



Structure and electrophysical properties of nanocomposites based on thermoplastic polymers and carbon nanotubes

Volodymyr Levchenko

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par

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**Morphologie et propriétés électrophysiques de
nanocomposites à base de polymères thermoplastiques
et de nanotubes de carbone**

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Structure and electrophysical properties of nanocomposites based on thermoplastic polymers and carbon nanotubes

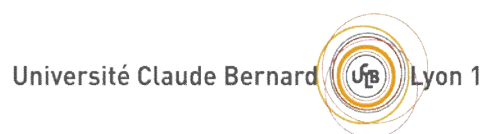
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GENERAL INTRODUCTION

Lately electro-conductive polymer composites are intensively investigated due to their valuable properties and perspectives of the application both for the research purposes and in the industry. These materials are of high interest for the practical use, as their electro-physical characteristics are close to those of metals, whereas the mechanical properties and processing methods are typical for plastics. By this time the conductive composite materials are represented by the thermoplastic or thermoset polymers filled with dispersed conductive component, such as metals, carbon fillers, conductive ceramic etc.

The usage of new nanofillers provides to the increased interest to obtain the polymer composites filled with carbon nanotubes (CNTs). Owing to the unique mechanical, electrical and thermal properties, CNTs are expected to be an ideal filler for the electro-conductive polymer composites. Thus, due to the high anisotropy of the carbon nanotubes, their application enables to obtain polymer materials with a very low percolation threshold, i.e. with a low filler content. Such materials filled with CNTs are characterized by a wide range of unique physical properties and can be used as sensors, electrodes, supercapacitors, special coatings protecting from electromagnetic radiation etc. The characteristics of such materials can be also changed via the influence of electric and magnetic fields, temperature, etc. Therefore, a special attention should be paid to the study of the electro-conductivity, dielectric and thermo-physical properties of such nanocomposites.

The urgency of the topic. An intensive development of the state of the modern technologies, which demands the manufacture of materials with new specific properties, results in the widening of the potential application of composites, filled with nanoparticles, and, particularly, with carbon nanotubes. In spite of the wide possible use of electroconductive polymer composites filled with CNTs, nowadays they are mostly studied in order to satisfy the scientific interests. This is caused by the dependence of the characteristics of the electro-conductive composites on a lot of factors, such as: space distribution of the filler and its

content in the polymer matrix; the electro-conductivity of the filler; the shape and size of the particles; the existence of the interphase interactions polymer-filler; the regimes of composite formation. Owing to the nanosize of the particles, the formation of the conduction phase in the composites is characterized by special properties, which had not been studied by now. Besides, there is another factor, which diminishes the effectiveness of the CNTs usage as electrical filler – their ability to create aggregates during the introduction into the polymer matrix.

Thus, one can conclude, that a possibility to control the structure formation of the filler conduction phase becomes especially important, as this process determines the electro-physical properties of the polymer. In this connection it is necessary to provide the theoretical and experimental investigations of the correlation between the conditions of the formation of composites and their morphology and properties. The ascertainment of such a correlation will make it possible to create the compositions with the preassigned electro-physical properties.

The connection of the Thesis with the scientific programs, plans, themes. The Thesis was performed in the Department of polymer composites in the Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine according to the scientific planes of the Institute according to the Government's themes: «The basics of conductive cluster creation in organic-inorganic polymers», 2007-2011, 2.1.11.5-10 (registration number – 0106U010376); «Synthesis and investigation of hybrid organic-inorganic systems containing dispersed oxides and metals», 2008-2013, 2.1.11.5-11 (registration number – 0108U010723).

A part of the experimental research was performed in the Laboratory IMP@LYON1, UMR CNRS 5223 "Ingénierie des Matériaux Polymères", University Claude Bernard Lyon 1 (CNRS, France) according to the «Agreement on the joint International supervision of the Thesis» between the Institute of Macromolecular Chemistry NAS of Ukraine and the University Claude Bernard Lyon 1 (CNRS, France) in the framework of the international scientific cooperation program between the Institute of Macromolecular Chemistry NAS of Ukraine and the Laboratory of Polymer Materials and Biomaterials, University Claude Bernard

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The purpose and tasks of the research. The aims of the Thesis investigation are as follows:

- to determine the peculiarities of the formation of the filler conductive structure in polymer nanocomposites filled with carbon nanotubes and combined nanofillers;
- to investigate the influence of the morphology of the heterogeneous structure of the composite and interaction of nanofillers on the electrical, dielectric, thermophysical and mechanical properties of the composites.

The attainment of the above described purposes provided for the following objectives:

- to investigate the processes of CNTs conductive phase formation in polymer nanocomposites based on thermoplastic polymers and their blends;
- to study the influence of the interphase interactions between polymer and filler on the percolation conductivity of the heterogeneous polymer systems;
- to investigate the processes of CNTs conductive phase formation in the polymer matrix filled with combined fillers;
- to find out the influence of the interaction between nanofillers on the percolation conductivity and properties of polymer systems filled with combined fillers;
- to study the electrical, mechanical and thermo-physical properties of the segregated polymer systems, which include CNTs.
- to find out the correlations between the technological conditions of the nanocomposite processing and their electrical, dielectric, thermal and mechanical characteristics.

The object of the research – the regularities of conducting phase formation of the filler and its influence on the properties of structural composites.

The subject of research – the structural organization of carbon nanotubes in the composites based on thermoplastic polymers and its effect on electrical, mechanical and thermal properties.

Methods: differential scanning calorimetry method (DSC) was used to study structural changes and phase transitions; dielectric relaxation spectroscopy method (DRS) was applied to determine the dielectric parameters and electroconductivity in a direct current regime (σ_{DC}); two-electrode method of the electroconductivity measuring at direct current was used to study the conductivity σ_{DC} ; thermomechanical analysis method (TMA) was applied to define the elastic modulus and deformation properties of the composites; optical microscopy method was used to study the microstructure; in order to study the morphology and spatial distribution of composite fillings, transmission and electron scanning microscopy were applied; dynamic mechanical thermal analysis (DMTA) was applied for the detection of mechanical relaxation processes and the influence of the fillers on them.

Scientific novelty of the results:

- For the first time it has been shown that the simultaneous introduction of carbon nanotubes and layered silicate into the thermoplastic matrix decreases the percolation threshold of composites due to the interaction between the fillers and consequent better distribution of CNTs in the polymeric matrix.
- For the first time it has been demonstrated, that the introduction of Ni nanoparticles into the composites filled with CNTs results in the lower percolation threshold due to the fact that metal nanoparticles connect, while forming the conducting network (so-called "bridging"-effect).
- There have been found the laws of formation of CNT conducting phase structure in the polymer matrix based on the polymer blends; the basic factors, determining the space distribution of the filler in the polymer matrix were classified.
- For the first time it has been shown, that nanoscale fillers being introduced into the semi-crystal polymer affect only the crystalline phase of the polymer matrix.

- The conditions of the formation of the segregated polymer systems with ultra-low percolation threshold were determined, as well as thermomechanical, electrical and dielectric properties of such systems have been researched.

The practical significance of the results. A filling of polymer matrix with carbon nanotubes enables to form nanocomposites with a defined complex of electro-physical properties, what makes them promising materials for the use in various technical spheres. The obtained experimental results can be applied as a scientific basis for the search of the optimal conditions to form the structure of the conducting filler, which will enable to get the materials with necessary preassigned properties. Such composites can be widely used in the electronic industry as electroconductive adhesives, suitable for the manufacture of effective screening covers, protecting from the electromagnetic radiation. Moreover, these composites can be applied for the construction of various sensors, electrodes etc.

Applicant's personal contribution. The author took part in the the formulation of the main propositions and conclusions, in the experimental and theoretical investigations, analysis and interpretation of the results. The problem definition and determination of the research objectives, a part of theoretical and experimental studies were performed in collaboration with the Head of the Department of polymer composites of the Institute of Macromolecular Chemistry of NAS of Ukraine, Academician, Professor E.V. Lebedev and the research supervisor, Doctor Sci. Ye. P. Mamunya in collaboration with Doctor S.S. Ishchenko, Doctor V.V. Davydenko, Doctor M.I. Shandruk in the Department of polymer composites of Institute of Macromolecular Chemistry of National Academy of Science of Ukraine (Kyiv, Ukraine). Planning and realization of theoretical and experimental studies were also performed in conjunction with the scientific supervisor, the Head of research CNRS, Doctor G. Boiteux, involving Director of Laboratory of polymer materials and biomaterials of University Claude Bernard Lyon 1, CNRS, France, Doctor G. Seytre, Professor Ph. Cassagnau, Doctor A. Rybak in the Laboratory of polymer materials and biomaterials of the University Claude Bernard Lyon 1, CNRS, France (Lyon, France). The applicant

took part in preparation of publications and in presentations of the results on international conferences and symposia.

Approbation of the results. The main directions and results of the Thesis were submitted on the IV Saint-Petersburg Young Scientists Conference "Modern problems of polymer science" (Saint-Petersburg, Russia, 2008); 5th International Conference "Broadband Dielectric Spectroscopy and its Applications (BDS-2008)" (Lyon, France, 2008); VI Ukrainian Young Scientists Conference on Macromolecular Compounds "MC-2008" (Kyiv, Ukraine, 2008); 5th International Conference "Nanostructured Polymers and Nanocomposites" (Paris, France, 2009); World forum on advanced materials, "PolyChar17" (Rouen, France, 2009); International conference "Eurofillers 2009" (Alessandria, Italy, 2009); The 2nd International Meeting "Clusters and Nanostructured Materials (CNM-2)" (Uzhhorod, Ukraine, 2009); 11th Pacific Polymer Conference (Cairns, Australia, 2009); 6th International Conference "Nanostructured Polymers and Nanocomposites (ECNP-2010)" (Madrid, Spain, 2010); 14th International conference "Polymeric Materials" (Halle, Germany, 2010); XII Ukrainian conference on Macromolecular Compounds "MC 2010" (Kyiv, Ukraine, 2010); II International scientific conference „Nanostructured Materials – 2010" (Kyiv, Ukraine, 2010).

Publications. The applicant is the author of 15 scientific publications, 3 of which are articles in specialized scientific journals and 12 – are the conference abstracts.

