

Preparation and characterization of nano clay-biopolymer composites : new materials for eco-design

van Son Vo

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Présentée par : Van Son VO

Élaboration, caractérisation et simulation de nanocomposites argile/polymère : des nouveaux matériaux pour l'éco-conception

Date de soutenance : le 12 Décembre 2016

Membres du jury :

Bénédicte LEBEAU	Directeur de Recherche	Rapporteur
Ali ZAOUI	Professeur	Rapporteur
Jean-Michel GLOAGUEN	Professeur	Examinateur
Nhu-Cuong TRAN	Ingénieur de recherche	Examinateur
Benjamin CARBONNIER	Professeur	Directeur de thèse
Salah NAILI	Professeur	Co-directeur de thèse
Samia MAHOUCHE-CHERGUI	Maître de Conférences	Invité
Vu-Hieu NGUYEN	Maître de Conférences	Invité



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Elaboration, characterization and simulation of polymer/clay nanocomposites: new materials for ecodesign

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Members of the jury:

CNRS Senior Researcher	Reviewer
Professor	Reviewer
Professor	Examiner
Research Engineer	Examiner
Professor	Supervisor
Professor	Co-supervisor
Assistant Professor	Invited
Assistant Professor	Invited
	CNRS Senior Researcher Professor Professor Research Engineer Professor Professor Assistant Professor Assistant Professor

A ma famile, A ma chérie,

"Learning to know Learning to do Learning to live together Learning to be"

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Résumé

Les nanoparticules d'argile sont des ressources naturelles largement disponibles et peu coûteuses présentant de nombreuses caractéristiques telles qu'une grande surface spécifique, une imperméabilité aux gaz, ainsi que des propriétés mécaniques et thermiques élevées. Elles ont donc attiré depuis plus de trois décennies une attention particulière, notamment pour le renforcement des matériaux à base de polymères. Cependant, les nanoparticules d'argile à l'état natif souffrent d'une incompatibilité, donc de faibles interactions interfaciales et d'une mauvaise dispersion avec/dans la plupart des matériaux polymères organiques à cause de leur hydrophilie intrinsèque et des fortes interactions entre les feuillets constitutifs. Ainsi, l'un des principaux défis dans le développement de nanocomposites polymères à base d'argile (NAPs) avec des propriétés mécaniques avancées repose sur le contrôle à l'échelle moléculaire des propriétés interfaciales entre l'argile et la matrice polymère.

En tenant compte des critères du développement durable, du génie civil et de l'économie verte, nous avons développé, dans la première partie de cette thèse, des nano-renforts réactifs et pré-exfoliés qui peuvent être incorporés dans une grande série de matrices (bio)polymères en donnant lieu à de fortes interactions avec les dites matrices et conduisant à des comportements mécaniques améliorés. Afin de mieux répondre à ces spécificités, nous avons mis en œuvre des approches vertes pour la préparation de ces nano-renforts génériques, à savoir la photopolymérisation a été utilisée comme une méthode rapide et peu énergivore pour la fonctionnalisation de surface des argiles, un protocole sans solvant a été utilisé pour préparer des nanocomposites ternaires, tandis que des biopolymères (amidon, cellulose) ou des précurseurs d'origine biologique (huiles végétales époxydées) ont servi de milieux de dispersion.

Les résultats principaux issus de cette première partie peuvent être résumés comme suit :

- La morphologie et la réactivité des nano-renforts d'argile sont aisément contrôlées en ajustant le temps de photo-polymérisation et en choisissant un monomère vinylique approprié.
- Les méthodes de préparation permettent la préparation d'échantillons à l'échelle du gramme.
- La chimie surface des nano-renforts réactifs et pré-exfoliés peut être ajustée afin d'assurer la compatibilité avec des biopolymères préformés thermoplastiques et des résines thermodurcissables, tels que l'amidon et les résines époxy biosourcées, respectivement.
- Les propriétés mécaniques des nanocomposites ternaires ainsi obtenus sont fortement améliorées en comparaison des matrices polymères pures grâce à la dispersion homogène et fine des feuillets du nano-renfort dans la matrice polymère et aux fortes interactions interfaciales entre ces deux constituants.

En raison de la complexité des composants chimiques à l'échelle nanométrique et les incertitudes dans le contrôle de la dispersion des nano-charges, des techniques de caractérisation expérimentales ne peuvent pas donner suffisamment d'informations lesquelles permettraient d'expliquer explicitement le mécanisme de renforcement des propriétés mécaniques des NAPs. Dans ce contexte, la deuxième partie de cette thèse a porté sur le développement des modèles numériques multi-échelles pour étudier la structure ainsi que les propriétés thermomécaniques des NAPs.

A l'échelle atomistique, l'intérêt principal est d'étudier la structure moléculaire de différentes phases constitutives du NAPs (feuillets d'argile, matrice de polymère et organomodifiant), et en particulier, dans l'interphase argile-polymère. En utilisant le code DL_POLY, des simulations de dynamique moléculaire (MD) ont été effectuées, fournissant des informations sur l'interaction moléculaire des structures nanocomposites intercalées et exfoliées. Les propriétés thermo-dynamiques des polymères confinés entre les feuillets d'argile ont été également étudiées afin de clarifier l'influence de ces feuillets sur les propriétés des nanocomposites. En outre, ces modèles moléculaires nous ont permis d'estimer les propriétés élastiques effectives des nanoparticules argile-polymères à différentes températures.

A l'échelle micrométrique, un modèle tridimensionnel utilisant la méthode des éléments finis a été développé pour calculer les propriétés élastiques macroscopiques des NAPs en fonction de leurs microstructures et des propriétés mécaniques des composants constitutifs. Différents types de microstructures de NAPs ont été étudiées : intercalée, exfoliée et partiellement exfoliée (structure mixte). Une étude paramétrique de l'influence des paramètres structuraux des nanoparticules d'argile telles que l'état d'exfoliation, le facteur de forme, la distance interfoliaire, le fraction volumique aux propriétés macroscopiques des NAPs a été rigoureusement éffectuée. Le rôle de l'interphase sur le mécanisme de renforcement des propriétés mécaniques des NAPs a été mis en évidence. Les résultats obtenus par ce modèle ont été comparés avec ceux expérimentaux/théoriques extraits de la littérature.

Mots clés : nanoparticules d'argile, nano-renforts réactifs, nanocomposites argile/polymère, polymérisation *in situ*, relations structure-propriété, méthode des éléments finis, simulation de dynamique moléculaire.

Abstract

Clay nanoparticles (CNP) are abundantly available low-cost natural resources with numerous positive attributes such as large surface area, impermeability to gas, superior mechanical and thermal properties so that they have attracted over the last three decades significant attention, notably for the reinforcement of polymer-based materials. However, CNP suffer from incompatibility, hence weak interfacial interactions and poor dispersion with/in most of organic polymeric materials because of their intrinsic hydrophilicity and strong interlayer interactions. Thus, one of the key challenges in developing claybased polymer nanocomposites (PCNs) with advanced mechanical properties relies on the control at the molecular level of the interface properties of clay nanoplatelets-filled polymer resins.

Taking into account the criteria for sustainable development, civil engineering and green economy, we have developed, in the first part of this thesis, reactive and pre-exfoliated clay nanofillers that may be further incorporated in a diverse set of biopolymer matrices and giving rise to strong energy interactions with the said matrices for improved mechanical behavior. To ensure a closer fit of these specifications we have implemented green approaches for the preparation of these generic nanofillers, namely photopolymerisation was used as a low energy consumption and fast method for the surface functionalization of native clays, solvent-free protocols were applied to prepare polymer nanocomposites, while biopolymers (starch, cellulose) or bio-based precursors (epoxidized vegetal oils) served as dispersion media.

Our major results from the first part can be summarized as follows:

- Morphology and reactivity of clay nanofillers are easily controlled though adjusting the photopolymerization time and selecting adequate vinyl monomer.
- The newly preparation methods allow preparation of samples beyond the gram-scale.
- Reactive and surface chemistry of pre-exfoliated clay nanofillers can be tuned to provide compatibility with both conventional preformed biopolymers and bio-based epoxy resins.
- The mechanical properties of the resulting polymer nanocomposites are improved as compared to the neat polymeric matrices owing to the strong interface interaction between fillers and dispersion matrices.

Due to the complexity of chemical components at the nanoscale and the uncertainties in controlling the dispersion of nanofillers, experimental characterization techniques may not be sufficient for understanding most important factors that improve the expected behavior of developed PCNs. Therefore, the second part of this thesis focused on developing some models and numerical frameworks for investigating the multiscale mechanical behavior of the PCNs.

At the nanoscale, the main interest is the arrangement of constitutive components of PCNs, particularly in the interphase zone. By using the research code DL_POLY, molecular dynamics (MD) simulations were performed, providing insights into the molecular interaction in the interphase zone for nanocomposite structure with different morphological configuration such as exfoliation or intercalation. The thermodynamic properties of the confined polymer in each structure are also investigated in order to clarify the influence of silicate layer on the properties of nanocomposites. In addition, these molecular models allow us to numerically estimate the effective elastic properties of the PCN models at different temperatures.

At the microscale, a 3D finite element model has been developed to compute the macroscopic elastic properties of the PCNs according to their microstructures and the mechanical properties of each of the constitutive components. Microstructural parameters of clay or clay stacks such as elasticity modulus, aspect ratio, basal spacing, and its volume fraction have been taken into account in the model. A parametric study on effects of these parameters on the macroscopic effective elastic properties of the PCNs has been carefully investigated. The important role of interphase on the mechanical properties enhancement of PCNs has also been demonstrated through our numerical models. The comparison with the experimental result or analytical prediction extracted from the literature has been performed.

Keywords: clay nanoparticles, reactive clay nanofillers, polymer/clay nanocomposites, *in situ* polymerization, structure-property relationships, finite element method, molecular dynamics simulation.

List of Abbreviations

ACN	Acetonitrile
AFM	Atomic force microscopy
AGET ATRP	activators generated by electron transfer for atom transfer radical polymerization
AIBN	Azobisisobutyronitrile
APTMS	(3-aminopropyl)trimethoxysilane
ATNRC	Atom transfer nitroxide radical coupling
ATRP	Atom transfer radical polymerization
BIBB	α -bromoisobutyryl bromide
BuA	Butyl acrylate
CMC	Contrast of stiffness between clay and polymer matrix
CROP	Cationic ring opening polymerization
CRP	Controlled radical polymerization
CuAAC	copper(I) catalyzed alkyne azide cycloaddition
CuBr ₁	Copper(I) bromide
CuBr ₂	Copper(II) bromide
DA	Diels-Alder
DMA	Dynamic mechanical analysis
DMAP	4-dimethylaminopyridine
DMF	N,N-dimethyl formamide
DMPA	2,2-dimethoxy-2-phenylacetophenone
DMSO	Dimethyl sulfoxide
DSC	differential scanning calorimetry
EHA	2-ethylhexylacrylate
EP	Effective particles
EtOH	Ethanol
FEM	Finite element method
FMA	Furfuryl methacrylate
FTIR	Fourier transform infrared spectroscopy
GMA	Glycidyl methacrylate
GMC	Contrast of stiffness between gallery and polymer matrix
HCl	Hydrochloric acid
IMC	Contrast of stiffness between interphase and polymer matrix
MD	Molecular dynamics
MMA	Methyl methacrylate
MMT	Montmorillonite
MMT-Br	α -bromoisobutyryl grafted bromideMontmorillonite
MMT-MAPS	3-(trimethoxysilyl) propyl methacrylate grafted montmorillonite
MMT-Na	Pristine montmorillonite
MMT-NH ₂	3-aminopropyl trimethoxysilane grafted montmorillonite

MMT-OH	Activated montmorillonite
MMT-PGMA	Poly(glycidyl methacrylate) grafted montmorillonite
MMT-PPGM	Poly(propargyl methacrylate) grafted montmorillonite
MSD	Mean square displacement
NaN ₃	Sodium azide
NMP	Nitroxide-mediated radical polymerization
NMR	Nuclear magnetic resonance spectroscopy
Nn	The number of clay layers by block
PCL	Poly(epsilon-caprolactone)
PCN	Polymer/clay nanocomposite
РЕНА	Poly(2-ethylhexylacrylate)
PFMA	Poly(furfuryl methacrylate)
PFPA	2,2,3,3,3-Pentafluoropropyl acrylate
PGM	Propargyl methacrylate
PGMA	Poly(glycidyl methacrylate)
PMDETA	Pentamethyldiethylenetriamine
PMMA	Poly(methyl methacrylate)
Poly(BuA-co-MMA)	Poly(butyl acrylate-co- methyl methacrylate)
PPGM	Poly(propargyl methacrylate)
PTHF	Polytetrahydrofuran
PS	Polystyrene
RAFT	Reversible addition-fragmentation chain transfer
rDA	Retro-Diels-Alder
RDF	Radial distribution function
RVE	Representative elementary volume
SEC	Size-exclusion chromatography
SEM	Scanning electron microscope
SI-ATRP	Surface initiated atom transfer radical polymerization
SI-CRP	Surface initiated controlled radical polymerization
SIP	Surface initiated polymerization
TEA	Triethylamine
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray diffraction
α	The aspect ratio of clay layer
γ -MAPS	3-(trimethoxysilyl)propyl methacrylate

Introduction générale

Les nanostructures hybrides à architecture macromoléculaire contrôlée sont considérées comme des outils importants pour élaborer des nanomatériaux avancés ayant des propriétés structurelles et des fonctionnalités ajustées sur mesure [1]. Le terme générique "nanomatériaux" recouvre les nanocomposites à matrice polymère chargés par des nano-objets qui continuent de susciter un grand engouement en raison de leur fort potentiel dans des domaines d'application variés.

Du fait de leur facilité de fabrication, leur légèreté, leur ductilité, ainsi que leur fonctionalisation aisée, les matériaux polymères organiques connaissent une utilisation de plus en plus croissante. Cependant, leurs faibles propriétés mécaniques par rapport à celles des métaux et des céramiques limitent leur utilisation. L'importance commerciale de ces matériaux polymères ainsi que leurs applications dans divers domaines rendent l'amélioration de leurs propriétés, en particulier les propriétés mécaniques, cruciale. Les renforts de taille nanométrique sont des candidats parfaits pour satisfaire cette demande tout en préservant les propriétés intrinsèques intéressantes des matériaux polymères, telles que la légèreté et la nature ductile. Particulièrement, ces nanocomposites présentent un grand potentiel de croissance avec le développement sans cesse des biopolymères ou polymères biosourcés ces dernier temps [2, 3, 4].

En effet, l'incorporation des objets dont au moins une des dimensions est à l'échelle nanométrique (<100 nm) dans des matériaux polymères, même à de faibles quantité (1-5% en masse), permet d'amliorer nettement leurs propriétés mais aussi de leur apporter de nouvelles caractéristiques et performances remarquables, telles que la rigidité, la tenacité, les propriétés barrières au gaz, l'inflammabilité, et les propriétés électriques et thermiques [5, 6, 7, 8, 9].

Parmi les différents types de nanoparticules utilisés pour renforcer des matrices polymères, les argiles connaissent un grand intérêt sur les plans industriel et académique. En effet, les argiles grâce à leur facteur de forme élevé (longueur/épaisseur > 100 avec une épaisseur de 1 nanomètre), leur importante imperméabilité, leur grande disponibilité, leur faible coût, ainsi que leurs propriétés mécaniques élevées, sont des renforts efficaces pour les matrices polymères [8, 10, 11].

Toutefois, les nanoparticules d'argile à l'état natif en raison de leur caractère hydrophile intrinsèque ainsi que des fortes interactions électrostatiques entre les feuillets constitutifs, souffrent d'une mauvaise dispersion dans et d'une incompatibilité avec les matrices polymères organiques conduisant souvent à une perte des propriétés mécaniques. Afin de surmonter ces limitations et d'améliorer les interactions interfaciales entre argile et matrice organique, la fonctionnalisation de surface de l'argile avec des matériaux polymères organiques s'est révélée être une stratégie très efficace [12, 13, 14].

Les smectites appartenant à la famille des phyllosilicates, constituent un bon choix pour l'élaboration de nanocomposites polymères, car leur structure organisée en feuillets bidimensionnels construits par l'empilement de couches tétraédriques (SiO_4) et octaédriques $Al(OH)_6$ de type (TOT) et séparées par un espace ou distance dite interfoliaire, rend facile leur modification chimique. Le but de cette étape de fonctionnalisation étant de permettre la compatibilisation des argiles avec la matrice polymère d'intérêt.

Cependant il est à noter que les propriétés finales des nanocomposites ne dépendent pas que des propriétés intrinsèques du renfort et de la matrice polymère mais elles sont aussi gouvernées par des effets de synergie qui résultent directement de la nature des interactions interfaciales mises en jeu entre les deux constituants et de la dispersion et l'orientation des nano-objets dans la matrice polymère [2, 15, 16, 17]. Ces deux phénomènes son bien souvent intercorrélés.

C'est dans ce contexte que s'inscrit ce projet de thèse, qui porte sur l'élaboration par des méthodes de synthèse élégantes et, si possible, respectueuses de l'environnement (économie d'atomes, économie d'énergie, biodégradables...) de nanocomposites argile-polymère (NAPs). L'accent a été porté sur la modification chimique de la surface d'argile et la réactivité de ces lamelles argileuses vis-a-vis de molécules modèles et de biopolymères ou de leurs précurseurs.

Cette thèse, réalisée en collaboration entre deux équipes de recherche, des chimistes des matériaux et des mécaniciens, a deux objectifs principaux:

- Assurer une dispersion fine et homogène des nanoparticules d'argile utilisées comme nanorenforts dans la matrice polymère sélectionnée. Pour cela, dans la partie réalisée à l'Institut de Chimie et des Matériaux Paris Est, nous nous sommes intéressés à l'ajustement de la chimie de surface departicules de montmorillonite, afin d'une part, de contrôler la morphologie et la structure des dites particules, et d'autre part d'assurer des interactions interfaciales fortes entre nanoparticules avec idéalement une morphologie pré-exfoliée et la matrice. Nous avons choisi de modifier la surface de la montmorillonite par des polymères réactifs par des méthodes de photopolymérisation in situ. Les nanocomposites binaires ainsi obtenus possèdent une forte densité de fonctions réactives en surface facilitant leur incorporation, au cours d'une étape ultérieure, dans des matrices biopolymères. De tels nanocomposites ternaires sont caractérisés par la nature covalente des liaisons matrice-renfort qui est un atout incontestable pour l'amélioration des propriétés mécaniques.
- Comprendre les phénomènes régissant les propriétés finales de nanocomposites argile-polymère et identifier les paramètres importants qui gouvernent les interactions interfaciales entre les constituants organique et inorganique. A ce sujet, la stratégie de modélisation et de simulation multiéchelle est devenue un outil précieux pour mieux comprendre la structure et le mécanisme de renforcement des propriétés macroscopiques des NAPs. Pour cela, des modèles numériques à l'échelle nanométrique ainsi qu'à l'échelle micrométrique ont été modélisés et simulés au laboratoire Modélisation et Simulation Multi Echelle. D'une part, la simulation à l'échelle atomistique est cruciale pour comprendre l'arrangement des phases constitutives de NAPs, l'interaction entre celles-ci ainsi que pour déterminer l'influence des feuillets d'argile aux propriétés thermody-namiques de polymères. D'autre part, un modèle l'échelle micrométrique nous permet d'étudier explicitement l'influence des paramètres liés aux microstructures et aux propriétés des phases constitutives, aux propriétés macroscopiques de NAPs. La méthode dynamique moléculaire et la méthode des éléments finis sont choisi grâce à leur potentiel pour la simulation des nanomatériaux dont NAPs.

Ce manuscrit se décline sous forme de recueil d'articles ou projets d'articles que nous présentons dans deux parties, la première partie comporte quatre chapitres, et la seconde est composée de deux chapitres.

Dans le chapitre 1, les caractéristiques principales des argiles, et plus particulièrement la montmorillonite, qui sont habituellement utilisées pour l'élaboration de nanocomposites sont brièvement présentées. Les différentes méthodes de caractérisation physico-chimique des feuillets d'argile (naturelle ou organomodifiée), ainsi que des nanocomposites polymères sont également mentionnées. Ensuite sont présentées les méthodes récentes utilisées pour la préparation de nanocharges lamellaires argile/polymère avec un accent particulier sur les méthodes de synthèse avancées, telles que la polymérisation amorcée à partir de la surface des argiles, la polymérisation radicalaire contrôlée, la chimie *"click"*, le greffage et la polymérisation photo-induites.

Le chapitre 2 est dédié à la synthèse de nanocharges d'argile intercalées et *photoclickables* par la méthode de la polymérisation radicalaire par transfert d'atomes. Des chaines de poly (méthacrylate de propargyle) sont générées directement à l'intérieur de la structure lamellaire des argiles préalablement traitées par une étape de silanisation et le greffage d'un amorceur de type de bromobutyrate. Le caractère générique des argiles *clickables* est démontré par le greffage de l'(azidométhyl)benzène et l'acide mercaptosuccinique *via* respectivement des réactions de chimie *click* de cycloaddition de Huisgen et d'addition radicalaire de type thiol-ène, activées photochimiquement. Cette étude constitue un des premiers exemples si ce n'est le premier, traitant de la mise en œuvre de la polymérisation radicalaire par transfert d'atomes combinant un amorçage en surface et par voie photochimique pour le greffage de polymères à la surface d'argile. Cette stratégie a permis un contrôle fin de la longueur des chaines de polymères, et donc de la distance interlamellaire. Des argiles intercalées fonctionnelles ont été élaborées in fine.

Dans le chapitre 3 et 4, nous proposons une méthode simple et efficace pour l'exfoliation totale des lamelles d'argile. Cette méthode est basée sur le greffage interfaciale de chaînes de poly méthacrylate de glycidyle, un monomère contenant des unités d'époxy et très réactif via la polymérisation radicalaire. Ici encore une approche par polymérisation in situ a été sélectionnée en utilisant une argile vinylique préparée par silanisation avec le méthacrylate d'aminopropyle silane. Les nanocharges ainsi exfoliées présentent une forte réactivité vis-à-vis d'espèces moléculaires nucléophiles, *i.e.* amines fonctionnelles, ce qui a été mis à profit pour réaliser facilement et efficacement leur dispersion à la fois dans une matrice polymère thermodurcissable à base de résine d'époxyde biosourcée et une matrice thermoplastique dérivée de l'amidon. La forte réactivité des argiles greffées avec les polymères portant le groupement époxyde permettant l'établissement de liaisons fortes, covalentes, entre matrice polymère et nanolamelles d'argile a permis un renforcement des propriétés thermomécaniques des nanocomposites.

Tous ces matériaux nanostructurés ont été caractérisés par différentes méthodes telles que les spectroscopies infra-rouge, les microscopies électroniques à balayage et à transmission, la diffraction des rayons X, l'analyse thermogravimétrique, l'analyse mécanique dynamique mécanique, dans le but d'établir des relations propriété-structure.

Dans le cinquième chapitre, un modèle de NAP à l'échelle atomistique est proposé dans le but de mieux comprendre leur structure et leur comportement thermomécaniques. A cette échelle, le terme nanocomposite est pour indiquer les nanoparticules d'argile-polymère. La définition de la structure de NAPs est basée sur la distance entre deux feuillets consécutifs. A notre connaissance, les modèles de NAPs dans lesquels les organomodifiants ou polymères sont greffés de manière covalente à la surface d'argile ne sont pas encore proposés dans la littérature. Un modèle de l'argile greffé avec des aminosilanes a été introduit pour la première fois par simulation de dynamique moléculaire (DM) dans le travail de Piscitelli et al. [18]. De plus, le système argile/polymère thermodurcissable est également très peu étudié dans la littérature par DM. Ainsi, en s'inspirant du modèle de l'argile silanisée de Piscitelli et al. [18], on développe un modèle de DM dans lequel ces argiles sont combinées avec la matrice de résine époxyde donnant différentes structures de NAPs. L'originalité de ce modèle réside dans la possibilité de tenir en compte de la réactivité de la surface d'argile grâce aux groupements fonctionnels (amine) des aminosilanes qui sont préalablement greffés de manière covalente à celle ci. L'objectif de ce chapitre est d'étudier la morphologie des différentes structures de NAPs où l'accent est porté sur l'identification de l'interphase en se basant sur le profil de distribution de densité des matières organiques. De plus, l'influence des feuillets d'argile réactifs sur les propriétés mécaniques et thermodynamiques de polymères est étudiée en détails.

Le sixième chapitre a pour but de déterminer les propriétés élastiques macroscopiques des NAPs en se basant sur leurs microarchitectures et le comportement élastique des éléments constitutifs, c'està-dire, l'argile, l'interphase, la galerie et la matrice de polymère. Le calcul des propriétés effectives est effectué par la méthode des éléments finis en se basant sur le volume élémentaire représentatif en trois dimensions. Une étude paramétrique sur les effets des paramètres structuraux de NAPs tels que l'état d'exfoliation, les propriétés d'élasticité des éléments constitutifs, le facteur de forme de l'argile et la fraction volumique de l'argile sur leur propriétés d'élasticité macroscopique est soigneusement menée. En particulier, la présence de la zone de l'interphase ainsi que la structure partiellement exfolié de NAPs est également intégrée dans notre model numérique. Ainsi, l'originalité de cette étude réside dans la possibilité de tenir en compte des nombreux paramètres structuraux de manière explicite pour expliquer le mécanisme de renforcement des propriétés mécaniques de NAPs. La comparaison des résultats obtenus par ce modèle avec les données expérimentales ainsi que ceux obtenus par des modèles analytiques issues de la littérature est effectuée pour mettre en évidence la pertinence du modèle proposé.

Ce travail de thèse se termine par un résumé des résultats importants obtenus. A la fin, des perspectives sont proposées pour développer et élargir ce travail.

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Chapter 1

Chemical and photochemical routes towards tailor-made polymer/clay nanocomposites: recent progress and future prospects

The work developed in this chapter has been submitted to:

V-S. Vo, S. Mahouche-Chergui, V-H. Nguyen, S. Naili, N.K. Singha, B. Carbonnier: Chemical and photochemical routes towards tailor-made polymer/clay nanocomposites: recent progress and future prospects, in Clay-Polymer Nanocomposites: Morphology, Structure, Properties and Applications, Elsevier, Edited by Dr. Mohamed M Chehimi, Prof. Sabu Thomas, Dr. Khouloud Jlassi Chapter 1. Chemical and photochemical routes towards tailor-made polymer/clay nanocomposites: recent progress and future prospects

1.1 Introduction

Polymers are fascinating molecules that dominate our day to day lives starting from diapers, toys, clothes, smart devices chassis, comfortable foam mattress and cushions, food and beverage packaging, trash bags, air/rail/road/water transportation, construction and even implantable sensors for in vivo glucose detection, heart patches, joint prosthesis and dentures. Natural polymers are widely found in nature and have been a keystone of human's development and technology since the dawn of time, urging inventors to develop synthetic substitutes. Camphor-plasticized cellulose provides inexpensive imitation of ivory giving rise to the *Golden Age of Natural vs. Artificial*. Since then, synthetic polymers have been designed in a variety of topology and chemical composition leading to the concept of complex macromolecular architectures (Figure 1.1). Fine tuning of polymer topology, chemical composition as well as distribution of the chemical functions along the polymer backbone were made possible through progress in macromolecular synthesis toolbox including controlled [1, 2] and living [3] free radical polymerization, anionic [4] or cationic [5] ring opening polymerizations.



Figure 1.1 – Schematic illustration of selected macromolecular architectures with varied topologies. Examples are given for homopolymers and copolymers.

Similarly to natural polymers, properties of synthetic polymers are intimately related to their structures. For instance, highly branched polymers exhibit unique chemical and physical properties in comparison with their linear analogues, such as improved solubility, low solution and melt viscosities, making them good candidates for coating applications, while the large number of functional end groups allows for further modification to meet specifications for high performance applications [6]. Star polymers exhibit distinct physicochemical properties as compared to their linear analogues including chain morphologies, solution behaviors and mechanical properties [7]. Liquid crystalline polymers exhibit optoelectronic properties which are dictated by the self-assembly ability of their polymer backbone and side segments [8, 9]. As an important branch of polymer science with significant industrial output, polymer blends technology has since long taken advantage of synergistic effects of mixing polymers with additives, blending two or more polymers [10], combining polymers with fibrous [11] or spherical [12] particulate materials. Such strategies may offer improved processability, time-effective formulation changes, improved dielectric properties plant flexibility and high productivity proving to be economically profitable [13]. Indeed, polymer-based materials with a large panel of specific properties, e.g. strength, toughness, flame retardancy, solvent resistance, can be obtained at rather low price as compared to the investment efforts required for the design of new monomers, catalysts and/or polymerization methods [14, 15, 16]. However, remembering basis of thermodynamics where the Flory-Huggins model (Eq. 1.1) is described by the Gibbs free energy of mixing (ΔG_m) composed of both entropic (ΔS_m) and enthalpic (ΔH_m) contributions, polymer blends are homogeneous at the molecular scale only if $\Delta G_m < 0$. Taking into account that the entropic term increases upon mixing, i.e. $T\Delta S_m > 0$ 0, it results that achievement of single phase polymer blends exhibiting optimal end-use properties is

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possible only in $T\Delta S_m > \Delta H_m$.

$$\Delta G_m = \Delta H_m - T \Delta S_m. \tag{1.1}$$

With the recent emphasis on nanotechnology, the "generic" area of polymer mixing has been extended to the incorporation of nanofillers into linear [17], crosslinked [18], conducting [19] or even porous [20] polymers as well as block [21], gradient [22], comb-branched [23] copolymers. Because nanosized objects are usually free of defects, they are considered as high-potential candidate as filler materials in comparison to their conventional microscaled analogues. However, to benefit of the often-promised nano-effect, it is crucial to achieve homogeneous dispersion of single nanoparticles within the polymeric matrix allowing for the development of large interfacial area. This prerequisite leads to a significant volume fraction of polymer surrounding the particle and whose properties differ from the ones of bulk polymer. Similarly to polymer blending, the main challenges in producing homogeneous polymer nanocomposites are to achieve (*i*) chemical compatibility between the polymer matrix and the nanofiller at the nanoscale and (*ii*) homogeneous dispersion of the nanofiller within the polymer matrix. These two intercorrelated features determine the nanocomposites' morphology and thus final bulk properties such as strength, elastic modulus, gas barrier resistance, heat distortion temperature, self-healing and shape memory abilities and thermal stability [24, 25].

From a thermodynamic point of view, here again the interplay between entropic and enthalpic contributions will determine whether functionalized clay will be aggregated, dispersed, intercalated or exfoliated in a polymer. In most cases, nanofillers, when used in their native form, exhibit poor interfacial adhesion with organic polymers resulting in poor improvement of, if not being detrimental to, the composite materials' properties. The two most efficient strategies to compatibilize both partners rely on the chemical modification of nanofillers' surface through the surface adsorption of grating of either low molecular weight molecules, generally referred to as coupling agents [26] or macromolecules [27]. The former approach can be combined to the use of a polymeric compatibilizer providing ternary nanocomposites with improved physical properties [28]. The latter enables designing polymer-grafted particles with a nearly limitless range of surface functionality through proper selection of monomers and grafting conditions [29]. These approaches have been developed to date, for both organic [30, 31] *-carbon nanotubes, graphene...* -and inorganic [30] *-silica, titanium oxide, clay, polyhedral-oligomeric silsesquioxane...* -nanostructures.

This chapter is presented as a mini-review discussing the preparation of polymer nanocomposites through original and recent synthesis methods with a specific focus on the surface modification of inorganic nanofillers to provide improved dispersions in organic solvents or polymeric matrices. The inorganic nanostructures usually used to prepare nano-composites mainly include layered silicate clays, metal powder and a variety of inorganic oxides. Herein, in regard to the theme of the Elsevier monograph "*Clay-Polymer Nanocomposites: Morphology, Structure, Properties and Applications*" our words are purposely restricted to the case of clay nanoparticles. In this respect, the use of the nanocomposite term is sometimes extended to polymer-grafted nanoclays, which are not true polymer nanocomposites, but should be better viewed as functional nanomaterials. Besides reviewing synthesis methods towards organic-inorganic polymer-clay materials preparation, specific characteristics and various applications of the modified nanoparticles and nanocomposite materials are also discussed.

1.2 Scope and aim

In this contribution, we discuss recent routes to the preparation of polymer/clay nanocomposites with a specific focus on advanced synthetic methods, such as surface initiated polymerization (SIP), controlled radical polymerization (CRP), click coupling chemistry, photo-driven grafting and polymerization. All

these methods have been successfully implemented for either the chemical modification of clay surface or the covalent grafting of the clay to the dispersion polymeric matrix (Figure 1.2) [32]. The former provides reactive nanofillers with intercalated morphology, the extent of which being related to the amount of organics incorporated with the clay layer. The latter ensures a strong interaction between the reinforcement and the matrix that is crucial for improved thermo-mechanical properties. Hence, the deliberate choice done by the authors is to discuss well-selected studies independently of chronological considerations but mainly guided by relevance and benefits allowing scientific breakthrough in the design of polymer/clay materials with well-controlled morphologies. Application and/or properties improvement of the as-prepared polymer nanocomposites are also covered, and rationalized on the basis of the chemical nature of the nanocomposites-forming partners. The discussion encompasses all type of clay nanoparticles, although abundant literature is devoted to montmorillonite.



Figure 1.2 – Schematic illustration summarizing trendy *in situ* methods applied to the preparation of polymer/clay nanocomposites. Reproduced from reference [32] with permission by Wiley.

As this contribution, presented in the book chapter format, is not intended to be exhaustive in terms of preparation methods; the reader is kindly invited to refer to previous research papers [33] and reviews [34, 35, 36] in the field highlighting manufacturing techniques such solution mixing and melt mixing in presence of clay.

1.3 Key features of layered clay

Clay minerals which are made of the most abundant elements in the Earth's crust have been exploited all around the world since long, and their presence on Mars soil has been suspected about more than 3 decades ago [37]. Natural clays have been categorized depending on their geological origin and their structure is now well-established. Smectite clays are well-defined layered structures made of multiple sheets including a large number of ionic charge sites. Among them, the phyllosilicate clays of the 2:1 type exhibit a platy morphology consisting of two sheets of silicate/aluminum oxide with a corner-linked tetrahedra structure and an edge-shared octahedral sheet sandwiched in between (Figure 1.3) [38]. The nature of the cations in the octahedra depends on the phyllosilicates origin. The tetrahedral and octahedral sheets are joined together via a plane of oxygen atoms and constitute the modular build-

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ing elements of the phyllosilicate layered structure. Because of valence considerations, some of the oxygens from the tetrahedral sheets belong to the octahedral layer. The 2:1 phyllosilicate clays include bentonite, montmorillonite, hectorite and saponite, to cite but a few, and in the case of montmorillonite (MMT), the primary units have average dimension of ca. $100 \times 100 \times 1 nm^3$ for individual sheets agreeing fully with the specifications for nanoparticles. Another important feature of clay is the so-called isomorphous substitution corresponding to the substitution of one chemical element for another. Although isomorphous substitution does not affect substantially the layered structure of clay it induces a net negative charge. For instance, although the predominant atom in the tetrahedron sheet is the *S i*⁴⁺ cation, *Al*³⁺ cation occurs at some sites. Similarly, chemical composition variations involving Al, Fe, Mg and Li may occur in octahedral cation sites. To fulfill the general principle of electrical neutrality, charge deficiency must be balanced within the clay structure by Na^+ , Ca^{2+} , Mg^{2+} . These cations present at the interlamellar interface can be easily interconverted with any other species as long as they are positively charged, rather hydrophilic in essence and with atomic or molecular dimensions.



Figure 1.3 – Structure of 2:1 phyllosilicates. Reproduced from reference [38] with permission by Elsevier.

The chemical composition, layered structure made of crystals with nanosized dimensions, ion exchange ability are key parameters responsible for some of the unique properties of clays such as large surface area, chemical surface reactivity, high cation exchange capacity, interlamellar hydration ability (Figure 1.4) [36]. Large volume applications of natural smectice clays encompass varied industrial domains depending on their cation composition such as foundry applications, civil engineering, oil well drilling, iron ore industries, and wine production. The ion exchange-mediated intercalation of organic cations within clay layered structures may alter the hydrophilic/hydrophobic balance of natural clays. This process has been widely applied to the preparation of hydrophobic and engineering polymer-compatible organoclays [39]. This beneficial compatibilization effect arises from the decrease in the surface energy of the inorganic filler. To date, cationic surfactants, including primary, tertiary and quaternary ammonium ions, have been applied and gave rise to commercially available organoclay.