Chapter 1

Modern concepts of structure and properties of conductive polymer nanocomposites

Introduction

1.1. General characteristics and properties of the conductive polymer composites filled with carbon nanotubes.

1.1.1. *The properties of carbon nanotubes.*

1.1.2. *The formation of the conductive cluster in the polymer composites.*

1.2. Methods of formation of the conducting polymer composites.

1.2.1. *Conductive polymer composites prepared by solution mixing.*

1.2.2. *Formation of conducting polymer composites by "in situ"-polymerization.*

1.2.3. *Formation of the conducting polymer composites by melt mixing method.*

1.3. Conducting polymer composites based on polypropylene filled with CNTs.

1.4. Segregated electro-conductive nanocomposites.

1.5 Polymer blends, filled with electro-conductive filler.

1.6. Polymer composites filled with combined nanoparticles.

Introduction

Nowadays, carbon nanotubes (CNTs) are considered as one of the most promising fillers for polymer composites. The first idea of introduction of the CNTs into the polymer matrix has been formulated by Ajayan et al. [1]. After that similar materials were widely investigated in the whole world. The introduction of CNTs into the polymer matrix is the basis for the formation of the various functional materials. These CNTs are characterized by unique physical and chemical properties [2]. These materials with a wide range of the specific properties can be used as chemical and biological sensors, electrodes for batteries, supercapacitors, protective coatings from electromagnetic radiation, aerospace structural materials, etc. [2-12]. The improving of the electrical conductivity of polymer composites by introducing of the carbon nanotubes, can play an important role in a numerous of applications [10]. In particular, the growth of conductivity of some elements of aerospace apparatus provides the protection from electromagnetic interference [11].

Such composite materials can also be used as case for computers and the external parts of the cars. The properties of polymer nanocomposites filled with CNTs depend on many factors, in particular: the types of polymer matrix and CNTs, the number of impurities in the CNTs, the ratio of length and radius of CNTs, the polymer-filler interaction, the degree of the distribution and orientation of the filler in the polymer matrix, the parameters of the composite [7].

1.1. General characteristics and properties of the conductive polymer composites filled with carbon nanotubes.

1.1.1. *The properties of carbon nanotubes.*

As it was notice by different authors, first, carbon nanotubes were reported in 1991 by S. Iijima [2, 6, 7]. Carbon nanotubes are long cylinders of covalently bonded carbon atoms. The ends of the cylinders may be capped by hemi-fullerenes [7]. In the nature there exist two types of carbon nanotubes single-walled and multi-walled [13]. Ideal single-walled carbon nanotube (SWCNT) is a

graphene sheet rolled in a cylinder, i.e. the surface of CNTs contained regular hexagons of the carbon atoms. The various ways of rolling graphene into tubes are described by the tube chirality, i.e. the angle of the orientation of graphene sheet relative to the axis of the tube. Electrical properties of CNTs are defined by the chirality namely. Fig. 1.1 shows the graphene sheet with marked possible directions of its rolling. The chirality of the nanotubes are identified by symbols (m, n) which indicate the number of steps along the unit vectors $(\vec{a}_1$ and \vec{a}_2) [7]. The chirality of CNT can be also identified by the angle θ between the direction of nanotube rolling and the direction in which adjacent hexagons have a common side. Depending on the chirality single-wall carbon nanotubes are divided into three types: "armchair" (n, n) ; "zigzag" $(n, 0)$; and "chiral" (n, m) (Fig. 1.2). In the simplified model, the single-wall CNT does not form the seams during rolling and ending by hemi-fullerenes, which contain regular hexagons and six regular pentagons. However, idealized CNT structure differs from the experimentally observed.



Fig. 1.1 The graphene sheet with marked possible directions of its rolling.

Carbon nanotubes can be metallic or semiconductor, what depended on their diameter and chirality. During synthesis a mixture of nanotubes is usually received, two-thirds of which have semiconductor properties and one-third – metal ones. All the carbon atoms in nanotubes have ternary coordination, therefore nanotubes are conjugated aromatic systems. In such structure each

three of four valent electrons of carbon atom form sp^2 -hybrid orbitals with localized σ -bonds C-C and the fourth electron is involved in the formation of the delocalized π -system [13]. These π -electrons are weakly connected with their atoms, so that they are involved in charge transport. High (metallic) conductivity appears when occupied π -states are not separated by energy gap from vacant π -states. If this condition is not fulfilled and the energy gap is quite narrow, the carbon nanotube is semiconductor; when a gap is wide, then a CNT is insulator. The conduction takes place along the nanotube, which makes the CNTs the functional quantum wires.

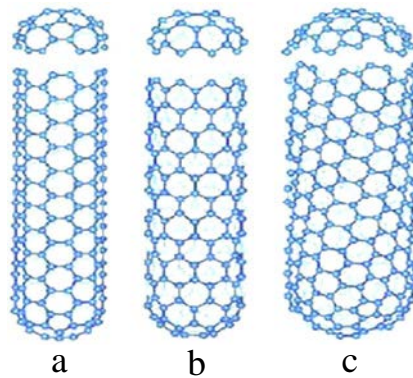


Fig. 1.2. Carbon nanotubes are divided into three types: "armchair" (a); "zigzag" (b); and "chiral" (c).

All armchair SWCNTs are metallic with a band gap of 0 eV. SWCNTs with $n-m=3i$ (i being an integer and is not equal to 0) are semimetallic with a band gap about few meV, while SWCNTs with $n-m \neq 3i$ are semiconductors with a band gap of (0.5÷1) eV [7].

In the nature there are also multiwalled carbon nanotubes (MWCNTs) which differ from single-walled with wider variety of shapes and configurations [14]. There are several types of multi-walled structures of CNTs. The first structure is known as the Russian dolls and the second structure is a roll (Fig. 1.3).

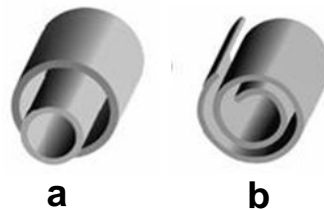


Fig. 1.3. The models of multi-walled CNTs: Russian dolls (a) and a roll (b).

With the increase of the numbers of walls the deviation from the ideal cylindrical shape occurs. In some cases the outer wall of the nanotube takes a shape of polyhedrons. Also on the outer wall such defects as pentagons and heptagons can be formed, and they lead to the disruption of cylindrical form. The presence of similar defects leads to the appearance of curved and spiral carbon nanotubes [13].

Carbon nanotubes are also characterized by unique mechanical properties, in particular - strength and stiffness. It is explained by the fact that CNTs have a high degree of structural perfection, i.e. a small number of structural defects. In addition, carbon rings of walls which form a regular hexagon, being bent can change its structure. This is caused by the fact that C-C bonds can be sp^2 -hybridized and change the hybridization during bending [13]. This property of carbon nanotubes provides them with great values of Young modulus and ultimate tensile strength. In the polymer/carbon nanotubes composites external tensile loads were successfully transmitted to the nanotubes across the tube/polymer interface [11]. Thus, polymer composites filled with carbon nanotubes composites demonstrate excellent mechanical properties and high mechanical module values.

Table 5.1. Theoretical and experimental properties of single- and multi- walled carbon nanotubes.

| Property | CNTs |
|----------------------|--|
| Specific gravity | 0.8 g/cm ³ for (SWCNTs) 1.8 g/cm ³ for (MWCNTs) |
| Elastic modulus | ~ 1 TPa for (SWCNTs) ~ 0,3-1 TPa for (MWCNTs) |
| Strength | (50÷500) GPA for (SWCNTs) (10÷60) GPA for (MWCNTs) |
| Resistivity | (5÷50) μOhm·cm |
| Thermal conductivity | 3000 W/(m·K) (theoretical) |
| Thermal expansion | Negligible (theoretical) |
| Thermal stability | >700 °C (in air) 2800 °C (in vacuum) |
| Surface area | (10÷20) m ² /g |

Moreover, except unique mechanical and electrical properties, carbon nanotubes have very interesting magnetic, optical and thermal characteristics [2, 13, 15-27]. The basic properties of CNTs calculated theoretically and obtained experimentally are listed in Table 1.1. [2].

Analyzing the above mentioned data, one can suggest that CNTs is a good filler for making electrically conductive polymer systems.

1.1.2. *The formation of the conductive cluster in the polymer composites.*

The conductive polymer composites are thermoplastic or thermoset polymers filled with dispersed conductive components such as metal, carbon black, carbon nanotubes etc. The composites which contain an electro-conductive filler in insulating polymer became electroconductive at certain value the so-called percolation threshold φ_c (i.e. the critical concentration of filler above which the conductivity appears) [28, 29]. The percolation threshold is very important parameter of such systems, and the lower it is, the better is the structural organization of conductive phase. In two-component system, some components of which are characterized by high and low conductivity, the distribution of filler particles in the volume of the polymer can be random or ordered. Formally, such systems can be characterized as a combination of conductive and non-conductive particles. The conductivity of the first one is indicated as σ_1 , and another one as σ_2 , ($\sigma_2 < \sigma_1$). During the growth of the filler content (from very small values) in the system small associates start to form, and then conductive separate clusters are formed. The average size of the clusters is characterized by the so-called correlation length ξ . At a certain concentration of conductive particles φ_c , between the isolated clusters conductive bridges are formed and they can consist both of individual particles and of their aggregates. This way the connection of the initially isolated clusters into the infinite conductive cluster takes place. At this moment a stepwise of transition system from the non-conductive to conductive state is observed. At further increase of the concentration of conducting phase the infinite cluster grows, absorbing some small clusters, what results in the monotonous increase of the system conductivity. Percolation threshold is

characterized by the sharp change of the conductivity by several orders of magnitude, what is connected with the creation of three-dimensioned conductive network of the filler inside the matrix. In numerous reports there were presented different models, which characterize the dependence of percolation threshold on the composite conductivity and on the content of the conductive filler [30-36].

The composites polymer/CNTs are characterized by the low percolation threshold because of the great value of the ratio between the length and diameter of the CNTs, which reaches (100 ÷ 1000). The dependence of the composite conductivity on the CNTs content and polymer matrix conductivity and on the percolation threshold were introduced by D. S. McLachlan et al. [31]:

$$|\sigma_f| \rightarrow \infty: \quad \sigma_c = \sigma_i \left(\frac{\varphi_c}{(\varphi_c - \varphi)} \right)^s, \quad \varphi < \varphi_c \quad (1.1)$$

$$|\sigma_i| \rightarrow 0: \quad \sigma_c = \sigma_f \left(\frac{\varphi - \varphi_c}{(1 - \varphi_c)} \right)^t, \quad \varphi > \varphi_c \quad (1.2)$$

where σ_c – is the conductivity of the composite, σ_f – is conductivity of CNTs, σ_i – is the polymer conductivity, φ_c – is the percolation threshold, φ – is CNT concentration, s and t – are critical exponents.