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Chemical structure of commonly used 2:1 phyllosilicates^a

2:1 Phyllosilicate	General formula
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$
Saponite	$M_xMg_6(Si_{8-x}Al_x)O_{20}(OH)_4$

^a M=monovalent cation; x=degree of isomorphous substitution (between 0.5 and 1.3).

Figure 1.4 – Cation exchange capacity and particles' dimensions of major layer clay. Reproduced from reference [36] with permission by Elsevier.

Moreover, the use of short chain ammoniums bearing a functional end group allows incorporation of reactive units within the interlayer spacing. These reactive moieties may provide anchoring or initiation sites for the covalent attachment of the filler with the polymer matrix or inducing the polymerization from the clay surface, respectively. This approach allow strengthening of the interface between both inorganic and organic components and are discussed in more details in the following sections of this contribution.

Although considered as an historical and classical method, original approach and new trends in the literature described the use of cationic diazonium salt (N,N-dimethylbenzenediazonium tetrafluoroborate) [40] and clickable [41] (propargyldimethylstearylammonium bromide) and azo-type free radical initiator derived from 4,4'-azobis(4-cyanovaleric acid) [42] surfactants for ion exchange with sodium of montmorillonite. X-Ray Diffraction (XRD) analysis indicated a slight increase in the interlamellar space upon intercalation of the diazonium derivative, while X-ray photoelectron spectroscopy (XPS) and fourier transform infrared spectroscopy (FTIR) provided evidence for the presence of $N \equiv N^+$ triple bond from arising from the diazonium [40]. Presence of the propargyl-containing intercalator within the clay galleries was evidenced by an increase in the d-spacing from 1.42 nm to 3.73 nm for the native and clickable montmorillonite samples, respectively [41]. Moreover the FTIR spectrum of the clickable clay indicated a strong absorption peaks at 1033 cm⁻¹ (Si – O – Si bond in the montmorillonite silicate), 2800-2950 cm⁻¹ (alkyl chain of the stearyl segment), and 2128 cm⁻¹ (acetylene unit) suggesting that the ordered layered structure remained. Exfoliation of the clay layers was finally obtained via the reaction with mono- and multi-functionalized azido polyhedral oligomeric silsesquioxane nanoparticles.

1.4 Key features of polymer-clay nanocomposites characterization

A crucial issue in investigating polymer-nanocomposites is the determination of the state of dispersion and exfoliation of nanoparticles within the polymeric matrix. Indeed, as announced in the above section, polymer nanocomposites belong to the class of materials exhibiting morphology-controlled properties and the implementation of complementary experimental methods enabling gathering structural, thermal and mechanical information is essential to establish structure-property relationships.

The most commonly applied method to assess clay structure is XRD. Through monitoring position, shape, and intensity of the Bragg reflections measured for chemically modified or in-polymer dispersed clays, and comparison with the corresponding signal from native clay one may easily determine the degree of intercalation for organoclay, or identify delamination or even exfoliation in organic matrices (Figure 1.5) [43]. In the former case, increase in the interlayer spacing is ascertained from the shift of the basal reflections toward lower 2θ diffraction angles in concordance to the inverse proportionality of the by-XRD calculated correlation distance *d* to the scattering vector S (Eq. 1.2) as the expression:

$$S = \frac{1}{d} = \frac{2\sin\theta}{\lambda},\tag{1.2}$$

where λ is the radiation source's wavelength.

The increase in the *d*-spacing is generally within 1-4 nm, depending on the chemical structure of the chemical modifier. For intercalated nanocomposites with layer spacing exceeding 6 nm or for exfoliated nanocomposites exhibiting disordered layered arrangement, XRD analysis may not be relevant providing conclusive-less data.



Figure 1.5 – Representative XRD profiles showing the shift of the Bragg's peak towards lower 2θ values upon chemical modification of the silicate clay with initiator and grafting of block copolymer. Reproduced from reference [43] by permission of ACS.

For exfoliated structures, total disappearance of Bragg reflections (both 1st and higher order) is obtained suggesting the disruption of the layer structure and thus the distribution of single clay layer, or sheet aggregates with short-range layer-type order, within the dispersion polymer. Although XRD offers a simple method requiring no specific sample treatment prior to measurement to determine the interlayer spacing of silicate layers in both their pristine and intercalated forms, it does not provide reliable information about the spatial distribution of the silicate layers including structural inhomogeneities in nanocomposites. Additionally, in some cases, layered silicates, even in their native form, do not exhibit clear basal reflections, moreover peak broadening and intensity changes as observed for samples with varied degree of intercalation are very complicated to interpret unambiguously. Therefore, drawing final conclusions about nanocomposites' structure based solely on XRD data can only be tentative and it is often necessary to complement XDR analysis with electron microscopy observations. Transmission electron microscopy (TEM) allows a thorough understanding of the internal structure, dispersion and spatial distribution of the clay particles within the polymer matrix (Figure 1.6). Moreover, TEM allows direct visualization structural defects although sample treatment and preparation are required to observe representative cross section sampling.

One may also mention that bulk characterization techniques conventionally applied in polymer science, including differential scanning calorimetry (DSC), size-exclusion chromatography (SEC), thermogravimetric analysis (TGA), rheology, nuclear magnetic resonance spectroscopy (NMR), dynamic mechanical analysis (DMA), spectroscopies are useful to gather additional information about structure



Figure 1.6 – Representative TEM image epoxy/clay nanocomposites showing the clear co-existence of exfoliated/disordered montmorillonite layers (A structures in the image) and intercalated tactoids (B structures in the image).

and dynamics of polymer chains confined within the interlayer space. Precise and fine knowledge of the nanocomposites structure and morphology is essential to understanding the change in properties. Hopefully, the incorporation of clay at the nanometer scale enables "general" improvement of bulk characteristics of the resulting polymer nanocomposites for low or moderate (1-5 wt%) clay loading. Briefly mentioning, enhancement of scratch resistance, tensile strength, reduction in permeability to liquids and gases, decrease in flammability, higher heat deflection temperature and solvent uptake accompanied with weight lighting are common beneficial "clay" effects [39].

1.5 Polymer-clay nanocomposites and click chemistry methods

Numerous research efforts have been devoted to the development of efficient and versatile methods for the chemical modification of (nano)materials surface, with a special focus over the last 15 years on using click chemistry [44]. The term click chemistry, originally used by Sharpless and coworkers to describe the copper-catalyzed azide-alkyne Huisgen dipolar cycloaddition reaction (CuAAC), has been generalized to a set of particular organic reactions exhibiting specific synthetic features. Indeed, according to Sharpless, such click reactions should be regio- and even stereo- selective, carried out in mild conditions and provide thermodynamically stable products with high yields and very few inoffensive byproducts, if any, without the requirement for tedious purification protocols [45]. These reactions encompassing the copper-catalyzed azide-alkyne Huisgen dipolar cycloaddition reaction, the radical-mediated addition of thiols on ene (thiol-ene) and yne (thiol-yne), the thiol-(meth)acrylate Michael addition, the thiol-epoxide and the Diels-Alder reactions, have been successfully implemented for controlling the interface properties of nanoparticulate structures [29], including clay [46]. However, implementation of the click & clay pair remains a niche and the few other examples in the literature deals with the design of functional clay for depollution applications [46].

Achievement of click coupling reactions requires the presence of complementary functional groups on both partners. Polymers can be designed in a nearly limitless range of click variants and many examples can be found in the extensive literature including excellent reviews [47, 48]. Both strategies implying either azide [49] or alkyne [41] montmorillonite have been evaluated for the preparation of chemically modified and exfoliated montmorillonite via the copper(I) catalyzed alkyne azide cycloaddition (CuAAC). Montmorillonite (Cloisite 30B) with azide interlamellar functionality was prepared following a two-step process involving (*i*) the conversion of hydroxyl groups of the silica nanolayers into methanesulfonate groups using methanesulfonyl chloride, (*ii*) subsequent reaction with sodium azide [50]. Step (*i*) was achieved in tetrahydrofuran (THF) in presence of trimethylamine as catalyst and the reaction was allowed to proceed over night from 0°C to room temperature. Step (*ii*) was performed at reflux overnight. As schematically presented in Figure 1.7, chemical modification of hydroxyl groups was not complete providing unreactive *OH* sites.



(T) = Tallow (~65% C18; ~30% C16; ~5% C14; fat product)

Figure 1.7 – Schematic illustration of the preparation of azide-functionalized montmorillonite via the initial conversion of the surface hydroxyl groups into methanesulfonate units and further reaction with sodium azide. The so-designed clay can be applied in a subsequent step to grafting methacrylate units or polymer (PTHF) via copper(I) catalyzed alkyne azide cycloaddition click reaction. Reproduced from reference [50] by permission of American Chemical Society.

The as-designed functional clay was reacted with poly(epsilon-caprolactone) (PCL) prepared by ring opening polymerization of the corresponding monomer [49]. Bulk polymerization was performed using tin(II) 2-ethyl-hexanoate ($Sn(Oct)_2$) and propargyl alcohol as a catalyst and an initiator, respectively. The latter allowing introducing click compatible alkyne units at one of the polymer chains end. Nanocomposites with varied clay loading were prepared via the CuAAC (70°C, overnight) in the presence of copper(II)sulfate ($Cu(II)SO_4$) and sodium ascorbate in a mixture of water and dimethyl sulfoxide (DMSO) (Figure 1.8).

TEM images of PCL-Clay nanocomposites revealed the presence of stacks of intercalated montmorillonite together with exfoliated silicate sheets, consistent with TGA suggesting limited enhancement of the thermal stability. Click chemistry was also implemented for the preparation of polytetrahydrofuranclay nanomaterials [50]. Alkyne-functionalized polytetrahydrofuran was obtained by cationic ring opening polymerization (CROP) at 20°C using methyl triflate and propargyl alcohol as an initiator and a terminating agent, respectively. Variation in the polymerization from 15 to 60 min provided polymers with molecular weight in the range 38000-11300 g/mol (Mn as determined by size exclusion chromatography using polystyrene as a standard and a correction factor of 0.44 as measured for linear polytetrahydrofuran) with polydispersity indices below 1.26. Click coupling between azidefunctionalized montmorillonite clay and alkyne-functionalized PTHF was achieved in DMSO through Chapter 1. Chemical and photochemical routes towards tailor-made polymer/clay nanocomposites: recent progress and future prospects



Figure 1.8 – Schematic illustration of the preparation of poly(epsilon-caprolactone)/clay nanocomposites via copper(I) catalyzed azide/alkyne cycloaddition (CuAAC) "click" reaction. The synthetic path implies the preparation of alkyne-terminated poly(epsilon-caprolactone and azide-functionalized montmorillonite. Reproduced from reference [49] with permission by Elsevier.

subsequent addition of water solution of $CuSO_4$ and sodium ascorbate followed by overnight heating at 70°C (Route b in Figure 1.7).

The nanocomposites exhibited improved thermal stability as compared to native polymer as concluded from the significant shift of decomposition onset and midpoint degradation temperature toward a higher temperature. These results are well correlated with the TEM investigations showing random distribution of thin clay nanoplatelets in PTHF matrices. This is reflected in the presence of thin contrasted filaments corresponding to edge side view of finely dispersed nanolayers (Figure 1.9).





Daoxing Sun *et al.* [51] designed azide-montmorillonite using 3-azidopropyltriethaoxysilane as a silanizing agent that was simply prepared *via* the reaction between 3-chloropropyltriethoxysilane

and sodium azide. The reaction was performed at reflux in acetonitrile during 18 hours and under nitrogen atmosphere in the presence of tetrabutyl ammonium bromide. Evidence for the click grafting was provided by a combination of FTIR, elemental and XRD analyses. The clay loading affected significantly the properties of the polymer nanocomposites as follows: tensile strength was increased by more than 270% upon addition of 5 wt% of clay, improvement of heat, flame and water resistance was obtained for montomorillonite content below 4%. These effects were attributed to both hydrogen bonds and covalent linking between intercalated montmorillonite and polyurethane.

Other implementation of the polymer-clay coupling *via* Cu(I) catalyzed alkyne-azide cycloaddition reaction, involved the reversed strategy where azide and alkynyl moieties were present on polymer and clay, respectively [52]. To this aim, two silanization agents, namely N-(3-(triethoxysilyl)propyl)propiolamide and (3-azidopropyl)triethoxysilane were prepared following the synthesis paths illustrated in Figure 1.10.



Figure 1.10 – Schematic illustrations of the preparation routes to clickable derivatives with alkynyl and azide functionality applied to the silanization of clay and cellulose, respectively. The approach for preparing the corresponding cellulose clay nanocomposite is also presented. Reproduced from reference [52] by permission of Springer.

Effective attachment of click-reactive units to the silane precursors was confirmed by ¹3*C* nuclear magnetic resonance (NMR) and the Click chemistry product was obtained using *CuBr* as a catalyst in *DMSO* at 150°C. The formation of triazole was suspected based on a qualitative FTIR investigation showing the disappearance of the characteristic bands of $-C \equiv C$ - and N_3 at 2055 cm⁻¹ and 2117 cm⁻¹, respectively. Cui and Kuo reported on the introduction of exfoliated montmorillonite into polybenzoxazine [53, 54]. The polymeric matrix was prepared at 140°C from a reactive mixture containing paraformaldehyde, aniline, and phenol. Exfoliation of the montmorillonite prior to the polymer nanocomposites preparation was achieved *via* the reaction between a polyhedral oligomeric silsesquioxane derivative bearing an azido functional group and a montmorillonite intercalated with propargyl-containing alkyl ammonium salt. Physical properties of the nanocomposites were controlled by the amount and dispersion homogeneity of clay, providing in the most favourable cases improvement of the polymer's glass transition, thermal decomposition temperatures, mechanical properties, and surface hydrophobicity.

Although beside the scope of this section, it is worth mentioning that photo-induced click polymerization based on thiol-ene radical addition has been applied to disperse nanoclay into photo-crosslinked polymer network [55]. Nanocomposite films were obtained via single one step polymerization using tetrafunctional thiol (pentaerythritol tetrakis(3-mercaptopropionate)) and triene (1,3,5-triallyl-1,3,5triazinane-2,4,6,-trione) as monomers, nanoclay surface hydrophobized with octadecylamine as inorganic filler and Irgacure 754 as phenylglyoxylate photoinitiator. Homogeneous dispersion of clay with either intercalated or exfoliated morphology was observed by transmission electron microscopy. Of particular importance, differential scanning calorimetry (DSC) profiles recorded for thin films contain-
ing 1 wt% of organoclay and UV-irradiated for 10 min suggested that the photopolymerization process was not significantly hindered by the presence of nanoclay. Indeed, while DSC traces indicated clear T_g signal, no exothermic peak assigned to residual thermal polymerization was observed. For clay loading up to 1 wt% nanocomposite films remained transparent and exhibited a decrease in thermal expansion coefficient (106 μ m .°C⁻¹) and provided oxygen permeability comparable with poly(ethylene terephthalate) films.

The potential and versatility of atom transfer nitroxide radical coupling (ATNRC) reaction was demonstrated for the preparation of polystyrene/clay nanocomposites with exfoliated morphology [56]. The general strategy relied on the intercalation of quaternary ammonium-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) with sodium montmorillonite was reported in the Figure 1.11. Then the nitroxide containing clay was coupled with the complementary bromide-end functionalized polystyrene. The latter was prepared by ATRP. The intercalable quaternary ammonium TEMPO was firstly synthesized from 4-dimethylamino-TEMPO and methyl bromide. The polymer-clay coupling reaction was performed in toluene under thermal conditions (120°C, 4 h) in presence of N,N,N',N'',N'',Pentamethyl diethylenetriamine and copper chloride.



Figure 1.11 – Schematic representation of the general strategy applied to the preparation of Polystyrenemontmorillonite nanocomposites via versible atom transfer nitroxide radical coupling. Reproduced from reference [56] with permission by Wiley.

Combining XRD and TEM, the authors came to the conclusion that both exfoliated and intercalated structures co-exist in the nanocomposites. From the TEM, it seemed that the latter morphology occurred more frequently for higher clay loading content (Figure 1.12).

1.6 Polymer-clay nanocomposites and radical-mediated polymerization methods

In this section, we mainly focus on surface-initiated controlled/living radical polymerization process for the preparation of polymer-decorated nanoclays. However, important reference on traditional free radical polymerization is also discussed. The basic advantage of surface initiated polymerization originates from a sound assumption that exfoliation could be facilitated by polymer chains growing from nanofiller surfaces, leading to fine dispersion. Traditional *in situ* intercalative polymerization meth-



Figure 1.12 – TEM micrographs showing the exfoliated/intercalated structure of polystyrene-montmorillonite nanocomposites via versible atom transfer nitroxide radical coupling Reproduced from reference [56] with permission by Wiley.

ods involves the initial swelling of layered silicates within the liquid monomer or a monomer solution to enable formation of the polymer within the monomer-intercalated sheets. In its simplest implementation, polymerization is initiated by simple diffusion of suitable initiator or catalyst (Figure 1.13) [57, 58, 59, 60].



Figure 1.13 – Schematic representation showing the various events, including surface clay polymer grafting and in-solution growth of polymer chains, occurring simultaneously during the preparation of polymer-clay nanocomposites. Reproduced from reference [60] with permission by American Chemical Society.

Herein, we have purposely concentrated our discussion to in situ processes involving initiation or propagation of the polymerization from the clay surface. In 2003, the group of C. Advincula discussed the grafting of polystyrene from the surface of clay via free radical polymerization [42]. Symmetric and asymmetric azobisisobutyronitrile (AIBN)-analogue initiators bearing two cationic groups at both chain ends and one cationic group at one end, respectively, were synthesized from 4,4'-azobis(4-cyanovaleric acid) precursor (Figure 1.14). Preparation of the asymmetric initiator involves blocking of one carboxyl acid end through esterification with butanol.

Thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) analyses suggested completion of the Na^+ ion exchange with the two types of initiators. However, organization of the mono- and di-cationic initiators differed significantly and was mainly controlled by the interaction between the surfactant cationic ends and the negative clay layer surface. The assumed intercalated organization is depicted in Figure 1.15. On the basis of the XRD-determined *d*-spacing values, the authors suggested two intercalation patterns for the dicationic initiator where the quaternary ammonium



Figure 1.14 – Schematic illustration of the preparation routes to mono- and di-cationic free radical initiators for the chemical modification of clay interlayer space allowing further growth of polymer chains via surface initiated process. Reproduced from reference [42] with permission by the American Chemical Society.

end-groups may interact electrostatically either with the surfaces of two neighbouring sheets or with the surface of a unique clay layer. This type of molecular arrangement at layer surface leads to larger *d*-spacing as compared to what was observed for the monocationic *AIBN* derivative.



Figure 1.15 – Schematic illustration of organization of mono- and di-cationic free radical initiators within clay interlayer space. Reproduced from reference [42] with permission by the American Chemical Society.

Presence of polystyrene on clay surface was evidenced for the two types of surface-initiated polymerization (SIP) initiator by FTIR spectroscopy. The polymerization reactions were conducted at 60 °C for 72 h under a N_2 atmosphere. Size-exclusion chromatography analyses (SEC) suggested that the presence of clay nanostructures in the polymerization mixture definitely affects the growth of the free polymer chains and that monocationic initiator enabled formation of polymer with higher molecular weight leading to a completely exfoliated structure. In contrast, the XRD data indicated intercalated clay when the dicationic initiator was used. This difference in behavior was rationalized based on time scale of diffusion of the monomer and kinetics of free radical polymerization in solution. This fundamental study clearly highlighted important features of preparation of polymer clay nanocomposites via surface initiated polymerization, i.e. polymer can only grow within the clay gallery when monomer effectively diffuses into the radicals within the interlayer spacing, clay dispersion and monomer diffusion are crucial factors in performing a successful SIP and in achieving complete exfoliated clay structures.

Cui *et al.* [61] discussed the first preparation of exfoliated poly(methyl methacrylate)(PMMA)/clay nanocomposites *via* in situ polymerization method initiated with a coordination catalyst. The strategy involved the anchoring of the polymerization catalyst, namely, nickel(II) acetylacetonate, onto the surfaces and/or into the interlayer of the clay and the subsequent polymerization of MMA (Figure 1.16).



Figure 1.16 – Schematic illustration of synthesis path towards the formation of PMMA-clay nanocomposites using clay-anchored nickel-based catalyst. Reproduced from reference [61] with permission by American Chemical Society.

In order to control length and length distribution of surface-grafted polymer chains as well as to provide opportunity for designing grafted block copolymers, controlled/"living" radical graft polymerization was applied to design polymer/clay nanocomposites. Bifunctional intercalator containing a quaternary ammonium end for anchoring to montmorillonite surface via cation exchange with Na^+ ions and either a bromine terminus [62] or nitroxide end moiety [63] to activate atom transfer radical polymerization (ATRP) or nitroxide-mediated radical polymerization (NMP), respectively (Figure 1.17). ATRP initiator-modified montmorillonite exhibited improved solubility in acetone that was selected as polymerization solvent to favor accessibility towards the within-layered silicate incorporated initiating sites. First-order kinetic behaviour was observed for the polymerization of MMA at 60°C in presence of *CuBr* and 1,1,4,7,10,10-hexamethyltriethylenetetramine as transition metal catalyst and ligand, respectively. SEC analysis using multi angle light scattering detection was performed on cleaved polymer grafts confirmed that the molecular weight increases with by-TGA determined conversion and the polydispersity index remained below 1.14. For polymerization time lower than 4 h, the layered structure of polymer-grafted clay was preserved while after 4 h of polymerization no diffraction peak was observed in the XRD patter suggesting delamination of clay layers.

No TEM morphology investigation was reported by the authors however, this initial study on implemented surface initiated controlled radical polymerization (SI-CRP) for the design of polymer clay nanocomposites inspired over research groups enlarging the scope of in situ ATRP to styrene and n-butyl acrylate [64] and glycidyl methacrylate (GMA) [65]. Prior to polymerization the montmorillonite was ion-exchanged with pre-synthesized 11'-(N,N,N-trimethylammonium bromide)-undecyl-2-bromo-2-methyl propionate (Figure 1.18). Chemical modification improved significantly the dispersion ability of the nanofiller due notably to the compatibility of surface-grafted polymer chains - PGMA - with the polymeric matrix - epoxy resin with triamine hardener - yielding an increase in the storage modulus in the rubbery plateau domain.

Roghani-Mamaqani *et al.* [66] combined the use of ARTP initiator, namely ethyl α -bromoisobutyrate, dissolved in styrene with vinyl-clay, prepared *via* cation exchanged of native clay with quaternary



Figure 1.17 – Schematic illustration of the intercalation an ATRP-initiator (11-(N,N,N-trimethylammonium bromide)undecanyl-2-bromoisobutyrate) containing an ionic anchoring group for intercalation between individual layers of a silicate via cation exchange. Reproduced from reference [62] with permission by the Royal Society of Chemistry.

benzylic ammonium cation with a vinyl end group - *vinylbenzyltrimethylammonium* - to prepare tailormade polystyrene nanocomposites. The approach was extended to atom transfer radical polymerization using activators generated by electron transfer (AGET ATRP) for the synthesis of poly(styrene-co-butyl acrylate)/clay nanocomposite [67]. Dodecyltrimethylammonium bromide (DDTMAB) was combined to vinylbenzyltrimethylammonium chloride (VBTMAC) to chemically modify the surface of sodium montmorillonite (Figure 1.19). The former enables increasing the interlayer *d*-spacing while the latter provides reactive double bond to firmly anchor the poly(styrene-*co*-butyl acrylate) chains in the course of the propagation process.

Intercalation of a trifunctional ATRP initiator containing a cationic ammonium anion and a *C*18 aliphatic arm, afforded a series of well-defined A(3)-type star polymer/clay nanocomposites (Figure 1.20) [68]. Methyl methacrylate was polymerized *in situ* in toluene in presence of N,N,N',N",N"-pentamethyldiethylenetriamine and copper(I) bromide at 90°C for 16 h. Linear kinetic plot together with the increase in molecular weight with conversion suggested controlled radical polymerization MMA. Complex morphology, with partial intercalation/exfoliation, was obtained depending on clay loading.

Survey of the polymer-clay nanocomposites literature indicates the covalent anchoring of controlled radical polymerization initiators. For instance, ATRP-initiator modified clay was obtained *via* a two-step process [69]. First, clay with nucleophilic surface reactivity was obtained *via* silanization with 3-aminopropyltriethoxysilane. Second, aminated clay was allowed to react 12 h at room temperature with 2-bromoisobutyryl bromide in presence of trimethylamine. The as-designed macroiniator proved suitable for the polymerization of glycidyl methacrylate. X-ray diffraction measurements, thermogravimetric analysis and XPS analyses suggested that the nanocomposites exhibit exfoliated morphology with PGMA-like bulk and surface characteristics. Graft polymer loading up to 65 wt% was obtained. Karejosa *et al.* followed another approach relying on the use of presynthesized initial synthesis of tom transfer radical polymerization (ATRP) initiator-bearing silane derivative [70]. 11-(2-Bromo-2-methyl)propionyl-oxy-undecyl trichlorosilane the Karstedt catalyzed adduct from 10-undecen-1-ylbromo-2-methylpriopinate and trichlorosilane, was reacted with ion exchanged (octadecylamine) and acid treated (*HNO*₃) clay. The macroinitiator particles were used to the thermal (90°C) polymerization



Figure 1.18 – Schematic illustration of the intercalation of an ATRP-initiator (11'-(N,N,N-trimethylammonium bromide)-undecyl-2-bromo-2-methyl propionate) containing an ionic anchoring group for intercalation between individual layers of a silicate via cation exchange. Reproduced from reference [64] with permission by Wiley.



Figure 1.19 – Schematic illustration of the combined intercalation a polymerizable surfactant (vinylbenzyltrimethylammonium chloride together with an interlayer spacer (dodecyltrimethylammonium bromide) containing both an ionic anchoring group for intercalation between individual layers of a silicate via cation exchange. Reproduced from reference [67] with permission by Springer.

in bulk monomer solution or in DMSO of butyl acrylate (BuA) and methyl methacrylate (MMA) on the clay surface (Figure 1.21). Success of the copolymerization process was ascertained by FTIR and TGA measurements.

Preparation of tailor-made hybrid nanostructures through surface initiated ATRP (SI-ATRP) of ethyl acrylate was reported by Singha's group based on the esterification of the surface hydroxyl groups of clay (Cloisite 30B) with 2-bromopropionyl bromide in anhydrous tetrahydrofuran using triethylamine as catalyst (Figure 1.22) [71, 72]. The so-designed bromopropionate-containing clay was to prone to thermally initiate (90°C) controlled radical polymerization of ethylacrylate in presence of CuBr, 2,2'-bipyridine and methyl 2-bromopropionate as sacrificial initiator. Qualitative and quantitative data confirming the grafting of the initiator were obtained by means or FTIR. Indeed, on the one hand, characteristic vibration of the carbonyl group was observed at 1746 cm⁻¹ ascertaining the presence of the propionate moiety. On the other hand, monitoring of the intensity ratio of the said absorption band at 1746 cm⁻¹ to the intensity of the one at 1049 cm⁻¹ (Si-O in plane stretching that is unaffected for grafted clays) yielded to carbonyl index determination. Grafting percentage up to 40% was obtained for the initiator on clay depending on the feed ratios used in the esterification step.



Figure 1.20 – Quaternization of trifunctional ATRP initiator serving for the preparation of A(3)-type star polymer/clay nanocomposites by in-situ atom transfer radical polymerization. Reproduced from reference [68] with permission by Wiley.



Figure 1.21 – Schematic illustration of the preparation of an ATRP-initiator (11-(2-Bromo-2-methyl)propionyloxy-undecyl trichlorosilane) containing a trichloro silane anchoring group for incorporation between individual layers of a silicate via silanization. Reproduced from reference [70] by permission of Wiley.

Complementary data obtained by XPS, XRD and TGA pointed out the success of both initiator grafting and growth of poly(ethyl acrylate) chains. For instance, the *d*-spacing increased from 1.85 nm to 2.31 nm after esterification while no diffraction peak was seen after polymerization. These results were fully substantiated by TEM observations showing an increase in the interlamellar distance and dispersion of disordered clay platelet for the initiator- and polymer-functionalized clays, respectively (Figure 1.23).

With the aim of prepared dielectric elastomer materials, poly(BuA-*co*-MMA)-grafted nanofiller was mixed with poly(BuA-*co*-MMA) [70]. Composite films were obtained *via* a solvent evaporation process involving initial dispersion of copolymer-grafted clay in toluene and poly(BuA-*co*-MMA) matrix. Although the presence of surface grafted poly(BuA-*co*-MMA) enhanced significantly the homo-



Figure 1.22 – Schematic illustration of the strategy applied to prepare polyacrylate-clay nanocomposites via the combined used of surface-attached and sacrificial ATRP initiators. Reproduced from reference [72] with permission by Wiley.

geneous dispersion of the clay into the corresponding matrix, XRD measurements revealed superiority of the solution (DMSO) polymerization process other the bulk one. Indeed, diffraction peak corresponding to a layer distance of 1.87 nm was observed for the polymer grafted clay synthesized in a bulk monomer, while for the in-solution polymerized sample, only a diffuse halo reminiscent of the amorphous polymeric matrix was observed. This was further confirmed by TEM observations (Figure 1.24).

Comprehensive investigation reported by Singha and co-workers highlighted the role of nanoclay as an additive in the ATRP of ethyl acrylate (Figure 1.25) [73]. The polymerization was performed in bulk in presence of methyl 2-bromopropionate, *CuBr* and 2,2-bipyridine. Importance of interaction between the nanoclay and the monomer was evidenced by using native (Cloisite Na^+) and hydrophobized (Cloisite 30B, and Cloisite 20A) clays exhibiting variations in their gallery heights. The authors demonstrated thorough investigation of polymerization kinetics the accelerating effect induced by nanoclay additives. This effect was controlled by dispersion time of the clay particles in the monomer prior to polymerization as well as the clay loading. Indeed, significant increase in the polymerization rate was noticed as the value for the apparent rate constant increased by 62% for 1 h dispersion, 247% for 10 h, and 866% for 20 h.

Although the reported route did not utilize surface initiation, it is worth to mention as it allowed one pot preparation of tailor-made polymer nanocomposites, i.e. with controlled molecular weights and well-defined end functionalities and mostly exfoliated structure (Figure 1.26).

Influence of nanoclay on bulk polymerization of MMA was further investigated by the group of P. Karayannidis using commercially available organically modified montmorillonite clays (Cloisite 15A, Cloisite 25A, and Cloisite 30B) and benzoyl peroxide as free radical initiator [60]. The authors pointed out the crucial role of the organic montmorillonite modifier. Indeed, while sodium MMT induced a retarding effect, some of the organoclays enhanced both reaction rate and conversion over the same period of time. This feature was assigned to the role of the ammonium salt diffusion-controlled phenomena occurring during polymerization.



Figure 1.23 – TEM micrographs showing the structures of (a) initiator grafted clay and (b) functionalized polyacrylate-clay nanocomposites casting from diluted THF suspension. Reproduced from reference [72] with permission by Wiley.

Synthesis of hybrid architectures with well-defined structure, morphology and composition remains a hot topic in current materials science as it is expected to provide scientific breakthrough beyond traditional polymer chemistry and physics and to affect other fields as medicine, biology, nanotechnology... One of the keys towards such complex organic-inorganic nanostructured materials consist in combining polymerization processes followed, eventually, by post-polymerization decoration of monomers' functional groups or end-functionalization of the polymer chains via advanced coupling methods [74]. Here-below we report on the major advancements discussed in the recent literature about combination of such synthesis methods for the design of tailor made clay-containing polymer nanocomposites. This contribution, as a part of our ongoing research on implementation of radical-mediated both polymerization and radical addition reactions, initiated from the surface of or organic (carbon nanotubes, monoliths-constituting polymer nuclei) [44, 75] and inorganic particles (clay, metal oxide-based nanomagnet) [29, 76] we mainly focused on multi-mechanisms-based methods involving, in the course of at least one of the synthetic step, free radical species.

1.7 Polymer-clay nanocomposites and tandem preparation methods

Marrying click chemistry with living/controlled polymerization methods has proved a smart and elegant route to design an impressive library of tailor-made macromolecular architectures [77, 78] and composite materials [79, 80]. This success results from the versatility and robustness of both these processes including tolerance toward a plethora of solvents and functional groups, use of, including water, and relatively inexpensive and benign starting materials such as commercially available vinyl monomers, technical grade solvents or water.

The general idea associated with the use of block copolymers-modified nanoparticles for compatibilizing the said nanostructures with polymer blends relies on the possibility for the blocks to provide fa-



Figure 1.24 – TEM micrographs showing the structures of related poly(BuA-*co*-MMA)-clay nanocomposites (3% loading) obtained via (left) bulk and (right) solution (DMSO) processes. Reproduced from reference [70] with permission by Wiley.



Figure 1.25 – Semilogarithmic kinetic plots for the ATRP of ethylacrylate in bulk at 90°C in presence of Closite 30B. The plots illustrate the beneficial effect of the clay of the polymerization rates. Reproduced from reference [73] with permission by American Chemical Society.

vorable interactions and/or form entanglements with the appropriate partners of the blend. This strategy has been successfully applied to polymer blends since long and has be envisioned in the case of dispersion of clay particles in polymer blends over the last years [81, 82]. Jianbo Di and Dotsevi Y. Sogah reported on the synthesis of poly(styrene-b-caprolactone)/silicate nanocomposites *via* a one-step, one-pot *in-situ* block copolymerization approach relying on the simultaneous living free radical polymerization and anionic ring-opening polymerization of styrene and epsilon-caprolactone, respectively [43]. Multifunctional initiator containing a benzyltrimethylammonium group allowing anchoring onto silicate layers surface via ion exchange, together with a primary alcohol and alkoxyamine providing initiating sites for living ring opening polymerization of heterocyclic ethers/lactones and for nitroxide-mediated living free radical polymerization was synthesized using benzoic acid 2-(4-(chloromethyl)phenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl ester as starting material [5]. By using initiator bearing orthogonal reactive sites, the authors expected producing in a straightforward way block copolymer/silicate nanocomposites with exfoliated morphology which had been demonstrated by previous literature to be highly challenging [83]. The originality of the approach relied on the attachment of the PS and PCl chains to the surface of the silicate layers at the junction between the two blocks (Figure 1.27).

XRD measurements brought evidence for the successful intercalation of the bulky initiator (increase in the interlayer spacer from 1.18 nm to 2.03 nm, the crystalline structure of PCL (with peaks



Figure 1.26 – TEM micrograph showing the exfoliated nature of Cloisite 30B dispersed during 10h in the monomer prior to bulk polymerization at 90°C. Reproduced from reference [73] with permission by American Chemical Society.

at 21.5° and 23.8°) and exfoliated morphology (absence of diffraction peaks in the range 2θ between 0 and 16°). The latter feature was complemented by scanning transmission electron microscopy clearly showing dispersion of silicate particles into single layers with random orientation within in the polymer matrix (Figure 1.28).

The group of Singha extended its investigation on the use of bromide-clay as ATRP macroinitiator to the preparation of all acrylic block copolymer/clay nanocomposites [84]. Bromo-functionalized poly(hydroxyl ethylacrylate)-grafted clay as prepared in reference [72] served as macroinitiator for the preparation of block copolymer-nanofiller with MMA. Linear kinetic plot and linear increase in molecular weight vs reaction time were considered as indicative of the controlled character of the EHA polymerization. ¹*HNMR* spectroscopic analysis of cleaved copolymer evidenced the successful block copolymerization of EHA with MMA and confirmed the presence of living -Br end units.