It should also be noted that polymer nanocomposites filled with CNTs are characterized by the electrical conductivity values which are significantly lower than the conductivity of individual carbon nanotubes. This is caused by the fact that a polymer can create a thin insulating layer in the contact point between nanotubes. This thin layer can not prevent the tunneling process between neighboring nanotubes, however, it can significantly increase the value of contact resistance between them.

1.2. Methods of formation of the conducting polymer composites.

As it was mentioned above, carbon nanotubes, owing to their unique mechanical and electrical properties (see Table 1.1.), are an ideal filler for the manufacturing of the polymer nanocomposites. In general, the process of the CNT

introduction into thermoplastic and thermoset polymers can be achieved by three methods, namely:

- solution mixing;
- "*in situ*"-polymerization;
- melt mixing;

Each of these methods has its advantages and disadvantages as well as certain restrictions in the formation of the polymer composites and in the achievement of uniform distribution of the nanotubes in a polymer matrix.

1.2.1. *Conductive polymer composites prepared by solution mixing.*

The solution mixing is one of the commonly used methods of the preparation of polymer composites filled with CNTs [37-45]. The advantage of this method is low viscosity of the system, what provides a high degree of random distribution of the nanotubes in a polymer matrix. This method is used to form a thermoset and thermoplastic composites. The principal stages of the formation of the polymer nanocomposites based on polycarbonate (PC) and prepared by solution mixing are presented in Fig. 1.4. [37]. First, nanotubes have been oxidized in nitric acid to form carboxyl groups on their surface, which can interact with the carbonate groups of the polymer. After that, the oxidized nanotubes have been dissolved in the tetrahydrofuran (THF) and mixed with the polycarbonate, also dissolved in THF. Further, the precipitate of the nanocomposite material, which was formed during introduction of the obtained suspension into methanol, was removed by filtration. The scanning electron microscopy (SEM) images have confirmed the uniform distribution of nanotubes in polycarbonate matrix. The introduction of CNTs into the PC matrix has provided the growth of the elastic modulus of the composites, compared to the pure PC.

The method of solution mixing was also used for the synthesis of the nanocomposites based on the epoxy matrix and filled with chemically modified carbon nanotubes [38]. The transmission electron microscopy (TEM) microimages have revealed that ultrasound treatment of the polymer solution, filled with modified CNTs, provide the random distribution of carbon nanotubes in the polymer matrix. The authors have found that the introduction of a small

number of CNTs into the polymer matrix causes a significant increase of the thermal conductivity of the composites compared to the pure epoxy. Solution mixing is a quite effective method for the introduction of carbon nanotubes into the polymers which have high viscosity and can not be processed on extruders. The solutions of high viscose polymers have low viscosity, thus the filler can be easily distributed in the matrix. Particularly, there have been reported about the introduction of nanotubes in a solution of polyvinylchloride (PVC) [39, 40]. After that in order to obtain polymer composite the solvent was evaporated in a vacuum heater.

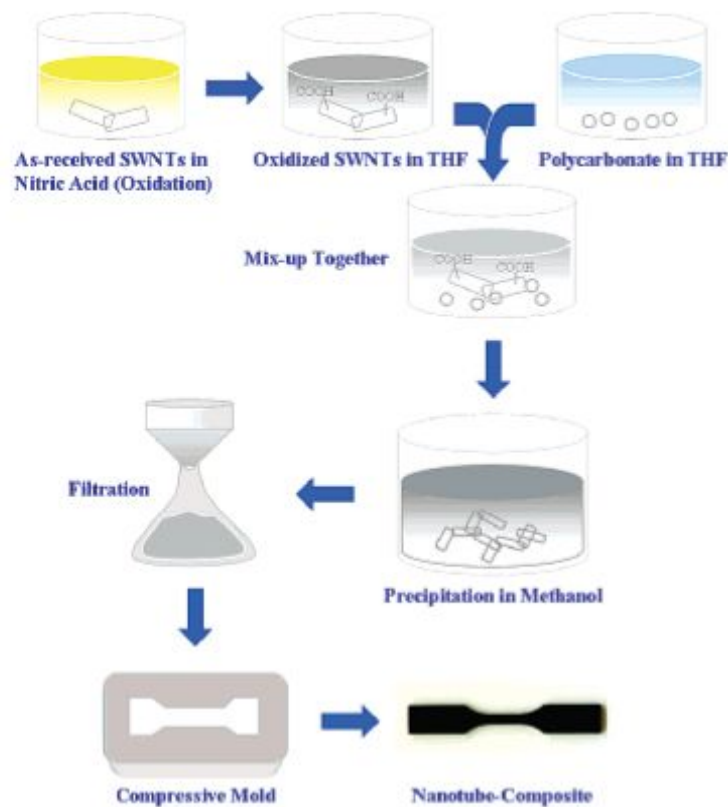


Fig. 1.4. Fabrication of nanocomposite samples: (a) Schematic of the solution-mixing technique used for dispersing oxidized SWNT in the polycarbonate matrix [37].

In addition, a significant advantage of this method is the possibility to treat by ultrasound a polymer solution filled with nanotubes [37, 39, 40]. G. Broza et al. [40] have noted that ultrasonic treatment of PVC dissolved in THF and filled with carbon nanotubes, provides a random distribution of CNTs in the composite. Obtained in such a way composites are characterized by low percolation

threshold, as far as nanotubes have introduced into low viscous environment with further ultrasonication of the solution. For example, the composites based on polymethylmethacrylate filled with CNTs are characterized with low percolation threshold - $\varphi_c=0.11$ vol. %. It has been also shown that when a content of nanotubes is such small, the mechanical properties of the composites improved significantly [40].

Better dispersion of CNTs in the polymer solution can be realized by the functionalization of the carbon nanotubes surface. The modification of the CNT surface by functional groups can provide the increase of the interaction between the filler and the polymer chains, which will promote a more random dispersion of CNTs in the composite [37, 44, 45]. H. K. Lee et al. [45] have found that the presence of diazo-compounds on the external wall of functionalized carbon nanotubes has significantly increased the interfacial interaction between the CNTs and polyisoprene matrix. A strong interaction between the filler and the polymer has been confirmed by a significant increase of the viscosity of the investigated composites.

Thus, the advantage of solution mixing method is the low viscosity of the polymer solution, what makes easier the distribution of CNTs in the polymer matrix. The disadvantage of this method is the requirement to dissolve the polymer, what is quite difficult for some types of polymers, such as polyethylene and polypropylene. Moreover, such a method demands to use a huge amount of solvents, which may be harmful for ecology. This factor is a significant disadvantage for this composite preparation method to be used in the industry.

1.2.2. Formation of conducting polymer composites by "in situ"-polymerization.

The method of "in-situ"-polymerization is applied to improve the dispersion of nanofiller and to increase the interaction between the filler and the polymer matrix. Polymerization "in-situ" occurs at the simultaneous presence of carbon nanotubes and monomer in a solvent. A low viscosity of the system ensures the distribution of nanotubes in a polymer matrix and subsequent

polymerization of monomer leads to a random polymer interaction with the surface of the nanotubes. In many cases the synthesized polymer can be chemically deposited on the surface of the CNTs through the functional groups or through direct grafting of the polymer chains on the surface of nanotubes in the presence of initiators [46-52]. C. Velasco-Santos et al. [46] have compared the properties of the composites filled with functionalized CNTs (f-CNTs) and non-functionalized CNTs (n-CNTs) obtained by "*in-situ*"-polymerization of methylmethacrylate. The results have revealed that n-CNTs can chemically interact with the polymer through the open π -bonds. However, the reaction groups of f-CNTs were more effective for the formation of the bonds with the polymer chains during polymerization. The investigation of the composite characteristics has revealed that the mechanical properties of composites with f-CNTs were much better than those, containing n-CNTs. This difference appears in enhance of the elastic modulus and increase of glass transition temperature by 33 °C.

The growth of polymer chains from the surface of nanotubes has also been studied. S. Qin et al. [47] have investigated polymer composites based on *n*-butyl methacrylate obtained by controlled polymerization from the surface of carbon nanotubes. H. Kong et al. have described a similar method of composite preparation [48], when methyl methacrylate was polymerized on the surface of CNTs by radical polymerization with the atom transfer. The use of "*in-situ*"-polymerization in the presence of nanotubes for the formation of the conductive composites has both advantages and disadvantages. On the one hand, the polymerization around CNTs provides better interaction between the filler and polymer matrix. On the other hand the polymer formed the layer around the surface of carbon nanotubes, which prevents the formation of contacts between them and reduces the conductivity of composites. It should be noted that the formation of composites by "*in-situ*"-polymerization requires the functionalization of CNTs surface, which can affect their properties negatively. In particular, S. M. Yuen et al. [53] reported that prolonged modification of carbon nanotubes can reduce their length, as well as facilitate the formation of the defects on their surface.

1.2.3. Formation of the conducting polymer composites by melt mixing method.

The melt mixing of polymer with inorganic filler and, in particular, with carbon nanotubes is a very attractive method for the formation of the nanocomposites based on a wide range of polymers. The advantage of this method is a direct mixing of the polymer with the filler at high temperature without the solvent. Thus melt mixing is easier to use and more environmentally friendly compared to the other methods. However, melt mixing requires high-quality mixing equipment what enables to apply high shear forces to blend the polymer melt with nanofiller.

The random distribution of the filler in the polymer matrix can be achieved, mainly due to high shear deformations in the extruder. Also, better mixing of the organic and inorganic components can be improved by the increase of the composite mixing time or by the regulation of the mixing temperature, which affects the viscosity of the polymer. Formation of composites by melt mixing has been described in [54-58]. P. Pötschke et al. [59] have obtained the nanocomposites based on polycarbonate by melt mixing in twin-screw mini extruder at the temperature of 240 °C and rotation speed of 280 rpm. The authors reported that such mixing parameters provided random distribution of CNTs in the polymer matrix. The parameters of the composite preparation influence significantly the final characteristics of the conductive systems. In particular, the prolonged mixing with high shear deformation applied can reduce the length of CNTs [60, 61]. Thus the value of the conductivity of nanocomposites can be decreased as well. R. Andrews et al. have reported that the length of CNTs decreased by 25%, when mixing of the material in the extruder was longer than 15 minutes [60].