The successful click-mediated intercalation step, presented in Figure 1.7 and affording methacrylic units into the interlayer regions of organophilic clay, was followed by typical free-radical photopolymerization (300 nm, 3 mW cm⁻¹) of the said-particles and MMA [85]. Benzoin was used as photoinitiator. Random dispersion of silicate layers in the PMMA matrix with exfoliation/intercalated structures depending on the clay loading was suggested based on XRD, TEM and atomic-force microscopy (AFM) measurements.

Singha *et al.* described the combined use of surface-initiated ATRP from nancoclay surface and post polymerization functionalization via Diels-Alder (DA) and retro-DA (rDA) click reactions to prepare thermoreversible polymer which can have potential applications in paints and coating (Figure 1.29) [86].

Poly(2-ethylhexylacrylate)/clay (PEHA) nanocomposite was prepared in a first polymerization step via the SI-ATRP of 2-ethylhexyl acrylate from bromo-functionalized nanoclay and was further used as macroinitiator for the preparation of block-copolymer-clay nanocomposites using furfuryl methacrylate (FMA), as reactive methacrylate comonomer. Furfuryl groups of PFMA unit of block copolymer PEHA-b-PFMA/clay nanocomposite was used as a diene in DA reaction with bismaleimide as dienophile. XRD and TEM investigations revealed the dispersion of the nanoclay within the polymeric matrix (Figure 1.30) while differential scanning analysis was applied to investigate the thermoreversible property of the polymer/clay nanocomposite.

Success of both disconnection, *i.e.* rDA occurring at $(160^{\circ}C)$ and reconnection, *i.e.* DA [4+2] cycloaddition (60°C), of linkage between the fufuryl and maleimide functionalities provided block



Figure 1.27 – Schematic illustration of the general strategy applied to the preparation of poly(styrene-b-caprolactone)/silicate nanocomposites via a one-step, one-pot in-situ block copolymerization approach. The particularity of the so-designed polymer-clay nanocomposites rely on the attachment of the two homopolymeric segments at the junction between the two blocks. Reproduced from reference [43] with permission by American Chemical Society.

copolymer-clay nanocomposites with reversible crosslinking ability.

1.8 Polymer-clay nanocomposites and radical-mediated photopolymerization methods

As for thermal processes, photo-driven polymerization enables preparation of polymers and copolymers with well-controlled molecular weight and topology starting from a broad range of functional monomers with the additional advantages of fast polymerization rates, easy process, and low temperature. To date, photo-polymerization in its large variety of implementations has also been successfully applied to the synthesis of tailor made polymer-based nanocomposites [87]. Although they are wellestablished methods and particularly well-suited to the field of polymer nanocomposite preparation, we do not emphasize herein of thiol-mediated processes involving polymerization with acrylate or ene derivatives [88]. The group of Yagci (2006) discussed the use of intercalated phenacyl pyridinium salt initiators to grow to grow polymer chains inside the montmorillonite galleries upon UV-irradiation [89]. N-phenacyl N,N-dimethylanilinium hexafluorophosphate, the product from the reaction between bromoacetophenone and N,Ndimethylaniline, was inserted via an ion exchanged with $MMT - Na^+$ leading to an increase in the basal spacing from 1.21 nm to 1.76 nm. The as-designed macroinitiator served for the polymerization of MMA. The authors assumed that electronically excited N-phenacyl N,N-dimethylanilinium hexafluorophosphate underwent homolytic cleavage leading to the formation of free radicals able to initiate the polymerization (Figure 1.31). Nitrogen-degassed homogeneous mixture of MMA and initiator-modified clay (1, 3, and 5% of the monomer by weight) was placed in a reactor emitting light at $\lambda > 300$ nm equipped with 16 Philips 8W/06 lamps and a cooling system, ensure true photo-process.

For the nanocomposites containing 3 wt% of inorganic component, large aggregates (with size



Figure 1.28 – STEM micrograph showing the dispersion of poly(styrene-b-caprolactone)-grafted clay platelets. Reproduced from reference [43] with permission by American Chemical Society.



Figure 1.29 – Schematic illustration of the reversible crosslinking of poly(2-ethylhexylacrylate)-block-poly(furfuryl methacrylate)-clay nanocomposites via thermally driven Diels-Alder (DA) and retro-DA (rDA) click reactions. Reproduced from reference [86] with permission by Columbia International Publishing.

up to 11.11 μ m) together with small aggregated particles were observed by SEM (Figure 1.32 part a). These structural elements were assigned to intercalated or partially exfoliated structure suggesting poor interaction of the initiator-modified interlayer galleries with PMMA matrix. Decreasing the clay content to 1wt%, was found beneficial to exfoliation as solely small clay particles' clusters (with size of one order of magnitude lower at about 1.18 μ m) were seen by SEM (Part b in Figure 1.32). This finding was further confirmed by TEM.

In a 2008 report, Tan *et al.* investigated the incorporation of an organic silane photoinitiator obtained through the reaction of (3-isocyanatopropyl) triethoxysilane (IPS) and 2-hydroxy-2-methyl-1phenylpropane-1-one (1173) [90]. As schematically shown in Figure 1.33, the originality of the approach relied on the implementation of sol-gel reaction between cationic triethoxysilanepropylamineformylethyl trimethyl ammonium iodide (APS) and the initiator silane to afford quaternary ammonium species bearing photo-cleavable units. The sol-gel step was achieved at 50°C in the dark to avoid any photolysis events. After 24 h of reaction, a water dispersion of sodium montmorillonite was added for the ion exchange process.



Figure 1.30 - TEM micrographs showing the (c, d) intercalated morphology of thermoreversible block copolymer-clay nanocomposites where no aggregates were observed as for (a, b) native clay. Reproduced from reference [86] with permission by Columbia International Publishing.



Figure 1.31 – Scheme of the mechanism for the initiation of the free radical polymerization of MMA via hemolytic cleavage of electronically excited N-phenacyl N,N-dimethylanilinium hexafluorophosphate. Reproduced from reference [88] with permission by Wiley.

The functionalized clay (5 wt% loading) was further mixed with 1,6-hexanediol diacrylate (30%) and urethane acrylate oligomer (70%) to produce polyurethane-montmorillonite nanocomposites through photo-irradiation under a 2 kW mercury lamp. Ratio between the two silanes was changed (from 1/1 to 1/5 for quaternary ammonium silane/photo-initiator silane) and corresponding effects on XRD patterns and TEM morphologies of modified clays and polymer nanocomposites were estimated. XRD measurements confirmed the effective incorporation of the sol-gel products providing increase in the basal spacing from 1.31 nm up to 3.65 nm. The larger increase was obtained for the initiator silane rich formulations. After photopolymerization, the XRD traces recorded for the clay-polyurethane nanocomposites demonstrated the disappearance of all diffraction peaks disappeared, independently of the silane composition. The authors rationalized these observations on the basis of either by the ordered exfoliation of the silicate or high disordering of the clay, referred to as disordered exfoliation. TEM morphology investigations displayed the presence of 1 nm thick intercalated layers stacked together in parallel, while dispersion of monolayer in the polyurethane matrix was not observed (Figure 1.34).

Cationic exchange process for the within clay galleries incorporation of organoclays exhibiting



Figure 1.32 – SEM micrographs comparing fracture surfaces of PMMA-clay nanocomposites with (top) 3% and (bottom) 1% clay loading content. Reproduced from reference [88] with permission by Wiley.



Figure 1.33 – Schematic illustration of ammonium moiety-containing photo-initiator prepared by sol-gel from the corresponding silane precursors and further intercalated within clay layers via ion exchange process. Reproduced from reference [90] with permission by Elsevier.

a dual role as intercalant and initiator for photopolymerization has been exploited by other research groups. Tertiary or quaternary amine derivatives have thus been synthesized using hydroxy-2-methyl-



Figure 1.34 – TEM micrographs showing the morphology of polyurethane-clay nanocomposites (5% clay loading) prepared via photoprocess using various content of quaternary ammonium/photo-initiator silanes. Reproduced from reference [90] with permission by Elsevier.

1-phenylpropane-1-one [91], benzophenone [92], or 2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl) phenyl]-1-butanone [93] as precursors with free radical generation ability. In the latter case, the initiator bared two cationic charge providing two possibilities for interactions with the clay layer as discussed here-above (Figure 1.35). Upon exposure to 30 mW cm⁻¹ light intensity, cleavage of the α -amino ketone bond, two type of radicals were formed initiating the growth of urethane acrylate oligomers.



Figure 1.35 – Schematic illustration of the general synthetic route applied to the preparation of polymer-clay nanocomposites by photopolymerization using intercalated photoinitiator bearing two cationic groups. Reproduced from reference [93] with permission by Elsevier.

Real-time infrared spectroscopy monitoring enabled studying photopolymerization kinetics, optimizing the irradiation time and evaluating the effect of the presence of nanoclay in the reactive mixture on the polymerization process. The content in initiator containing montmorillonite was the key parameter affecting both photopolymerization rate and final double bond conversion. As expected, the higher the modified clay concentration, the earlier the polymerization started and the faster the polymerization rate was. For instance, when 1 wt% of modified clay was added, the polymerization started after 60s while it was nearly instantaneous when the loading was increased to 5 wt%.

Other studies reported on the use of polymerizable dispersants acting as both intercalating agent and reacting monomer in the course of the photopolymerization step [94]. Representative examples mention the use of acrylamide [95], tetradecylethylmethacrylate dimethylammonium bromide and undecylmethacrylate trimethylammonium bromide [96], tetradecyl-2-acryloyloxy(ethyl)dimethylammonium bromide, and octadecyl-2-acryloyloxy(ethyl)dimethylammonium bromide [88]. Covalent strategies for the robust incorporation of either initiator/catalyst, polymerizable groups or free radical providers have also been described in the context of photopolymerization.

Thiolated-bentonite served as chain transfer agent for the bulk polymerization of glycidyl methacrylate initiated by 2,2' azobisisobutyronitrile [97]. The chains growth was achieved upon exposure to UV light in the (365 nm, 5 mW.cm⁻¹) for 2000 s under magnetic stirring. Surface analysis by XPS was primarily used to ascertain not only the grafting of (3-mercaptopropyl)-trimethoxysilane within the clay layers but also the surface attachment of in solution grown PGMA chains. PGMA mass loading up to 81 wt% was determined depending on the preparation conditions. Oxirane-decorated clay nanofillers were dispersed within epoxy matrix based on di-glycidyl ether of bisphenol A through thermal reaction (curing 4 h at 180°C followed by post curing at 200°C for 1 h) using 4,4-diaminodiphenyl sulfone as hardener. Bulk propertied of the as-designed polymer nanocomposites with a pure clay loading of 3% were investigated by means of dynamic mechanical analysis and modulated force thermomechanometry. Tan δ spectra revealed a shift in the main relaxation peak towards higher temperatures upon addition of polymer-functionalized nanoclays. General improvement in the mechanical properties, namely increase in the storage modulus E_0 and drop in the loss factor, was consistent with the fracture behavior as observed by SEM. In another study, the grafting of methacrylate monomer onto the hydroxyl groups of organo-modified clay [98]. Cloisite 30B containing intercalated methylbis(2-hydroxyethyl)(tallow alkyl)ammonium via cationic interaction was allowed to react with methacryloyl chloride in presence of trimethylamine. The monomer-containing clay was dispersed in polysulfone dimethacrylate in CH_2Cl_2 solution, and the polymerization was initiated after precautious stirring and homogenization of the reactive solution upon UV-exposure for 4h under UV lamps emitting light at $\lambda > 350$ nm using 2.2dimethoxy-2-phenylacetophenone as photo-initiator. A cooling system was employed to avoid any side thermal effect. Such in situ photo-triggered crosslinking polymerization afforded exfoliated morphology of the silicate layers. Yagci et al. explored the chemical modification of bentonite with N,Ndimethylaminopropyltrimethoxysilane to prepare clay particles bearing hydrogen-donor groups (Figure 1.36) [99]. When used in combination with benzophenone as photosensitizer, the dimethylaminografted bentonite could initiate the photo-triggered polymerization (365 nm, 5 mW.cm⁻¹, 2000 s) of glycidyl methacrylate. Optical observations of chloroform suspensions of native clay, clay macroinitiator and PGMA/clay nanocomposites pleaded for the success of each functionalization steps affording improved solubility. Quantitative date were gathered from XRD and TEM analyses showing an increase in the interlayer spacing from 1.2 nm for purified clay to 1.8 nm after silanization and up to ≈ 5 nm for the polymer grafted clay.

In their work, Xie *et al.* prepared nanocomposites *via* intercalating triacrylated siloxane into the cetyltrimethyl ammonium bromide-modified montmorillointe layers prior to performing thiol-ene polymerization reaction by exposure to light source the reactive clay formulation based on bisphenol A epoxy acrylate and tri-functional thiol (Figure 1.37) [100]. Combination of FTIR, XRD, and TGA



Figure 1.36 – Schematic representation of the synthetic route applied to the preparation of polymer-clay nanocomposites by photopolymerization using clay-grafted dimethyl amine as hydrogen group in combination with benzophenone as photosensitizer. Reproduced from reference [99] with permission by Wiley

measurements ascertained the successful grafting of the triacrylate derivative to the clay interlayers. The *d*-spacing was enlarged from 1.55 nm for the pristine material to 2.23 nm for the polymerizable clay. Accordingly, TGA confirmed the increase in organics content following successive incorporation of surfactant and triacrylate. The latter gave rise to the characteristic signals of carbonyl group in ester moiety and acrylate double bond at 1732 cm^{-1} and 1410 cm^{-1} , respectively, after clay modification.



Figure 1.37 – Schematic representation of the synthetic route applied to the preparation of crosslinked polymerclay nanocomposites by photopolymerization using clay-grafted triacrylate derivative in combination with cation exchanged hydrophobic quaternary ammonium. Reproduced from reference [100] with permission by Elsevier.

On the basis of a qualitative analysis of HR-TEM micropgraphs, the authors concluded that the thiol-ene photopolymerization process occurring in the confine of the interlayer of reactive montmorillonite afforded intercalated structure and random orientation of layers in the matrix. Thermomechanical behavior of the nanocomposites was also analyzed. Although the polymer nanocomposites exhibited similar thermal behavior as pure polymer, the onset temperature of thermal decomposition and the char residue slightly rose as the clay loading increased. DMA also suggested an increase if the glass temperature transition of about 4°C when the clay loading reached 5 wt%. The presence of a unique peak without any multimodal behavior in the tan δ curves, was considered as indicative for improved compatibility of the organic-modified clay with the polymeric matrix (Figure 1.38).



Figure 1.38 – Plots of the temperature dependences of the storage modulus (E') and Tan δ for crosslinked polymer-clay nanocomposites obtained by photopolymerization using clay-grafted triacrylate derivative in combination with cation exchanged hydrophobic quaternary ammonium. Reproduced from reference [100] with permission by Elsevier.

As a part of our ongoing research project aiming at designing polymer-nanoparticle composite materials with well-defined surface functionality [76, 101, 102], we developed a set of generic polymergrafted nanofillers with versatile reactivity towards (meth)acrylic polymeric matrix [103]. As schematically depicted in Figure 1.39, hydroxylated clay particles are reacted with silane dervatives providing either methacrylic- or bromide-modified clays. The former can react in the course of free radical polymerization while the latter enables initiation of controlled radical polymerization processes. Experimental conditions for both approaches were adapted to photo-driven initiation enabling fast and efficient polymerization. As evidenced by the here-above discussion, implementation of photo-triggered ATRP as not yet been proposed for the design of reactive polymer-clay nanofillers and here we present fragmentary results for the case of propargyl methacrylate [103]. Of particular interest, the interlayer d-spacing exhibited direct dependence on the polymerization time allowing the design of tailor made reactive nanofillers with predictable interlayer spacing. The so-obtained polymer-grafted clays exhibit versatile clickable and electrophilic characters as they can be reacted with low (mercaptosuccinic acid and azidomethyl benzene) and high (polysaccharides, bio-based epoxy resins from epoxidized vegetable oils) molecular weight compounds, via thiol-ene, thiol-yne, thiol-epoxy, CuAAC and ring opening reactions.

Silicate layers chemically modified with dithiocarbarmate photoiniferter, namely 4-(N,N-diethyldithiocarbamylmethyl)benzyltrimethylammonium bromide, were applied to living free radical polymerization of a variety of monomers, including styrene, methyl methacrylate, tert-butyl methacrylate [104]. In all the cases, the polymer chains were attached to the silicate layers through ionic interactions. Of particular interest, the method worked reproducibly and enabled the preparation of well-dispersed polymer nanocomposites, even for nanocomposites with high (above 20 wt%) silicate contents. The PMMAbased nanocomposites exhibited higher storage moduli compared with neat PMMA.

1.9 Polymer-clay nanocomposites and miniemulsion methods

Hybrid materials consisting in polymer-encapsulated nanostructures can be readily prepared via emulsion polymerization and the process has been considered for the preparation of varied polymer-clay



Figure 1.39 – Schematic illustration of the general synthetic route developed for the preparation of a series of generic clay-based nanofillers with reactivity towards epoxy resin precursors and functional thiols and azides Click partners.

nanocomposites including PMMA-[105], PS-[106], [107], poly(vinyl chloride-) [108], poly(styreneco-methyl methacrylate)-montmorillonite [109]. The mini-emulsion method exhibits specific attributes as compared to other polymerization methods such as elimination of harmful solvents, high monomer conversion and molecular weight, nucleation step is not as complex as in emulsion polymerization accounting for its success to encapsulate both non-exfoliable and exfoliable organic and inorganic particles. Major studies published before 2010 and dealing with the implementation of miniemulsion polymerization for the design of structured clay/polymer nanocomposites have been discussed by Faucheu *et al.* in a review article publish in Polymer [110]. Of particular relevance to the topic of the present contribution, one may cite the study by Roghani-Mamaqani and coll. dealing with implementation of miniemulsion technique to disperse montmorillonite (Cloisite 30B) platelets within poly(methyl methacrylate) matrix (Figure 1.40)[111].



Figure 1.40 – Schematic representation of the general synthetic route applied to the preparation of poly(methyl methacrylate)-clay nanocomposites by miniemulsion. Reproduced from reference [111] with permission by Springer.

ATRP was used as the polymerization method employing simultaneous reverse and normal ini-

tiation. AIBN, selected as an oil soluble radical initiator, was added to the organic phase containing classical ATRP formulation made of monomer (methyl methacrylate), radical deactivator (copper (II) bromide), ligand (4,4'-dinonyl-2,2'-bipyridine) and initiator (ethyl alpha-bromoisobutyrate) as well as organoclay. The latter was initially dispersed in MMA (1, 2 and 3 wt% vs MMA). The polymerization was initiated via mixing the organic solution with the aqueous surfactant (cetyltrimethylammonium bromide) solution and increasing the temperature to 80°C. In the course of the polymerization performed, the reaction mixture changed from light green to light brown. Droplet size as estimated by DLS measurements on samples taken before the polymerization process was in the range 145-185 nm with low polydispersity index. Correspondingly, SEM imaging revealed homogeneous distribution of spherical polymer particles with sizes around 170 nm (Figure 1.41) while TEM suggested partially exfoliated morphology. Some of these authors extended their miniemulsion approach to the use of activators generated by electron transfer for atom transfer radical polymerization (AGET ATRP) of styrene and butyl acrylate [112]. Ascorbic acid was added as a reducing agent to reduce termination reactions. Latexes with sphere-like morphology were in the size range 140 - 170 nm as determined by dynamic light scattering. Although XRD analysis evidenced the interlayer space increase upon copolymerization, the low molecular weight of the poly(styrene-co-butyl acrylate) did not permit full exfoliation of the clay stacks.





In a recent study, Singha *et al.* reported an interesting alternative for the preparation of polymerdecorated clay particles by cationic reversible addition-fragmentation chain transfer (RAFT) assisted pickering miniemulsion polymerization (Figure 1.42) [113]. 2,2,3,3,3-Pentafluoropropyl acrylate (PFPA), methyl methacrylate (MMA), and n-butyl acrylate (nBA) were copolymerized in miniemulsion using laponite-RDS as stabilizer and S-1-dodecyl-S-(methylbenzyltriethylammonium bromide) trithiocarbonate as RAFT agent. The later played a key role in the preparation process promoting ionic attractiondriven interaction between polymer and clay.

Optimization the laponite (30 wt %) content as well as nature (2-cyano-2-propyl dodecyl trithiocarbonate vs. S-1-dodecyl-S-(methylbenzyltriethylammonium bromide) trithiocarbonate) and content of RAFT (1.2 wt % for S-1-dodecyl-S-(methylbenzyltriethylammonium bromide) trithiocarbonate) agent allowed a drastic increase in the polymerization rate. The miniemulsion was characterized by particle



Figure 1.42 – Schematic representation of the general synthetic route applied to the preparation of polymerclay nanocomposites by cationic reversible addition-fragmentation chain transfer assisted pickering miniemulsion polymerization using a RAFT agent bearing a quaternary ammonium. Reproduced from reference [113] with permission by American Chemical Society.

with sizes in the range between 200 nm and 300 nm resulting in laponite armored spherical copolymer particles as observed by atomic force microscopy and transmission electron microscopy (Figure 1.43).



Spherical orientation of Laponite

Figure 1.43 – TEM micrographs showing fluorinated copolymers-clay nanocomposites obtained by cationic reversible addition-fragmentation chain transfer assisted pickering miniemulsion polymerization. Reproduced from reference [113] with permission by American Chemical Society.

Because of low surface energy, the as-obtained fluorinated copolymer/Laponite are expected to be specialty candidates for hydrophobic coating surfaces or fire-retarding applications because of the presence of polyphosphate in the laponite-RDS.

1.10 Polymer-clay nanocomposites besides radical-mediated polymerization methods

Just thinking about achieving anionic polymerization in the presence of clay-particles may give headaches to most of materials scientists. Indeed, the highly challenging nature of such a process is inherent to the intrinsic hydration characteristics of clay. The on silicate layers-adsorbed water molecules may interfere with growing anion leading to termination of the living propagation step. As such, one may acknowledge the work by Zhang *et al.* who implemented in situ living anionic polymerization to butadiene, styrene and isoprene to prepare a set rubber/clay nanocomposites incorporated homo- and co-polymeric partners [114, 115, 116]. Z. Yenice *et al.* described the preparation of poly(styrene-b-tetrahydrofuran)/clay nanocomposites by mechanistic transformation [82]. Montmorillonite was first modified with 6-[(2-bromo-2-methylpropanoyl)oxy]hexan-1-ammonium chloride via a cation exchange reaction and then used to initiate in situ the atom transfer radical polymerization of styrene. The presence of both intercalated and exfoliated structures were evidenced by TEM. poly(styrene-block-tetrahydrofuran) was finally obtained by mechanistic transformation from ATRP to cationic ring opening polymerization (CROP) using silver hexafluorophosphate as initiator. The so-designed polymer/clay nanocomposites exhibited exfoliated structure. In two reports, Advincula's group investigated the beneficial effects of living anionic surface initiated (SI) polymerization to improve the stabilities and grafting of polymers on clay [117, 118]. The montmorillonite clay surface and intergallery interfaces were intercalated with an organic cation derived from 1,1-diphenylethylene, enabling initiation of anionic polymerization (Figure 1.44).



Figure 1.44 – Schematic illustration of the synthetic route applied to the preparation of polymer-clay nanocomposites by living anionic surface initiated polymerization from clay surface. Reproduced from Reference [118] with permission by ACS.

Dealing with in situ ring opening polymerization, a lot of effort has been devoted to polymerizing ϵ -caprolactone to prepare clay-grafted PCl chains with controlled molecular weight and delaminated morphology [119, 120, 121]. Liao *et al.* proposed the use of microwave-assistance to initiate the polymerization of ϵ -caprolactone in presence of unmodified (Cloisite Na^+) and modified clay (Cloiste 30B) [121]. In the latter case, the intercalated surfactant contained hydroxyl groups. The microwave-assisted ring opening polymerization afforded higher monomer conversion and number average molecular weight (*Mn*) as compared to what was observed with conventional thermal ring opening polymerization. The microwave approach was also applied to the preparation of polycarbonate [122], poly(ethylene oxide) [123], polyepoxy[124], clay-nanocomposites including the use montmorillonite, hectorite, and laponite. Here again, the reader is referred to original papers and review articles [32, 36, 38] to learn more about original and efficient polymer-clay nanocomposites preparation based, for instance, ring opening metathesis polymerization [125, 126].

1.11 Future prospects

Functionalization of clay surface with molecular or polymeric segments bearing reactive groups has emerged over the last years as a trendy strategy to develop a new generation of reactive nanofillers. Indeed, taking advantage of the intrinsic properties of both partners, *i.e.* compatibility/reactivity with/towards the dispersion polymer matrices or their precursors, and favourable surface area, excellent mechanical performances for the organic layer and inorganic clay, respectively, allows for the design of ternary nanomaterials, true nanocomposites, with advanced properties. As witnessed by the numerous examples cited here-above, the *in situ* polymerization of reactive monomers is by far the most widely applied method. This success arises undeniably from the possibility to adjust the grafted amount of organics and thus to control the clay interlayer spacing by changing the polymerization conditions. Polymerization time, monomer concentration, in solution vs. from clay surface initiation, thermally or photochemically driven initiation... to name but a few, are as many parameters polymer-grafted clay with pre-exfoliated morphology and dispersion matrix-compatible character. The combination of *in situ* polymerization with efficient coupling methods is a key to successfully achieve the most important challenge inherent to the fabrication of polymer/clay nanocomposites that is, the effective clay dispersion, in the form of individual platelets, in the polymer matrix. The covalent coupling between nanofillers and the matrix ensures improved mechanical properties to the final polymer nanocomposites. In this regard, the currently in vogue click chemistry reactions, including the azidation of oxirane, thiol-epoxy click chemistry, thiol-ene and thiol-yne click chemistries and copper-catalyzed azide-alkyne cycloaddition, are good candidates for being implemented subsequently or concomitantly to *in situ* polymerization, and for sure, although first examples have been recently described in the literature [103], the potential of such a tandem has not yet been fully explored. The new generation of citizens has been immersed since its childhood in the era of sustainable development and responsible consumption, and for sure this will guide their future choices as consumers. Taking into account the reduction of fossil resources and the need to preserve and protect our environment, the design of bio-inspired materials which has known a fast growth over the last 10 years is expected to provide turnkey for various scientific and technological fields such as building and transport industries. Bio-nanocomposites are an emerging group of nanostructured organic-inorganic materials derived from natural polymers and inorganic solids, such as polysaccharides and clay for instance, interacting at the nanometric scale.

1.12 Conclusion

Polymer-clay nanocomposites have been synthesized using a plethora of synthetic routes aiming at controlling both the surface chemistry of clay nanoplatelets and bulk properties of the corresponding polymer nanocomposites (Table 1.1). The former affords improved miscibility of the clay layers through grafting of matrix-compatible chemical units and intercalation or exfoliation of the silicate layered structure. Undoubtedly, the *in situ* approach has allowed developing fast and robust, sometimes one-step if not one-pot, preparation methods for highly functional nanofillers providing advanced solutions in materials science.

Preparation method		Functional clay	Monomer/polymer	Ref
Clay- polymer coupling	CuAAC	Azide-Cloisite	Alkyne-PCL	49
		Alkyne-Kaolinite	Azide-Cellulose	52
		Azide-Montmorillonite	Alkyne-polyurethane	51
In situ polymerization	Free radical polymerization	Azo-initiator intercalated cloisite Na+	St	42
	ATRP	Vinyl-clay (CE) ^{a)}	St	66
		Bromine-terminated clay	MMA	62
		(CE)	St, MMA, BuA	64
			MMA	
				68
		Bromine clay	EHA	86
		(Graft) ^{b)}		
		Vinyl clay	St	66
		(CE)		
	AGET ATRP	Vinyl benzyl trimethylammonium chloride modified montmorillonite	poly(St-co-BuA)	67
	Initiation with a	Triethylaluminum	MMA	61
	coordination catalyst	(TEA)-modified clay		
	Living free radical polymerization	Nitroxide end moiety (CE)	St	63
	atom transfer radical nitroxide coupling	Nitroxide clay (CE)	PS with bromide-end	56
	ATRP	Bromine clay	GMA	69
		(order)	BuA, MMA	70
	Block copolymerization living ring opening polymerization of heterocyclic ethers/lactones and for nitroxide-mediated living free radical	Primary alcohol and alkoxyamine clay	St, epsilon-CL	43
	Surface-initiated photo-induced ATRP	Bromine clay (Graft)	Propargyl methacrylate	103

Table 1.1 – Synthetic routes for the preparation of PCNs

	Photopolymerization	phenacyl pyridinium salt clay ion exchanged	MMA	89
		and 2-hydroxy-2-methyl-1- phenylpropane-1-one clay ion exchanged	1,6-hexanediol diacrylate (30%) and urethane acrylate oligomer	90
		benzophenone	urethane acylate oligomer (CN964) and tripropylene glycol diacrylate	92
		2-benzyl-2-(dimethylamino)-1- [4-(4-morpholinyl) phenyl]-1- butanone	urethane acrylate oligomers	93
		acrylamide-treated organophilic clay hosts (CE)	Acrylamide, Benzyl as initiator	95
		Acrylate clay (CE)	1,6-hexanediol diacrylate (HDDA) and tripropylene	96
		Thiolated-clay	GMA	97
		silanized		
		Methacrylate clay	polysulfone dimethacrylate	98
		Grafted ester		
		N,N-dimethylamino-grafted clay	GMA	99
			benzophenone as co-initiator	100
	UV thiol ene	Triacrylate clay (Graft)	bisphenol A epoxy acrylate and tri-functional thiol	100
Emulsion	-	MMT-Na+	MMA	105
		MMT-Na+ or Ca ²⁺	St	106,
		MMT-Na+	vinyl chloride	107
				108
	Miniemulsion	Hydroxylated clay ion exchange	MMA	111
	ATRP with reverse and normal initiation			
	Minismulsion		St and BuA	112
	AGET ATRP			
	Pickering emulsion cationic RAFT	Trithiocarbonate-modified clay ion exchanged	PFPA, MMA, BuA	113
^{a)} indicates t	hat the interaction between organic and	inorganic components is of ionic	nature and arises from cation e	xchange.

b) indicates that the interaction between organic and inorganic components is of covalent nature and arises from a grafting reaction at the clay

surface.

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Chapter 2

Photo-induced SI-ATRP for the synthesis of photoclickable intercalated clay nanofillers

Design of functional and hairy nanoclay intercalated assemblies using tandem photoinduced surface initiated ATRP-1,3 dipolar cycloaddition/thiol-yne click reactions



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2.1 Introduction

In situ photoinduced SI-ATRP is reported as a novel and efficient route for preparing intercalated nanoclay fillers bearing clickable functions. Poly(propargyl methacrylate) chains are grown inside the clay interlayer after silanisation and grafting of bromine ATRP initiator. The generic clickable character is demonstrated through grafting with azidomethyl benzene and mercaptosuccinic acid *via* photodriven 1,3-dipolar cycloaddition and thiol-yne click reactions, respectively.

Clay nanoparticles due to their high aspect ratio, great surface area, impermeability, superior mechanical and thermal properties, low-cost and availability [1, 2, 3, 4], have attracted significant academic and industrial attention for potential applications in many areas such as sensing [5, 6], heterogeneous catalysis [7], pollutants removal [8], energy storage [9], drug delivery [10, 11], as well as reinforcement of nanocomposites [12, 13, 14, 15, 16, 17]. Despite attractive properties, clay nanoparticles suffer from incompatibility, hence weak interfacial interactions and poor dispersion with/in most of organic materials because of their intrinsic hydrophilicity and strong interlayer interactions [18, 19]. This is detrimental to the preparation of clay-based nanocomposites with exfoliated morphology but can be overcome by functionalizing the clay surface with organic modifiers, typically polymers, via either blending or in situ polymerization [20]. The latter approach is compatible with both aqueous and organic solvents, tolerates a wide range of monomers and functional groups and provides densely grafted polymer brushes as well as uniform dispersion of clay layers within polymeric matrices [21, 22, 23, 24]. The group of Singha prepared tailor-made poly(2-ethylhexyl acrylate) clay nanocomposites through thermally triggered living radical polymerisation using copper(I) halide, as catalyst, and N,N,N', N",N"-pentamethyl diethylenediamine, as ligand [25]. The initiator/ligand pair was simply added to the polymerization mixture containing organically modified clay providing high degree of intercalation.

Among the various *in situ* polymerization routes, the surface-initiated variant of controlled radical polymerization (SI-CRP) has been successfully applied as a versatile and promising approach in designing polymer brushes with narrow molecular weight distributions, predetermined molecular weights and controlled architecture and functionality. Growing polymer chains from nanoparticles *via* SI-CRP strategy permits tailoring both chemical and physical properties of a wide variety of nanoparticles [26, 27, 28, 29, 30, 31]. SI-CRP enables notably to control polymer length via variation of monomer conversion affording, in the case of clay nanoparticles, tunable increase in the interlayer spacing over polymerization time. Using this approach for the fabrication of clay/polymer nanocomposites implies firstly the surface functionalization of silicate layers with polymerization initiator by either physical adsorption or chemical attachment, and then, *in situ* growing of the polymer chains from these macroinitiators.

To date, polymerization processes have been mainly initiated by using heating or chemical external stimulation. Montmorillonite clay layers have been effectively coated by homopolymers and block polymers *via* various thermal CRP methods, such as atom transfer radical polymerization [32], reversible addition fragmentation chain transfer polymerization, and nitroxide-mediated polymerization, using quaternary ammonium initiators [33]. In the cited examples, initiators have been incorporated inside the clay galleries by interlayer cations exchange. Thermal-assisted CRP initiated from silanised clay surface bearing initiating end-units has been demonstrated to be effective in increasing the basal plane spacing [34]. In other implementations, activated hydroxy groups on the clay surface were chemically modified with bromine-ATRP initiator, RAFT transfer agent, and NMP nitroxide terminating agent through esterification reaction and subsequent initiation of the polymerization process yielded intercalated or/and exfoliated layered silicates [35]. In other implementations, Singha *et al.* described the esterification of hydroxylated montmorillonite (Cloisite 30B) to graft ATRP initiator [36, 37]. Herein, we opted for a three-step approach, involving acid activation of the clay prior to silanization with an aminosilane and subsequent grafting of the ARTP initiator *via* amidification reaction. Such acid treated clay exhibits increased density of surface silanol groups providing grafting of larger amount of organosilane as compared to native clay [38]. Silane grafting induces an increase in the basal spacing and a change in montmorillonite characteristics from hydrophilicity to lipophilicity [39]. Thus, the presence of an aliphatic segment arising from the 3-aminopropyl trimethoxysilane is expected to induce interaction with the propargyl methacrylate monomer favouring its incorporation within the interlayer galleries and thus the growth of the polymer chains. Only a few reports addressed the implementation of photochemically-driven strategies for such a purpose. Physically adsorbed quaternary ammonium salts based on dimethylaniline served as type II photo initiators in tandem with benzophenone (UV-light) or camphorquinone (visible light) for the *in situ* free radical polymerization of methyl methacrylate providing exfoliated nanocomposites as ascertained by the disappearance of the XRD peak [40]. As for thermal methods, photo-induced polymerization enables preparing polymers and copolymers with well-controlled molecular weight and topology from a large range of monomers and functional groups with the additional advantages of fast polymerization rates, easy process, and low temperature.

To the best of our knowledge there is no report on combination of photochemical strategy with surface initiated atom transfer radical polymerization (SI-ATRP) method to design polymer grafts on clay platelets bearing surface-grafted initiator, hence the motivation for this study. Considering the previous report by Yagci's research group on preparation of well-defined bulk polymer chains through photochemical generation of copper (I) complex from copper (II) species without using any reducing agent [22], we expanded this attractive strategy to the area of the interfacial chemistry of clay.

Herein, we discuss the unprecedented room temperature preparation of azide- and thiol-sensitive clay/polymer intercalated nanofillers via photoinduced SI-ATRP. By combining this route with the surface grafting of ATRP initiator, we have successfully confined the growth of poly(propargyl methacrylate) chains from silicate layers for producing clickable and intercalated organoclay bearing alkynyl pendant groups. We also report here our preliminary results on click functionalization of the clay nanoparticles taking advantage of the alkyne-decorated polymer grafts as anchoring interface for azidoor thiol-containing agents *via* azide-alkyne cycloaddition and thiol-yne radical addition click reactions, respectively [41, 42, 43]. Both click reaction were performed at room temperature under photodriven irradiation conditions.

2.2 Materials and Method

To establish the method, montmorillonite clay (MMT - Na) was firstly activated with diluted HCl 0.1M solution in order to increase the surface density of hydroxyl groups and to improve the surface area as previously reported by He et al [44]. The activated clay (MMT - OH) was then functionalized by 3-aminopropyl trimethoxysilane by reaction of the trimethoxysilane moieties with OH groups on clay surface; the as-obtained $MMT - NH_2$ was then grafted with bromoisobutyryl bromide via amide bonds to prepare ATRP macroinitiator (MMT - Br). Finally, polymerization of propargyl methacrylate (PGM) from the bromine-clay was carried out at room temperature for 2 h under stirring using a UV irradiation at 365 nm in presence of CuBr/PMDETA complex as catalyst and 2,2-dimethoxy-2-phenylacetophenone (DMPA) as photoinitiator yielding clickable clay nanofillers (MMT - PPGM). The polymerization time was optimized on the basis of qualitative and macroscopic optical observations of the dispersion stability of polymer-grafted clays in common organic solvent. As a representative example, Figure 2.6 shows DMF solutions as observed for native MMT - Na (a) and MMT - PPGM(b, c) after standing for a period of 24 h. It is seen that native MMT is insoluble and sediment in DMF while increasing the polymerization time from 1 h (b) to 2 h (c) improves significantly the dispersion behaviour of the polymer-grafted clays. To fully evidence the reactivity of the alkynyl pendant groups, MMT – PPGM were allowed to react with mercaptosuccinic acid and azidomethyl benzene under UV-
irradiation in presence of a catalytic amount of photoinitiator. The schematic procedures for making MMT - PPGM and their subsequent photoclick functionalization are is shown in Figure 2.1 and Figure 2.7, respectively. Experimental details are also available in the supporting information.



Figure 2.1 – Schematic representation of the preparation of poly(propargyl methacrylate)-grafted clay (MMT-PPGM) *via* (*i*) acidic activation and (*ii*) silanisation of clay surface, (*iii*) surface-grafting of ATRP initiator and (*iv*) photoinduced surface initiated atom transfer radical polymerization. The clay modification is illustrated on one clay layer for clarity purpose. Although the scheme is not to scale, the increase in the interlayer distance is shown following successive chemical modification steps.

2.3 **Results and Discussions**

Chemical structures of the neat and modified clays were analyzed by infra-red spectroscopy (FTIR) as shown in Figure 2.2. For comparison purposes, all spectra were normalized to the area under the Si - O vibration band (at about 1000 cm⁻¹). It can be observed for all samples, a weak peak at 3620 cm⁻¹ corresponding to the inner *OH* stretching vibration of Si - OH and Al - OH in the smectite type clays, a strong peak centred at 1000 cm⁻¹ assigned to the Si - O band, and a deformation band at 1647 cm⁻¹ indicating the presence of adsorbed water. Expanded spectrum between 3500 and 3900 cm⁻¹ (noted A in Figure 2.2) is shown in order to better highlight the effect of the mild acid treatment on the clay surface. The intensity increase of the band at 3620 cm⁻¹ corresponding to hydroxyl groups suggests increase in the *OH* density, demonstrating thus success of the clay surface activation. After silanisation reaction, two weak bands appeared at 2930 and 2867 cm⁻¹ corresponding to the asymmetric and symmetric stretching of *CH*₂ groups, respectively.45-47 The two large bands centred at 3300 and 3367 cm⁻¹ (expanded spectra noted B) can be assigned to the vibrations of *NH*₂ from the organosilane. It is worth noting that the silanisation step is accompanied by a slight intensity decrease in *OH* stretching vibrations at 3620 cm⁻¹, thus suggesting the consumption of the silanol groups *via* grafting of silane molecules [45, 46, 47].

Initiator grafting is evidenced by the apparition of characteristic signals of C=O stretching vibration at 1630, 1680 and 1712 cm⁻¹, assigned to the amide groups. In addition, appearance of new peak at 1530 cm⁻¹ typical for the *NH* of O=C-NH clearly indicates the successful reaction between the amine



Figure 2.2 – FTIR spectra of (a) pristine clay (MMT-Na), (b) activate clay (MMT-OH),(c) silanised clay5MMT-NH2) (d) ATRP initiator-graftedclay (MMT-Br)and (e) poly(propargyl methacrylate)/clay nanocomposite (MMT-PPGM).

groups and bromoisobutyryl bromide. After the polymerization reaction, one can observe the increase of the intensity of the carbonyl stretching vibration due to the presence of C=O ester groups of poly (propargyl methacrylate) accompanied with a shift from 1712 to 1732 cm⁻¹. Success of the chain growth in the clay intergalleries is further confirmed by the apparition of a new peak at 3293 cm⁻¹ corresponding to the stretching vibrations of terminal alkyne (\equiv C-H). From these results, one can state that the poly(propargyl methacrylate) chains are well grown from the clay surface leading to clickable nanofillers.

Thermogravimetric analysis (TGA) has been further used to gather quantitative information about surface functionalization. Clearly, degradation of organic content was observed in the temperature range from 100 to 800° C, indicating the successful grafting of organic molecules (Figure 2.3). The decrease in mass loss at $\approx 100^{\circ}$ C attributed to the amount of physically adsorbed water as observed upon successive functionalization steps reveals conversion of clay surface from hydrophilic character to hydrophobic one.

In addition, one can note that the onset temperature of neat clay is remarkably decreased after surface clay modification from approximately 600°C for MMT-Na to approximately 350°C for MMT- NH_2 and 300°C for both MMT-Br and MMT-PPGM. This finding indicates reduced thermal stability providing further evidence for the grafting of organic moieties at the inorganic clay surface. Weight losses of 12.5, 11.9, 19.3, 27.5 and 37.3% are observed for MMT - Na, MMT - OH, $MMT - NH_2$, MMT - Br and MMT - PPGM, respectively. Such a continuous increase in the weight loss confirms the grafting of organic moieties at each step [48].

As well known, the interlayer spacing plays a decisive role in the compatibility and dispersion ability of organo-modified clays with organic materials. To access this parameter, X-ray diffraction (XRD) measurements were conducted on all clay samples and the interlayer d-spacing was calculated according to Bragg equation (Figure 2.4). Pristine montmorillonite (MMT - Na) exhibits a strong diffraction peak at $2\theta = 7.58^{\circ}$, corresponding to the (001) basal reflection of the silicate layers and giving a d-spacing of 1.16 nm which is in well concordance with the value given by Southern Clay Products (1.17 nm). The d_{001} peak was shifted to about 4.93° after silanisation and 4.12° after bromination. This suggests a clear increase in the interlayer spacing from 1.16 nm for the MMT - Na clay



Figure 2.3 – TGA curves of (a) pristine clay (MMT - Na), (b) activate clay (MMT - OH), (c) silanised clay $(MMT - NH_2)$, (d) ATRP initiator-grafted clay (MMT - Br) and (e) poly(propargyl methacrylate)/clay nanocomposite (MMT - PPGM).

to 1.79 nm for the $MMT - NH_2$ and 2.13 nm for the MMT - Br.



Figure 2.4 – **a**) XRD patterns of (a) pristine clay (MMT - Na), (b) silanised clay $(MMT - NH_2)$, (c) macroinitiator clay with surface grafted ATRP initiator (MMT - Br) and (d) poly(propargyl methacrylate)/clay nanofiller (MMT - PPGM). **b**) Plot of the variation of the interlayer spacing as a function of the mass loss variation. The linear dependence suggests preservation of the layered structure. Pristine clay was considered as reference, and the plot is representative of $MMT - NH_2$, MMT - Br and MMT - PPGM.

It should be underlined that the d-spacing value obtained after silanisation step is comparable to the one given by Piscitelli et al. [45] fitting with a bilayer organization of aminosilanes within the clay interlayer. Moreover, the absence of the d_{001} peak after polymerization in the studied angle region ((2 θ from 4 to 10°)), may be explained by a shift towards a lower diffraction angle (2 θ < 4° for MMT - PPGM). In addition, one can note the apparition of new diffraction peak for all modified clays, which can be attributed to the (002) plane. A shift is also observed for the 002 peaks, from $2\theta = 9.66^{\circ}$ for $MMT - NH_2$ to $2\theta = 8.01^{\circ}$ for MMT - Br. This behavior is to be correlated to the shift in the d_{001} peak as discussed here above and corresponds to the incorporation of ATRP initiator between aluminosilicate layers.

As expected for layered structures, all d_{002} diffraction peaks appeared at positions corresponding to about twice the 2θ values of the corresponding d_{001} peaks, so intuitively position of the d_{001} peak of MMT - PMMG may be estimated to appear at $2\theta = 2.96^{\circ}$ corresponding to a *d*-spacing of 3 nm. This finding suggests growing of the polymer chains from clay surface with conservation of the parallel layers organization which is in full line with our aim to preserve the intercalated structure for the polymer-grafted nanofillers. This XRD-calculated *d*-spacing agrees well with morphological investigations performed by electron microscopy.

Figure 2.5 shows the TEM micrographs together with SEM images of (a) MMT - Na and (b) MMT - PPGM. The hydrophilic pristine clay forms agglomerates, with stacks of multiple parallel layers. The basal spacing of MMT-Na is around 1.1 nm, which corresponds well with the value measured by XRD. For the polymer-grafted clay, the flakes became smaller and their surface is much smoother due to wrapping with *PPGM*. The average interlayer space increased from 1.1 ± 0.1 nm for MMT - Na to 3 ± 0.2 nm for MMT - PPGM. In addition, the TEM image of MMT - PPGM shows clearly the individualisation of the layers through an increase in the interlayer distance while maintaining their parallel organisation. This behaviour is in good agreement with the tendency shown in Figure 2.4(b). In this figure, change in *d*-spacing is plotted versus variation in weight loss, considering the values characteristic for pristine clay as references. A direct proportionality is nearly observed confirming preservation of the intercalated morphological regime. Moreover, the increase in the *d*-spacing is nearly strictly governed by the amount of organics incorporated between the clay layers. Due to clickable character and intercalated morphology of the as-prepared clay-poly(propargyl methacrylate) nanofillers, the interlayer spacing may be further increased by coupling of azide- or thiol-functionalized (macro)molecules and thus favouring random dispersion of silicate layers [49, 50].



Figure 2.5 – TEM images of (a) pristine clay and (b) poly(propargyl methacrylate)/clay nanocomposite. The insets show SEM micrographs for the corresponding samples.

Surface reactivity of the as-synthesised clickable clay nanohybrids was evaluated towards coppercatalysed Huisgen cycloaddition (*CuAAC*) and thiol-yne radical addition (Figure 2.7). Both reactions were performed under UV irradiation conditions with model molecules and the resulting functional clay nanofillers, named MMT - COOH and MMT - Phe in Figure 2.7, were analysed by infrared spectroscopy (Figure 2.8). Success of both the thiol-yne (Figure 2.8(a)) and *CuAAC* cycloaddition (Figure 2.8(b)) click reactions is firstly demonstrated by the complete disappearance of the terminal alkyne characteristic absorption peaks detected at 3293 cm⁻¹ in the MMT - PPGM spectrum (Figure 2.2(c)). Moreover, the apparition of a broad band centered at 3250 cm⁻¹ together with the intensity increase of the peak at 1720 cm⁻¹ assigned to the C - OH and C = O stretching vibrations in carboxylic acid functions are clearly seen after thiol-yne coupling of mercaptosuccinic acid molecules. The *CuAA* cycloaddition between MMT - PPGM and azidomethyl benzene was further revealed by the appearance of C = C stretching typical for aromatic ring at 1227 and 1497 cm⁻¹, $N \equiv N$ vibration band at 1455 cm⁻¹, as well as the triazole breathing mode at 1129 and 1142 cm⁻¹[51]. In addition, one can notice the absence of peaks at 2555 and 2089 cm⁻¹ attributed to thiol and azide antisymmetric stretch from mercaptosuccinic acid and azidomethyl benzene respectively, indicating that the clay nanocomposite functionalization is achieved via covalent click coupling [42]. The so-designed functional nanoclays, with robust and hydrolytically stable anchoring of the polymer grafts on the clay surface may be used as adsorbents for the removal of metal ions and aromatic pollutants from wastewater [52].

2.4 Conclusions

In summary, photoinduced SI-ATRP approach has proved effective for producing intercalated clickable clay nanofillers. Through this strategy, clay surface was firstly functionalized with amino silane coupling agent, followed by grafting of bromine ATRP-initiator, and finally growth of poly(propargyl methacrylate) chains has been UV-initiated from the silicate layers in presence of free photoinitiator. The as-obtained clickable alkynyl nanohybrids were readily coupled with azidomethyl benzene and mercaptosuccinic acid small molecules through photo-initiated Huisgen cycloaddition and thiol-yne click reactions, respectively. These results revealed that the strategy of photoinduced SI-ATRP easily provides generic clay-based nanoplatforms for the preparation of a variety of new multifunctional nanomaterials.

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2.6 Supporting information

2.6.1 Materials

Soda montmorillonite clay (*MMT-Na*: CEC = 92 mequiv./100g, $d_{001} = 11.7$ Å, surface area 750 m^2/g) sample was kindly donated by Southern Clay Products. 3-aminopropyl trimethoxysilane *APTMS*, α -bromoisobutyryl bromide *BIBB*, propargyl methacrylate *PGM*, copper (I) bromide (*CuBr*), copper (II) bromide (*CuBr*₂), pentamethyldiethylenetriamine (*PMDETA*), triethylamine (*TEA*), 4-dimethylamino-pyridine (*DMAP*), 2,2-Dimethoxy-2-phenylacetophenone (*DMPA*), Irgacure 819, ethylenediaminete-traacetic acid (*EDTA*), mercaptosuccinic acid (*MSA*), bromomethyl benzene (*C*₆*H*₅ – *Br*) were purchased from Sigma-Aldrich and used as received. The solvents hydrochloric acid (*HCl*), anhydrous toluene, anhydrous N,N-dimethyl formamide (*DMF*), ethanol (*EtOH*), sodium hydroxide (*NaOH*), dichloromethane (*DCM*), and acetone were purchased from Alfa-Aesar and used without further purification. Ultrapure water was purified using a Milli-Q plus purification system.

2.6.2 Synthesis methods

2.6.2.1 Activation of clay, step (i) in Figure 2.1 (MMT - OH)

2 g of MMT - Na were introduced in 200 mL of 0.1 M *HCl* during 24 h under stirring at room temperature. Then, this activated powder was collected by centrifugation and thoroughly washed with ultrapure water until total removal of chlorine ions (as tested by $AgNO_3$). The resulting clay was finally dried in a vacuum oven at 60°C for 24 h. This sample is denominated as MMT - OH.

2.6.2.2 Silanisation of clay, step (*ii*) in Figure 2.1 (*MMT* – *NH*2)

1 g of MMT - OH was first dispersed for 1 h in 25 mL of anhydrous toluene using magnetic stirring, and then sonicated for 5 min in order to obtain well-dispersed solution. To this suspension, 1 mL of 3-aminopropyl trimethoxysilane (APTMS) was added and the silanisation reaction was carried out under stirring for 16 h at reflux under N_2 inert atmosphere. The functionalized clay was then centrifuged and washed several times with toluene, dichloromethane and ethanol and then dried in a vacuum oven at 60° C for 24 h, the resulting sample is denominated $MMT - NH_2$.

2.6.2.3 Grafting of ATRP initiator on clay, step (*iii*) in Figure 2.1 (*MMT – Br*)

1 g of the $MMT - NH_2$ was dispersed in 25 mL of anhydrous dimethyl formamide DMF. After 10 min of stirring at room temperature, 6 mL of anhydrous triethylamine (*TEA*) and 100 mg of DMAP were added to the suspension. The mixture was degassed by bubbling with nitrogen and left to stir for 30 min and then cooled down to 0°C in an ice bath. To this dispersion, were added drop wise 6 mL of bromoisobutyryl bromide (*BIBB*) solubilized in 10 mL of anhydrous DMF. Subsequently the reaction was allowed to proceed under stirring for 24 h at ambient temperature, while maintaining the suspension under nitrogen atmosphere. The obtained clay was collected by centrifugation and successively washed with DMF, ethanol, and acetone and then dried in a vacuum oven at 60°C for 24 h. This procedure yields bromine-terminated clay denominated as MMT - Br.

2.6.2.4 Synthesis of poly (propargyl methacrylate)/clay nanofiller *via* photoinitiated SI-ATRP, step (*iv*) in Figure 2.1 (MMT-PPGM)

Polymerization of propargyl methacrylate from the bromine-clay surface was carried out using UV irradiation at 365 nm in a spectrolinker XL-1500 UV under stirring. Typically, 100 mg of MMT-Br were introduced in a deoxygenated three-necked flask containing 25 mL of anhydrous DMF, where was added a mixture of 52 mg of CuBr, 8 mg of $CuBr_2$, 84 mL of PMDETA, and 48 mg of DMPA was added under stirring, while maintaining a nitrogen stream. On the other hand, 5 mL of MPG and 2 mL of anhydrous DMF were bubbled with nitrogen for 10 min, and then were injected via a degassed syringe into the clay suspension. The mixture was then irradiated at 365 nm under stirring for 2 h to initiate the polymerization from the clay surface. Subsequently, the suspension was centrifuged, and the modified clay was thoroughly washed with DMF and EtOH followed by a Soxhlet extraction in chloroform. Finally, the clay was dispersed in a 10 mL solution of 0.1 M of EDTA in 0.1 M *NaOH* overnight in order to remove the copper ATRP-catalyst and then followed by washing with water and drying in a vacuum oven at 60°C for 24 h.

2.6.2.5 Functionalization of clickable clay nanofillers *via* photo-initiated thiol-yne click reaction, acid-(MMT-COOH)

20 mg of MMT-PPGM were dispersed in 2 mL of methanol for 10 min under stirring, and then 300 mg of mercaptosuccinic acid were added. The mixture was degassed under nitrogen flow for 10 min. On the other hand, 30 mg of DMPA photoinitiator, were solubilised in 1 ml of methanol and bubbled with nitrogen for 5 min, and then introduced in the clay suspension via a degassed syringe. The mixture was then irradiated at 365 nm under stirring for 3 h. Subsequently, the suspension was centrifuged, and the modified clay was thoroughly washed with methanol and EtOH followed by drying in a vacuum oven at 60° C for 24 h.

2.6.2.6 Azidation of bromomethyl benzene $(C_6H_5 - N_3)$

1 g of bromomethyl benzene and NaN_3 were solubilized in 13 mL of DMSO. After 2 h of stirring at room temperature, the mixture was diluted with 50 mL of water and then the organic product was extracted using ether for three times followed by washing with water and saturated NaCl solution and finally dried over $MgSO_4$. The mixture was then filtered and the solvent was evaporated. The obtained product was analyzed by IR ($\nu = 2090 \text{ cm}^{-1}$; $-N_3$) and by ¹H NMR ($\delta = 4.33$ (s, 2 H); $CH_2 - N_3$)

2.6.2.7 Functionalization of clickable clay nanofillers via photo-initiated CuAAC click reaction (MMT-Phe)

20 mg of MMT-PPGM were dispersed in a 4 mL of DMF for 10 min, and then 100 mg of azidomethyl benzene, 335 mg of $CuBr_2$, and 470 µL of PMDETA were added. The mixture was degassed under nitrogen flow for 10 min. On the other hand, 385 mg of Irgacure 819 photoinitiator were solubilised in 1 ml of DMF and bubbled through nitrogen for 5 min, and then introduced in the clay suspension via a degassed syringe. The mixture was then irradiated at 365 nm under stirring for 3 h. Subsequently, the suspension was centrifuged, and the modified clay was thoroughly washed with DMF and EtOH followed by drying in a vacuum oven at 60°C for 24 h.



Figure 2.6 – Comparison of dispersion state of 2 mL DMF suspensions of 10 mg of (a) MMT-Na, (b) MMT-PPGM after SI-ATRP time of 1 h (c) MMT-PPGM after SI-ATRP time of 2 h. The digital photos are taken after 1 h stirring followed by 24 h standing period.



Figure 2.7 – Schematic illustration for the surface functionalization of MMT-PPGM with mercaptosuccinic acid and azidomethyl benzene via photodriven thiol-yne and 1,3 dipolar cycloadditon click strategies, respectively.



Figure 2.8 – FTIR spectra of (a) acid- (MMT-COOH) and (b) benzene-functionalized (MMT-Phe) clay nanofillers via thiol-yne and Huisgen cycloaddition surface Click grafting reactions, respectively.

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Chapter 3

Versatile highly exfoliated epoxy-rich interlayer clay: nanofillers for thermoset and thermoplastic biobased nanocomposites

The work developed in this chapter is intended to be submitted to ACS Applied Materials & Interfaces

Abstract: In this letter, we are proposing a simple approach for the fully exfoliation of montmorillionite clay layers by interfacial grafting with a highly reactive epoxy-containing polymer, and facile and good dispersion both in biobased thermoset and thermoplastic matrices. The approach is based on the *in situ* photo-induced polymerization of the epoxy-like monomer on vinyl-functionalized clay silicate layers. As a proof of concept, both starch and Green epoxy resin biomatrices exhibited high reactivity towards the as-prepared epoxy organo-functionalized clay nanoplatelets. Preliminary results demonstrate the potential use of the nanofillers in reinforcement of environment-friendly polymers.

3.1 Introduction

Since the pioneering work of the Toyota research group on clay-filled nylon-6 nanocomposites [1, 2], clay nanoparticles have gained great interest as reinforcing nanofillers for organic polymers [3]. Due to the remarkable physical properties and morphological structure of the clay silicate layers, their incorporation onto polymer matrices even at small amounts has already been reported to significantly improve their mechanical, thermal, barrier, flammability properties. However pristine clay nanoparticles because of their intrinsic hydrophilicity and strong interlayer interactions, suffer from incompatibility and poor dispersion with/in organic matrices causing frequently a loss in mechanical properties. To overcome these inherent limitations and to improve the interfacial interactions between clay and organic matrices, functionalization of clay surface with organic polymeric materials have been reported as suitable strategy [4]. Out of various possible ways to prepare intercalated or exfoliated polymer layered silicate nanocomposites, using functional quaternary ammonium modified clay as macroinitiator in the growing of the polymer chains via in situ polymerization is quite common. This success can be rationalized by the simplicity of insertion of the exchangeable cations inside the clay galleries and their ability to delaminate the micro-size tactoids for generating individual nanometric silicate layers which favor penetration of monomer molecules and thereby lead to their homogeneous distribution within polymer matrix [5, 6, 7].

However, the non-covalent strategy for the preparation of binary nanocomposites could be disadvantageous because the physical attachment of the polymer chains to the clay layers surface may lead to macroscopic phase separation and hence fast degradation rate which could limit their potential use as nanofillers in ternary nanocomposites [8, 9].

Alternatively, the presence of silanol reactive groups at the silicate platelets edges and in the interlayer-generated via proton exchange reaction using acid treatment-permits chemical grafting of functional organosilane coupling agents on the clay surface. This may be further exploited for covalent bonding of polymers on the clay platelets surface [10]. The as designed strong clay-polymer interfacial interactions should lead to high degree of exfoliation of the nanofillers before their introduction in the polymer matrices which should facilitate their uniform distribution and therefore promise significant enhancement of mechanical and physical properties of the fabricated ternary nanocomposite [9, 11, 12].

However, exfoliation structure of nanofillers alone can be insufficient for ensuring appropriate interfacial interactions and effective synergistic effect with the matrix. It has been established that for enhancement of the properties of epoxy thermosetting polymers, chemical reactivity between the grafted polymer and the thermosetting matrix is required and this for Al_2O_3 , Fe_3O_4 , carbon nanotube, SiO_2 , clay nanoparticles [13, 14, 15, 16, 17].

Nowadays, several works have reported on the compatibilization, dispersion and interfacial interaction of polymer-modified clay into petroleum based polymer matrices [8, 17]. Nevertheless study of the interfacial interactions with biobased polymer matrices was not well described yet.

In the present work, epoxy and starch bio-biobased ternary nanocomposites filled with clay monotmorillonite were successfully prepared. First, the clay surface (MMT) was grafted with poly(glycidyl methacrylate), PGMA, as highly reactive polymer for the functionalization with amine and azide groups. Effects of clay acid activation and monomer concentration on the structure of the MMT-PGMA nanofillers were investigated. The morphology, the thermo stability, and the chemical and crystalline structures of the nanofillers were studied by transmission electronic microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD), respectively. Chapter 3. Versatile highly exfoliated epoxy-rich interlayer clay: nanofillers for thermoset and thermoplastic biobased nanocomposites

3.2 Results and Discussions

We report here our preliminary results of morphological structure and the mechanical properties of epoxy filled with MMT-Na and MMT-PGMA ternary nanocomposites using TEM and dynamic mechanical analysis (DMA). As well as results of incorporation of MMT-PGMA nanofillers into starch matrix are achieved taking advantage of the azide-functionalized polymer grafts as anchoring interface for propargyl starch *via* photo-induced azide-alkyne cycloaddition click reaction.

Figure 3.1 depicts the synthetic pathway of the clay-grafted poly(glycidyl methacrylate) nanofillers and their integration in two type of biobased materials, namely starch as thermoplastic matrix and GreenPoxy bio resin as thermoset matrix. The experimental and the measurement methods details are provided in the supporting information. It is worthy to note that for comparison purposes, all FTIR spectra were normalized to the area under the Si-O vibration band (at about 1000 cm⁻¹).



Figure 3.1 - Schematic illustration of the stepwise sequence for fabricating epoxy and starch filled clay ternary nanocomposites using epoxy-rich polymer as a bridge ensuring covalent attachment between the clay montmorillonite and the polymeric matrices (epoxy and starch). The clay modification is illustrated on only one clay layer for clarity purpose and the scheme is not to scale.

It is well known that in pristine montmorillonite clay structure, the hydroxyl groups, which could provide possible reactive sites for organosilane grafting, are located at the layer edges [18]. So, prior to the silanisation step with 3-(trimethoxysilyl) propyl methacrylate in water, the clay platelets (MMT-Na) are first activated with a 0.05 M hydrochloric acid solution at 60°C for 3 h in order to replace the exchangeable interlayer sodium cations with protons. This acid activation step permits to introduce a high concentration of reactive hydroxyl groups in the interlayer surface allowing a covalent attachment

of the silane coupling agent at the internal clay surface [19]. This treatment has an additional advantage of swelling the clay platelets which facilitate the introduction of the 3-(trimethoxysilyl)propyl methacrylate molecules in between the layers [20, 21].

The pristine clay FTIR spectrum in Figure 3.2(a) shows characteristic smectite familly inner OH stretching vibration at 3626 cm⁻¹, a sharp and intense band centered at about 1000 cm⁻¹ representing the Si-O groups, and the characteristic deformation band of adsorbed water at 1635 cm⁻¹. As can be seen from comparison of the expanded spectra between 3200 and 3900 cm⁻¹ (See Figure 3.5 in the supporting information), the MMT-OH spectrum shows increased intensity of the OH stretching vibration at 3626 cm⁻¹ resulting from the silanol groups formation.

Silanised clays prepared from both pristine (MMT-Na-MAPS) and activated montmorillonite (MMT-OH-MAPS) using methacrylate silane and water as solvent exhibit apparition of new peaks at 2945, 1634, 1726 cm⁻¹, attributed to $-CH_2$ antisymmetric stretching vibration, the carbonyl groups, and the terminal C=C bonds, respectively (Figure 3.2(a)). Moreover, a decrease of the OH peak intensity at 3626 cm⁻¹ is observed, indicating the transformation of the Si-O-H groups to Si-O-Si bonded ones, confirming the chemically attachment of the vinyl silane molecules on the clay surface [22]. A comparison of the two spectra clearly indicates that the intensity of all the silane characteristic peaks is much higher in the case of MMT-OH-MAPS than for the MMT-Na-MAPS, confirming beneficial effect of the acid treatment step.

The presence of a high amount of the polymerizable vinyl groups should ensure dense and covalent attachment of the poly(glycidyl methacrylate) chains on the clay platelets surface, which could favor exfoliation structure of MMT-PGMA binary nanocomposite [23, 24, 25].

XRD measurements give another evidence for the success of the nanoclay surface chemical functionalization and provide information on the induced morphological change of the montmorillonite platelets structure. Indeed, introduction of organic molecules in between the self-parallel organized platelets may allow changes in the interlayer distance (*d*-spacing). This can result in either intercalated or exfoliated nanocomposite, *i.e.* conserving the parallel organization of the layers or generating random orientation of single sheets. It is noteworthy that the presence of diffraction peaks in the XRD diffractograms reflects an intercalated morphology while its absence can either indicat an important interlayer distance or an individualized layers randomly dispersed. To assess the interlayer distance, Bragg's equation 2 $d_{001}sin\theta = n\lambda$ was used. From the XRD patterns shown in Figure 3.2(b), sodic montmorillonite (MMT-Na) shows a broad and an intense diffraction peak at around 2θ =7.58°, corresponding to a layer-to-layer stacking distance of about 1.16 nm, which is in well concordance with the 1.17 nm value provided by Southern Clay Product. However, acid activation of the montmorillonite (MMT-OH) shifts slightly the peak towards lower diffraction angle of 2θ = 7.2° increasing the interlayer spacing to only 1.23 nm, indicating that the platelets are still closely stacked. Such shift of diffraction peak is due to the generation of interlayer hydroxyl groups [26].

It's worthy to note that the intensity as well as the width of the diffraction peak were conserved after the acid activation indicating that this treatment did not affect the MMT crystallinity [27]. Previous works have demonstrated that the chemical modification of clay by silanes can be achieved at three different clay-sites, "broken" layer edges, external surface, or in between platelets, depending both on the silane structure and the solvent surface energy [28, 29].

Here, we used a trifunctional silane as coupling agent and water as silanisation solvent. As it reported by Herrera [10] and He and co-workers [18] these conditions favor interlayer insertion of the silane coupling agents and their covalent grafting via the accessible activated hydroxyl groups which would ensure a quantitative silane grafting and thus a good dispersion of the clay sheets [26, 30]. After silanization reaction, the d_{001} peak was shifted to about 7.02° for MMT-Na-MAPS and 5.43° for MMT-OH-MAPS, corresponding to a basal spacing of about 1.26 and 1.64 nm, respectively, which is in full

accordance with the FTIR results. One can also note from the MMT-OH-MAPS pattern that the peak becomes weaker and broader, which reflects the intercalation of silane molecules into the clay gallery. The XRD results revealed further evidence of the influence of clay activation on its structure. Separation of the clay layers should promote facile insertion of hydrophobic GMA monomers within the platelets which can facilitate linking of polymer chains at the surface and the important delamination of these platelets.

The above claims are strongly supported by the obtained TGA results. Figure 3.2(c) shows clearly the degradation of organic content in the temperature range from 200 to 800 °C, indicating the successful grafting of organic molecules on the clay surface. As can be seen from TGA and DTG thermogram profiles (see Figure 3.6 in the supporting information), unmodified and activated clays show both two decomposition steps. The first step occurs below 150 °C showing a slight weight loss of about 7.3 % for MMT-Na and 10 % for MMT-OH, which is assigned to both the surface and the interlayer adsorbed water evaporation [31]. One can highlight the greater intensity of the water release peak of MMT-OH than that of MMT-Na explained by the presence of a high hydroxyl groups density at the clay surface making it more hydrophilic than the unmodified clay. The second step showed weight loss of 5.2 % for MMT-Na and 3.9 % for MMT-OH between 470 - 730°C, corresponding to the dehydroxylation of the clay layers [31]. The total weight loss of unmodified clay is close to 12.5 %, whereas the one of activated clay is close to 13.9 %, indicating only a very few difference.

It can obviously be seen that the MMT-Na-MAPS and MMT-OH-MAPS organo-modified clays become less stable than the pure MMT and the main decomposition occurs in the temperature range of 200-450°C due to the thermal degradation of the grafted organic moieties. Total weight losses close to 15.8 and 31.8% are obtained for the silane grafted clays prepared from untreated and activated ones, respectively. This quantitative data confirms the importance of the clay surface activation in its grafting. The increase in the onset degradation temperature of the as prepared organoclays comparing to the pristine clay is a further confirmation of its transformation from hydrophilic to hydrophobic material. Silanized clay involves four decomposition steps (see Figure 3.6 in the supporting information) with maximum rates at 70, 231, 379 and 567°C, which may be attributed to physisorbed water evaporation, decomposition of the intercalated MAPS which are hydrogen bonded, degradation of interlayer MAPS which are covalently grafted and dehydroxylation of montmorillonite, respectively [32]. Interestingly, comparison between the Hydrogen bonded and the covalent grafted MAPS shows obviously more intense peak for the latter one, indicating very high density of grafting MAPS moities on montmorillonite. In addition, one note clear decrease of the temperature of dehydroxylation of the clay, which is in good agreement with result previously reported by Shen *et al.* [33].

In the second step, glycidyl methacrylate was polymerized in the presence of the vinyl-functionalized clay for 2 h via UV induced *in situ* radical polymerization at 365 nm using the 2,2-dimethoxy-2-phenylacetophenone photoinitiator. The obtained binary nanocomposite was washed abundantly with acetonitrile (ACN), ethanol, and then followed by Soxhlet extraction with chloroform to remove the physisorbed polymer. Initial monomer concentration can affect considerably the growth of polymer chains and hence the clay layers structure. The influence of this parameter was investigated for three GMA concentrations (1.5, 3, and 4.5 mM) and the structural and morphological results (denominated MMT-PGMA-1, MMT-PGMA-2 and MMT-PGMA-3, respectively) are reported for the three nanocomposites in the Figures 3.2(d-f,h,i).

The significant decrease of the signature of C=C bond, the appearance of epoxyde characteristic peaks at 904, 845 and 757 cm⁻¹, and the increase in the intensity of the carbonyl stretching vibrations peak at 1726 cm⁻¹ are clear proofs for the PGMA grafting on the silicate layers [34]. It can be noticed that the clay signals are completely masked by those of PGMA for the GMA concentration above 3 mM, indicating a high density grafted polymer. The organo functionalization of the clay layers could reduce their strong attraction which prevent their aggregation and therefore improve their compatibility with

the organic biobased matrices. Clearly, increasing the GMA initial concentration induces progressive increasing of the grafted PGMA amount as demonstrated by both FTIR and TGA as shown in Figures 3.2(d) and 3.2(f). One can note a clear increasing of the C=O vibration intensities and weight losses of 49 % for MMT-PGMA-1, 80% for MMT-PGMA-2 and 90 % for MMT-PGMA-3.

For a deeper understanding of the nanofillers structure, XRD analyses were performed at 2θ between 4 and 10° (Figure 3.2(e)). By comparison of the different patterns, it can be concluded that the stacked platelets of the multilayer structure detected in the case of sodic clay (Figure 3.2(b)) were efficiently separated upon the grafting of PGMA whatever the GMA concentration (Figure 3.2(e)). XRD pattern of the clay-grafted poly(glycidyl methacrylate) prepared from GMA 1.5 mM shows a shifted diffraction peak at 4.74° resulting in an increasing of the average interlayer distance from 1.52 to 1.87 nm which could reveal conservation of the intercalated structure of the montmonrillonite layers. In fact, as it can be observed, the peak is broader and smaller than the peak detected for MMT-MAPS, suggesting a disordered morphological structure of clay,*i.e.* lower degree of clay layers organisation [35]. TEM analysis Figure 3.2(h) confirms this structure, revealing mainly parallel individual sheets however their number per stack is significantly smaller comparing to the pristine clay stacks (Figure 3.2(g)).