The materials can be also received by the combining of several methods. In particular, M. X. Pulikkathara et al. have obtained the composites, combining the methods of the melt and solution mixing [62]. First, CNTs and PE powder of were dissolved in chloroform. The solvent was removed by the drying of the solution in

the thermal heater. Then the obtained material was melt mixed in the extruder at 110 °C during 10 min.

In conclusion, it should be noted that melt mixing is the most appropriate method of the preparation of the nanocomposites based on thermoplastic polymers being filled with nanofillers. However, this method does not provide a uniform distribution of the filler particles in a thermoplastic matrix, particularly in polypropylene - due to the high viscosity of the polymer melt and low wettability of the filler by the polymer.

1.3. Conductive polymer composites based on polypropylene filled with CNTs.

Polypropylene (PP), which belongs to the group of polyolefins and has a valuable complex of potential applications, is one of the mostly used polymers. Because of the low cost, low density, high thermal stability and corrosion resistance, PP is widely used in various fields of industry [63]. The introduction of the fillers gives an opportunity to steer the properties of the materials, obtained from PP.

Last decade a great attention has been paid to the formation of the nanocomposites based on polypropylene and carbon nanotubes. Introduction of carbon nanotubes into polymer matrix results in the significant enhancement of thermophysical properties of the polypropylene matrix. It is well known that the properties of polymer composites strongly depend on the distribution of the filler, and, therefore, all properties of PP/CNTs composites depend on the morphology of the composites.

The effect of the CNT concentration on the electrical properties of PP/CNT composites was intensively studied [64-74]. It was found that the conductivity of the composites increased with the increase of the CNT content. The percolation threshold for the PP/CNTS composites was in the range of (0.6÷3) vol. % [64-68, 73]. Electrical conductivity of PP/CNT composites depends on many factors, in particular - the types of CNT and PP [75], viscosity of PP [64] and parameters of the composite preparation [70]. M. Mičušík et al. [64] have found that the content

of CNT aggregates, and, thus, the value of the percolation threshold significantly depends on the viscosity of the polymer matrix. In particular, the increase of melt flow index $MFI_{210/2.16}$ of polypropylene from 2 g/10 min to 12 g/10 min (i.e., viscosity is diminished) results in the percolation threshold decrease from 2 vol. % to 1.18 vol. % of CNT, that is less viscous the polymer the lower value of φ_c . The percolation threshold value also depends on the parameters of composite preparation, such as speed of mixing in extruders. S. C. Tjong et al. [70] have observed a significant decrease of the percolation threshold when the mixing speed increased from 60 rpm to 200 rpm. The value of the percolation threshold at 200 rpm was only 0.22 vol. %. However, as it was mentioned above, a high speed of mixing may reduce the length of the nanotubes.

A huge amount of works have been devoted to the study of the influence of the carbon nanotubes on the crystallization of the polypropylene matrix [65, 76-84]. In most of them it has been shown that when the content of carbon nanotubes in the composites increases, the crystallization temperature of PP shifts to higher values. This indicates that the CNTs act as the crystallization centers [65, 76, 79, 81]. Also, the presence of CNTs leads to the growth of crystallinity degree χ_c of PP. In particular, the degree of crystallinity increased by 3 % and by 4 % at concentration of CNTs equal to 5 wt. % of CNTs [65] and 1 wt. % of CNTs [80], respectively. One can conclude that the improvement of mechanical properties of the PP/CNT composites is caused by two factors: the reinforcement effect of CNTs and increase of the crystallinity degree. The reverse effect of CNTs on the degree of crystallinity of PP was also observed [79, 81]. D. Bikiaris et al. [79] have found that when the concentration of carbon nanotubes was 6 vol. %, the degree of crystallinity χ_c have decreased by 5% compared to the pure polypropylene matrix. This effect can be attributed to the fact that the functionalized carbon nanotubes were used and they interact with the polymer chains preventing the formation of the crystal structure of PP. It has also been noted that CNTs, can act as crystallization centers and cause a faster growth of crystals and formation of large number of small-sized spherulites [79]. H. Zhang and Z. Zhang [80] have also found the reduction of spherulites size with the introduction of CNTs into PP matrix.

A significant value of elasticity modulus of CNTs (~ 1 TPa) and a great value of the ratio between the length and diameter ($100\div 1000$) make carbon nanotubes an effective filler for the enhancement of mechanical properties of polymers. It was found that Young's modulus, elastic modulus and strength of composites PP/CNT increased with the introduction of CNTs into the polymer matrix [79, 85-89]. In particular, G.-W. Lee et al. [85] have found that the introduction of CNTs into the PP matrix caused the increase of elastic modulus by 8 GPa at -140 °C and on 1 GPa at 100 °C. However, it should be noted that in some cases, the increase of the CNT content does not result in the change of the mechanical properties or they even can be retrogressed. This effect is due to the ability of CNTs to form the agglomerates. M. Mičušík et al. [64] have studied the PP/CNT composites and observed the presence of the aggregates of large sizes which were in some composites about $100\text{ }\mu\text{m}$. Their presence was explained by the semicrystalline structure of polymer matrix and weak interaction between non-polar PP and CNTs. In semicrystalline polymers the CNTs are localized only in the amorphous phase.

The review of the methods of forming of the electro-conductive polymer systems has shown that a great amount of experimental reports is devoted to the formation of the polymer composites, filled with CNTs. Nevertheless, the uniform distribution of CNTs in polymer matrix is a very actual problem. The successful solution of this problem will give the possibility to use all unique properties of CNTs for the realization of desirable properties of the composites. In order to solve this problem a lot of methods were proposed and described, in particular, CNT functionalizing for the enhancement of the interaction with the polymer links; preparing of the composites by the solution mixing method; changing of the composite forming parameters, such as temperature and shearing deformation value. However, the mentioned above methods have also their significant shortcomings along with the advantages. Thus, there appears a problem to search new, economically sound ways to form the composites, which would be able to provide a uniform CNT distribution.

Another important problem is to search the regimes of formation of electro-conductive composites with rather high conduction level and low

percolation threshold, which would affect the electro-physical properties of the composites. In order to reach low percolation threshold values, one has to obtain a uniform distribution of the CNT in polymer matrix, what is realized in so-called “segregated systems” and in the filled polymer blends.

1.4. Segregated electro-conductive nanocomposites.

First the term “segregated system” was introduced by R. P. Kusy and R. D. Corneliussen [90] and referred to the electroconductive composites based on polymers and metal filler. So-called “*segregated systems*” differ from the usual filled systems by the fact, the filler is distributed not uniformly, but creates an ordered structure in the form of a framework (or lattice) in polymer matrix, wherewith one can achieve significantly lower φ_c value in comparison with common filled polymers [91-94]. Such an ordered filler distribution is realized, for instance, in the polymer mixture, when a filler is localized in one polymer phase or on the interphase boundary [95-97]. Because of the presence of two phases, crystal and amorphous ones, semi-crystalline polymers can also be considered as segregated systems, as far as the filler is localized only in the amorphous phase, while diminishing the percolation threshold of the composite.

One of the available methods of the formation of the segregates system is compacting (pressing of the mixture of polymer and filler powders) on conditions that the size of polymer particles D exceeds the size d of the filler particles significantly ($D \gg d$). Nowadays there are a lot of reports devoted to the study of the segregate systems obtained by compacting method. In particular, there were studied segregated composites based on the polymers filled with metal nanoparticles [92, 93, 98-104], carbon-black [105-107], ceramics [108] and carbon nanotubes [94, 109].

The main factors, which define the electrical properties of the segregated systems can be listed as follows.

- The ratio of the radii of polymer and filler R_p/R_f .
- The types of the filler and polymer matrix.

- The form of the filler and matrix particles.
- Viscosity and mechanical properties of polymer.
- Interaction between polymer and filler.
- Conditions and ways of composite forming.

A. Malliaris and D. T. Turner have shown that if the ratio of PE and Ni particles increases from 7.5 to 30, the percolation threshold of PE/Ni composites will decrease from 14 vol. % Ni to 6 vol. % Ni [99]. R. P. Kusy and R. D. Corneliusen have shown, that for PE/Ni composites at $R_p/R_f \approx 2$, the percolation threshold was extremely high and reached 36 vol. %, while at $R_p/R_f > 30$ the percolation threshold has decreased more than 10 times and was equal just 3 vol. % of Ni [90]. J. Bouchet et al. have compared the electrical properties of two segregated systems based on ultrahigh molecular weight polyethylene (UHMWPE) with the sizes of polymer particles – 30 μm and 150 μm and titanium carbide with the sizes of filler particles – 0.8 μm and 0.5 μm [108]. In the case when polymer particle size was 150 μm the percolation threshold was significantly lower.

The type of polymer matrix influences significantly the properties of the segregated systems and formation of the conductive cluster [98]. B. Bridge et al. studied the segregated systems based on polymethylmethacrylate (PMMA) and polyethylene, which were filled with gold particles [98]. It was found a significant difference between the formation of the conducting cluster for amorphous and semicrystalline polymer. It has also been shown that introduction of Au particles results in the gradual increase of the electroconductivity of PMMA/Au, and at filler content $\varphi=34$ vol. % it becomes 3 orders of magnitude more in comparison with the electroconductivity of pure polymer matrix [98]. At the same time, PE/Au composites have demonstrated absolutely different conductivity character dependently on the content of the filler [98]. The conductivity of the polymer decreased with filler content increase and reached minimum at $\varphi=50$ vol. %. For semicrystalline polymers filled with Au, metal particles can play a role of crystallization centers, and then the polymer layer, formed around the particles, will prevent the formation of the contacts between filler. Thus, it is necessary to have a great amount of conductivity filler for the formation of the conducting

cluster. G. D. Liang et al. have found that in PP/Ag composites silver particles play a role of the crystallization centres for PP molecules [110]. Thus, the amorphous polymers are more effective to form the segregated systems filled with metal particles.

The filling of polymer with carbon-black results in the significant decrease of the percolation threshold of the segregated conducting composites, what is caused by the specific structure and by the form of the carbon-black particles [105-107]. For PE/carbon black composites the percolation threshold value varied from 0.25 vol. % to 0.65 vol. % dependently on the carbon-black type [107]. Because of the low filler concentration and its selective localization a positive temperature coefficient of resistance was found for the PE/carbon-black composites. This effect is caused by the breaking of the conducting lattice due to the space widening of the polymer matrix at crystal melting process [106]. C.-M. Chan et al. have also shown the correlation between the parameters of composite forming and their morphology [106]. It has been found, that pressure change from 13.8 MPa to 44.2 MPa did not influence the composition morphology, whereas high temperatures and a prolonged pressing resulted in the mixture of carbon-black and polymer particles, what caused, in one's turn, the resistance increase of the composites.