However, both MMT-PGMA-2 and MMT-PGMA-3 patterns do not present any visible diffraction peak, indicating clearly an important interlayer distance which attests to the good dispersion of the silicate layers. Nevertheless, the absence of diffraction peak alone cannot predict partial or complete exfoliation structure of the obtained nanocomposite, therefore TEM characterization was required for MMT-Na, MMT-PGMA-1 and MMT-PGMA-3 to provide additional information. TEM micrographs (Figure 3.2(g, h, i)) of the untreated and polymer modified clays reflect clearly an important change in the clay platelets morphology revealing different dispersion states as well as different organization structures for MMT platelets within the matrix and this depending on their surface modification. For untreated clay, tactoids and stacks are observed which can be explained by the strong diffraction peak detected in the XRD pattern. TEM images of MMT-PGMA-1 and PGMMA-2 show separated clay layers. However a great difference is observed in their orientation, where the single platelets in the MMT-PGMA-1 nanocomposite almost still maintain a parallel organization; however with the increase of the GMA concentration from 1.5 to 3 mM, the clay platelets reach a random orientation. Additionally, one can note the detachment of some individual platelets from each other for MMT-PGMA-1. These observations combined with the XRD results which revealed the presence of a small and broad diffraction peak for MMT-PGMA-1 and the absence of any peak for MMT-PGMA-2 proved partial intercallated and highly exfoliated structures, respectively.

Due both to the high degree of exfoliation of the prepared MMT-PGMA-2 and the important reactivity of the pendant epoxide moieties of PGMA chains, this binary nanocomposite was chosen as nanofiller in two types of biobased materials, namely starch as thermoplastic matrix and GreenPoxy bio resin as thermoset matrix. Two ways were employed for the dispersion of the nanofiller into the matrix.

In the case of the bioepoxy resin, the MMT-PGMA-2 binary nanocomposite fillers (5 wt.% of the total weight of resin and hardener) were first mixed with the Green epoxy resin (GreenPoxy 56) using an ultra-turrax at 80°C for 1 h in order to obtain homogeneous dispersion of the nanofillers. Then an amino hardener was added at the epoxy/hardener of 42/40 weight ratio. The mixture was then poured into silicon mold and cured 24 h at 60°C followed by 48 h at room temperature. The well-known reactivity of epoxide with amine groups via nucleophilic attack could ensure crosslinking of the system containing MMT-PGMA, amino hardener and Green epoxy resin [36, 37]. Although presence of high nucleophilic nitrogen could promote high reactivity to amines, their chemical structure has a key role. To study the reactivity of the polyamine hardener used in this work (SD Green Pox 505 V2) with the MMT-PGMA nanofillers and to better understand the mechanism of formation of the MMT-PGMA/Green epoxy resin ternary nanocomposite, FTIR was used to investigate the reaction between the hardener and both the



Figure 3.2 – (a) FTIR spectra, (b) XRD patterns, and (c) TGA curves of pristine clay (MMT-Na), activated clay (MMT-OH), silanised clay prepared from pristine clay (MMT-Na-MAPS), and silanised clay prepared from activated clay (MMT-OH-MAPS) (d) FTIR, (e) XRD, and (f) TGA of silanised clay (MMT-OH-MAPS), polymer-grafted clay prepared using 1.5, 3 and 4.5 mM of GMA monomer concentration (MMT-PGMA-1, MMT-PGMA-2, and MMT-PGMA-3), respectively. TEM images of (g) MMT-Na, (h) MMT-PGMA-1, and (i) MMT-PGMA-2.

MMT-PGMA and the epoxy resin. FTIR spectrum (Figure 3.3(a)) of the resulting material obtained by mixing of the MMT-PGMA nanofillers with the amino hardener in ACN at 60°C for 6 h under stirring, shows appearance of a new broad peak centered at 3333 cm⁻¹, it is attributed to the N-H and OH stretching vibrations, whereas the epoxy bands detected in the MMT-PGMA spectrum at 904, 845, 757 cm⁻¹ (Figure 3.3(a)), have disappeared, confirming the reaction between amine of the hardener and epoxyde of the PGMA grafted on clay layers.

FTIR spectrum (Figure 3.3(a)) of the MMT-PGMA/Green epoxy resin nanocomposite cured 24 h at 60°C exhibits similar observations, indeed disappearance of the epoxy bands and appearance of amine and hydroxyl peaks. It should be noted that the signatures of the clay as well as ones of PGMA are almost covered by the strong bands of the resin, explained by the very small amount of the nanofiller (5 wt.%) compared to resin content in the nanocomposite. FTIR results have proved that the hardener could react with the PGMA epoxy groups from the clay surface as well as the epoxy of resin (bottom spectrum in Figure 3.3(a)), which should promote both high crosslinking degree of the ternary nanocomposite and a well dispersion of the nanofillers within the resin.

Figure 3.3(d) shows typical TEM micrograph of MMT-PGMA/Greenepoxy nanocomposite with nanofiller content of 5%. It can be observed that almost all the nanoplatelets are in the form of single-layer and homogeneously distributed in the resin matrix, however certain platelets maintain the intercalated order which led to the formation of some dark areas. These observations obviously reveal that the nanocomposite is mostly exfoliated although it contains small percentage of intercalated structures. It can also be highlighted that the nanoplateletes are homogeneously dispersed throughout the resin. Additionally, the photograph of the nanocomposite film (the inset of the Figure 3.3(b)) shows that it is transparent to visible light which confirm the nanoscale dimension thus the fine dispersion of the incorporated nanofillers.



Figure 3.3 – (a) FTIR spectra of polymer-grafted clay (MMT-PGMA), Amine hardener-functionalized polymer grafts (MMT-PGMA-hardener), epoxy resin, epoxy resin reacted with hardener, epoxy filled clay ternary nanocomposite (MMT-PGMA/epoxy); (b) DMA results of pure epoxy resin, epoxy filled pristine clay, and epoxy filled clay ternary nanocomposite, the inset shows the photograph of the film of MMT-PGMA/epoxy ternary nanocomposite; (c) TEM image of the epoxy filled pristine clay ternary nanocomposite.

To investigate the effect of the MMT-PGMA nanofillers on the mechanical and viscoelastic properties of the as prepared ternary biobased nanocomposite, pristine resin, resin filled with unmodified MMT (MMT-Na/epoxy) and resin filled with polymerized MMT (MMT-PGMA-2/epoxy) were studied using dynamic mechanical thermal analysis (DMA). The figure of the storage modulus E' as a function of temperature in the temperature range of 0 to 145° C ((Figure 3.3(b)), indicates that the E' value of the pristine resin and the resin filled with MMT-Na are similar. This result demonstrates that the incorporation of the unmodified clay in the resin matrix is of no effect in its mechanical properties, which can be explained by the poor interfacial interaction between the two materials and thus the aggregation of the clay layers within the matrix as supported by TEM image ((Figure 3.3(c)).

Whereas, E' of MMT-PGMA/Greenepoxy of both glassy state (< 60° C) and rubbery state (>110°C) are much higher than those of the pristine resin. Even at the temperatures below glass transition temperature (T_g), incorporation of MMT-PGMA nanofillers into the Green epoxy resin enhanced significantly the storage modulus. For example at room tempearture, E' increased from 2007.5 to 3055 MPa which corresponds to 52.2 % increase.

Moreover, a very great improvement of the mechanical performance of the epoxy nanocomposite was observed above Tg, with a maximum increasing of E' of about 208.7 % (98°C). This can be attributed to the high dispersion of the nanofillers within the Green epoxy matrix but also significantly

to the strong interfacial adhesion between them due to chemical crosslinking reaction caused by the reaction between epoxy groups of PGMA-grafted clay and those of the biobased resin via the amine hardener, as demonstrated above by FTIR results. Noticeably, the clear increase of the stiffness after introduction of MMT-PGMA nanofillers can be explained by the reinforcement brought by crosslinked network as well as by the limited mobility of the polymer chains of the resin, originating from the confinement of the polymer chains of the resin in between the silicate platelets as a result of the strong interfacial interactions between the nanofillers and the matrix.

To fully demonstrate the versatility approach and further extend the use of poly epoxy-decorated clay nanofiller, we investigated incorporation of the said clay nanofiller into the starch matrix using a covalent attachment strategy, *i.e.* click chemistry. Herein, we present preliminary results on starchbased nanocomposite using the photo-triggered CuAAC click chemistry. Starch polymer was propargylated using propargyl bromide, while the MMT-PGMA nanofiller was azidised through the epoxide ring-opening reaction of poly(glycidyl methacrylate) grafts using sodium azide. Subsequently, the propargyl-functionalized starch and the MMT-PGMA- N_3 were coupled via a photo-triggered CuAAC cycloaddition reaction.



Figure 3.4 – FTIR spectra of (a) clay-grafted polymer (MMT-PGMA), (b) azide-functionalized polymer grafts (MMT-PGMA- N_3), (c) starch (d) propargyl-functionalized starch (e) starch filled clay ternary nanocomposite (MMT-PGMA-Starch).

Direct evidence for the successful grafting of the nanofillers was provided by FTIR analysis, as shown in Figure 3.4. Comparison between the MMT-PGMA and the MMT-PGMA- N_3 spectra shows apparition of new peaks at 2103 and 3434 cm⁻¹ assigned to the azide and the hydroxyl groups vibration, respectively. The pristine starch spectrum shows a strong peak at around 1010 cm⁻¹ attributed to ether groups. In addition, two OH bands, a broad one centered at 3300 cm⁻¹ and a smaller peak at 1640 cm⁻¹ are detected; they are assigned to the hydroxyl groups of the starch backbone. After its chemical modification, the starch spectrum reveals the appearance of two bands, a narrow peak at 2116 cm⁻¹, attributed to the C≡C stretching vibration functions, and a peak at 3280 cm⁻¹ assigned to the terminal alkyne C-H vibrations. The success of the covalent coupling reaction between the azide-modified nanofiller and the propargylated starch was further demonstrated by a significant decrease of both the azide and the propargyl signatures, as well as by the appearance of the OH bands of starch at 1640 and 3382 cm⁻¹. In addition, one can observe decreasing of the PGMA carbonyl peak intensity which can be explained by a dense covering of clay by starch.

3.3 Conclusions

In summary, we have successfully developed an original and simple route for the preparation of highly exfoliated versatile clay nanofillers using photopolymerization green process. The morphology as well as the structure of the prepared nanocomposite were dependent on the surface clay treatment and the monomer concentration which influence directly the clay interlayer distance. Exfoliated structure of nanofillers was obtained with a monomer concentration of 3 mM using silanized clay prepared from an acid activated one. The as obtained exfoliated organic nanofillers show a homogeneous dispersion both in thermoset and thermoplastic matrices producing highly exfoliated ternary nanocomposites with great improved mechanical properties (49 % higher storage moduli in the case of epoxy resin) relative to the pristine matrix at even very small nanofiller loading (5 wt.%). This can be rationalized by both the nanofillers fine dispersion and the chemical surface reactivity ensuring strong interfacial adhesion with the matrix. Based on these results, chemical and morpholigical structures of MMT-PGMA nanofillers might open up new pathways to biobased nanocomposites owing to the plethora of methods for the reaction with nanomaterials.

3.4 Supporting information

3.4.1 Materials

Natural sodium montmorillonite (MMT-Na) was supplied by Southern Clay Products (ion-exchange capacity = 92 mequiv/100g, d_{001} = 1.17 nm, surface area 750 m^2/g). Silver nitrate ($AgNO_3$), 3-(trimethoxysilyl)propyl methacrylate 98% γ -MAPS), glycidyl methacrylate (GMA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), sodium azide (NaN_3), propargyl bromide, ammonium chloride (NH_4Cl) and starch were purchased from Aldrich and used as received. The hydrochloric acid 37% (HCl), ethanol (EtOH), acetonitrile (ACN), chloroform, dimethyl formamide (DMF), and acetone solvents were purchased from Alfa-Aesar and used without further purification. Ultrapure water was purified using a Milli-Q plus purification system. In this study a commercial bio-based epoxy resin containing 56% of carbon from bio-renewable sources "Greenpoxy 56", and a polyamine hardener (SD GP 505 V2) containing around 58% of "green" carbon were used. Both were purchased from Sicomin composites, France.

3.4.2 Preparation of clay-grafted PGMA nanofillers (MMT-PGMA)

The synthesis strategy of PGMA/Clay nanofillers is carried out in three steps as illustrated in Figure 3.1. The montmorillonite clay was first acid activated, briefly, 2 g of MMT-Na were dispersed in 100 mL of 0.05 M HCl under continuous stirring at 60°C for 3 h. The clay powder was then collected by centrifugation and washed several times with ultrapure water until total removal of chlorine ions (as tested by $AgNO_3$), and finally dried in a vacuum oven at 60 °C for 24 h, it was abbreviated MMT-OH. In the second step, the activated MMT-OH was functionalized by grafting of a vinyl silane molecules. 1 g of MMT-OH was first dispersed in 100 mL of ultrapure water under continuous stirring at 60°C for 1 h. The mixture was sonicated for 5 min in order to obtain a stable suspension and then kept under nitrogen flow for 15 min, before adding 1mL of γ -MAPS. The suspension was then continuously stirred under nitrogen at 80°C for 24 h. Subsequently, the powder was collected by centrifugation and washed abundantly with water, ethanol, followed by Soxhlet extraction with EtOH to remove the physisorbed silanes. Finally, the obtained organoclay was abbriviated as MMT-MAPS was dried in a vacuum oven at 60°C for 24 h.

As the last step, 100 mg of prepared MMT-OH-MAPS were dispersed in 10 mL of ACN and continuously stirred under nitrogen flow for 15 min, followed by sonication for 5 min. Then, GMA monomer and DMPA photo-initiator (1% in respect to the monomer) were added to the previously prepared suspension. Three monomer concentrations (1.5, 3, and 4.5 mM) are used to study the influence of this parameter on the structure and the morphology of the obtained nanocomposites was abbreviated as MMT-PGMA-1, MMT-PGMA-2 and MMT-PGMA-3. The obtained mixture was continuously stirred and degassed under nitrogen flow for 15 min before UV irradiation at 365 nm in a spectrolinker XL-1500 UV. The polymerization reaction was performed under continuous stirring. After 2 h of polymerization, the powder was collected by centrifugation and washed abundantly with ACN, ethanol, and then followed by Soxhlet extraction with chloroform. Finally, the obtained nanofillers were dried in vacuum oven at 60°C for 24 h.

3.4.3 Functionalization of clay-grafted PGMA nanofillers (MMT-PGMA-hardener), study of the nanofillers reactivity towards amines

100 mg of MMT-PGMA were dispersed in 20 mL of ACN for 10 min under stirring, and then 2 mL of the amine hardener were added. The suspension was then continuously stirred at 60° C for 6 h. Subsequently, the powder was collected by centrifugation and washed abundantly with ACN and ethanol and then dried in a vacuum oven at 60° C for 24 h.

3.4.4 Fabrication of MMT-PGMA/Green epoxy resin nanocomposites

The ternary nanocomposites MMT-PGMA/epoxy were prepared following two steps, using a solvent-free process. Firstly, the MMT-PGMA nanofillers were dispersed in the Greenpoxy 56 resin under ultrasonicationat 80°C for 1 h. Then, the MMT-PGMA/epoxy prepared mixture was cooled down to room temperature, and the polyamine hardener (SD Green Pox 505 V2) was added to the MMT-PGMA/epoxy mixture at the epoxy/ hardener ratio of 42/40 weight ratio. The mixture was stirred for 5 min, then poured into silicon mold and degassed under vacuum to remove trapped air bubbles and finally cured 24 h at 60°C and then 48 h at room temperature. The ternary nanocomposite was prepared using 5 wt.% of nanofiller of the total weight of resin and hardener. Using the same procedure, MMT-Na/epoxy nanocomposite was prepared and used as reference. It is worthy to mention that the MMT-PGMA contains about 80 wt% of organic modifier and thus the true content of clay in the ternary nanocomposite is only about 1 wt.%.

3.4.5 Synthesis of MMT-PGMA/Starch nanocomposite

Prior grafting starch, it was functionalized with propargylic clickable groups. 1g of starch were solubilized in a mixture of 50 mL of distilled water and 10 mL of NaOH (1 M), then 4 mL of propargyl bromide were added. After 24 h of stirring at room temperature, the functionalized-starch was precipitated in a mixture of H_2O /EtOH (25/75, v/v), and then mixture was then filtred and the obtained product was washed with water and ethanol, then dried at 40°C.

While MMT-PGMA nanofillers were functionalized by the antagonist azide clickable groups. 100 mg of MMT-PGMA were dispersed in 10 mL of DMF and then were added 100 mg of NH_4Cl , and put under stirring at 0°C, then 300 mg of NaN_3 were added. After 30 min, the mixture was put at 50°C for 3 h under nitrogen, and the suspension was centrifuged, and the azide-functionalized clay (MMT-PGMA- N_3) was thoroughly washed with DMF and then with EtOH followed by drying in a vacuum oven at 60°C for 24 h.

20 mg of MMT-PGMA- N_3 were dispersed in a 4 mL of DMF for 10 min, and then 100 mg of propargyl-functionalized starch, 167 mg of $CuBr_2$, and 470µL of PMDETA were added. The mixture was heated at 60°C for 15 min under nitrogen flow to ensure complete dissolution of starch. On the other hand, 10 mg of DMPA photo-initiator were solubilised in 1 ml of DMF and bubbled through nitrogen for 5 min, and then introduced in the clay suspension via a degassed syringe. The mixture was then irradiated at 365 nm under stirring for 3 h. Subsequently, the suspension was centrifuged, and the modified clay was thoroughly washed twice with hot DMF and then with hot EtOH twice followed by drying in a vacuum oven at 60°C for 24 h.

3.4.6 Characterization

Fourier Transform Infrared spectroscopy (FTIR) measurements were conducted on a Bruker TENSOR 27 FTIR spectrometer in the wavenumber range of 400-4000 cm⁻¹ at a resolution of 4 cm⁻¹. For comparison purposes, all spectra were normalized to the area under the Si-O vibration band at about 1000 cm^{-1} .

Thermogravimetric analyses (TGA) were performed on a SetaramSetsys Evolution 16 apparatus in the temperature range of 20-800°C at a heating rate of 10°C/min under argon flow rate of 20 mL/min.

XRD measurements were carried out on a Bruker D8 Advance diffractometer using Cu K α source $(\lambda = 1.54 \text{ Å})$ and 2θ scans were obtained from 4 to 10° . The basal distance of the silicate layer (d_{001}) was calculated using the Bragg's equation $(n\lambda = 2.d_{001}.sin\theta)$ where n=1 and θ is the diffraction angle.

Transmission electron microscopy (TEM) analyses were performed on a FEI Tecnai F20 microscope operating at an accelerating voltage of 200 kV. The modified clay powders were dispersed in ethanol under ultrasonication, and the suspension was dropped onto the Formvar carbon film-coated copper grid. In the case of the ternary nanocomposite films, the samples were prepared using an ultramicrotome equipped with a diamond knife to obtain ultrathin specimens.

Dynamic mechanical measurments (DMA) were performed on a TA Q800 Dynamic apparatus in the tension mode with a constant frequency of 1 Hz, and a heating rate of 5° C/min in the range of 0-145°C. The nanocomposite samples were cut into rectangular specimens of 20 x 5 x 1 mm³.



Figure 3.5 – Expanded FTIR spectra of (a) pristine clay (MMT-Na), (b) activate clay (MMT-OH).



Figure 3.6 – DTG curves of (a) pristine clay (MMT-Na), (b) activate clay (MMT-OH), (c) vinyl-functionalized clay (MMT-MAPS).

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Chapter 4

Green epoxy resin filled with poly epoxy-functionalized clay hybrid nanofillers: preparation, characterization and mechanical properties

The work developed in this chapter is intended to be submitted to ACS Sustainable Chemistry & Engineering.

Abstract This study reports the synthesis of highly exfoliated poly epoxy-functionalized montmorillonite/green epoxy resin ternary nanocomposites. The homogenous filled resin network was produced following a four-step procedure: (i) acid activation of clay montmorillonite, (ii) vinyl-functionalization of the clay interlayer spacing, (iii) in-situ photo-induced polymerization of glycidyl methacrylate on the vinyl-functionalized clay interlayer spacing, and (iv) incorporation of the poly(glycidyl methacrylate)grafted clay montmorillonite in the epoxy resin using a green polyamine as hardener. The materials structure and the morphology were characterized by FTIR, TGA, XRD, SEM and TEM. The results show that silanization of the acid-treated montmorillonite clay (hereafter MMT-OH) using water as solvent ensured efficient grafting of vinyl silane moities inside the clay layers, resulting in an increase of the clay interlayer d-spacing from 1.23 nm to 1.48, 1.52, and 1.64 nm for 0.5, 0.75, and 1 mL of initial vinyl silane amount, respectively. Increasing polymerization reaction time from 1 to 3 h increased the PGMA loading giving a mass content of 32.82 wt.% and 91.3 wt.%, providing an intercalated and an exfoliated structures, respectively. The incorporation of different contents of poly epoxy-functionalized clay layers enhanced continuously the mechanical properties of the epoxy resin, increasing remarkably the storage modulus and the glass transition temperature. For example at 25°C, 10 wt.% of MMT-PGMA nanofillers increased E' and T_g by 87.7% and 26.5°C, respectively.

4.1 Introduction

Along with the great development of the polymer-based materials industry, increasing sensitiveness towards eco-conception has to be considered as an important objective nowadays. The use of polymeric materials must move towards renewable resources in order to adapt to sustainable development criteria. These new materials allow not only replacement for fossil fuels by limiting the use of petroleum-based polymers but also reduction or even elimination of the use or the generation of substances harmful to the environment. This is particularly accentuated in the case of composite materials since great amounts of petroleum-based polymers have been routinely used. Among the original developed biomass polymers for composite materials, bio-based epoxy resins are in full development owing to their interesting thermal and chemical properties which permitted their various applications such as paints and coatings, adhesives, electronic components and composites [1, 2, 3, 4, 5].

However, a low glass transition temperature, a low stiffness and a low elongation at break of bio-based epoxy resin films limit their expansion in the industrial field. Liu *et al.* [6] prepared epoxidized soybean oil based "green" composites with triethylenetetramine (TETA) as curing agent. Glass-transition temperature (T_g) of 11.8°C and storage modulus of 590 MPa were determined within the glassy state for the obtained film by dynamic mechanical analysis. Identically, epoxidized soybean oil-based film prepared in presence of methylhexahydropthalic anhydride as curing agent and 2-ethyl-4-methylimidazole as catalyst was reported by Tan *et al.* [7]. The so-obtained material showed a storage modulus of 400 MPa and a T_g of 62°C, hence their mechanical properties are not enough for an applicable composite material.

In the work of Lu *et al.* [8], biobased composites have been prepared by the cationic polymerization of conjugated soybean oil (CSOY) or conjugated LoSatSoy oil (CLS) with styrene (ST) and divinylbenzene (DVB). The storage modulus (< 1 GPa) and T_g (<20 °C) of both cases are dissatisfied for commercial application.

Several efforts have been made in order to increase these properties, by applying the chemical modifications way or by using different kinds of fillers [6, 9, 10, 11, 12]. These reinforcement materials allow for tailoring the properties of the composites to fit the requirements of structural or functional materials.

Among various proposed reinforcing fillers, nanoclays have occupied a large proportion of the efforts of researchers around the world because of their natural origin, low-cost aspect for the particles and promise of improving barrier as well as mechanical properties of related nanocomposites. Thus, it is only understandable that they appear frequently in the literature as proposed reinforcements for plant oil-based nanocomposites. It is well known that the dispersion level of silicate layers into polymer matrices is one of the key factors contributing to the control of the microstructure, thus thermo-mechanical properties of polymer clay nanocomposites (PCNs). A good dispersion requires however an efficient processing such as three-roll mill, high shear mixing, or by combining with thermomechanical or sonication effects [13, 14, 15, 16, 17, 18, 19].

Besides, to improve the dispersion level of clay in thermoset polymer matrices, use of solvent such as acetone, chloroform have been usually applied for the processing of PCNs [19, 20, 21]. It is also important to note that the use of such solvents for solution dispersion process can give some potential environmental and health problems [22]. The application of more eco-friendly and high efficient methods such as solventless are desirable for the processing of epoxy clay nanocomposites [23, 24]. Unfortunately, the morphology of the nanocomposites obtained without using solvent is usually intercalated or partial intercalated but rarely fully exfoliated, hence the optimal mechanical properties inherent to the exfoliated morphology cannot be achieved [6, 7, 8, 23, 17, 25].

Besides, strong interaction between polymer matrix and fillers has a crucial role in affording ad-

vanced mechanical properties to the composite materials since it allows good load transfer from the matrix to the reinforcement. Thus, the organo chemical modification of clay surface step is necessary to make it compatible with the polymer matrix [26, 27]. The use of silane coupling agents or alkyl ammonium cations (primary, secondary, tertiary or quaternary) has been widely reported in the literature to facilitate dispersion and to improve the adhesion between the clay layer and polymer matrix, leading to an increasing of the physical, mechanical, and chemical properties of the nanocomposite [27]. Indeed, effective improvement of nanocomposites' mechanical properties requires random organization of the clay layers which ensures facile penetration of matrix chains in between permitting uniform dispersion in the nanocomposite. Many researches in the clay-based nanocomposites domain have shown that this can be achieved *via* polymer functionalization of the clay surface [28, 29].

In this contribution, we discuss an efficient approach to elaborate GreenEpoxy/Clay nanocomposites. First, to ensure robust interfacial interactions at the molecular level, montmorillonite clay surface (MMT) was chemically modified *via* silanization using 3-methacryloxypropyl trimethoxysilane (γ -MAPS). Next, polyglycidyl methacrylate (PGMA) chains were grafted onto the organoclay interface *via* photo-initiated free radical polymerization through the vinyl-grafted functions. Finally, the as-obtained epoxy-rich clay nanofillers (MMT-PGMA) were dispersed in a Green epoxy matrix to obtain exfoliated ternary nanocomposite films. Green epoxy matrix was selected due to its high renewable content (> 56%). Moreover, it can be cured under ambient conditions using a stoichiometric resin/hardener ratio. It is also to note that on the one hand, the hardener contains more than 58% of "green" carbon and, on the other hand, the epoxy-clay nanocomposites were processed under environmental friendly conditions (solventless) ensuring a "green" label to the final nanocomposites.

4.2 Experimental section

4.2.1 Chemicals

Natural sodium montmorillonite (MMT-Na) was supplied by Southern Clay Products (ion-exchange capacity = 92 mequiv/100g, d001= 1.17 nm, surface area 750m2/g). Silver nitrate ($AgNO_3$), (trimethoxysilyl) propyl methacrylate 98% γ -MAPS), glycidyl methacrylate (GMA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), were purchased from Aldrich and used as received. The hydrochloric acid 37% (HCl), ethanol (EtOH), acetonitrile (ACN), chloroform, and acetone solvents were purchased from Alfa-Aesar and used without further purification. Ultrapure water was purified using a Milli-Q plus purification system. In this study a commercial bio-based epoxy resin containing 56% of carbon from bio-renewable sources "Greenpoxy 56", and a polyamine curing agent (SD GP 505 V2) containing around 58% of "green" carbon were used. Both were purchased from Sicomin composites, France.

4.2.2 Characterization and Instruments.

Fourier Transform Infrared spectroscopy (FTIR) measurements were conducted on a Bruker TENSOR 27 FTIR spectrometer in the wavenumber range of 400-4000 cm⁻¹ at a resolution of 4 cm⁻¹. For comparison purposes, all spectra were normalized to the area under the Si-O vibration band at about 1000 cm⁻¹. Thermogravimetric analyses (TGA) were performed on a SetaramSetsys Evolution 16 apparatus in the temperature range of 20-800°C at a heating rate of 10°C/min under argon flow rate of 20 mL/min. X-ray diffraction measurements were carried out on a Bruker D8 Advance diffractometer using Cu K α source (λ =1.54 Å) and 2 θ scans were obtained from 4 to 10°. The basal distance of the silicate layer (d_{001}) was calculated using the Bragg's equation ($n\lambda = 2.d_{001}.sin\theta$) where n=1 and θ is the diffraction angle. Transmission electron microscopy (TEM) analyses were performed on a FEI Tecnai F20 mi-

croscope operating at an accelerating voltage of 200 kV. The modified clay powders were dispersed in ethanol under ultrasonication, and the suspension was dropped onto the Formvar carbon film-coated copper grid. In the case of the ternary nanocomposite films, the samples were prepared using an ultramicrotome equipped with a diamond knife to obtain ultrathin specimens. Dynamic mechanical measurments (DMA) were performed on a TA Q800 Dynamic apparatus in the tension mode with a constant frequency of 1 Hz, and a heating rate of 5°C/min in the range of 0-145°C. The nanocomposite samples were cut into rectangular specimens of 20 x 5 x 1 mm³.

4.2.3 Activation of clay (MMT-OH)

2 g of MMT-Na were dispersed in 100 mL of 0.05 M HCl under continuous stirring at 60°C for 3 h. The clay powder was then collected by centrifugation and washed several times with ultrapure water until total removal of chlorine ions (as tested by AgNO3), and finally dried in a vacuum oven at 60°C for 24 h. The activated clay was abbreviated as MMT-OH.

4.2.4 Silanisation of clay (MMT-MAPS)

1 g of MMT-OH was first dispersed in 100 mL of ultrapure water under continuous stirring at 60°C for 1 h. The mixture was sonicated for 5 min in order to obtain a stable suspension and then kept under nitrogen flow for 15 min, before adding the desired amount of γ -MAPS. The suspension was then continuously stirred under nitrogen at 80°C for 24 h. To optimize the silanization reaction on the activated clay, three amounts of γ -MAPS (0.5, 0.75 and 1mL) were used and the obtained silanized clays were abbreviated MMT-MAPS-0.5mL, MMT-MAPS-0.75mL, and MMT-MAPS-1mL, respectively. Subsequently, the powder was collected by centrifugation and washed abundantly with water, ethanol, followed by Soxhlet extraction with EtOH to remove the physisorbed silanes. Finally, the obtained vinyl-functionalized clays were dried in a vacuum oven at 60°C for 24 h.

4.2.5 *In situ* photo-induced polymerization of glycidyl methacrylate in presence of vinyl-functionalized clay (MMT-PGMA)

100 mg of prepared MMT-MAPS were dispersed in 10 mL of ACN and continuously stirred under nitrogen flow for 15 min, followed by sonication for 5 min. Then, GMA monomer and DMPA photo-initiator (1% in respect to the monomer) were added to the previously prepared suspension. The obtained mixture was continuously stirred and degassed under nitrogen flow for 15 min before UV irradiation at 365 nm in a spectrolinker XL-1500 UV. The polymerization reaction was performed under continuous stirring. The polymerization time was optimized to produce exfoliated nanocomposite. For this, three polymerization reaction times were investigated, *i.e.* 1, 2 and 3 h, and the obtained polymer-grafted clays were abbreviated as MMT-PGMA-1, MMT-PGMA-2 and MMT-PGMA-3. After the desired polymerization time, the powder was collected by centrifugation and washed abundantly with ACN, ethanol, and then followed by Soxhlet extraction with chloroform. Finally, the obtained nanofiller was dried in vacuum oven at 60°C for 24 h.

4.2.6 Fabrication of MMT-PGMA/Green epoxy resin nanocomposites.

The ternary nanocomposites MMT-PGMA/epoxy were prepared following two steps. Firstly, the MMT-PGMA nanofillers were dispersed in the Greenpoxy 56 resin under high shear mixing at 80°C for 1 h. Then, the MMT-PGMA/epoxy prepared mixture was cooled down to room temperature, and the

polyamine hardener (SD Green Pox 505 V2) was added to the MMT-PGMA/epoxy mixture at the epoxy/ hardener ratio of 42/40 weight ratio. The mixture was stirred for 5 min, then poured into silicon mold and degassed under vacuum to remove trapped air bubbles and finally cured 24 h at 60°C and then 48 h at room temperature. The ternary nanocomposite was prepared varying the amount of nanofiller from 1 to 15 wt.% of the total weight of resin and hardener. Using the same procedure, MMT-Na/epoxy nanocomposite was prepared and used as reference using 2 wt.% of MMT-Na.

4.3 Results and discussion

4.3.1 Fabrication of green epoxy nanocomposites filled with MMT/PGMA.

The preparation of the MMT-PGMA/Green epoxy ternary nanocomposite can be divided into two main parts, where the first one combines the three-step procedure of PGMA-grafted clay nanofillers synthesis and the second one deals with the incorporation of the as-prepared nanofillers in a green epoxy resin, as illustrated in Figure 4.1.



Figure 4.1 - Preparation procedure of the MMT-PGMA/Green epoxy ternary nanocomposites.

In the part one, first, the montmorillonite clay surface was activated using chlorhydric acid with the aim to introduce hydroxyl groups in between the clay layers (abbreviated as MMT-OH). Next, methacrylate silane was covalently attached at the interlayer clay surface through silanization reaction with the internal silanol groups resulting on vinyl-functionalized clay (abbreviated as MMT-MAPS). This step has three objectives, (i) conversion of the clay surface from hydrophilic to hydrophobic in order to ensure its compatibility with the monomer used in the following polymerization step, (ii) separation of the clay layers from each other which facilitates the penetration of the monomer, and (iii) finally functionalization of the clay layers surface with vinylic groups in order to ensure their covalent bonding with the polymer chains in the course of the polymerization procedure. Finally, *in situ* photoinduced polymerization of glycidyl methacrylate in presence of the vinyl-functionalized clay, leading to the growing of poly(glycidyl methacrylate) chains inside the clay layers and covalent tethering to their surface (abbreviated as MMT-PGMA). Grafting of polymer ensures more separation of the clay layers which facilitates the insertion of resin matrix chains in the step of fabrication of the ternany nanocomposites, and the choice of PGMA polymer is related to the its highly epoxy reactive groups able to ensure strong interactions with the epoxy matrix through reaction with multi-amine hardener playing also the role of covalent bridge between clay and matrix.

In the second part, the MMT-PGMA nanofillers were dispersed in a green epoxy resin for 1 h at 80°C using an ultra-turrax before adding the polyamine hardener. It should be pointed out that high temperature, high speed, high pressure, an ultrasound sonication at the mixing step were demonstrated favorable to obtain highly exfoliated nanocomposites [17, 23, 30, 31]. Besides, rapid curing and effective degassing during processing were reported to contribute to the reinforcement of the tensile modulus, and tensile strength of the resultant nanocomposites [18, 32]. Thus, the mixture was then transferred into a silicon mold and cured at 60°C for 24 h. Optimization of the preparation parameters of nanofillers as well as epoxy nanofiller filled nanocomposites is crucial to ensure fine and homogeneous dispersion of the clay nanofillers in the epoxy resin matrix and thus produce performant final epoxy-clay nanocomposites. For this, we were interested in investigated both the effect of the amount of silane coupling agent and photopolymerization time on the structure of the nanofillers. Then, we have evidenced the great influence of the method used for dispersing the nanofillers in the epoxy matrix on the morphology of prepared nanocomposite. Ultra-turrax instrument was adopted for mixing the nanofillers with the epoxy matrix under heating as these conditions facilitate dispersion of the nanofillers in the viscous epoxy resin; details are given in Figure 4.2.



Figure 4.2 – Schematic illustration of dispersion of clay and epoxy-rich clay nanofillers into the green epoxy resin matrix.

4.3.2 Characterization of vinyl-functionalized clay layers

After reaction between γ -MAPS at the three different amounts and the acid-activated clay, the structures of resulting MMT-MAPS were characterized by infra-red spectroscopy as shown Figure 4.3. As it can be observed, the spectrum of MMT-OH shows a large band centered at 3626 cm⁻¹ and a sharp peak at 1634 cm⁻¹, corresponding to the silanol groups and the deformation band of adsorbed water, respectively [33]. Previous reports have shown three possible reactive clay-sites, "broken" layer edges, external surface, or in between platelets for grafting of silane coupling agents, this depending both on the silane structure and the solvent surface energy [34, 35].

As our aim was to exfoliate the clay layers, we have selected the conditions allowing to grafting silane inside the clay platelets, *i.e.* trifunctional silane and water as silanization solvent. After the silanization reaction, FTIR spectrum displays decrease of the intensity of the silanol band, indicating reaction *via* this group and thus their transformation to Si-O-Si groups. Two bands appeared at 2945 and 2890 cm⁻¹, attributed to the asymmetric and symmetric stretching of $-CH_2$ groups in the alkyl



Figure 4.3 – (a) FTIR spectra, (b) TGA curves of activated clay (MMT-OH) and silanised clay prepared from activated clay at different silane concentration 0.5, 0.75 and 1 mL.

chains of MAPS, respectively [36, 37]. Moreover, the new characteristic peaks detected at 1726 and 1634 cm⁻¹ are ascribed to C=O and C=C groups, respectively [37, 38]. The effect of the initial silane concentration has been investigated for three MAPS amounts (0.5, 0.75, and 1 mL) and FTIR results show obvious increase of the C=O stretching mode peak intensity with increasing silane concentration, indicating that the degree of silane grafting increased accordingly. These FTIR results provide an evidence for the successful silanization reaction [39].

TGA analysis was further employed to quantify the grafting amount on the clay layers. One can note from Figure 4.3(b), a clear decrease of both amount of physically adsorbed water at about 100°C and the onset temperature attributed to the reduced thermal stability after silanization reaction, revealing conversion of clay surface from hydrophilic character to hydrophobic one. The total weight loss showed for activated clay MMT-OH corresponding to the evaporation of physisorbed water at about 100°C and the irreversible dehydroxylation of clay at 639°C were found to be of about 13.9 wt.% [36]. After silanization reaction, the weight loss increased to approximately 18.8 wt.% for MMT-MAPS-0.5mL, 28 wt.% for MMT-MAPS-0.75mL and 31.8 wt.% for MMT-MAPS-1mL, fully confirming the FTIR results.

To gather information about structure of the clay layers, XRD measurements were conducted on clay before and after silanization reaction and the interlayer d-spacing was calculated according to Bragg equation (Figure 4.4). An intensive diffraction peak was detected at $2\theta = 7.2^{\circ}$ for MMT-OH, reflecting an interlayer spacing of about 1.23 nm. After silanization reaction, the diffraction peak continuously shifted towards lower 2θ angles, decreased in intensity and became broader with increasing of initial silane amount, which implies a good intercalation of the silane coupling agent moieties into the clay interlayer. The vinyl-functionalized clays show an interlayer spacing of about 1.48, 1.52 and 1.64 nm for MMT-MAPS prepared using 0.5, 0.75 and 1 mL of γ -MAPS, respectively. MMT-MAPS-1 mL was retained for the preparation of the binary nanocomposites, due to its highest interlayer spacing facilitating penetration of monomer molecules inside the clay layers.

4.3.3 Chemical and morphological structures of polymer-grafted clay layers

The FTIR results (Figure 4.5(a)) for polymer-grafted clay layers prepared from MMT-MAPS-1mL, exhibited obvious changes in the spectra of MMT-PGMA with respect to the spectrum of their precursor



Figure 4.4 – XRD patterns of (a) activated clay MMT-OH, (b) vinyl functionalized- clay (MMT-MAPS) at different concentrations of silane.

MMT-MAPS, confirming the success of the growth of poly epoxy polymer chains in the clay interlayers through UV-initiated free radical polymerization. The effects of the polymerization reaction time (varied from 1 h to 3 h) on the loading with PGMA on the clay layers is demonstrated through the increasing intensity of the polymer characteristic signals (Figure 4.5(a)). First, appearance of new peaks at 904, 845 and 757 cm⁻¹, related to stretching of epoxide groups, and great diminution (MMT-PGMA-1 and MMT-PGMA-2) or complete disappearance (MMT-PGMA-3) of the peak of the vinyl groups at 1634 cm⁻¹, and finally increase in the intensity of the carbonyl stretching vibrations peak at 1726 cm⁻¹ are clear proofs for the PGMA grafting on the silicate layers as well as its continuous growth from 1 to 3 h.

Vinyl-functionalized clay prepared using 1 mL of γ -MAPS has been selected for the following steps because it exhibited higher surface grafting of PGMA, as expected from XRD results. Indeed, comparison of FTIR spectra (see Figure 4.13 in the supporting information) of MMT-PGMA prepared using MMT-MAPS-0.75 mL and MMT-MAPS-1mL indicates clearly that the peak intensities of epoxide (904, 845 and 757 cm⁻¹) and carbonyl (1726 cm⁻¹) characteristic PGMA signals are much higher in the case of γ -MAPS 1 mL.

The TGA analysis provided information about the PGMA grafted amount and confirmed the FTIR results, showing that the grafted amount increased with reaction time. MMT-PGMA-1, MMT-PGMA-2 and PGMA-3 show weight losses of about 38.8, 79.8 and 91.3 wt.%, respectively (Figure 4.5(b)).

XRD analysis was used to characterize the structure of the MMT-PGMA binary nanocomposites. XRD pattern of MMT-MAPS is shown again in the Figure 4.6 for comparison purposes. MMT-PGMA-1 pattern shows shift of the sharp diffraction peak toward lower angles ($2\theta = 4^\circ$), indicating an increase in the interlayer spacing from 1.64 nm (MMT-MAPS) to 1.88 nm for the MMT-PGMA-1. Both MMT-PGMA-2 and MMT-PGMA-3 do not show any visible diffraction peak, indicating disordered structure with high interlayer spacing. As the absence of diffraction peak alone is not sufficient to predict fully exfoliation structure of the clay layers, TEM analysis was used to provide additional information.

As can be seen in the top of the Figure 4.7, SEM micrographs show an obvious change in the montmorillonite surface morphology after polymer grafting. The MMT-Na exhibits agglomerates of sharp flakes, while the MMT-PGMA shows much smoother surface due to the surface coverage with amorphous polymer chains. TEM images (bottom of the Figure 4.7) confirmed the suggested morphological structures based-on XRD characterization, revealing an intercalated morphology for the MMT-PGMA-



Figure 4.5 - (a) FTIR spectra, (b) TGA curves of silanised clay and polymer-grafted clay prepared with different polymerization times 1, 2 and 3 h.



Figure 4.6 – XRD patterns of silanized clay MMT-MAPS, and polymer-grafted clay prepared with different polymerization time 1 (MMT-PGMA-1), 2 (MMT-PGMA-2) and 3 h (MMT-PGMA-3).

1 and an exfoliated one for MMT-PGMA-2 and MMT-PGMA-3. The clay layers in MMT-PGMA-1 remain parallel with an increased interlayer spacing from about 1.64 nm before polymerization reaction (as calculated from XRD) to 1.9 nm after 1 h of polymerization time (as shown by TEM). The MMT-PGMA-2 image showed that most of the clay platelets are sufficiently separated from each other, giving more increased interlayer spacing and random structure. In the case of MMT-PGMA-3 nanocomposite, fully delamination and random distribution of the clay layers are observed. The TEM observations are in well agreement with the XRD results, and both of them showed that the polymerization time affects strongly the binary nanocomposite structure.

Taking in account the different obtained results and the preparation conditions, MMT-PGMA-2 has been selected to be incorporated in the epoxy resin as nanofiller. As it showed exfoliated structure, high amount of grafted epoxy groups at the surface of clay, and short time of polymerization, MMT-PGMA-2


could predict facile and homogeneous dispersion in epoxy matrices.

Figure 4.7 – (Top images) SEM micrographs of pristine clay (MMT-Na) and poly(glycidyl methacrylate)-grafted clay binary nanocomposites. (Bottom images) TEM micrographs of or poly(glycidyl methacrylate)-grafted clay binary nanocomposites at polymerization time of 1 h (MMT-PGMA-1), 2 h (MMT-PGMA-2) and 3 h (MMT-PGMA-3).

4.3.4 Structural characterization of the epoxy-rich clay/green resin ternary nanocomposite

In order to study the reactivity of the curing system, FTIR analysis was performed to follow the conversion of the epoxy groups from the resin via reaction with the polyamine hardener at three different times, T0 corresponds to the resin/hardener mixture just after mixing, T1 is typical for 40 minutes of mixing at 60°C and T2 corresponds to overnight mixing at 60°C. Note that the mixtures were prepared using epoxy/hardener system of 42/40 weight ratio. Figure 4.8 shows that the characteristic signals of epoxide groups detected at 758 and 913 cm⁻¹ decreased from T0 to T1, to completely disappear in the case of T2. The change in the chemical structure was accompanied by appearance of a large band centered at 3364 cm⁻¹, ascribed to hydroxyl groups coming from the epoxides ring opening reaction with the amine function from hardener. Complete conversion of all the epoxy groups reflects the high reactivity of the used curing agent toward the green epoxy resin.

XRD patterns of the epoxy resin filled with 2 wt.% of MMT-Na and 5wt.% of MMT-PGMA together with the ones for each of the system-building constituents are displayed in Figure 4.9. The ternary nanocomposite prepared using pristine clay MMT-Na as nanofiller revealed a diffraction peak at the same 2θ position as pure pristine clay, indicating that the epoxy resin chains did not intercalate into the clay interlayer and therefore all clay platelets remained completely stacked. This is explained by the incompatibility between clay and epoxy resin which leads to very poor interfacial interactions. However, no peak was detected in the XRD pattern of the epoxy-functionalized-clay nanofillers filled resin, indicating highly dispersion of the clay platelets in the epoxy resin matrix, which can be due to both the pre-exfoliated structure of the used nanofillers as shown by Figure 4.9(c) and the strong interfacial adhesion between the nanofillers and the matrix. Indeed, the rich-epoxy groups at the surface of clay ensure chemical bonding with the matrix via amine hardener.

The XRD findings were supported by TEM observations (Figure 4.10) which gave clear morpho-

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Figure 4.8 – IR spectra of system resin epoxy-hardener at 60° C and at different crosslinking times T0 (0 minute), T1 (40 minutes) and T2 (12 h)



Figure 4.9 – XRD patterns of (a) MMT-Na, (b) MMT-Na/Greenepoxy nanocomposite 2 wt.%, (c) MMT-PGMA and (d) MMT-PGMA/Greenepoxy nanocomposite avec 5 wt.%.

logical structure of the nanoscale dispersion state of the clay platelets in the ternary nanocomposites prepared by incorporation of 2 wt.% of MMT-Na pristine clay, and different amounts of MMT-PGMA-2 polymer-grafted clay (2, 5, and 15 wt.%).

Incorporation of the unmodified clay in the epoxy resin matrix appears to lead to high degree of agglomerated morphology consisting of stacked layers in the matrix. This is explained by both the incompatibility of the hydrophilic pristine clay with the organic epoxy resin matrix and its small interlayer spacing preventing the polymer chains to access into the interlayer. TEM images of the MMT-PGMA/epoxy resin ternary nanocomposites prepared with 2 and 5 wt.% show that the clay platelets are predominantly thin and randomly dispersed in the matrix. Several individual platelets were detected for 5 wt.% loading. Nevertheless, more layers are assembled to form tactoids randomly distributed in the matrix in the case of nanocomposites containing 15 wt.% of nanofillers. The pre-exfoliated structure of the epoxy-rich clay as well as the presence of reactive and hardener-compatible groups at the clay surface demonstrated their positive effect in the homogeneous dispersion of clay layers in polymer matrix.

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Figure 4.10 – TEM images of MMT-Na/Green epoxy with 2 wt.% and MMT-PGMA/Green epoxy nanocomposite with 2, 5 and 15 wt.% of MMT-PGMA nanofillers.

4.3.5 Dynamic mechanical properties of the ternary nanocomposite

The mechanical reinforcing effect of the epoxy-rich clay and its content on the epoxy resin was investigated using dynamic mechanical analysis (DMA) by measuring the storage modulus E' and determination of loss factor tan δ as a function of temperature in the temperature range of 0 to 145°C. For this, unfilled and filled resin films with MMT-Na and MMT-PGMA at different contents have been prepared. From Figure 4.11, it should be noted that incorporation of pristine clay did not induce any variation of the storage modulus and the tan δ of the resin because of its stacked structure in the matrix as shown by XRD and TEM analyses. This leads to limited interfacial interactions and thus conservation of the resin structure. Whereas, MMT-PGMA filled epoxy resin nanocomposites show a higher storage modulus than the pure epoxy resin throughout the whole temperature range and this behavior is displayed for any nanofiller content. Storage modulus and loss factors of the ternary nanocomposites, for different nanofillers content are summarized in Table 4.1 at three temperatures as representative examples of the behavior observed below, close and above the glass transition temperature.

It can be noted that even at temperatures below the glass transition temperature (T_g) , incorporation of MMT-PGMA nanofillers into the Green epoxy resin enhanced significantly the storage modulus. For example at 25°C, incorporation of 2 wt.% and 10 wt.% of MMT-PGMA in the resin increased the storage modulus from 1984.5 to 2403 and 3725 MPa, which corresponds to 21% and 88% increase, respectively. In can be noted that above T_g , greater improvement of the mechanical performance of the epoxy nanocomposite was observed for all nanofiller contents. Nanofiller content of 2 wt.% and 10 wt.%, for examples, induced an increase of the storage modulus of about 53.6% and 489 %, respectively.

The improvement in resin nanocomposites storage modulus as observed in presence of MMT-PGMA nanofillers can be attributed to the homogenous and fine distribution of the nanofillers within the epoxy resin matrix as demonstrated both by TEM and XRD results. Due to the delaminated morphology, the matrix chains can easily penetrate into the clay interlayer leading to their confinement in the crosslinked network which reduces significantly their movement and therefore increases the stiffChapter 4. Green epoxy resin filled with poly epoxy-functionalized clay hybrid nanofillers: preparation, characterization and mechanical properties



Figure 4.11 – Storage modulus and loss factor (tan δ as function of temperature of neat green epoxy resin and MMT-PGMA/Green epoxy nanocomposite at different nanofillers contents. The MMT-Na/Green epoxy nanocomposite at 2 wt.% is reported by the dash line.

ness of the clay-functionalized nanofillers filled resin. In addition to their morphology, nanofillers are multifunctional as they are densely decorated with epoxy groups as demonstrated by FTIR and TGA results, which permits chemical reaction during synthesis of the nanocomposite between the multi amine hardener and both nanofillers and epoxy resin via epoxide ring opening with nucleophilic amine groups. This chemical crosslinking generates strong interfacial adhesion between nanofillers and epoxy resin matrix, which plays a key role in the enhancement of the mechanical properties of the resin [12, 14, 16].

However, the reinforcement effect was decreased when the amount of incorporated nanofiller was increased to 15 wt.%, which can be explained by less fine dispersion of the nanofillers because of presence of some tactoids in the epoxy resin matrix as shown by TEM analysis (Figure 4.10).

As can be seen from Figure 4.11, obvious continuous increase of the glass transition temperature was shown with increasing of the nanofillers content in the ternary nanocomposites comparing to the pure epoxy matrix. This is attributed to the increase of the amount of dispersed platelets resulting in more confinement of the molecular polymer chains which could restrict further their mobility. The green epoxy resin shows a peak at 85.4 °C, corresponding to its transition from the glass to the rubbery state. Incorporation of 10 wt.% of nanofillers in the resin shifts T_g to 111.8°C which corresponds to an increase of 26.5°C [32, 40]. These results demonstrated the benefic effect of the epoxy-functionalized clay-based nanofillers in the mechanical reinforcement of the ternary nanocomposites.

In addition, on can note that $\tan \delta$ of ternary nanocomposites was lower than that of pure epoxy resin, which can be ascribed to the interfacial interactions between nanofillers surface with the resin matrix [32, 16, 40]. It should be noted that both T_g and $\tan \delta$ of the nanocomposite containing 15 wt.% of nanofillers are lower than that filled with 10 wt.%, which can be explained by the partial exfoliation of the nanofiller morphology, *i.e.* less individual dispersed layers (Figure 4.11), generating less chain confinement.

To better understand and explain the effect of the nanofillers in the reinforcement of mechanical properties of the epoxy resin nanocomposites, the microstructures of tensile fracture surface of the pure epoxy resin, pristine clay and epoxy resin nanocomposites filled with polymer functionalized-clay were investigated by SEM. As it can be observed from Figure 4.12, the pure epoxy resin exhibits a smooth and flat fracture surface with occasional linear cracks. It can be seen that the lines are parallel to the

Table 4.1 – Storage modulus and glass-transition temperature (T_g) of neat green epoxy resin and MMT-PGMA/Green epoxy nanocomposites at different nanofillers contents.

MMT-PGMA	Stora	Tg (°C)		
(wt %)	3 °C	90 °C	140 °C	
0	2076 ± 25	33.7 ± 2,5	14.3 ± 0,5	85.3 ± 0,12
2	2535 ± 46	111.4 ± 6,4	$\textbf{20.1} \pm \textbf{0,6}$	$\textbf{91.2} \pm \textbf{0,14}$
5	3095 ± 63	583.6 ± 17,2	$30.1 \pm 1,1$	97.5 ± 0,17
7	$\textbf{3620} \pm \textbf{79}$	$\textbf{1274.6} \pm \textbf{29,5}$	50.7 ± 1,6	$\textbf{105.1} \pm \textbf{0,21}$
10	3886 ± 87	1883.6 ± 45,4	69.2 ± 2,1	$\textbf{111.6} \pm \textbf{0,24}$
15	3688 ± 75	$\textbf{1883.5} \pm \textbf{34,7}$	46.5 ± 1,7	$\textbf{109.69} \pm \textbf{0,19}$

direction of the crack propagation. This phenomenon is typical of a brittle failure and is well-known in the cured epoxy materials [13, 16, 41]. Nevertheless, the fracture surface changes significantly after addition of clay nanoparticles into the resin, it becomes clearly rougher. It should be also noted that the continuous cracks direction seen in the pure epoxy resin was lost in both epoxy resin filled with MMT-Na and MMT-PGMA due to the limited propagation of the cracks induced by the presence of the clay platelets [42].



Figure 4.12 – Microstructure of tensile fracture surface of pure GreenEpoxy film and its nanocomposites.

In the case of MMT-Na/epoxy resin nanocomposite, due to aggregated clay nanoparticles and poor interfacial interactions with the epoxy resin, separation between the two constituents and appearance of voids around the clay tactoids were observed. These voids act as points of stress concentration which generated some new fracture surfaces in the nanocomposite [16, 43].

MMT-PGMA/epoxy sample is much more uniformly distributed, and displayed smoother fractured surface than that seen for the MMT-Na. Furthermore, there is no void around the clay particles, thus it is clear that the polymer-functionalized clay has a good adhesion with the polymer matrix. This further demonstrated the strong effect of the surface chemistry of the clay layers on not only their dispersion in the polymer matrix but also in the significant improvement of their adhesion with the matrix.

4.4 Conclusions

Green epoxy resins filled with epoxy functionalized-clay were prepared as ternary nanocomposites through high shear mixing and thermal curing by incorporation of poly epoxy-functionalized montmorillonite nanofillers in a green epoxy resin in the presence of polyamine hardener. The novel experimental procedure proposed herein for the synthesis of MMT-PGMA nanofillers permits controlling the grafting density of PGMA coating though the polymerization time, and thus adjusting the interlayer spacing. FTIR and TGA analyses confirmed that the poly(glycidyl methacrylate) chains are densely grafted onto clay layers surface, while both XRD and TEM results indicated a highly exfoliated morphology for the clay layers in the MMT-PGMA at polymerization times of 2 and 3 h. As the exfoliated MMT-PGMA nanofillers are selected to be incorporated in the epoxy resin, significant improvement of clay layers dispersion homogeneity and exfoliation in the epoxy resin have been shown. In addition to the initial random morphological structure of the nanofillers, their surface functionality plays crucial role. Indeed, the poly amine hardener is able to react with both epoxy groups from PGMA grafts and those coming from epoxy resin *via* epoxide ring opening reaction, playing a role of interfacial bridge between the resin and the clay surface. As such strong interactions between clay and epoxy resin were obtained resulting in significant improvement of the storage moduli and increasing of glass temperature transition in the MMT-PGMA filled epoxy resins.

4.5 Supporting information

Effect of the grafting density of vinyl-functionalized clay on the polymerization efficiency



Figure 4.13 – FTIR spectra of polymer-grafted clay (MMT-PGMA) prepared from γ -MAPS volume of (a) 0.75 mL, (b) 1 mL.

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Chapter 5

From morphology to thermodynamics and mechanical properties of epoxy/clay nanocomposite: investigation by molecular dynamics simulation

Abstract In this work, we proposed a molecular model to investigate the morphology and thermomechanical properties of thermoseting clay nanocomposites. The clay surface has been modified by using the functional covalent coupling agents aminosilanes. The epoxy matrix is composed of several representative cross-linked epoxy units. Different structures of PCNs, which correspond to intercalated or exfoliated status have been taken into account by varying the amount of polymer phase in the interlayer space. By using the code DL_POLY, molecular dynamics simulations were performed, providing insights into the arrangement of constitutive components of PCNs and the molecular interaction, particularly in the interphase zone, for different nanocomposite structures. The thermodynamic properties of the confined polymer in each structure are also investigated in order to clarify the influence of silicate layer on the properties of nanocomposites. In addition, these molecular models allow us to numerically estimate the effective elastic properties of the PCN models at different temperatures.

5.1 Introduction

The advanced polymer/clay nanocomposites (PCNs) materials are obtained by adding small amounts of clay nanofillers that have an extremely high aspect ratio and great mechanical properties (strength and flexibility) to a polymer matrix. It has been shown that PCNs exhibit significant enhancements in mechanical, thermal and barrier properties while maintaining the lightweight characteristic, optical clarity of polymer-based materials [1, 2, 3, 4]. To date, the physical behavior of this kind of nanomaterial is not yet well understood and still stimulate numerous research activities [5, 6, 7, 8, 9, 10].

Experimentally, several structural characterizations such as X-ray diffraction (XRD), transmission electronic microscopy (TEM), small-angle neutron scattering, nuclear magnetic resonance (NMR) have been performed in order to investigate the dispersion states of clay layer into the polymer matrices as well as the influence of these silicate layers on the structure and properties of PCNs [11, 12, 13, 14]. However, due to the complexity of chemical components at the nanoscale, nowadays the characterization equipments can not easily ascertain details about the molecular structures particularly in the vicinity of clay surface [15, 16].

As a consequence, molecular dynamics (MD) simulation has become an emerging and a powerful tool to gain insight into the structure and behavior of such nanocomposite materials. In many works in literature, the molecular structures, the interactions between constitutive components of PCNs (*i.e.* silicate layer, organomodifiant and polymer), the thermodynamic and mechanical properties of organically modified montmorillonite (OMMT) systems [5, 6, 17, 18, 19] or of polymer clay nanocomposite (PCNs) [7, 8, 9, 10, 20, 21, 22, 23, 24] have been thoroughly investigated.

The molecular structures of intercalated and exfoliated poly ϵ -caprolactone (PCL) nanocomposites have been investigated in several MD simulation works [8, 20]. Indeed, by changing the number and length of polymer chains in the gallery, Gardebien *et al.* [8] have varied the amount of PCL to examine the influence of the interlayer density on the molecular structure of intercalated nanocomposites. It should be noted that the montmorillonite layers have been modified with alkylammonium as surfactants. By examining the interlayer density profiles, the authors observed that the interlayer phase organized into four layers while the charged heads of the surfactants remained stuck to the surface. Moreover, both polar and non-polar interactions between PCL and the clay surfaces have been revealed, .

For the case of exfoliated nanocomposites [20], it was found a layered structure with high density of organic phase near the clay surface. This high density profile of organic phase, particularly in the nearest layer, shows the strong affinity between the polymer and the clay platelet.

The difference between the arrangements of poly(ethylene oxide) (PEO) in the intercalated and exfoliated nanocomposites has been studied by Suter and Coveney [9] by using large-scale molecular dynamics simulations. Non-modified montmorillonite (MMT-Na) was used as inorganic phase. It was found that the PEO chains were organized in layers parallel to the clay surface. For the exfoliated structure, the polymer conformation at the clay surface was significantly different from the others because of the presence of the sodium ions and the charges within the clay surface.

The dependence of the interlayer distance, *d*-spacing, on the amount and structures of organic phase has been studied in several MD works [25, 18, 6, 26]. By studying different organoclays, Paul *et al.* [6] showed that *d*-spacing increases linearly with the mass ratio of organic surfactant to clay. The presence of hydroxyl-ethyl units on organoclays was found to have a positive effect to increase the packing density of the interlayer structure. This phenomenon can be attributed to the hydrogen bonding between these surfactants themselves and between the surfactants and the oxygen of the clay surface.

By using the MD simulation, the changes in the dynamic properties of surfactants or polymers confined between the clay layers were also investigated. These complementary information can help

us to better understand the influence of clay layer on the dynamic properties of organic phases, and more importantly, to identify the constrained zones of the PCNs [9, 17, 19, 24, 27]. Besides, the interactions between polymer and organoclays attracted many attention because it was believed that the binding energy is directly related to the mechanical performance of nanocomposites [21, 22]. However, as suggested by Chen *et al.* [28], there is no direct evidence or theory to support this hypothesis, particularly for the complex interfaces in nanocomposites where most of them possess complex phases with various molecules [28].

Elasticity properties of PCN clusters is an important parameters that can be used in continuum models for estimating the macroscopic properties of PCNs [29, 30]. However, to date, few studies that have been undertaken to predict the mechanical properties of PCN clusters *via* MD simulations [24, 26]. In the work of Xu *et al.* [24], only longitudinal and lateral Young's *moduli* have been determined for exfoliated clay and partially intercalated/exfoliated clay clusters. The effect of temperature in the determination of elasticity properties of PCNs has not been taken into account.

It should be noted that in all cited works, the pristine clay or organically modified clays which are obtained by using the cationic surfactants have been considered. The modification of clay surface by the covalent grafting was for the first time introduced in MD simulations in the work of Piscitelli *et al.* [31]. These authors studied the effect of the concentration and the chain lengths of different aminosilanes on the *d*-spacing of montmorillonite. The MD simulations revealed that the increase of aminosilanes concentration and the use of shorter aminosilanes chains contributed to the extent of the clay's *d*-spacing. These numerical results were in excellent agreement with the results of their experiments. Note that there is no MD study in which these silanized clays served as fillers in polymer matrix, even if these techniques were extensively used in the processing of PCNs, particularly for epoxy/clay nanocomposites [32, 33, 34].

To the best of our knowledge, there is really few studies that consider the molecular structure and properties of thermosetting polymer/clay nanocomposites [28]. In the cited work, the authors investigated intercalated and exfoliated clay-nanocomposites based on epoxy matrix cross-linked from Diglycidyl ether of bisphenol-A and Diethylmethylbenzenediamine (DGEBA and DETDA). A series of surfactants with a single ammonium head group and one alkyl chain of various length were used. The failure behavior of the interphase in terms of quantifiable parameters including peak strength, fracture energy and final separation distance have been determined by using the traction-separation relationship. However, details of the molecular structures and overall thermomechanical properties of these nanocomposites were not studied.

Except for epoxy/clay nanocomposites, the pure thermosetting polymer [35, 36, 37, 38, 39, 40, 41] and its nanocomposites containing carbon nanotubes [42, 43], nanoparticles [44, 45, 46] or graphene [47, 48, 49] have been extensively studied by using MD simulations. Based on these epoxy-based nanocomposites models and the silanized-clay model of Piscitelli *et al.* [31], in the present study, we modeled the PCN systems composed of silanized-clay and thermosetting epoxy resin. Three different nanocomposite structures, which have different numbers of representative cross-linked epoxy molecules representing intercalated or exfoliated structure, were studied.

The influence of the silanized clay on the morphology and density of polymers were examined. The issue of the resulting interphase region was clarified. In addition, the effect of the end functional groups of the grafted aminosilane molecules, on their interactions with the host epoxy polymer was also discussed by examining the local structure of nanocomposites. The thermodynamics and mechanical properties, including glass transition temperature, time-dependent mean squared displacement (MSD), elasticity coefficients, isothermal bulk *modulus* of the epoxy matrix and PCNs were determined.

After this introduction on the rationale for studying the polymer/clay nanocomposites materials, the paper is organized as follows. In section 5.2, we present the molecular dynamics methodology.

This methodology is based on the construction of the chemical structures of sodium montmorillonite and polymer clay nanocomposites, the specification of the force fields and the molecular dynamics simulation procedure. The methods in order to determine the glass transition temperature and the mechanical properties are given in this section. We thoroughly present and discuss our numerical results in section 5.3 underlining the differences amongst the different molecular configurations for which the local structure of atoms is studied *via* the radial distribution function, such as the glass transition temperature, the translational dynamics of polymer and the elasticity properties. Finally, in section 5.4, we draw the conclusion of this work and set forth future research directions.

5.2 Molecular dynamics methodology

5.2.1 Model construction

5.2.1.1 Model of pristine and silanized clay

Let us consider a sodium montmorillonite $(MMT - Na^+)$ which has the chemical structure $Na_xSi_8Al_{4-x}-Mg_xO_{20}(OH)_4$ where x = 0.67 presents a cation exchange capacity of 91meq/100g. This structure corresponds the sodium montmorillonite provided by Souther Clay Products. First, based on the coordinates data extracted from X-ray identification of clay minerals reported in [50], an unit cell of 40 atoms was built. We define an orthogonal basis for which the Z-axis is perpendicular to the clay surface of the cell. Next, this unit cell was replicated 4 times according to the X-axis and 3 times according to the Y-axis. Then, 8 atoms of Al^{3+} were randomly chosen and replaced by Mg^{2+} in the octahedral layer, resulting a charge deficiency -8 for clay layer. Finally, 8 sodium ions Na^+ were added in the interlayer space to obtain the complete $MMT - Na^+$ cell. The size of the $MMT - Na^+$ cell were 21.12 × 27.42 × 6.56 Å³. It should be noted that the isomorphous substitutions herein were not performed in two consecutive octahedra as suggested by Sainz-Díaz *et al.* [51] in order to ensure the stability of the clay structure. Moreover, the sodium ions were positioned at about 1 Å from the clay surface following the suggestion of Heinz *et al.* [52].

For the silanized clay, the size according to the Z-axis of the $MMT - Na^+$ cell was fixed at 18 Å, which fits with a bilayer organization of aminosilanes within the clay interlayer space [31, 32, 33, 34, 53]. Grafting of aminosilanes onto the clay surface was carried out following the procedure proposed in the work of Piscitelli *et al.* [31]. Herein, it is assumed that the silane molecules can be grafted covalently with the oxygen atoms on the surface of clay [31]. For the sake of simplification, we only considered the case where the 3-aminopropyltrimethoxysilane molecules were linked with clay surface through three covalent bonds [31]. The molecular structure of this aminosilane molecule is shown in Figure 5.1(a). In this model, 8 aminosilanes were grafted on each clay surface. This corresponds to the number of monocationic surfactant needed to obtain a fully treated clay surface based on its cation-exchange capacity.

5.2.1.2 Model of polymer clay nanocomposites

In our PCN model, the polymer matrix consists of representative cross-linked molecules [44]. This kind of representative structure has also been used in the literature for simulating thermoset polymers in order to reduce the computational cost, particularly for large models of molecular structures [46, 47, 48, 54]. In addition, the use of these representative cross-linked molecules has also been shown to be suitable for estimating thermodynamic and mechanical properties of thermoset polymer [44]. Figure 5.2 shows the curing reaction mechanism between the epoxy group and the primary amine group. The carbon-oxygen



Figure 5.1 – The molecular structure of (a) aminosilane molecule, (b) epoxy monomer molecule, (c) amine-based hardener molecule and (d) the representative cross-linked molecule. The cross-linked molecule (d) is obtained by using the cross-linking reaction between three epoxy monomers (b) and one hardener (c). Some typical atoms and the color legend of all atoms are also indicated.

bond in the epoxy monomers is broken and opens the epoxy ring. The oxygen-end of the opened epoxy ring takes over the hydrogen atom from a nearby amine group in the hardener molecule and leaves a dangling nitrogen in the hardener molecule. This dangling nitrogen forms a covalent bond with the carbon-end of the opened epoxy ring. This process allows the epoxy monomer to link to an amine based hardener.



Figure 5.2 – Curing reaction mechanism between the epoxy resin and amine based hardener.

Figures 5.1(b) and (c) show the atomistic structure of the used epoxy monomer and the hardener, respectively. Each epoxy monomer has two reactive epoxy groups and the hardener has six reactive

amine groups. The representative cross-linked molecule was build from the cross-link process between three linear epoxy monomers and one chain of curing agent. Therefore, as suggested in the work of Yu *et al.* [44], a cross-linking ratio of 50 % is used for this representative molecule based on the consummation of the reactive functions on both epoxy monomer and hardener molecules. Figure 5.1(d) shows the configuration of the representative cross-linked molecule.

The procedure for building the nanocomposite structures from the organically modified clay was performed following the work of Anoukou *et al.* [26]. Firstly, the silanized system was relaxed in NVE ensemble for 200 ps. Next, the simulation cell was replicated 2 times in both X- and Y-axes in order to have enough surface before adding the representative cross-linked molecules. As a consequence, its surface dimensions become 42.24×54.84 Å² in the XY-plane geometry. The size according to the Z-axis of the simulation box was shifted to insert the cross-linked molecules in the interlayer space. In this work, three cases of the number of cross-linked molecules 20, 60 to 100 were used for studying three PCN structures, denoted by N-20E, N-60E and N-100E, respectively, which represent different exfoliated status of the PCN structure. For the purpose of comparison, a model that contains only cross-linked molecules (100 molecules), designated as pure epoxy, is also built. Note that the orthorhombic symmetry was assumed for all molecular systems in this study. The orthorhombic symmetry corresponds to $\alpha = \beta = \gamma = 90^{\circ}$, where the three angles α, β and γ are the angles between the Y- and Z-axes, between the X- and Z-axes, and, between the X- and Y-axes respectively. The aminosilane and cross-linked molecules have been built by using the Aten package [55].

5.2.2 Force fields description

Electrostatic charges and potential parameters for all atoms in montmorillonite layer $MMT - Na^+$ were taken from CLAYFF [56]. For the organic phase, the geometries of both organosilane and cross-linked molecules were optimized by using the DFT method at $B3LYP/6 - 311^{++}G^*$ level implemented in Gaussian 09 program [57]. The electrostatic charges of these molecules were calculated at $B3LYP/6 - 311^{++}G^{**}$ level from optimized geometries by using the mulliken population analysis. The potential parameters for the organic phase were determined from the INTERFACE-FF force field [58]. To make equivalent between the 9-6 van der Waals (vdW) potentials in INTERFACE-FF and the 12-6 Lennard-Jones potentials in CLAYFF, we used the 12-6 vdW form instead of 9-6 vdW in the INTERFACE-FF for polymer and aminosilanes molecules. The conversion method between these two vdW types was shown in the work of Heinz *et al.* [58]. The potential parameters of the polymer were determined by using DL_FIELD program [59].

5.2.3 Molecular dynamics simulation procedure

The molecular dynamics (MD) simulations were performed using the code DL_POLY 4.5 [60]. The integration algorithms are based on a Verlet leap-frog scheme. Periodic boundary conditions are applied to three directions of the simulation box. The Nosé-Hoover algorithm was used to control the temperature and pressure of molecular systems. The long-range electrostatic interactions between the charges of all species were computed using the Smoothed Particle Mesh Ewald (SPME) method with the relative error of 10^{-6} [61]. The time step of 0.5 fs was chosen for all MD simulations to maintain the system stability. The system properties including structure, averaged properties, which are needed for computed the atom densities and the radial distribution functions, were recorded every 5 fs, whereas the mean square displacements of atoms are recorded every 2 ps.

The molecular system were sequentially simulated in two types of thermodynamic ensembles NVT (constant-temperature, constant-volume) and NPT (constant-temperature, constant-pressure) in order to

reach the equilibrium state with minimized potential energy. At first, simulations in the NVT ensemble at 600 K and 200 ps have been carried out for all initial configurations. The objective of this step is to provide a sufficient kinetic energy to the cross-linked epoxy molecules, so that the homogeneous polymer network can be achieved near the clay surface. Then, the MD simulations in NVT ensemble were conducted again at 300 K and for another 200 ps. After this step, the size according to Z-axis of the simulation box was more optimal to have an equilibrium configuration of the molecular system. As a consequence, the computation time may be reduced.

Next, the MD simulations in the NPT ensemble were conducted at 0 atm and 500 ps for achieving a stress-free state of the system [48]. Finally, relaxation of the system in NPT ensemble was carried out at room temperature (300 K) and atmospheric pressure (1 atm) for 2000 ps. During the simulation process, the atoms in two silicate layers are fixed whereas the atoms in all organic components are free to move. The stabilization of the total energy, pressure and temperature of the molecular system was considered as the evidence for the state of equilibrium in MD simulations. The configurations at equilibrium state of the pure epoxy matrix (N-20E) and of the nanocomposites (N-20E, N-60E and N-100E) are shown in Figure 5.3. Note that at the equilibrium state, the *d*-spacing value of these systems shows a value of 3.01, 5.57 and 7.77 nm respectively (see Table 5.1). The density of all molecular systems at the equilibrium state is also reported in Table 5.1.