I. J. Youngs has investigated the dependence of the percolation threshold on the size ratio of polymer and filler particles in conductor-insulator composites [111]. The composites were prepared by cold compacting method. The compacting process was carried out at pressure value of 500 MPa during 5 min from the mixture of polytetrafluoroethylene (PTFE) and carbon-black particles. The PTFE particle sizes varied in the range of (1÷100) μm . The lowest percolation threshold value was found to be 1 vol. %, when the size of the polymer matrix particles was 100 μm . And when the latter value was equal to 1 μm , the percolation threshold value was found to be 5 vol. %. The authors have found the discordance between the theoretical and experimental data, which has been explained by the possible change of the shape of matrix particles (from spherical to disc-shaped) during pressing [111]. It is connected with the fact that surface area of the disc is larger than that of the sphere at equal volumes of these

geometrical objects. Thus, in order to form the conducting network it is necessary to take a greater amount of the filler.

In order to form segregated conducting systems, polymer emulsions filled with carbon-black [112-114] and carbon nanotubes [115,116] are also often used. S. M. Miriyala et al. have compared mechanical and electrical properties of the composites based on the emulsions and polyvinyl acetate (PVA) solution, filled with carbon-black (Fig. 1.5). It has been shown, that during the emulsion drying, carbon-black particles segregated around the polymer particles, while forming the conducting network, what enabled to obtain a low percolation threshold value – 1.2 vol. % of carbon-black. In the case of formation of composite from the solution, the nanotubes were uniformly distributed in the polymer matrix, what resulted in the high value of the percolation threshold, which was equal to $\varphi_c=8.18$ vol. %. It has also been found that at filler concentrations below 5 vol. % the elastic modulus of the segregated system grows impetuously; however, it decreases at filler high content above 6.5 vol. %, what is related to the pore formation.

The composites, formed from the solution, revealed better mechanical properties, and elastic modulus increased in the whole range of the carbon-black content. The comparing of the composites, formed by two different ways has revealed that a segregated system formation enabled to decrease the percolation threshold of the PVA/carbon-black composites almost by 8 times. However, these systems at significant filler concentrations revealed worse mechanical properties as compared to the composites, obtained from a melt.

A similar comparison of the composites with the uniformly distributed Ni particles and segregated filler network was reported by Ye. P. Mamunya et al. [101]. It has been found that for epoxy/Ni composites, in which Ni particles were uniformly distributed in the whole polymer matrix, the percolation threshold was 10 vol. % of Ni, whereas for the PVC/Ni segregated systems φ_c value was much lower and equalled 6 vol. % of Ni.

Y. S. Kim et al. have analyzed the connection between the elastic modulus E' of the polymer matrix and formation of the conductive filler network in it [113].

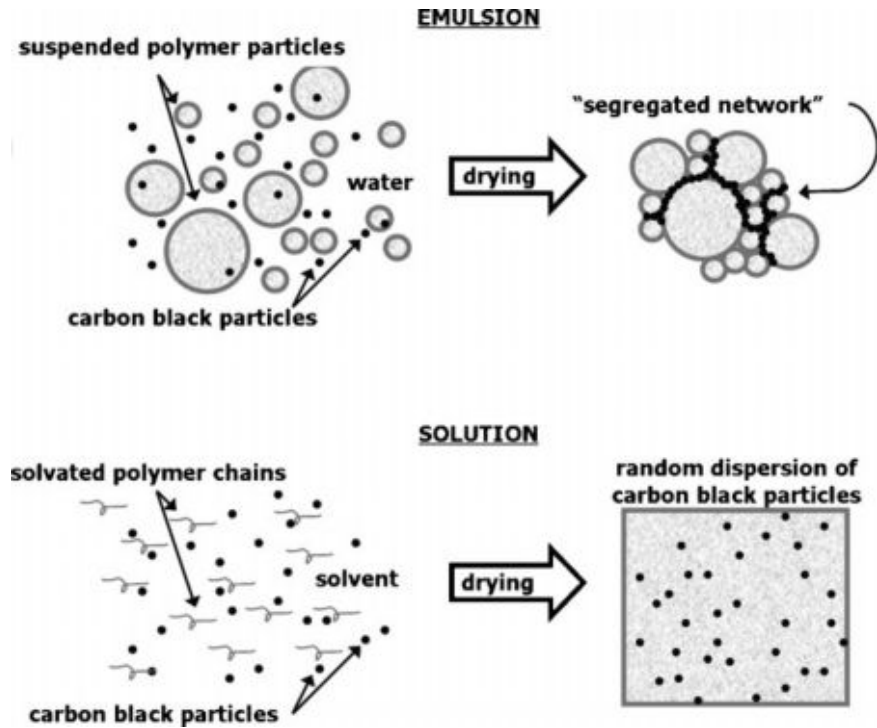


Fig. 1.5. A schematic image of the conduction phase formation in the PVA/carbon-black composite, which was formed by the compacting method (a) and melt mixing (b) [112].

There was investigated a series of co-polymers filled with carbon-black and synthesized on basis of butyl acrylate and methyl methacrylate. While changing the ratio between the initial components of the co-polymer, the authors obtained polymer matrixes, which were characterized by the different values of the elastic modulus. It has been shown, that a polymer with a high value of elastic modulus is more effective for the formation of the segregated network of the filler. However, the particles of the polymer, which has a low elastic modulus, are deformed easily by the carbon-black particles. Thus, the carbon-black migrates inside the polymer particles and the segregated structure of the filler undergoes destruction. A co-polymer, characterized by the elastic modulus of $E'=640$ MPa (at $T=20$ °C) had the percolation threshold value $\varphi_c=1.5$ vol. % of carbon-black, whereas for the matrix with $E'=3.6$ MPa, the percolation threshold was 4.9 vol. % of carbon-black.

While studying the segregated systems based on the ultra-high-molecular-weight polyethylene, filled with carbon nanotubes, C. Zhang et al. have found that the percolation threshold of such composites significantly depend on the viscosity of the polymer matrix [117]. It has been found that in more highly viscosity

systems a filler did not migrate into the polymer phase at composite formation, what resulted in low value of the percolation threshold.

For the segregated systems a non-typical dependence of the thermal conductivity λ on the filler content was observed. First R. P. Kusy and R. D. Corneliussen found that for the segregated systems PVC/Cu even at low filler content a thermal conductivity increased by one order of magnitude in comparison with pure PVC [90]. In order to correct the equation, which described the concentration dependency of the segregated systems, the authors proposed to introduce the “coefficient of metal conductivity”. Ye. P. Mamunya et al. [92] have observed a non-linear dependence of the thermal conductivity on the filler content and corrected the equation by the introduction of the exponent N . A non-typical character of the $\lambda=f(\varphi)$ dependence was explained by the fact that for the non-segregated conducting network for which $\varphi_{loc}>\varphi$, a filler compacting is more dense, what results in the best condition of the heat transfer.

The use of CNTs as a filler for segregated systems seems to be rather perspective. It is caused by the high length/diameter ratio, which can reach for CNTs, as it was mentioned above, (100÷1000), and due to this fact the contact between separate nanotubes can be achieved at their low concentration. Nowadays there are only some reports, devoted to the study of the segregated systems, filled with CNTs [94, 109, 115, 118, 119]. The described in these papers investigations have shown that in segregated systems based on PVC and PE, filled with CNT it was succeeded to reach ultra-low percolation threshold value $\varphi_c=0.04\%$ [94]. This effect was achieved both due the length/diameter ratio of nanotubes and due to the ordered distribution of the filler in the polymer matrix. While having such interesting properties, segregated systems, filled with nanotubes demand more detailed investigation of their electrical, dielectric and mechanical characteristics.

1.5 Polymer blends, filled with electro-conductive filler.

One can significantly decrease the percolation threshold of the composites by means of introduction of the conductive filler into the polymer matrix, what is

realized due to the so-called "double percolation" effect, which was proposed by M. Sumita et al. for the first time [120]. This effect is caused by the formation of the co-continuous morphology of the phases of two polymers, where the conductive filler is localized in one polymer phase or on the boundary of the phases [95, 97, 121-130]. A lot of factors influence the distribution of the conducting filler in the heterogeneous polymer matrix. In particular, the viscosity of the blend components, the wettability of the filler with the polymers, the parameters of the conduction blend formation and the order of the introduction of the components into the composite [95, 122, 131].

The distribution of the conducting filler in the polymer blend dependently on the ratio of the surface tensions of the composite components was investigated in [95, 132-135]. A.-C. Baudouin et al. have shown that during the dilution of the concentrate based on the co-polyamide (CPA) by the co-polymer ethylene-methacrylate (EMA) the nanotubes remained in the CPA phase, what did not correlate with the thermodynamical calculations [135]. At the same time, when the concentrate based on EMA and CNT was diluted with CPA, the nanotubes were localized on the boundary of the phases of two polymers, what correlated to the theoretical calculations. Thus, the authors have found that the localization of CNTs in the composite depends both on the thermodynamic factor (the ratio between the values of interphase tensions $\text{polymer}_1\text{-filler}$, $\text{polymer}_2\text{-filler}$, $\text{polymer}_1\text{-polymer}_2$) and on the technological one (the way of introduction of the filler into the heterogeneous polymer matrix).

A significant influence of the technological factor on the filler distribution was fixed by Ye. P. Mamunya et al. [95]. Thus, it has been shown that at the dilution of the conducting concentrate PE/carbon-black with the polypropylene, the carbon-black particles remained in the PE phase, whereas in the composites, obtained by the dilution of the PP/carbon-black concentrate with the polyethylene, the filler was uniformly distributed by the whole heterogeneous polymer matrix.

In order to decrease the interphase tension between the polymers and to reach the stability of the polymer blend, the compatibilizers are often used. In particular, maleated polypropylene (mPP) was introduced into the PA6/PP blend

filled with CNTs [134]. It was shown, that the thermal stability of the blend had increased significantly at the introduction of CNT and mPP. In addition the rheological investigations have shown that both fillers – CNT and mPP – increase the viscosity and mechanical modulus of the composites.