Figure 5.3 – The configuration at equilibrated state of (a) pure epoxy matrix 100*E*, (b) nanocomposite containing 20 representative molecules N - 20E, (c) nanocomposite containing containing 60 representative molecules N - 60E and (d) nanocomposite containing 100 representative molecules N - 100E

5.2.4 Determination of glass transition temperature

Glass transition temperature T_g is one of the most important thermal properties of amorphous polymers at which the polymer changes from a glass (an amorphous solid trapped in a non-equilibrium state) to a rubber (for cross-linked systems over the gel point) or liquid (when chains are not covalently bonded to each other as in the thermoplastics) [62]. The T_g value of a molecular system is defined by the temperature at which the density-temperature relation becomes discontinued. The motion of polymer chain segments dramatically speeds up and the mechanical properties of polymers become very different from those below it. The transition temperature T_g is governed by local chain dynamics and represents an intrinsic signature of the molecular structure [62].

The determination of T_g was performed by varying the system temperature from 300 K to 500 K at a constant heating rate of 20 K/500 ps and at 1 atm. Herein, at each temperature, the density was only averaged over the last 200 ps.

Besides of using the density-temperature relationship, the quantity T_g can also be obtained from the mean squared displacement-temperature relationship of some typical atom types where the mean squared displacement (MSD) stands the time-dependent. The determination of the MSD as a function of temperature was performed in the same thermal history that for the determination of the density profile.

5.2.5 Determination of mechanical properties

In this work, the strain fluctuations method has been employed for estimation of the rigidity of considered PCNs. The strain fluctuations method for estimation of elasticity properties of a molecular system was initially proposed by Parrinello and Rahman [63]. It is then developed in the work of Ray [64] and de Pablo [65]. This approach allows us to directly determine the elasticity properties of a molecular system by using a single MD simulation. Particularly, the elasticity properties of the system can be determined at a specific temperature [66]. This is particularly important for the polymeric materials because their mechanical behaviors strongly depend on the temperature.

During the simulation, the system was subjected to a three-dimensional stress field in the N σ T ensemble (constant-temperature, constant-stress). The obtained strain field was determined in each case of temperatures. The components of the 4-th order effective compliance tensor s_{ijkl} of the considered molecular system are given by:

$$s_{ijkl} = \frac{\langle V \rangle}{K_b T} (\langle \epsilon_{ij} \epsilon_{kl} \rangle - \langle \epsilon_{ij} \rangle \langle \epsilon_{kl} \rangle), \tag{5.1}$$

where K_b , ϵ_{ij} , T and V are the Boltzmann constant, the components of strain tensor, the imposed temperature and the volume of the molecular system, respectively. Each index varies from 1 to 3 where each value of these index 1, 2 and 3 is associated with the X-axis, Y-axis and Z-axis, respectively.

In this work, we are also interested in determination of the isothermal bulk *modulus* κ_T . For this purpose, the temperature was set at 300 K and MD simulations were conducted in NPT ensemble with the different pressure values in range from 0.1 MPa (*i.e.* 1 atm) to 2.5 GPa (*i.e.* 25 katm) [26]. Each simulation was carried out for 500 ps and the average volume was taken for the last 200 ps.

The bulk *modulus* κ_T of a substance is a measure of how compressible that substance is. It is defined as the ratio of the infinitesimal pressure increase to the resulting relative decrease of the volume. As a consequence, the bulk *modulus* κ_T at temperature *T* is determined by using a relationship between *P* and *V* as follows [26]:

$$\kappa_T = -V \left(\frac{\partial P}{\partial V}\right)_T,\tag{5.2}$$

where *P* is pressure, *V* is volume, and $(\partial P/\partial V)_T$ denotes the derivative of pressure with respect to volume at constant temperature *T*.

5.3 **Results and discussion**

5.3.1 Molecular configuration

The molecular configuration of different simulation cases may be studied by observing the density distribution profiles in these systems. Figure 5.4 shows the density profiles of pure epoxy matrix and different nanocomposite systems at room temperature (*i.e.* 300 K). In these graphs, the position z = 0

according to Z-axis corresponds to the median plane of the simulation box, whereas two dash lines present the positions of clay surfaces. Note that the positions of clay surfaces were determined from the density profile of surface oxygen atoms of silicate layer.



Figure 5.4 – Density profiles of different simulation cases: (a) Pure epoxy matrix containing 100 representative molecules, (b) Nanocomposite containing 20 representative molecules N-20E, (c) Nanocomposite containing 60 representative molecules N-60E, (d) Nanocomposite containing 100 representative molecules N-100E. For the purpose of comparison, the density profile of the pure epoxy matrix is put together with that one of nanocomposite.

One can observe that in the pure epoxy matrix system (see Figure 5.4(a)), the density profile of polymer is almost constant along Z-axis with a mean value $d_m = 1.038 \text{ g} \cdot \text{cm}^{-3}$. This value is close to values derived from the diglycidyl ether of bisphenol F (DGEBF) cross-linked with curing agent diethyltoluenediamine (DETDA) ($d_m = 1.07 - 1.075 \text{ g} \cdot \text{cm}^{-3}$ given by Tack and Ford [36]) and from the epoxy network composed of EPON 862 epoxy resin and triethylenetetramine (TETA) curing agent ($d_m = 1.08 \text{ g} \cdot \text{cm}^{-3}$, given by Fan and Yuen [67]). These values are slightly smaller than the value determined from the experimental measurement of epoxy networks ($d_m = 1.13 \text{ g} \cdot \text{cm}^{-3}$ in [68], or $d_m = 1.16 \text{ g} \cdot \text{cm}^{-3}$ in [69]). It is worth noting that the density of epoxy cross-linked matrix in mentioned experimental works was determined with fully cross-linked epoxy resin. In this study, low cross-link density has been used. The polymer density in MD simulations has been found to highly depend on several factors such as the cross-link density, the topology of curing reaction, the force-fields as well as the nature of the epoxy resin and the hardener [35, 36, 38, 46]. Therefore, the difference between the result obtained herein and the ones presented in the other works may be because of small cross-link density and of different type of epoxy and hardener as well as the force-field.

In Figures 5.4(b), (c) and (d), significant variations of the organic density according to Z-axis may clearly be observed, showing the influence of silicate layers on the molecular configuration of the epoxy matrix. In all three nanocomposite structures, the confined polymer region near the clay surface becomes like a layered structure with the density much higher than the density of the bulk polymer.

Our results are similar than that reported by Suter and Coveney [9] when investigating poly ϵ caprolactone/clay nanocomposites or several other authors [47, 48, 49] when investing the graphene/epoxy
nanocomposites. Suter and Coveney [9] suggested that the high density of organic phase the region
close to the clay surface shows the strong affinity between the polymer matrix and the clay platelets.

On contrary, by studying an epoxy/clay nanocomposite models using MD simulations, Chen *et al.* [28] have shown that the density of epoxy resin near clay surface is slightly lower than that of bulk matrix. Moreover, no layering configuration has clearly been observed. This contrary statement may be explained by the fact that the surfactants used in their model and in our model are not the same. In fact, in our model, the grafted aminosilanes have reactive amino functions NH_2 to epoxy matrix, whereas in [28], different organic molecules composed of a single ammonium head group NH_3^+ and one alkyl chain of various lengths C_n have been used.

Therefore, one may suggest that the presence of the reactive functions NH_2 on the grafted aminosilanes herein is the main cause of the high density of organic phase near the clay surface. As a consequence, this interphase may enhance the mechanical properties as well as the adhesion between the clay layer and polymer matrix as explained in several previous experimental works [32, 34].

Besides, the results show that aminosilane molecules are always found in the range [0, 7] Åfrom the clay surface thanks to its covalent bonds with clay surface. Moreover, all sodium ions are close to clay surface due to its strong electrostatic interactions with the negatively charged silicate layer. By using the density profile of nanocomposite structures, we can also estimate the thickness of interphase region based on the concentration of organic phase near clay surface [24, 70]. In Figure 5.4, it can be observed that the thickness h_I of the interphase of the exfoliated (N - 100E) or nearly exfoliated structures (N - 60E) is approximately 15 Å. For the intercalated structure (N - 20E), only a 10 Å thickness interphase layer was found.

Now, we compare the density profiles in three nanocomposite structures presented in Figures 5.4(b,c,d). It can be observed that, for intercalated structure (N - 20E), the density of interlayer epoxy resin $(0.77 \text{ g} \cdot \text{cm}^{-3})$ is smaller than the bulk epoxy matrix $(1.038 \text{ g} \cdot \text{cm}^{-3})$. This statement is similar to the one given by Chen *et al.* [28] who found an average density of 0.76 g \cdot cm⁻³ for organic phase in case of intercalated nanocomposite. This phenomenon may be explained by strong confined effects in the narrow space between silicate layers, particularly for the non-flexible polymer as resin epoxy [28].

When the number of representative molecules increases, the configuration of nanocomposite structures change from intercalated to the exfoliated one. In Figures 5.4(c) and (d), one may observe that the density of polymer matrix in the region far way from the clay surface tends to that of the bulk polymer matrix. Therefore, the confined effects become less significant when the interlayer distance increases. In contrary to the intercalated structure, the exfoliated cases (N - 60E and N - 100E), individual silicate layers with reactive surface may locally reinforce the interphase while maintaining the behavior of bulk polymer matrix for the confined polymer.

5.3.2 Radial distribution function

The radial distribution function (RDF), so-called pair correlation function and denoted by g(r), is defined as the probability of finding a given particle at a distance r from a reference particle. In this work, the radial distribution functions of some specific groups of atoms for equilibrium systems were also studied in order to better understand its local structures.

For the pure epoxy matrix which is composed of numerous cross-linked representative molecules, Figure 5.5(a) compares the RDF of the reactive epoxy functions with the RFDs of other atom types in the hardener backbone such as reactive nitrogen N_T , hydrogen linked to nitrogen H_{NT} , carbon C_T and

hydrogen linked to carbon H_{CT} (see Figure 5.1).

It is observed that there are two peaks at 3 Å and 2 Å associated to the distances $O_E - N_T$ and $O_E - H_{NT}$, respectively. There is no peak smaller than 3.5 Å between reactive oxygen and two others non reactive atoms (C_T , H_{CT}) of the hardener backbone. As suggested by Shokuhfar and Arab [39], the peaks in the RDF curves smaller than 3.5 Å are mainly due to hydrogen and chemical bonds between atoms, whilst those beyond 3.5 Å correspond to the van der Waals and electrostatic interactions. Thus, small distances between these reactive atoms show their tendency to cross-link together. In fact, by checking this close contact between these pairs of reactive atoms and by creating a new bond between them, several authors simulated the cross-linking process of epoxy resin and hardener [37, 38, 39, 71]. Besides, some small peaks within the range [4, 7] Å could contribute to the inter- or intra-molecular RDF of the cross-linked representative molecules. The case with nearly exfoliated structure N - 60E is reported in Figure 5.5(b,) showing the same RDF profiles for epoxy matrices in PCN structures.



Figure 5.5 – RDF's of reactive oxygen atoms in epoxy functions (O_E) to other atoms in hardener backbone such as reactive nitrogen N_T , hydrogen linked to nitrogen H_{NT} , carbon C_T and hydrogen linked to carbon H_{CT} of two cases (a) pure epoxy matrix and (b) a nanocomposite that contains 60 epoxy representative molecules.

For a nanocomposite system, the local interactions between the confined polymer matrix and the grafted aminosilanes are also studied by using the RDFs. For this purpose, the RDFs of reactive nitrogen atoms of grafted aminosilanes N_S to some typical atoms in cross-linked representative molecules such as O_E , C_E , C_T and N_T are studied. In Figure 5.6, an intense peak at 3 Å can be seen in the RDF of N_S - O_E , showing a high reactivity between the nitrogen atoms of primary amine functions N_S on the grafted aminosilanes and the oxygen atoms in epoxy groups O_E . The profile of this peak is similar to the one of $O_E - N_T$ in pure epoxy matrix presented in Figure 5.5(a). Besides, a lower peak may be found at 3 Å between two atoms N_S from grafted aminosilanes and N_T from cross-linked molecule can be related to the hydrogen bond between two considered amine groups. Thus, these RDF's profiles show a strong affinity between the grafted aminosilanes and the cross-linked polymer matrix.

5.3.3 Glass transition temperature

Figure 5.7(a) shows the density's variation of the pure epoxy matrix and its nanocomposites as a function of temperature. For all systems, the density decreases with increasing temperature and there are two linear regions corresponding to the glass and rubber states of polymeric material. Basically, the abscissa of the intersection of two linear curves, which are obtained by taking a linear fitting of the data, was recognized as T_g of the sample. Hence, the result of T_g may be sensible to the fitting method. Chapter 5. From morphology to thermodynamics and mechanical properties of epoxy/clay nanocomposite: investigation by molecular dynamics simulation



Figure 5.6 – RDF's of reactive nitrogen atoms in grafted aminosilane molecules (N_S) to other atoms in the crosslinked representative molecule such as reactive oxygen O_E , carbon in epoxy backbone C_E , carbon in hardener backbone C_T , reactive nitrogen in hardener backbone N_T ,

There are some deviations from the obtained glass transition temperature according to the number of data used in linear regression. Therefore, it is more suitable to take into account a range of temperature in which there is a slope's change. One can observe that for the pure epoxy matrix, the T_g is found in the range [380, 385] K. This range of temperature are in line with the results reported in several other MD works for epoxy matrix [67, 45, 72, 48, 73].



Figure 5.7 – Estimation of glass transition temperature (T_g) for epoxy and epoxy/clay nanocomposites: (a) pure epoxy matrix, (b) nanocomposite containing 20 representative molecules (N20-E), (c) nanocomposite containing 60 representative molecules (N60-E), (d) nanocomposite containing 100 representative molecules (N100-E).

The results shown in Figure 5.7(b,c,d) highlight the influence of the presence of clay layers to the glass transition temperature T_g of the epoxy matrix. The intercalated structure (N-20E) has a biggest glass transition temperature T_g in range [415, 425] K. The glass transition temperature decreases when the number of cross-linked epoxy molecules increases, with values in range [395, 415] K for N-60E and in range [385, 395] K for N-100E systems, respectively. The exfoliated structure N-100E and pure epoxy matrix only have slight difference in T_g .

It can be explained by the fact that in the case where there are only few polymer molecules inserted into the interlayer space, all polymer molecules should be located close to the clay surfaces and the grafted aminosilanes. It is natural that these polymer molecules can strongly interact with the reactive grafted aminosilanes as well as the clay surfaces as shown by the RDF profiles in Section 5.3.2. Therefore, the mobility of polymer became slow, particularly in the interphase region, then the mobility of overall polymer is reduced. The proportion of polymer molecules which are far away from the clay surface increases with the increasing number of used cross-linked epoxy molecules in nanocomposite structures. Clearly, the interactions between the polymer molecules which are far away from clay surface with the grafted aminosilanes and clay surface are not significant. Therefore, the thermodynamics behavior of overall polymer systems have tendency to be close to the bulk polymer matrix.

5.3.4 Translational dynamics of polymer

The translational dynamics of polymer in pure epoxy matrix and its nanocomposites are represented by the mean square displacement of a specific atom. In this work, the carbon atoms in the epoxy backbone was considered. Figure 5.8(a) shows the graphs of the MSD of this typical atoms *versus* time for the first 200 ps at various temperatures in the case of nanocomposites containing 100 representative cross-linked molecules (N-100E). It is found that the diffusional behavior consistently increases with temperature, as expected. Besides, the mobility of the considered atoms in epoxy backbone shows transitional behavior as a function of temperature. In fact, the polymer shows much faster mobility at high temperature.

For the purpose of clarifying this phenomenon, the carbon atoms MSD's profiles of pure epoxy matrix and its nanocomposites at 100 ps for various temperatures are reported in Figure 5.8(b). As can be seen from the Figure 5.8, a gradual change in the MSD value of the pure epoxy matrix is found around 380 K, whereas it becomes bigger for all nanocomposite structures. As expected, the carbon atoms of the polymer in the intercalated structure (N-20E) show the highest value of transition temperature due to the strong interactions with clay surface. These results are consistent with the glass transition temperature as discussed above. Particularly, it is observed that the MSD value of the pure epoxy quickly increases once the glass transition temperature has been reached. This increase in all nanocomposite structures is much slower. It should be emphasized that the chosen time (100 ps) for the comparison purpose may have a certain influence on the obtained results. In order to ensure the reliability of the result, other choices have also been tested (50 ps, 150 ps and 200 ps) in the current work and the similar results have been observed. Thus, the reported results are the typical ones for our considered systems. Along with the results in the glass transition behavior, one can conclude that the addition of reactive clay layer significantly enhance the thermal stability of epoxy based materials.

5.3.5 Bulk modulus

The isothermal bulk *modulus* of pure epoxy system and nanocomposites have been determined by using Eq. (5.2). The obtained results at 300 K are shown in Tab. 5.1. It can be observed that isothermal bulk *modulus* of the pure epoxy matrix is more important than the ones of all nanocomposite structures. There is a slight difference between κ_T of the cases N-60E and N-100E. The bulk *modulus* of N-20E



Figure 5.8 – Mean square displacement of carbon atoms in the backbone of cross-linked molecules: (a) case of a nanocomposite containing 100 representative molecules (N-100E) at different temperatures; (b) pure epoxy and its nanocomposites at t = 100 ps.

structure (intercalated structure) is significantly smaller than the ones of two others cases (N-60E and N-100E). Note that the isothermal bulk *modulus* represents the volume variation of the molecular system with respect to the pressure. This volume variation mainly depends on the volume change of the organic phase and its density. A small volume of organic phase in the intercalated structure seems to be the reason for the observed results.

Table 5.1 – Physical and structural properties of several molecular systems at 300 K determined by using MD simulations. κ_T is the isothermal bulk modulus.

Molecular systems	κ_T (GPa)	Density (g/cm ³)	<i>d</i> ₀₀₁ (nm)
Pure epoxy 100E	15.65	1.038	-
N-20E	12.20	1.70	3.01
N-60E	15.05	1.37	5.57
N-100E	15.28	1.24	7.77

5.3.6 Elasticity coefficients

The elasticity properties of the pure epoxy matrix and its nanocomposites at various temperatures were computed by using the strain fluctuations method (see Eq. (5.1)). The 4-th order tensors in three dimensions can be represented in a Euclidian six-dimensional space as (6×6) matrices. To this end, the representation adopted in this work is called the *Voigt*'s representation in which the new indexes *I* et *J* vary in the set {1, ..., 6} such as *I* = (*i*, *j*) and *J* = (*k*, *l*) where the indices *i*, *j*, *k* and *l* vary in the set {1, ..., 3}. The relation between these indices is the following 1 = (1, 1), 2 = (2, 2), 3 = (3, 3), 4 = (2, 3), 5 = (1, 3) and 6 = (1, 2). So, the symmetric matrix **C** associated with the 4-th order tensor **c** whose the components are c_{ijkl} is defined *via* these components by:

$$C_{IJ} = c_{ijkl}.\tag{5.3}$$

It may be observed that for all cases of temperatures, the elasticity tensor of the pure polymer matrix rests always nearly isotropic. In contrast, all nanocomposite structures exhibit highly anisotropic behaviors. Indeed, the elastic constants in XY-plane (C_{11} , C_{22}), which have the similar values, are

Molecular systems	Temperature	C_{11}	C_{22}	<i>C</i> ₃₃	C_{12}	<i>C</i> ₁₃	<i>C</i> ₂₃	C_{44}	C ₅₅	C ₆₆	
Pure epoxy Pure epoxy Pure epoxy	(300 K) (350 K) (400 K)	3.38 1.97 0.84	3.46 1.83 0.75	3.28 1.87 0.70	2.52 1.56 0.66	2.18 1.51 0.54	1.93 1.43 0.52	1.69 0.98 0.20	2.28 0.685 0.25	1.84 0.818 0.49	
N - 20E $N - 20E$ $N - 20E$	(300 K) (350 K) (400 K)	127 106 96.2	122 113 98.7	3.77 3.70 3.99	48.5 47.90 47.8	2.39 1.50 1.29	2.68 1.15 1.06	5.63 3.21 1.67	2.44 2.78 1.83	117 92.10 69.8	
N - 60E $N - 60E$ $N - 60E$	(300 K) (350 K) (400 K)	59.8 46.1 31.2	60.2 56.2 39.8	5.26 3.13 1.87	24.3 27.0 15.9	1.9 1.23 1.1	2.2 0.93 1.31	1.93 1.03 0.534	3.85 1.46 0.586	49.2 49.1 33.6	
N - 100E $N - 100E$ $N - 100E$	(300 K) (350 K) (400 K)	39.5 37.06 24.1	38.2 32.96 25.47	4.37 3.39 1.49	17.3 15.82 11.11	3.2 2.85 1.02	2.82 3.65 0.77	2.77 1.40 0.26	2.33 1.32 0.49	32.3 26.46 19.66	

Table 5.2 - The elastic constants (in GPa) at various temperature conditions

much more important than the one in Z-axis (C_{33}). The nanocomposites' stiffness in XY-plane strongly depend on the in-plane stiffness of clay platelets whereas its stiffness along Z-axis strongly depends on the soft polymeric phase. This observed result agrees well with several proposed theories for estimating the equivalent properties of clay cluster in continuum approaches [74, 75]. The results obtained from MD simulations suggest that the anisotropic properties of the PCN clusters should be taken into account in continuum approaches for estimating the macroscopic mechanical properties of PCNs.

In addition, as can be seen from the Tab. 5.2, the elastic constants in XY-plane decreases with increasing number of cross-linked polymers in nanocomposite structures. This phenomenon can be explained by the fact that the elasticity *moduli* in the lateral directions are strongly affected by the stiffness of clay layer due to the presence of small volume of organic phase for the intercalated structure. In this case, the high values (around 125 GPa) have been derived. When the number of polymer increases, the properties of the nanocomposites in lateral directions are becoming more pronounced by the elastic properties of polymer components, which shows an approximative value of 60 GPa and 39 GPa for the N-60E and N-100E systems respectively. Interestingly, it is found that the the elastic constant in the vertical direction of intercalated clay cluster (N-20E) is smaller than that for nearly exfoliated (N-60E) or exfoliated structures (N-100E). The small density of polymer phase in the intercalated structure (N-20E) as showed in the previous section could contributed to a bigger strain in the z direction, resulting a smaller stiffness in comparison with two others cases (N-60E and N-100E).

Besides, one can observe that the elasticity constants of pure epoxy matrix and its nanocomposites decrease with increasing temperature. This statement reflects well the typical behavior of thermoset polymer-based materials [45]. The stiffness of the pure epoxy matrix drastically decreases between 350 K and 400 K. However, much smaller change has been observed for the nanocomposite cases.

The elastic properties of intercalated structure is less sensible to the temperature than two other nanocomposite structures. These obtained results seem to be consistent with the thermodynamic behavior of polymer as discussed in the previous sections.

5.4 Conclusion

In the current work, we proposed a molecular model to investigate the morphology and thermomechanical properties of the epoxy/clay nanocomposites. The reactivity of the clay layer has been taken into account by using the reactive organomodifiant as aminosilanes, which are covalently grafted to clay surface. The cross-linked epoxy molecules have been used as the polymer matrix. Different molecular structures of PCNs, from intercalated to exfoliated one, have been developed based on the amount of the polymer phase between the interlayer space. The arrangement of organic components and their molecular interactions, particularly in the interphase zone have been investigated by using the research code DL_POLY. The identification of the interphase in term of thickness has been pointed out based on the high density of the organic phase near clay surface. The exfoliated structure shown a thicker interphase in comparison with the intercalated one. The reactivity of the clay surface has been investigated by using the RDF between the reactive atoms, which are in the polymer phase and aminosilanes. The thermodynamic properties of the confined polymer in each structure are also investigated in detail in order to clarify the influence of silicate layer on the properties of nanocomposites. It has been showed that the polymer located close to clay surface has a strong interaction with clay surface and aminosilanes, hence enhance its thermal stability. In addition, these molecular models allow us to numerically estimate the effective elastic properties of the PCN models at the nanoscale and at different temperatures. A high anisotropic behavior of the PCNs at the nanoscale has been observed.

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Chapter 6

Prediction of macroscopic elastic behavior of polymer/clay nanocomposites: a parametric study

Abstract In this work, a 3D finite element model has been developed to compute the macroscopic elastic properties of the polymer/clay nanocomposites (PCNs) from to their microstructures and the elastic behavior of constitutive components. Microstructural parameters of clay or clay stacks such as elastic properties, aspect ratio, interlayer spacing and the clay volume fraction have been taken into account in the proposed models. A parametric study on the effects of these parameters on the macroscopic elastic properties of PCNs has been carefully investigated. The obtained results show that the macroscopic rigidity of PCNs material depends not only on the clay volume fraction but also on the dispersion state of clay platelets in the polymer matrix. An exfoliated structure may improve the macroscopic rigidity of PCNs much more efficiently than intercalated ones, particularly at high volume fraction of clay. The important role of interphase on the mechanical properties enhancement of PCNs has also been demonstrated. In addition, the mixed morphology, in which clay platelets and clay stacks are simultaneous present in the polymer matrix, has been studied. The later morphology is commonly encountered in PCN processing, especially when important clay volume fractions are used. The comparison with the experimental and theoretical results extracted from the literature has been performed.

6.1 Introduction

In the last decade, polymer/clay nanocomposites (PCNs) have attracted considerable attention in academic and industry due to the exhibition of superior properties such as rigidity, thermal stability and flame retardant, gas barrier far from those of conventional micro-composites. In addition, these improvements are obtained without loss of optical clarify and recycling while keeping the light weight of polymeric materials [1, 2, 3].

Depending on several factors including the nature of constitutive components (silicate layer, surfactant and polymer matrix) and the preparation method, the dispersion state of fillers such as pristine or modified clay in a polymer matrix may be quite different from each other. When the polymer can not be intercalated between the silicate layers, the clay is found in aggregated form in the polymer matrix and a microcomposite is obtained. In a such phase-separated microcomposite, mechanical properties don't show significant improvement in comparison with that of bulk polymer matrix due to the poor adhesion between the polymer matrix and the micro-sized inclusions [3, 4].

A polymer/clay nanocomposite (PCN) is formed when polymer chains can successfully be intercalated between the silicate sheets. Two types of PCN structures may be distinguished: the *intercalated nanocomposite* and the *exfoliated nanocomposite* [3, 4]. In the first case, the intercalated nanocomposite (IN) is obtained when the polymer chains are inserted between the interlayer spaces between the stacked silicate layers and make increasing its interlayer distance (denoted by *d*-spacing or d_{001}). The obtained nanocomposite has a well ordered multilayer morphology with alternating polymeric and inorganic layers which improves the mechanical behaviors of PCN materials. In the second case, the exfoliated nanocomposite (EX), is achieved when all (or nearly all) individual clay layers are completely and uniformly dispersed in the polymer matrix. In this case, the polymer-clay interaction is present at entire surface of clay layers, which results in stronger mechanical behaviors of the nanocomposite in comparison with the first case. However, synthesized PCN structures in reality may have both intercalated blocks and exfoliated individual clay layers in its matrix polymer. A such nanostructure, so-called partial exfoliated (or mixed) nanostructure, is predominately obtained when the volume fraction of clay is important (more than 3% of weight fraction) [2, 5, 6].

Unlike the traditional microcomposites for which a high content of fillers is required for improving its mechanical behavior, the PCNs can exhibit a better improvement even at very low volume fraction of fillers thanks to the dispersion clay platelet with high stiffness and aspect ratio [5, 7, 8, 9, 10]. Many experimental results have showed the key role of the clay dispersion state in the polymer matrix on the mechanical properties of PCNs [7, 8, 11, 12, 13, 14]. For instance, Fornes *et al.* [7, 13] have shown that exfoliated structure in a nylon 6/clay nanocomposite may significantly improve its mechanical properties in comparison with the ones obtained by the intercalated or agglomerated structures at the same clay volume fraction. Similar observations have been reported by Yasmin *et al.* [8] and Borse and Kamal [14] while studying the epoxy/clay and polyamide-6/clay nanocomposites, respectively.

Another important factor that affects PCN's mechanical behavior is the polymer-clay interphase which is found in the region around the clay platelets. In this region, the density and the thermodynamic properties of polymer matrix are modified from those of pure polymer matrix by interracial interactions between the matrix and the clay surface. This modification has been reported by using molecular dynamics simulation [15, 16] or by experiments [17, 18, 19, 20]. As the contact surface area between the clay layers and the polymer matrix is considerable, especially when the nanostructure is exfoliated, the volume of the interphase is ineligible and would play an important role in the mechanical reinforcement of PCNs [21, 22, 23, 24]. Indeed, a good property of the interphase is expected to increase significantly the PCN's strength and *vice versa*. However, the influence of interphase characteristics (*e.g.*, thickness and stiffness) on the mechanical properties of PCNs has not been carefully studied.

Due to the complexity of chemical components at the nanoscale and the uncertainties in controlling the dispersion of nanofillers, the experimental characterization techniques could not provide enough information to explain the mechanism of mechanical reinforcement of PCN materials. Hence, theoretical modeling and numerical simulations are useful for establishing the microstructure-macroscopic relationship of mechanical properties in PCNs, which are considered as composite continua consisted of three phases: polymer matrix, clay platelet and interphase [25, 26]. In order to simplify the description of individual clay layers covered by interphases or intecalated blocks in the polymer matrix, so-called "effective particles" (EP) have been to be used [6, 23, 25, 27, 28, 29]. The effective elastic parameters of EPs, considered as isotropic or transversely isotropic media, have been derived in [6, 21, 25, 30].

In the literature, the effective properties of PCNs have been computed by using both analytical and the numerical methods. When using analytical methods, the EPs were idealized as spheroidal [23, 28] or ellipsoidal inclusions [6, 25, 30] which are embedded in a polymer matrix. The effects of structural parameters such as the dispersion state, the number of silicate layer per block, the *d*-spacing, the aspect ratio of clay platelet, etc. on the mechanical properties of PCNs have been investigated by using analytical methods [6, 23, 25, 27, 28, 29].

Although the analytical methods require less computational efforts for estimating the elastic behavior of PCNs, there are some drawbacks: the random distribution the clay layers in polymer matrix and the local stress and strain effects can not be described [26, 31, 32]; the interactions between the silicate platelets in PCN microstructures can not be accurately taken into account [22, 23, 33].

Along with the fast development of computer technologies, the finite element method (FEM) has been applied to for numerically computing the macroscopic behavior of PCN materials. As FEM allows us to deal with models with the complex geometry of microstructures, it has been used for checking the validity of models of which the inclusions are idealized forms or considered as "effective particle" [21, 25, 30, 31, 33]. Both 2D and 3D models have been studied by using FEM. However, the necessity of 3D FE modeling for correctly predicting behavior of PCNs was proved in several works [31, 22]. Mortazavi *et al.* [22] reported that the 2D finite element model could not accurately describe the fillers geometries in the fabricated nanocomposite samples. Hbaieb *et al.* [31] showed that 2D models may underestimate the rigidity of PCNs in comparison with the 3D models.

Exfoliated PCN structures of with random and preferential orientation of clay layers have been studied by Hbaieb *et al.* [31], Cricrì *et al.* [34], respectively. Description of the generation of microstructures, of the boundary conditions, and of the sensitivity of REV size have been addressed. Moreover, the correctness of these models in predicting the mechanical properties of PCNs has been shown and compared with results obtained using the Mori-Tanaka model [31]. Different clay's aspect ratio (denoted by α) have also been considered, for instance $\alpha = 50$ [31], $\alpha = 70$ [34], or $\alpha = 100$ [21, 22, 33]. However, the influence of a large range of clay's aspect ratio ($\alpha > 100$) on the reinforcement mechanism of PCN materials [3, 4] has not been numerically investigated. Here, the aspect ratio is defined as the ratio between the length and the thickness (1 nm) of clay layer.

The presence of interphase in 3D models of exfoliated microstructures has been considered [22, 35]. The interphase's thickness was taken by $h_i = 0.4$ nm [22] and a same elastic modulus as the one of the gallery layer was used [35]. However, the proposed thickness's value seems not to be coherent with the values about 1 - 3 nm found by using atomic force microscopy (Sikdar *et al.* [17]) or by analyzing the dynamic mechanical analysis results (Mesbah *et al.* [18]) or by using molecular dynamics (MD) simulation (Xu *et al.* [15]). Moreover, the mechanical properties of the interphase regions are believed to be quite different to the ones in the polymer matrix and in the gallery zone (see Shelley *et al.* [36], Mesbah *et al.* [18]). Pahlavanpour *et al.* [21, 33] have carefully studied the influence of the interphase's thickness and stifness on the mechanical properties of PCNs for a aligned exfoliated structure.

The objective of this work to perform an extensive parametric study in order to describe more real-

istic morphology of PCNs, especially for exfoliated microstructures which correspond to experimental processing described in the literature [8, 9, 37, 38]. Besides, parametric study on the influence of interphases with varied stiffness and thicknesses and of an extension of the clay's aspect ratio (in range of 100 - 400) would be interesting to clarify the mechanism of mechanical reinforcement of PCN materials. We are also interested on studying mechanical properties of the partial (mixed) exfoliated structure with the randomly oriented clay layers, which, with our best knowledge, have not been considered in 3D FEM models in the literature.

For these purposes, 3D FE models were developed for estimating the macroscopic elastic properties of a PCN from its microstructural characteristics. Several nanocomposite structures including exfoliated, intercalated and partial exfoliated were considered. Parametric studies were performed to highlight effects of nanocomposite morphologies, of the characteristics of inclusions (the aspect ratio, the average number of clay per intercalated block, the interlayer material, etc.) and of interphases (thickness, Young's modulus). The effects of structural parameters were demonstrated and compared with experimental and analytical results extracted from literature.

The paper is organized as follows: first, Section 6.2 describes the RVE model, the structural parameters, the material behavior and the finite element method used in this study. Next, Section 6.3 reports a parametric study on the mechanical properties and discussions. The results calculated by our model are also compared with the results of some typical experimental works in literature. Finally, Section 6.4 summarizes this work.

6.2 Materials and method

6.2.1 **REV** build et structural parameters

In this work, we are interested in the PCN microstructures where the intercalated blocks or the individual clay layers are randomly distributed in polymer matrix, which have been obtained in many experiments [8, 37]. In order to investigate the relationship between microstructure and macroscopic material properties of PCNs materials by using finite element analysis, a fundamental task is to establish a geometrical configuration that accurately reflects the morphologies of PCNs. In this context, the notion of representative volume element (RVE) has been introduced which has been shown to play an important role not only theoretically but also for the rational time consumed in the simulation by finite element method, in particular. Basically, the RVE is considered as a volume with enough large size that can statistically represent a heterogeneous material.

More precisely, this volume should include all microstructural heterogeneities that could be present such as inclusions, voids or interfaces in composite materials. However, it should also be small enough to be considered as a volume element of continuum mechanics [39]. The aforementioned multi-scale models yield the effective properties of material volumes theoretically much larger (one order of magnitude) than the microscale features. Accordingly, these models can be used to estimate effective properties in a material volume of several millimeter cubes, in which the microstructure possesses a well-defined regular or random pattern.

An in-house C++ and Python code has been used to generate the PCN structures, which are composed of the intercalated blocks or the individual clay layers that are randomly distributed in polymer matrix. The principle of this code is based on the random sequential adsorption (RSA) algorithm developed by Feder [40]. The clay platelets or intercalated blocks defined by their aspect ratio are randomly distributed in polymer matrix. The RVE size is adjusted as function of the inclusion aspect ratio and the inclusion number. During the construction of the RVE, each newly generated candidate clay particle is accepted only if it does not overlap with any existing clay particles in order to avoid the intersection of any two clay particles [41]. In addition, the RVE is constructed in a way to satisfy the continuity of a periodic microstructure [22]. As a result, in the generated structure, the inclusions within the domain do not overlap each to other and if one part of any inclusion intersect the outline, the lie party outside must be included in the opposite side of RVE. Therefore, all obtained PCN morphologies could be considered as the representation of a bulk composite material.