In the review, devoted to the filled polymer blends F. Fenouillot et al. [131] have noted that the transition of the filler from one phase into another one occurs more slowly, when the particles are localized first in the more viscous polymer. But at the significant difference of the thermodynamic interactions of the filler with each polymer, such regularity may not be fulfilled. It has also been noted [131] that at approximately equal values of viscosity of both polymers of the blend the key factor, which determines the space distribution of the filler is the values of the polymer/filler surface tension. In ones turn, F. Gubbels et al. came to a conclusion that the influence of viscosity on the distribution of the filler in the heterogeneous polymer matrix is weaker in comparison with the effect of the polar interactions between the system components [121].

As concerns the electrical characteristics of the composites, a low percolation threshold occurs, when the conducting filler is localized on the boundary of the polymer phases [95, 121, 135]. Thus, Ye. P. Mamunya [95] has shown, that for the composites based on the polyoxymethylene (POM) and for the PE, filled with carbon-black, the percolation threshold was $\varphi_c=4$ vol. %. At the same time for PE/carbon-black and POM/carbon-black composites the percolation threshold was 9 vol. % and 12 vol. %, respectively. A low percolation threshold value $\varphi_c=3$ wt. % was also found for PE/PS/carbon-black composites, in which the filler particles localized on the boundary of the phases [121].

The dependence of the electro-conductivity of the PS/PE blend, filled with carbon-black on blending time is reported by F. Fenouillot et al. [131]. At the beginning stage of the blending of PE with PS/carbon-black concentrate, the carbon black particles began to migrate from PS to PE phase. This resulted in the increase of the electro-conductivity of the composite, which has its maximum at the localization of the carbon-black on the boundary of the polymers. At further mixing carbon-black totally migrated into PE phase, what caused the conductivity

decrease. Thus, while regulating the time of mixing of the polymer blend, one can obtain a composite at non-equilibrium state with a high value of conductivity, which can be achieved at low filler content due to its localization on the boundary of polymer phases.

D. Yan and G Yang [136] have investigated the electrical properties and morphology of the PA6/PS polymer blend, filled with CNTs dependently on the ratio of the composite components. SEM and TEM micropictures have revealed that CNTs localized on the boundary of the polymer phases only. It was found, that at the introduction of the nanotubes into PA6/PS blend the resistivity of the composites decrease by 7 orders of magnitude. Besides, this effect was observed only for the samples with PA6 and PS ratio of 70 wt. % and 30 wt. %, respectively. As far as CNTs were localized only on the boundary of the phases, the continuous conducting network of the filler can be formed only in the composites with the continuous polymer structure in the blend, what was achieved at the component ratio 70:30.

Y. Li and H. Shimizu [137] found that the value of the rate of mixing during preparing of the filled blend influences significantly the distribution of CNTs in the polymer matrix and the electrical characteristics of the composite. TEM images have shown that in the composites based on the polyvinylidene fluoride (PVDF) and PA6, which were mixed at low rates, CNTs created aggregates and localized only in PA6 phase. However, at high mixing rates the nanotube aggregates were not formed, and nanotube distribution in the PA6 turned out to be more homogeneous, what, in one's turn, resulted in the enhancement of the electrical properties of the composites. The investigation of the mechanical properties of the filled blends, treated at different mixing rates revealed that the mechanical modulus remain almost invariable, whereas elongation at break was 200% more for the composites, treated at higher mixing rates. Y. Li and H. Shimizu have also noted the influence of CNTs on the composite morphology and on the parameters of component interactions [137]. It has been shown, that at the introduction in the polymer blend CNTs are localized in the PA6 phase only, what increases its viscosity significantly. Due to this fact the sizes of the particles decreased, and the composite transformed from the structure with isolated spherical inclusions PA6

in PVDF matrix to the co-continuous structure of both components. This, in one's turn, increased the polymer compatibility, and such a change of the structure also results in the enhancement of the mechanical properties of the composite.

Some papers were devoted to the investigation of the CNT distribution in the polymer matrix based on the PA6/PP [134, 138] and PE/PC [139], and to the influence of CNTs on the electro-conductivity of the compositions. It has been found, that when the content of the conducting filler PC-2% CNT in PE/PC blend reached 30 vol. %, a co-continuous structure formed in the composite, and its conductivity increased by 7 orders of magnitude [139]. At such ratio of the components a general content of the nanotubes in the composites was 0.41 vol. % of CNTs, whereas the percolation threshold for the individually filled PE or PC is more, than 1 vol. % of CNT. It is interesting, that the composite remained conductive after the removing of the PC phase with a dissolvent. P. Pötschke et al. propose to use such composites as conducting/antistatic membranes [139]. L. Zhang et al. reported about the initiation of the conductivity, connected with the double percolation effect and selective localization of CNTs in the PA6 phase [138]. When PP content increased from 50 wt. % to 80 wt. %, the structure of the conductive phase changed from co-continuous to the dispersed one, what was accompanied by the conductivity decrease.

Carbon nanotubes, due to their specific properties, turned to be rather effective filler for polymer blends. O. Meincke et al [140]. have compared the mechanical properties of both PA6 blends and acrylonitrile/butadiene/styrene (ABS), filled with CNT and carbon-black. For the unfilled blend the Young's modulus was 1.97 GPa, whereas the introduction of 7 wt. % of CNT resulted in the increase of its value up to 2.51 GPa (i. e. 27% more in comparison with the initial value). In the case of the blend, filled with 7 wt. % of carbon-black, the Young's modulus increased up to 2.08 GPa only. Break elongation decreases for both composites PA6/ABS/carbon-black and PA6/ABS/CNT, though in the latter case this decrease is not such pronounced, what illustrates the higher strength of the systems, filled with CNT.

Due to high ratio between the length and diameter, a nanotube can belong to every phase of the blend simultaneously, what increases the mechanical

properties of the composite significantly. In several papers [134, 138, 139, 141] the authors described a so-called “bridging”-effect, at which nanotubes localized simultaneously in two polymer phases, while forming singular “bridges” between them.

Some interesting results were also obtained for the blends of polycarbonate (PC) and PP, filled with CNT and montmorillonite (MMT) [141]. When PC/CNT and PP/MMT concentrates are mixed, montmorillonite localized on the boundary of the polymer phases, and prevented this way the migration of CNT from PC to PP phase. Thus, montmorillonite has provided the decrease of percolation threshold of the composites, while protecting the transition of CNT from one phase into another one.

CNTs also have a significant influence on the rheological properties of the polymer blends [134, 138, 139, 142, 143]. The presence of CNT in the PA6/PP blend resulted in the increase of the of the complex viscosity value (η^*), elastic modulus (G') and viscosity modulus (G'') in the whole frequency range [134]. Such a behaviour is connected with the fact that CNTs prevent the relaxation process of the polymer chains.

Temperature dependences of the conductivity revealed that electro-conductive polymer blends are characterized by positive [129, 130, 144, 145] and negative [146, 147] temperature coefficients (PTC and NTC, respectively). The basic factors, which influence PTC and NTC are the ratios between the composite components, the conducting filler content and the size of its particles. Thus, J. Feng and C.-M. Chan have shown, that the blends, filled with large particles of carbon-black reveal stronger PTC effect, besides, their room-temperature resistance is usually higher [146]. It has been shown, that one can reach the NTC of the composites, while using a semiconductor polymer with a high viscosity as one of the component. For the UHMWPE/PP/carbon-black systems it has been found a double PTC effect [144]. The initial growth of the resistance of the composite was connected with the melting of the UHMWPE particles, and the following PTC was related to the melting of the PP matrix.

I. Mironi-Harpaz and M. Narkis [148] have studied the influence of γ -radiation on the electric properties of UHMWPE/PE/carbon-black properties. In

the case of non-irradiated composite the carbon-black particles were segregated on the surface of the UHMWPE particles due to its high viscosity. The investigations have revealed that the irradiation of tree-component blend resulted in the increase of the composite conductivity, what was caused by the growth of the crystal phase of PE due to cross-linking of the macromolecules.

A polymer with inherent conductivity can also play a role of a conductive filler. M. Zilbermann et al. [149] have studied the composites based on the CPA and polystyrole (PS), filled with polyaniline (PANI). It has been found that PAN is more compatible with CPA, what provides more conductive structure with low percolation threshold in comparison with polymer blend based on the PS. When PAN is introduced into the blend of two CPA/PC polymers, PAN is localized in the co-polymer what results in the double percolation effect.

1.6. Polymer composites filled with combined nanoparticles.

Recently, the idea of simultaneous introduction of different type of fillers into polymer matrix seems very promising. The properties of such polymer nanocomposites depend greatly on the dimensions of nanofillers. The different dimensions of nanofiller determine the dispersion, interface, and distribution of nanofiller in polymer matrix. It is expected that the positive synergistic effect of these nanoparticles will improve the properties of polymer matrix. In contrast to conventional composites, in the systems filled with binary filler, the interaction between the nanoparticles should be also taken into account as well as the interaction between nanoparticles and matrix. In such composites, one type of nanofiller will affect the dispersion and distribution of another one, that may result in new synergistic effects in nanocomposites.

A fabrication of polymer nanocomposites is one of the most important applications of CNTs. Carbon nanotubes, due to their specific properties, may be a unique filler for conductive polymer composites with low percolation threshold. However, poor CNTs dispersion and weak interface interaction between CNTs and polymer matrix result in the limitation of the improvement of various properties,

and, thus the unique characteristics of CNTs can not be efficiently used in the nanocomposites. The ability to form the large aggregates also leads to the growth of the percolation threshold.

In order to form polymer nanocomposites it was proposed to use such combinations of the filler as clay/carbon black [150-152] and CNT/clay [153, 154]. Polymer/CNT/clay composite is one of the most important multiphase systems with an interesting synergistic effect, in which sodium based montmorillonite (MMT) is the most commonly used layered clay.

An interesting effect was observed for electrically conductive composites filled with carbon black and clay [150-152]. K. C. Etika et al. [150] have found that the adding of 0.5 vol. % of clay into epoxy/carbon black composites provided to the growth of the conductivity by more than one order. TEM micrographs have shown that around the clay particles a halo of carbon black particles was formed. The appearance of such halo is caused by the interaction between two types of filler. The interaction between the clay and carbon black leads to the improvement of the electrical properties of the composites. The similar effect was observed for the thermoplastic matrix filled with combination of carbon black/clay fillers [151]. In particular, in the composites based on PE/carbon black filled with clay, the electrical conductivity increased significantly. This effect was explained by the fact that clay interacted simultaneously with the polymer chains and with carbon black. On the one hand, the interaction between the organic components of the clay and the polymer chains results in the decay of interaction between the polymer particles of carbon black. On the other hand, the network of clay particles with the adsorbed carbon black particles on their surface owing to the interactions between the fillers was formed. Such interaction provides more uniform distribution of the fillers.

The incorporation of 3 vol. % of clay into composites PA6/carbon black results in the decrease of the percolation threshold φ_c from 0.155 vol. % to 0.058 vol. % of carbon black [152]. Besides, for the studied composites it was also found the disappearance of aggregates and a uniform distribution of carbon black in the polymer matrix. The interaction of clay platelets with carbon black prevented its

aggregation and has provided the formation of the continuous conductive network.

L. Liu and J.C. Grunlan [153] have investigated various epoxy/carbon nanotubes composites filled with clay, which were obtained by a mixture in solution. The presence of clay in composites epoxy/CNT provided the reduction of percolation threshold from 0.05 vol. % to 0.01 vol. % of CNTs. In addition, the introduction of clay resulted in the increase of the composite conductivity. For instance, for the composite containing 0.05 vol. % of carbon nanotubes the conductivity increased by more than four orders with the adding of 0.2 vol. % of clay. The photos of the optical microscopy showed that in the epoxy/CNT composites, the carbon nanotubes were present as isolated structures, while the introduction of the clay resulted in the formation of three-dimensional CNTs conductive network. The authors suggest several possible reasons, why the presence of the clay improves the electrical characteristics of the composite epoxy/CNT and provides the formation of the CNT network. First, the clay increases the viscosity of the composite mixture what complicates the re-agglomeration of CNTs in the solution after the ultrasound treatment. Second, CNTs interact stronger with the clay than with the polymer matrix, what results in the formation of segregated carbon nanotubes network.

A significant improvement in the mutual distribution of the fillers in the polymer matrix, and the absence of the aggregates leads to the improvement of not only electrical, but also the mechanical properties of the composites. In particular, Z. Wang and X. Y. Meng [154] have observed the effect of the clay/CNT filler combination on the mechanical properties of composites based on the polyethyleneoxide (PEO). The values of the yield strength, tensile strength at break and elongation at break for the composites PEO/clay/CNT were significantly higher than those for the composites PEO/clay and PEO/CNT. TEM micrographs have shown that the sizes of the clay particles in the composites filled with binary clay/CNT filler were significantly lower than in the PEO/CNT composite. It was found that the strong interaction between the clay platelets and CNTs prevented the formation of CNT and clay aggregates, and resulted in the formation of the specific network created by both fillers [154]. The results of

dynamic-mechanical analysis of the composites [153] showed that the introduction of a small number of SHS composites in clay/CNT, significantly increases their modulus of elasticity, which value was greater than for the composites filled only with clay or CNTs. A similar effect of fillers combination on the elastic modulus of the composites was reported by K. C. Etika et al. [150].

The influence of the clay on the carbon nanofibers (CNF) distribution in the polymer matrix was studied by J. A. Johnson et al. [155]. The authors have supposed that the effect of the improvement of CNF dispersion in the polymer matrix was caused by the penetration of the clay platelets into the pores of CNF aggregates.

A new type of materials based on the ethylene-vinyl acetate, filled with CNTs and clay and obtained by melt mixing were introduced by P. C. Ma et al. [156]. The thermal and mechanical properties of composites were significantly changed in the presence of both fillers. It was found that the thermal properties and fire resistance of the material had to be better in the presence of the filler combination.

The combination of CNT and carbon black particles were also found to be very effective. A low percolation threshold was achieved when the hybrid filler content of CNT and carbon black reached 0.2 wt. % and 0.2% wt. %, respectively [157]. Different shape and aspect ratio and different dispersion characteristics of two conductive fillers result in a unique synergy effect, which provides the improvement of the electrical properties of the nanocomposites. The conductivity of the composites based on PP and PE filled with carbon black has grown significantly after the introduction of a small amount of carbon fibers (CF) [158]. Such an effect was caused by the fact that CF has connected the divided particles of carbon black, while forming more conductive network in the composite. It has been also established that the composites filled with a hybrid filler show a higher value of the positive temperature coefficient effect, (so-called "PTC-effect"), compared to the composites filled with carbon black. The expansion of the polymer matrix during melting breaks the conductive bridges of CF which connect the carbon black particles. A similar effect of a hybrid filler on the PTC effect was found by W. Di et al. [159].

During the several previous years there were reported the experimental works, which show that the combination of metal nanofiller and CNTs can improve the electrical properties of the polymer composites. Nanotubes provide the decrease of the percolation threshold, and metal particles result in the appearance of the high conductivity of the composites. Thus, the combining of carbon nanotubes and metal nanofiller makes it possible to obtain the composites with low percolation threshold and high conductivity.

The combination of these two classes of materials (CNTs and metal nanoparticles) may result in a successful integration of properties of two components in new hybrid materials. The CNTs surface serves as a template, where metal particles are absorbed or, when they bear some functional groups, CNTs may be linked through the organic fragments. The composites of CNTs with metal nanoparticles can be formed by two different ways. Pure metal particles are grown and/or deposited directly onto the CNTs surface. Alternatively, metal particles can be pre-formed and connected to CNTs using covalent bonding of organic fragments, located on the both particles.

During the last decade the idea of decorating of metal nanoparticles on the surface of carbon nanotubes have been reported in some papers [160-167]. Due to the integration of the properties of two types of nanoparticles the new nanoscale fillers are obtained, which exhibit new properties, not inherent to pure carbon nanotubes or metal particles. P. C. Ma et al. [156] have compared the properties of three types of composites based on epoxy resin, filled with: 1) CNTs; 2) functionalized CNTs; 3) CNTs decorated with particles of Ag (CNT/Ag). In the process of decoration metal nanoparticles with the average size of $(2 \div 4)$ nm were uniformly distributed on the surface of nanotubes. The conductivity of the composites filled with the decorated carbon nanotubes was significantly higher than that for the composites with pure and functionalized CNTs. The lowest conductivity was observed for the composites with the functionalized CNTs. The presence of the functional groups on the surface of CNTs decreases the number contacts between the nanotubes and prevents the charge transfer between them. Also the length of CNTs can be reduced directly during their functionalization. In addition, the composites filled with CNT/Ag have shown a significant

improvement of their thermal conductivity. This value for the epoxy/CNT/Ag composites increased by 94% compared to the pure epoxy, while for the epoxy/CNT composites it increased by 71% only. In addition, all three fillers revealed the improvement of mechanical properties of the composites and the best result were obtained for the samples filled with functionalized NTD, because of their better interaction with polymer matrix.

Metal nanoparticles can be linked to the CNTs surface by the intermolecular or covalent bonds. In the beginning, the surface of metal nanoparticles should be modified by functional groups. They can form covalent bonds with functional groups on the surface of CNTs, or CNTs can interact with the surface by intermolecular or electrostatic interactions [168]. The filler, formed by the interaction of CNTs with metallic species can be used for the production of composites with several potential applications, such as gas sensors, biosensors, electronic nanodevices, polymer electrolyte fuel cells, etc. In many recent reports metal metal–CNTs are involved in catalytic systems [168].

A simple method for decorating the surface of the CNTs with gold particles without modifying of CNTs by the functional groups was reported by N. Salah et al. [169]. CNTs and solution of metal particles were irradiated by gamma rays. TEM images have shown that Au nanoparticles were localized on the surface of carbon nanotubes. K.-P. Lee et al. [170] have also used gamma-rays for the distribution of gold nanoparticles in the composites based on polyaniline and carbon nanotubes. Interesting results were presented by H. Yu et al. [171]. The suspension of water solution of CNT-AgNO₃ in the presence of 2-propanol were irradiated. The authors received silver nanofibers with the length of several microns, which were localized inside the carbon nanotubes.

The modification of carbon black surface with the particles of Ni and Au was very effective as well [172]. Nanometal particles filled holes and defects on the surface of carbon black, thereby significantly changing their properties. Such changes of the surface properties of carbon black particles resulted in the changes of the filler-matrix interactions, what influenced the characteristics of the resulting composite. The measurements of the electrical parameters of the composites have shown that the modification of carbon black with metallic

particles caused a reduction of resistivity of such systems in comparison with the composites, which contain carbon black only.

A significant improvement of electrical characteristics of PP/Ag composites was achieved by the introduction of CNTs [173]. At nanometal content below percolation threshold, the addition of nanotubes resulted in the increase of conductivity via a so-called "bridging"-effect, which means the following. The nanoparticles of metal connect the individual nanotubes and form, in such a way, a conductive network.

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Chapter 2

Objects and methods of research

2.1. Objects of research.

2.2. Preparing of the composites.

2.3. Methods for the research of the structure and properties of electro-conductive polymer composites.

2.3.1. *Methods for the electrical measurements.*

2.3.1.1. *Direct current (DC) conductivity.*

2.3.2.1 *A broadband dielectric relaxation spectroscopy.*

2.3.2 *Microscopy.*

2.3.2.1. *Scanning electron microscopy (SEM).*

2.3.2.2. *Transmission electron microscopy (TEM).*

2.3.2.3. *Optical microscopy.*

2.3.3 *Methods for the research of the mechanical properties of the composites.*

2.3.3.1. *The research of the mechanical properties by static method.*

2.3.3.2. *Thermomechanical analysis.*

2.3.3.3. *Dynamic mechanical analysis.*

2.3.4. *Differential scanning calorimetry.*

Objects and Methods of Research

2.1 Objects of research.

Electroconductive composites were based on thermoplastic polymers, and the thermoplastic MATRIX (basis) was prepared with the use of the following polymers:

- isotactic polypropylene EMC 76384 (Hostalen, Hoechst, Germany) in the form of powder and being characterized by the following properties: the density is $\rho_{pp} = 0.9 \text{ g/cm}^3$; the average size of the particles is $(200 \div 250) \text{ }\mu\text{m}$; melting temperature $T_m = 164 \text{ }^\circ\text{C}$; and melt flow index ($\text{MFI}_{210/2.16}$) is 2.25 g/10 min .
- isotactic polypropylene (Atofina, France) in the form of granules with a density of $\rho_{pp} = 0.9 \text{ g/cm}^3$ and melting temperature $T_m = 167 \text{ }^\circ\text{C}$;
- polyvinylchloride C-7058 M (Kalush, Ukraine) in the form of the powder, characterized by the density of $\rho_{pp} = 1.37 \text{ g/cm}^3$ and with an average size of the particles – $(100 \div 150) \text{ }\mu\text{m}$;
- aliphatic co-polyamide, obtained by the polycondensation of the monomers in the melt at the following molar ratio: ϵ -caprolactam: adipic acid: 1,6-hexane diamine: sebacic acid = $1 : 0.1 : 0.45 : 0.35$. The ratio between the co-polyamide components was $\text{PA6} : \text{PA6.6} : \text{PA6.10} = 70 : 6 : 24$. The melting temperature was $T_m = 125 \text{ }^\circ\text{C}$ and $\text{MFI}_{210/2.16} = 11.9 \text{ g/10 min}$. The co-polyamide was synthesized in the Institute of Macromolecular Chemistry "Petru Poni", Academy of Sciences of Romania, Iasi, Romania.
- polyethylene (of 158-03-020 and 181-02-007 types) in the form of a powder with a density of $\rho_{pp} = 0.92 \text{ g/cm}^3$, melting temperature of $T_m = 110 \text{ }^\circ\text{C}$ and $\text{MFI}_{210/2.16} = 0.97 \text{ g/10 min}$.