Moreover, the tool has been developed in Matlab software [42] allows us to distinguish the inclusion in different parts: clay layer, interphases layer and gallery layer. The sketch of an individual layer and an intercalated block is shown in Figure 6.1. Precisely, Figure 6.1 (a) shows inclusion made by one clay layer confined between two interphase layers. The thickness of clay layer, denoted h_c , is fixed at $h_c = 1$ nm, while the thickness of interphase, denoted h_i , can vary from 1 to 3 nm. The range of values 1 to 3 nm was the common interphase thickness of PCNs for several previous works [15, 17, 18]. It has been shown in the literature that the aspect ratio of clay layer, denoted α , could be varied in the range of value from 100 to 400 [3, 4, 5, 43, 44, 45, 46]. This range of value will be taken into account in our FE models. Except the case of the investigation of the influence of aspect ratio of clay, the typical value of $\alpha = 200$ is selected in our model as suggest in several works [23, 28, 32].

Figure 6.1(b) presents the arrangement of the three components: clay layer, interphase layer and gallery layer. As can be seen from the structure of intercalated blocks, the d-spacing is the distance between two consecutive clay layers.



Figure 6.1 – Two inclusion types: (a) the individual layer; (b) the intercalated block.

For all configurations studied, the volume fraction of nanoclays f_v in a REV varies in the range 0.1 to 2%. The relation between the volume fraction of clay f_v to the weight fraction f_m in the nanocomposite is given by the relation:

$$f_m = \frac{1}{1 + \frac{\rho_m}{\rho_c} \times \frac{1 - f_v}{f_v}},$$
(6.1)

where ρ_m and ρ_c are the mass densities of polymer matrix and of clay layer respectively.

The effective particle (EP) concept has been considered as an effective aid to facilitate the representation of PCN structures as well as to reduce the computation time in FE analysis for 2D FE models of intercalated structure [30] and 3D FE models of exfoliated structure with aligned orientation [21].



Figure 6.2 – Models of 2 % of nanoclay volume fraction RVEs: (a) exfoliated structure; (b) intercalated structure with 3 clay layers by block; (c) partial exfoliated structure

In this work, the effective properties of EP, which may be considered as a transversely isotropic material, was determined by using the method suggested by Luo and Daniel [6]. The formulas are shown in Appendix 6.5.

6.2.2 Material properties of the constituents

In this work, the constitutive relation of all materials (clay, matrix, interphase and galleries) is assumed to be the one of an isotropic linear elastic material. No thermal effect was considered in the simulation. For the sake of simplicity, the inclusions are assumed to be perfectly bond to the polymer matrix in all simulations. For the clay layer, it exists a large number of values of the Young modulus in literature which vary in the range of 178 to 400 GPa. This dispersion essentially depends on the experimental measurement or calculus method [15, 47, 48, 49, 50]. In this study, the material properties of the clay layer which are defined from the Young modulus and Poisson ratio are respectively given by $E_c = 400$ GPa and $v_c = 0.16$ and are based on the previous works [25, 32, 30]. In order to capture a large range of the clay stiffness as indicated above, the variation is taken into account by using the contrast of rigidity between the clay and the polymer matrix given by $CMC = E_c/E_m$, where E_m is the Young modulus of the polymer matrix.

The material properties of the polymer matrix are given by $E_m = 2.5$ GPa and $v_m = 0.4$ which are respectively the Young modulus and Poisson ratio. These values have been found within the range of typical values of elastic properties of several kinds of polymer matrices such as nylon [7], amide [10, 14] or epoxy [8] of which the Young modulus lie between 2 GPa-4 GPa GPa [30].

The effects of material properties of the interphase will be investigated *via* the rigidity contrast between the interphase and polymer matrix with the ratio defined by $IMC = E_i/E_m$, where E_i is the Young modulus of the interphase. The ratio *IMC* varies in the interval from 0.1 to 10 to consider the softer and stronger of interphase in comparison with the polymer matrix.

The effects of material properties of the gallery layer on the mechanical properties using the contrast of stiffness between gallery and polymer matrix expression (GMC). However, to the best of our knowledge, no data of elastic properties of the gallery layer is available in the literature. The density profile of polymer phase in the gallery space have been computed, showing a smaller density than the one of bulk polymer matrix [16, 51]. Despite that these authors haven't derived the equivalent elastic properties from these results, one may suggest that the stiffness of gallery layer would be smaller than the one of the bulk polymer matrix. The parameters used for similation are summarized in Table 6.1. For each parameter, we provide its refrence value and its range of variation for parametric study. In the parametric studies presented afterward, unless explicitly indicated, the reference values ($\alpha = 200$, CMC=160, IMC=1, GMC=1) will be used.

Table 6.1 – Parameters used for the parametric study. The subscripts c, i, g, m refer to the clay layer, the interphase layer, the gallery layer and the polymer matrix, respectively. * The value n = 1 corresponds to the exfoliated structure (EX)

Symbol	Meaning	Expression	value	reference value
α	The aspect ratio of clay layer	$\alpha = \frac{l_c}{h_c}$	100-400	200
СМС	Contrast of stiffness between clay and poly- mer matrix	$CMC = \frac{E_c}{E_m}$	40-400	160
IMC	Contrast of stiffness between interphase and polymer matrix	$IMC = \frac{E_i}{E_m}$	0.1-10	1
GMC	Contrast of stiffness between gallery and polymer matrix	$GMC = \frac{E_g}{E_m}$	0.5-1	1
Nn *	The number of clay layers by block	-	1-4	1

6.2.3 Modeling and finite element analysis

In this section, the problem solving method by using the finite element is described. The boundary value problem defined from the equations of linearized elasticity was solved with the commercialized finite element code COMSOL Multiphysics [52]. The domain and the equations were discretized on an unstructured mesh of tetrahedral finite elements and an interpolation quadratic polynomial of Lagrange. The meshing process was conducted in 2 steps starting by the nano-inclusions then the polymer matrix. The maximum element size imposed for the inclusion is 5 nm and the maximum element size imposed for the size of RVE. This choice is a compromise between the required accuracy and the computational cost. A meshed specimen of an exfoliated structure is shown in Figure 6.3.

The position is specified through the Cartesian coordinates (x_1, x_2, x_3) with respect to a Cartesian reference frame $\mathbf{R}(O; \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$, where O is the origin of the space and $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ is an orthonormal basis of this space. In the equations of linearized elasticity, the constitute relation is given by the Hooke law written under the form $\sigma_{ij} = c_{ijk\ell} \epsilon_{k\ell}$ for $i, j, k, \ell = 1, ..., 3$, where σ_{ij} are the components of second-order stress tensor, $\epsilon_{k\ell}$ are the components of the second-order strain tensor and $c_{ijk\ell}$ are the components of the fourth-order stiffness-tensor. The last tensor can be expressed as a stiffness matrix by using the Voigt notation given by C_{IJ} for I, J = 1, ..., 6. In what follows, the components of this matrix are simply denoted by C_{IJ} .

In order to determine the overall effective properties of PCNs based on the finite element method, each RVE was subjected successively to a six set of uniform displacements (KUBC, for kinematic uniform boundary conditions) boundary conditions following the procedure described for instance by Zohdi and Wriggers [53] that amounts to simulating longitudinal traction and shear tests in every direction defined by aligned directions with the edges of RVE. Each of these kinematic conditions leads to a homogeneous strain field on the boundary of the RVE.


Figure 6.3 – The meshed specimen of a REV of an exfoliated structure at 2% clay volume fraction.

Note that it is possible to subject successively to the RVE to a six set of uniform tractions (SUBC, for static uniform boundary conditions) or the periodic boundary conditions. For the PCNs materials, several authors have shown that the impact of boundary conditions was not significant when the size of RVE was large enough [21, 22, 31, 34].

It is worth noting that in some numerical works [22, 31, 35], the Young modulus of exfoliated PCNs was determined by measuring stress-train relation in only one direction of the RVE, assuming that the random dispersion of clay layer in polymer matrix can provide a isotropic behavior of PCNs. In this work, we estimated all components of elastic tensors, that allows us to check this proposed hypothesis.

In principle, the estimated elasticity tensor *C* is a full 6×6 matrix, so the equivalent isotropic elastic tensor needs to be determined. In the litterature, the simplest method consists of replacing the anisotropic material by its closest isotropic one may be found in [54, 55, 56, 57]. Given an anisotropic elastic tensor *C*_{IJ}, the equivalent Lamé constants (λ and μ) of the closest isotropic tensor are given by [57]:

$$\lambda = \frac{C_{11} + C_{22} + C_{33} + 4(C_{12} + C_{23} + C_{13}) - 2(C_{44} + C_{55} + C_{66})}{15},$$
(6.2)

$$\mu = \frac{C_{11} + C_{22} + C_{33} - (C_{12} + C_{23} + C_{13}) + 3(C_{44} + C_{55} + C_{66})}{15}.$$
(6.3)

The Young modulus and the Poisson ratio can be determined by:

$$E = \frac{\mu \left(3\lambda + 2\mu\right)}{\lambda + \mu}, \qquad \nu = \frac{\lambda}{2 \left(\lambda + \mu\right)} \tag{6.4}$$

6.3 Results and discussions

6.3.1 Verification of finite element results

We first check the correctness of the proposed model and of the computational procedure for estimating effective elastic coefficients. To do so, we consider two exfoliated nanocomposites with different clay volume fractions $f_v = 0.4\%$ and $f_v = 1\%$, respectively. For each case, we calculate all components C_{ij} of the effective elastic tensor of 5 RVEs of which the microstructural morphology were independently generated. Herein, 50 inclusions are chosen as the RVE' size for each case as suggest in several other numerical work [21, 31]. Figure 6.4 presents the these estimated elastic coefficients C_{ij} for both configurations in all 5 cases. We also show the equivalent the Young moduli and the Poisson coefficients calculated by using Eq. (6.4). In principle, as the orientations of clay platelets are randomly generated, these parameters are expected to be independent to the RVE's size if this size is sufficient large. In Figure 6.4, the variations of C_{11} , C_{22} and C_{33} are observed to be more important than those of others coefficients. Moreover, the results of estimated parameters of 5 cases are more uniform when $f_v = 0.4\%$ than when $f_v = 1\%$. Hence, one may suggest that a larger VRE's size would be needed when f_v is more important. Interestingly, in despite of these variations, the equivalent Young modulus and the Poisson coefficients which have been calculated from C_{ij} are almost constant.



Figure 6.4 – Variation of elastic constants for different configurations of exfoliated PCN at (a) $f_v = 0.4$ % and (b) $f_v = 1$ % of clay volume fraction. The RVE sizes were built with 50 inclusions in each case.

We also studied the influence of RVE's size (based on the number of clay layers) on estimated

effective elastic constants of exfoliated PCNs. Here, the size of RVE is determined by fixing $f_v = 1\%$ and varying the number of individual silicate layers from 35 to 180. For each ℓ_{VRE} , *E* and *v* have been computed from five random generations of morphological configuration. The results of Young's modulus presented in Fig. 6.5 show that it is nearly independent to the RVE size when more than 50 inclusions were generated. Note that in this case ($f_v = 1\%$), the ℓ_{VRE} is required to be at least 3 times bigger than the length of clay layer. This statement is coherent to the RVE sizes determined by using 3D FE simulations in the literature [31, 22, 34]. In order to obtain physical meaningfulness results with reasonable computational costs, all RVEs used for the parametric studies below are generated with about 50 inclusions.



Figure 6.5 – Effect of RVE size (presented by number of inclusions) on the equivalent Young modulus of exfoliated PCN at 1% volume fraction

In the following parametric study, the Young modulus will be normalized by the Young modulus of polymer matrix (E_m) .

6.3.2 Validation of the effective particle concept

By using the effective particle concept described before, one may replace the multilayer block (which represents the clay platelets, interphase and eventually gallery layers) by an effective particle (which is homogeneous block with equivalent elasticity properties). The equivalent properties of EP are determined from the expressions in Appendix 6.5. Here, numerical tests have carried out to check the validity of the use of effective particle concept for estimating the effective elastic constants E and ν of PCNs with exfoliated or intercalated structures. Figure 6.6 presents the effective Young modulus obtained by two models: the first one has multilayer blocks (which has 3 clay layers per block) and the second one uses effective particles instead. It shows that the model using EPs can reproduce the same equivalent Young modulus as the ones obtained by models with multilayed block. Therefore, thanks to its effectiveness in computation process and its ability to accurately determine the mechanical properties of PCN models, the EP concept will be used for all others studies in this work.

6.3.3 Effect of aspect ratio and elastic properties of clay layer

The typical characteristics of inclusions (such as stiffness, size and shape) in nano-scale are shown to play important role in the design of nanocomposite materials [22, 43, 46]. In this section, the influence of clay's aspect ratio (α), of the rigidity contrast between the clay and the polymer matrix (CMC), the



Figure 6.6 – Young's modulus of exfoliated nanocomposites (N1) and intercalated nanocomposites (N3) at different clay volume fraction. The FE models are established based on the use of effective particle concept (EP) or the multilayer representation

Poisson ratio of clay layer on the macroscopic mechanical behavior of exfoliated PCNs were investigated.

Firstly, exfoliated PCNs having different clay volume fraction (f_v between 0% – 2%) with clay's aspect ratio varied in the range 100 – 400 are considered. Figure 6.4(a) presents the variation of the Young modulus with respect to f_v in 3 cases of the aspect ratio α . It can be seen that the Young modulus proportionally increase with the volume fraction f_v and with the the clay's aspect ratio as well. Figure 6.4(b) shows a (nearly) linear relationship between *E* and α in the range $\alpha = 100 - 400$. The Poisson coefficient only varies from 0.38 (when $\alpha = 100$) to 0.36 (when $\alpha = 400$). The obtained results correspond well with several numerical results extracted from the literature [22, 58]. These results confirm the advantage of the using of the large aspect ratio platelet inclusions in the processing of nanocomposites for improving their mechanical behaviors. Indeed, clay platelet is one of the best candidate in several nanoparticles from this viewpoint with the presence of high aspect ratio [3, 4, 5, 43, 44, 45, 46].

The contrast of stiffness between clay and polymer matrix (CMC) is also investigated in this work because of the presence of a large range of clay's stiffness from literature and of various polymer types in PCN processing. The CMC value is considered in the range from 40 to 400 to cover all possibilities in PCN materials. Figure 6.8 shows the finite element results of the elastic modulus for exfoliated nanocomposites at different clay volume fraction, normalized by the matrix elastic modulus, E_m , as a function of the CMC. One can observe that of PCN Young's modulus increase with CMC and this effect is more significant for high clay volume fraction. These observations are different than those reported by Spencer and Sweeney [58] for 2D model in which the authors found that when CMC > 200, it doesn't significantly improve the rigidity of PCNs anymore.

The value of the Poisson ratio of clay layer is also found to have a large variation in the literature [17, 47, 48, 50]. Indeed, this value is determined in several MD works or experimental fitting with the value in the range of 0.28-0.47. However in almost numerical works, the value in the range of 0.16-0.28 has been chosen [21, 22, 25, 31, 34, 35]. Thus its influence on the mechanical properties of PCNs is also need to be clarify. In this work, the Poisson ratio is varied in the range of 0.16-0.35, while keeping all other parameters unchanged. The Young's modulus of exfoliated PCNs at different clay volume fraction as function of the Poisson ratio of clay layer is shown in the Figure 6.9. One can observe that the change in Poisson ratio didn't significantly change the Young's modulus of PCN material. The



Figure 6.7 – The influence of the clay's aspect ratio on elastic modulus of exfoliated PCNs at (a) different volume fraction and (b) at 1 % volume fraction. The corresponding Poisson ratio of PCNs is also reported in the case of 1 % volume fraction.



Figure 6.8 – The effect of the contrast of stiffness between clay and polymer matrix (CMC) on Young's modulus for exfoliated PCNs at different clay volume fraction.

difference in all case is negligible.

In summary, the aspect ratio and the stiffness of clay layer have an important role on the macroscopic mechanical properties of PCNs. However, variation of the Poisson ratio of clay layer seems to have negligible effect on the overall properties. Thus, the accurate identification of clay's aspect ratio and its stiffness is required to correctly estimate the effective properties of PCNs.



Figure 6.9 – The effect of Poisson ratio of clay layer on the mechanical properties of exfoliated PCNs at different clay volume fraction.

6.3.4 Effects of microstructural morphology

The influence of the structural parameters, *i.e.* exfoliated or intercalated structure with different clay layers per block (2, 3 and 4) as well as the interlayer distance (*d*-spacing), on the macroscopic properties of PCN materials are examined in this part. The *d*-spacing is first defined as 4 nm for all intercalated structures since this value is typical one as suggest from several works from the literature [5, 10, 25, 33]. The influence of the *d*-spacing on the elastic behavior of PCNs is also addressed by varying this value from 3 to 6 nm for the intercalated structure for which there are 3 clay layers per intercalated block. The influence of the gallery layer on the elastic behavior of the PCNs is also addressed by considering the intercalated structure in which there are 3 clay layers per intercalated block with the *d*-spacing of 4 nm.

Figure 6.10 shows the Young modulus of PCNs as a function of clay volume fraction in different structure types. It is clearly observed that in all cases, the Young modulus increase with the clay volume fraction and the exfoliated morphology shows a better enhancement capacity than the intercalated one. Moreover, this effect is highly pronounced at high volume fraction of clay. A simple explanation of this phenomena is given in the literature [27, 31], in which the authors concluded that an increase of the number of clay layers par stack inherently reduced the equivalent particle's aspect ratio of EP, thus mechanical properties of PCNs. Moreover, it is obvious to conclude that the nanocomposite structures can show a better dispersion state when smaller number of clay layers per block is used. Therefore, one can conclude that the dispersion state of inclusion into polymer matrix plays an important role in the mechanical enhancement of PCN materials. The influence of d-spacing is shown in the Figure 6.10(b). It is observed that at small clay volume fraction, the *d*-spacing didn't affect the mechanical properties of intercalated PCNs. The effect of *d*-spacing is only pronounced with the value bigger than 4 nm and at high volume fraction of clay > 1%. It should pointed out that the effect of the clay number per block is much more clear than the *d*-spacing effects. Besides, one can observe that for the intercalated structure, a weak gallery layer (GMC = 0.5) as shown in the Figure 6.10(b), may decrease the overall elastic modulus of the nanocomposite.

The presence of the mixed structure (MI) is also addressed in this part. For this purpose, the



Figure 6.10 – The influence of structural parameters on elastic modulus of PCNs: (a) the effect of number of clay layers per block, the intercalated structures have the *d*-spacing value of 4 nm and (b) the *d*-spacing effect of intercalated structure with 3 clay layers per block. In this case (b), the influence of the elastic modulus of the gallery layer is shown when the *d*-spacing is 4 nm.

mixed structure with the exfoliation ratio of 0.33 was built. Here, the exfoliation ratio is defined as the ratio between the number of individual clay layer and the total clay layer in the RVE. Two cases of mixed structures were considered based on the number of clay layers (2 and 3) per intercalated block, which are simultaneously present with the individual clay layer in the nanocomposite structures. These structures are denoted as MI.N2 and MI.N3 respectively. It can be seen from the Figure 6.11 that the Young modulus of the mixed structure is found between that of the intercalated and the exfoliated structure. It can be explained by the fact that in comparison with the intercalated structures, the presence of certain individual clay layers in the mixed structure contribute to a better dispersion state of clay in PCN structures, thus enhance its mechanical properties.

6.3.5 Effect of interphase

A parametric study was carried out to study systematically the influence of interphase's stiffness and thickness on the overall modulus of PCNs. For this purpose, only the exfoliated structure is considered since this structure presents the highest volume of interphase [4, 43, 46]. The contrast of stiffness between the interphase and the polymer matrix ($IMC = E_i/E_m$) is varied from 0.1 to 10 for investigating the weaker and the stronger interphase respectively. The interphase's thickness (h_i) was chosen as 1 nm to 2 nm as typical cases according to several studies [15, 17, 32, 33]. As can be seen from the Figure 6.12, a strong interphase can enhance significantly the mechanical properties of exfoliated



Figure 6.11 – The comparison of the Young modulus between the exfoliated, intercalated and mixed structure of PCNs. The exfoliation ratio of 0.33 is chosen for two considered mixed structures.

PCNs, particularly when the interphase's thickness is important. Indeed, an increase of 9% is observed for the exfoliated structure at $f_v = 2\%$ with the values IMC = 10 and $h_i = 1$ nm respectively 6.12(a). This value became 19% when the interphase's thickness is 2 nm 6.12(b). In contrast, a weak interphase may decrease significantly the stiffness of PCNs. Indeed, a reduction of 16% of the Young's modulus is found for the exfoliated nanocomposite to which the clay's volume fraction, the thickness and stiffness contrast values of interphase are $f_v = 2\%$, 1 nm and IMC = 1 respectively. Therefore, one can conclude that the interphase region plays an important role in the mechanism of mechanical reinforcement of PCNs. This result suggests that in processing of PCN materials, the reinforcement of the mechanical properties of the interphase may highly contribute to increase the overall mechanical properties of PCNs. The covalent liaison between clay surface and polymer matrix is believed to ensure the strong polymer-clay interactions, thus improve mechanical properties of the resulting nanocomposites.

6.3.6 Comparison with the experimental and numerical results from the literature

The comparison of the elastic modulus predicted by our model with that extracted from the experimental measurement in existing literature was performed in order to verify the robustness of our numerical model. Fur this purpose, the data concerning the elastic properties of polymer is taken from several experimental works of Anoukou *et al.* [10] and Fornes *et al.* [7], in which these authors reported the exfoliated structure of PCN. The aspect ratio of clay was fixed at $\alpha = 200$, which is the same as the value used in [10, 59]. The elastic modulus clay layer was varied in the range 170-400 GPa. Based on the density of polymer and clay, the volume fraction can be converted into the weight fraction by using Eq. (6.1). The interphase was not taken into account in this model.

Figure 6.13 presents the Young modulus predicted in 4 cases (3 exfoliated structures with different E_c and 1 mixte one) by using our model. We also present experimental and theoretical results given by Anoukou *et al.* [10]. The theoretical results have been derived by using self-consistant and mori-Tanake models. One may state that the model with $E_c = 400$ GPa seems to overestimate the stiffness of PCNs. When $f_v < 1.5\%$, the FE models with $E_c = 200$ GPa or $E_c = 170$ GPa lead to similar values equivalent Young modulus as experimental or analytical results. When $f_v > 1.5\%$, FE models of exfoliated structure give equivalent Young modulus slightly higher than the experimental ones. Interestingly, the results of the mixte model ($E_c = 200$ GPa) still match well with the experimental ones. Note that as the exfoliated status of specimen in experiments is difficultly achieved, only a qualitative comparison could



Figure 6.12 – The influence of the interphase's stifness (a) and thickness (b) on elastic modulus of exfoliated PCNs.

be made and further investigations need to be done. However, the value $E_c \approx 200$ GPa seems to be suitable for modeling the clay layer.



Figure 6.13 – Numerical predictions of the overall Young's modulus compared to the experimental data from Anoukou *et al.* [10] for the dry PA6/clay nanocomposites. The Mori-Tanaka and self-consitence predictions are also reused from the cited work for the purpose of comparison.

The comparison with the work of Fornes *et al.* [7] is also performed. As can be seen from the Figure 6.14 that the FE models in which the Young modulus of clay layer in the range of 170-200 GPa allow to very well reproduced the elastic behavior of PCNs.



Figure 6.14 – Numerical predictions of the overall Young's modulus compared to the experimental data from Fornes *et al.* [7] for the dry poly(nylon6)/clay nanocomposites.

As can be observed in all the comparison cases, the Young modulus of 400 GPa overestimated the mechanical properties of PCN materials. It may be explained by the fact that the value $E_c = 400$ GPa, which has been obtained by Manevitch and Rutledge [60] by using the MD simulation, is associated to a clay's thickness of 0.615 nm. In macroscopic models, it is generally accepted that the clay's thickness is about 1 nm. Thus, an adapted value of Young modulus that is about 250-260 GPa, which corresponds to the clay thickness h=1 nm, may be more appropriated. Suter *et al.* [48] presented several methods to determine the elastic modulus of clay layer by using MD simulation and obtained values in range 170-230 GPa when considering a thickness of clay layer of 1nm with or without interlayer. Besides, Chen and Evans [47] estimated the elastic modulus of smectite clay layer by using a empirical linear fit with the density of analogous materials. The Young modulus values in the range of 178-265 GPa has been obtained. In summary, based on the results presented herein and in the mentioned works in the literature, we may suggest that in practice, clay layers with E_c in a range between 170-230 GPa would be used for estimating the elastic properties of PCN materials.

6.4 Conclusions

This work was focused on the prediction of the overall mechanical properties of the polymer/clay nanocomposites by using the 3D FEM. Different kinds of PCN microstructures are taken into account: intercalated, exfoliated and the partial exfoliated (mixed structure). All the nanocomposite structures have been numerically generated with the random distribution and orientation of inclusion in the polymer matrix. The effective particle concept has been shown to be efficient for modeling the behavior of PCN microstructures and allows to reduce the computational time.

The influence of the key morphological parameters (clay volume fraction, clay's aspect ratio, contrast of stiffness between clay and polymer matrix, number of clay layers per intercalated block, interlayer distance, interphase's thickness and stiffness) on the overall mechanical properties of PCNs have been studied in detail. Our attention has been paid on the elastic properties as well as the aspect ratio of clay layers because of the large range of variation from the literature. The mechanical properties of clay layer have been chosen from MD simulations or empirical estimations. The aspect ratio and the stiffness of clay layer have been shown to play an important role on the macroscopic behavior of PCNs, while the Poisson ratio of clay layer has nearly no effects on the macroscopic properties. In addition, by comparing FE results with the ones extracted from the literature, we may suggest that for modeling PCNs behavior, E_c in range 170-230 GPa would be used.

The partial exfoliated structure has been shown to be more suitable for the prediction of PCN materials, particularly at high clay's volume fraction. Moreover, these studies highlighted the importance role of the interphase in terms of stiffness as well as thickness, modeled as a third constituent material, on the PCN's mechanical properties.

These obtained results may help the guidelines of PCNs design to obtain an optimized mechanical properties. For this purpose, a good dispersion of clay layers into polymer matrices is the key target. The modification of the clay surface to reduce the interaction between the clay layers, increase their interlayer distance and also to make it compatible with polymer matrix is an inevitable step. In addition, a good interface between clay and polymer matrix is an important factor for which the reinforcement of interphase by using the covalent graft or the reactive organomodifiant is highlighted. Besides, it is worth noting that the use of a stable thermal organomodifiant is mandatory for the melt processing of PCNs,.

6.5 Appendix. Determination of equivalent properties of the effective particle

Considering a representative intercalated block as shown in Figure 6.15. The block consists of two phases which represent the clay layer and the gallery, respectively.



Figure 6.15 – A representative element of an intercalated cluster

By assuming that both clay and gallery materials are isotropic elastic, the effective particle has a transversely isotropic behavior. Following Luo and Daniel [6], the effective elastic constants of EP may be given by:

$$E_{xx} = \chi E_c + (1 - \chi)E_g + (\nu_c - \nu_g)^2 \left(\frac{1 - \nu_c^2}{\chi E_c} + \frac{1 - \nu_g^2}{(1 - \chi)E_g}\right)^{-1},$$
(6.5)

$$E_{yy} = E_{xx},\tag{6.6}$$

$$\frac{1}{E_{zz}} = \frac{\chi}{E_c} + \frac{1-\chi}{E_g} + 2(\frac{\nu_c}{E_c} - \frac{\nu_g}{E_g})^2 \left(\frac{1-\nu_c}{\chi E_c} + \frac{1-\nu_g}{(1-\chi)E_g}\right)^{-1},\tag{6.7}$$

$$v_{xz} = v_{yz} = \chi v_c + (1 - \chi) v_g, \tag{6.8}$$

$$v_{xy} = \left(\frac{E_g (1-\chi) v_g}{1-v_g^2} + \frac{E_c \chi v_c}{1-v_c^2}\right) \left(\frac{E_g (1-\chi)}{1-v_g^2} + \frac{E_c \chi}{1-v_c^2}\right)^{-1},$$
(6.9)

$$G_{xz} = G_{yz} = \frac{G_c G_g}{\chi G_g + (1 - \chi) G_c},$$
(6.10)

$$G_{xy} = \chi G_c + (1 - \chi) G_g$$
(6.11)

where χ denotes the volume fraction of clay within the effective particle; the subscripts *c* and *g* refer to the clay layer and gallery, respectively.

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General conclusion and perspectives

Conclusion

The work developed in this thesis has encompassed two mains parts: the first part concerned the elaboration and characterization of the nanofillers and the ternary polymer/clay nanocomposites (PCNs), while the second one was dedicated to multiscale modelling and simulation of the said nano-materials.

Elaborations and characterizations of PCNs

In the first part, two different ways were proposed for preparing polymer-grafted clay reactive nanofillers:

The *in situ* photoinduced surface initiated atom transfer radical polymerization (SI-ATRP) has been reported as a novel and efficient route for preparing intercalated nano-clay fillers bearing *clickable* functions. The clay surface has been firstly functionalized with amino silane coupling agent, followed by grafting of bromine ATRP-initiator. The Poly(propargyl methacrylate) chains have been finally grown from the bromine-functionalized silicate layers in presence of free photoinitiator by using UV-initiated polymerization. The generic *clickable* character has been demonstrated through grafting with azidomethyl benzene and mercaptosuccinic acid via photodriven 1,3-dipolar cycloaddition and thiol-yne click reactions, respectively. This study constitutes the first example in the literature of implementation of photochemically-driven atom-transfer radical-polymerization in tandem with the use clay-grafted ATRP initiator for the robust grafting of polymer chains to clay surface. This strategy has allowed fine control of the length of the polymer chains and thus the interlayer distance.

With the aim to simplify further the preparation process of polymer-modified clay with tunable interlay-spacing and interfacial chemistry and to provide easy access to gram-scale preparation methods, we have proposed a new and simple route for the synthesis of reactive (pre)exfoliated fillers and ternary nanocomposites, respectively. The approach is based on the *in situ* photo-induced polymerization of epoxy-like monomer, namely glycidyl methacrylate, from vinyl-functionalized clay silicate layers. The morphology as well as the structure of the so-prepared nanofillers were strongly dictated by the surface clay treatment. A critical overview of the key parameters (silanes, and monomer concentration, polymerization time), influencing the effectiveness of the preparation process of clay nanofillers has been presented. The reactivity and homogeneous dispersion of the as-obtained nanofillers towards either modified starch, as thermoplastic matrix, and GreenPoxy bio resin, as thermoset matrix, have been investigated thoroughly *via* FTIR, TGA, XRD, SEM and TEM analyses. Incorporation of different contents of poly epoxy-functionalized clay layers enhanced continuously the mechanical properties of the final epoxy resin, through remarkable increase of the storage modulus and glass transition temperature. This study evidenced undoubtedly the direct relationship between morphology and chemical structure of the clay layers in the nanofillers and *in fine* the properties of the with these nanofillers-containing nanocomposites as well as the potential use of the reactive nanofillers in reinforcement of environmentally friendly polymers.

Multiscale modelling of PCNs

In the second part, numerical simulations of PCN materials have been carried out for investigating mechanical behavior these nanomaterials at both nanoscopic and microscopic scales.

- Firstly, at the nanoscale, different molecular structures of PCNs, which correspond to intercalated or exfoliated status of PCNs depending on the amount of polymer phase in the interlayer space, have been considered. The reactivity of the clay layer has been taken into account by using the reactive organomodifiant as aminosilanes, which are covalently grafted to clay surface. The representative crosslinked epoxy molecule has been used as polymer matrix. The arrangement of organic components and their molecular interactions, particularly in the interphase zone have been investigated by using molecular dynamics simulations. A strong affinity between the polymer matrix and the reactive clay platelets has been observed. The profile of the density of organic phase allows us to determine the thickness of the interphase. The exfoliated structure shown a thicker interphase in comparison with the intercalated one. The thermodynamic properties of the confined polymer in each structure have also been investigated in detail in order to clarify the influence of silicate layers on the macroscopic properties of nanocomposites. It has been shown that the mobility of polymer chains, which are located close to clay surface are quite different than that far away from the clay surface. In addition, these molecular models allow us to numerically estimate the effective elastic properties of the PCN models at the nanoscale and at different temperatures. A high anisotropic behavior of the PCNs at the nanoscale has been observed.

- Secondly, at the microscale, the equivalent elastic properties of the PCNs based on their microstructures and the mechanical properties of each constitutive components have been computed by using 3D finite element model. The key microstructural parameters of clay or clay stacks such as elasticity modulus, aspect ratio, basal spacing and its dispersion state as well as its volume fraction have been taken into account in the model. A parametric study on effects of these parameters on the macroscopic effective elastic properties of the PCNs has been carefully investigated. The results shown that the macroscopic rigidity of PCNs material depends not only on the clay's volume fraction but also on the dispersion state of clay platelets in the polymer matrix. An exfoliated structure may improve the macroscopic rigidity much more efficiently than intercalated ones, particularly at high volume fraction of clay. It has been shown that the aspect ratio and the stiffness of clay layer play important role on the macroscopic behavior of PCNs, while the Poisson ratio of clay layer has a negligible effect on the on macroscopic properties. The important role of interphase on the mechanical properties enhancement of PCNs has also been highlighted. The partial exfoliated structure has been shown to be more suitable for the prediction of PCN materials, in particular at high clay volume fraction. The comparison with the experimental result or analytical prediction extracted from the literature has been performed and the range of the clay elastic modulus has been proposed.

In summary, the work developed in this thesis has encompassed two main areas, with the aim of developing the synergy between chemical engineering and mechanical modelling. This strategy has been achieved with the support of two viewpoints. From chemical engineering to mechanical modeling, we were able to show different state of dispersion of clay layers in the polymer matrix, including exfoliated, intercalated as well as the partial exfoliated form. The used procedure to modification of clay surface confirmed the presence of the interphase zone for the modelling of this nanomaterial.

Conversely, from numerical modelling to chemical engineering, we showed the capacity to predict the mechanical properties of the PCN materials based on their elaborated conditions (material properties, volume fraction and estimated structure). In addition, the numerical framework was an efficient aid to identify the important factors that control the mechanism of thermomechanical reinforcement of the elaborated PCNs. Such information provided an important guide for the design of these nanomaterials.

Perspectives

The strategy aiming at functionalizing clay surface with molecular or polymeric segments bearing reactive groups allows for the synthesis of new ternary nanomaterials, with true nanocomposites features and advanced properties. Indeed, the generic strategy proposed in this work can be applied for other types of polymers in order to explore newsurface properties, notably in terms of reactivity and miscibility, of clay layers. Of particular interest would be the grafting of amino-containing polymer providing, similarly to molecular hardener, potential reactivity towards epoxy resins. Diol-containing may be of particular interest for dispersion with polysaccharides matrices through hydrogen bond-based interaction. One may also consider the use of such reactive nanofillers in combination with hardener (triethylenetetramine, aromatic polyamines) and epoxy-resins precursors to elaborate other kinds of thermoset polymer-based nanocomposites. Moreover, functional exfoliated nanoclays can be used for other applications such as sorbents for heavy metal of organic pollutants in waste water, or as supports for metal-based nanoparticle.

Concerning the multiscale modeling and simulation of PCNs, by using the developed DM model, we may investigate the effects of the graft density of the surfactant and of the crosslink density of the thermoset polymer on the molecular structure as well as the thermomechanical properties of PCNs. Besides, it is interesting to perform simulations on models using other surfactants, *e.g* cationic surfactant, and compare the results to the ones presented herein (which has been obtained by using covalent graft surfactant). Other types of hardened or epoxy monomers may be considered to study the influence of the polymer structures. Moreover, because the solvents (such as acetone, chloroform) are usually used in the processing of the thermoset polymer clay nanocomposites, the developed model may be enriched by adding these organic solvents in order to study the influence of these solvents on the properties of PCNs systems..

The viscoelastic or nonlinear behaviors of the PCNs can directly be taken into account by using the developed FE models. This will allow us to analyze the local damage mechanism occuring at the microscale and predict the rupture of PCNs. Furthermore, an extension of this model to compute the thermal and barrier properties of PCN materials may be developed.

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