The conductive fillers were:

- multi-walled carbon nanotubes (MWCNT) ("TM Spetsmash", Kyiv, Ukraine) obtained from ethylene by Chemical Vapour Deposition (CVD) method with $\text{FeAlMo}_{0.07}$, used as catalyst. In order to remove

the mineral impurities, the CNTs were treated by NaOH and HCL solutions.

- Multi-walled carbon nanotubes Nanocyl-7000 (Nanosyl S.A., Belgium), obtained from the ethylene by the CVD method (Fig. 2.1, a).

The main properties of the multi-walled carbon nanotubes, which were used in this work, are listed in the Table 2.1.

Table 2.1. The properties of the multi-walled carbon nanotubes.

| Properties | MWCNT („TM Spetsmash”) | MWCNT (Nanocyl S.A.) |
|---------------------------------|----------------------------|-------------------------------|
| Length | ~10 μm | 1.3 μm |
| External diameter | (12÷20) nm | 9.5 nm |
| Purity | 99% | 90% |
| Surface area | 190 m^2/g | 300 m^2/g |
| Density | 1.75 g/m^3 | (1.3÷2) g/m^3 |
| Length/diameter ratio (l/d) | ~1000 | >100 |

- Ni nanoparticles obtained by the decomposition of the nickel formate $\text{Ni}(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ at the temperature of $T = 210^\circ\text{C}$. The nickel formate powder was thermally treated in the vacuum heater during 12 hours. The average size of the obtained Ni particles was 60 nm (Fig. 2.1, b).

A well-known decomposition reaction of the nickel salt of formic acid $\text{Ni}(\text{COOH})_2$ (which was mentioned in the last item above) is very complicated. Its main direction is decomposition with the creation of the mixture of two gases – hydrogen and carbon dioxide gases in the ratio of 1:2, respectively:



Otherwise, this reaction is realized with a creation of the ternary system of H_2O , CO and CO_2 :



Apart from the main above mentioned decompositions, some second order reaction can also take place, which results in the creation of the organic acids, ethers and other substances. However, 75 % of the whole decompositions fall within the reactions, described by the (2.1) equation.

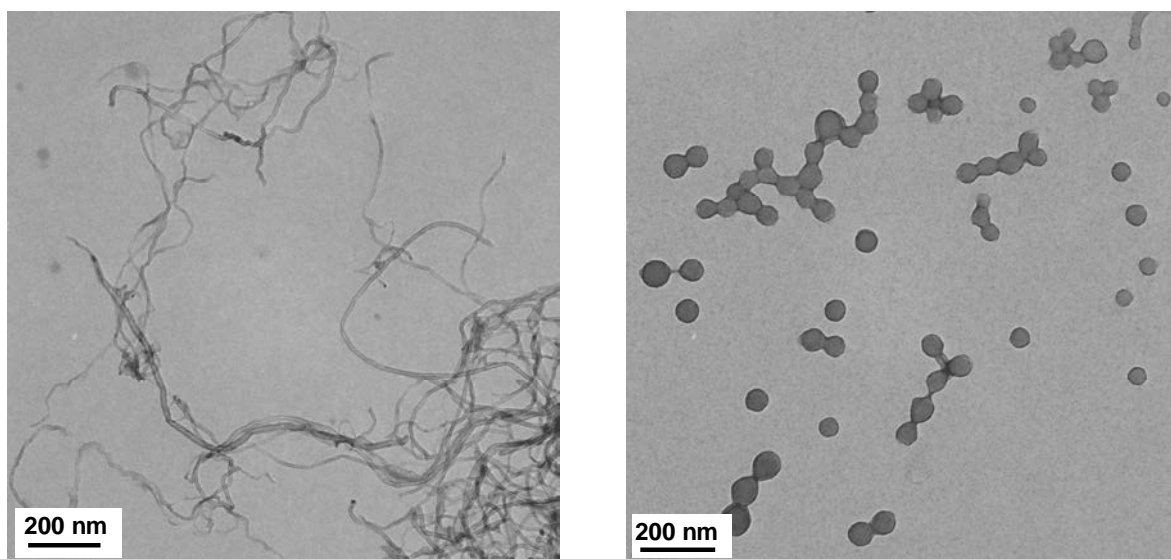


Fig. 2.1. Micro images of MWCNT (Nanocyl 7000) (a) and Ni nanoparticles obtained by TEM (b).

Organo-modified montmorillonite:

Montmorillonite (MMT), one of the most studied type of clay was used as a PP filler. It is characterized by the structure, which consists of a several layers (platelets), each of them 1.2-1.5 nm wide and about 100-200 nm long [1]. The platelets consist of two silicon-oxygen tetrahedral sheets (with the apexes located opposite each other), sandwiching a central of aluminum-hydroxide octahedral sheet (Fig. 2.2). In the interlayer gallery Na^{1+} , Li^{1+} , Ca^{2+} metal cations are usually present, and they can be substituted by other ions by ion exchange reactions. The introduction of modifier molecules into the interlayer gallery of clay can make the inorganic material organophilic. Moreover, the silicate layers can be exfoliated

before their incorporation into polymer matrix [2, 3], and the increasing of the interlayer distances will facilitate the dispersion of such clay in the composite.

Montmorillonite at a sodium form modified by cetyl-trimethyl ammonium bromide ($C_{16}H_{33}N(CH_3)_3^+ \cdot Br^-$, CTAB) was used in the study. The general formula of the montmorillonite is as follows $Na_{0.33}[(Al_{1.67}Mg_{0.33})(O(OH))_2(SiO_2)_4]$ [4]. The long chain cetyl-trimethyl ammonium bromide ions were chosen as a swelling agent for intercalation into MMT platelets, because they were shown to favour the formation of exfoliated composites [5-7]. In Fig. 2.2 one can see a schematic view of montmorillonite at sodium form and the process of its modification by the organic component. X-ray diffraction analysis was used to determine the distance between the montmorillonite plates at a sodium form and organomodified montmorillonite, which were found to be 1.26 nm and 2.45 nm respectively. The contents of MMT and organic component were 70 and 30 wt%, respectively.

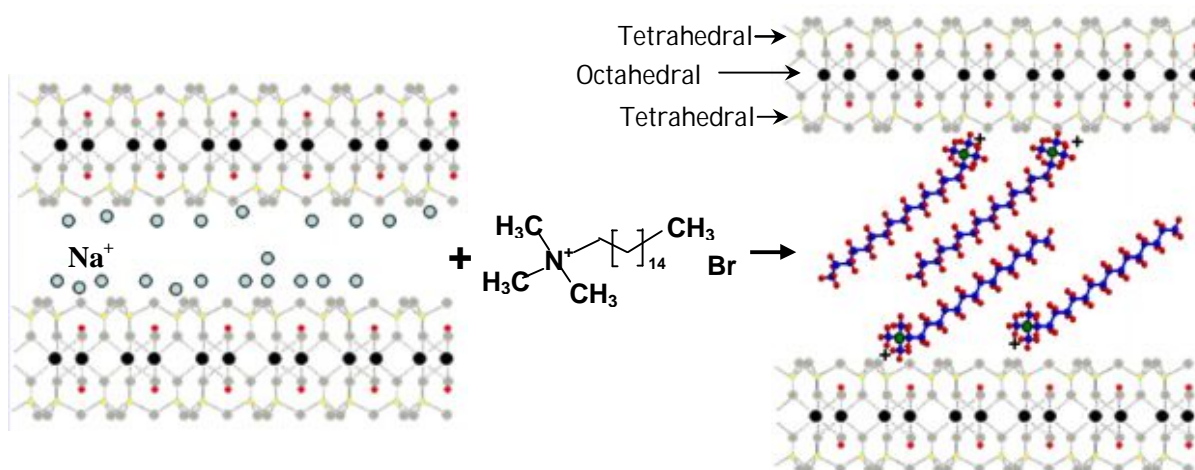


Fig. 2.2. A schematic view of the montmorillonite modification process by the organic component.

2.2. Preparing of the composites.

The three types of polymer composites, namely: segregated systems, conductive polymer blends and composites with combined fillers have been investigated.

The segregated systems based on PVC and PP filled with MWCNTs were formed by means of the hot compacting method used for preparation of composites. The MWCNTs were previously subjected to an ultrasonic action with

frequency of 22 kHz and power of 150 Wt during 20 min in the ethanol solution. The sonicated MWCNTs and PVC powders were homogenized by thorough grinding in a porcelain mortar to the visually homogeneous state. Homogenized composite was placed into a hot steel mold heated up to 145 °C and then pressed (hot compacted) during 5 min at 20 MPa with subsequent cooling of the mold in the air flow up to room temperature. The samples of pressed composites used for electrical and dielectric measurements were produced as discs with 30 mm in diameter and 1-1.5 mm in thickness. The samples for thermomechanical measurements were discs 12 mm in diameter and 1 mm thick.

In order to prepare thermoplastic composites, filled with MWCNTs ("TM Spetsmash") with organo-modified clay (OC) or with the combination of these two fillers (MWCNT/OC), a twin-screw mini-extruder (Micro 15 DCM XPlore Research, Netherlands) was used. The screws in this mini-extruder are located vertically, the mixing volume is 15 cm³ (Fig. 2.3). On the first stage of the mixing a filler or combination of fillers together with the polymer powder were mixed mechanically in a vessel. After that the mechanical blend of polymer powder and the filler was melted and mixed in the mini-extruder during 12 min. The screw speed rotation was 120 rpm, and the temperature during mixing was maintained at 210 °C. The extruded material was reduced to small particles and then placed into the steel mold heated up to 180 °C. Later it was compression moulded during 5 min at 12 MPa with the further cooling down to room temperature. The samples were disc-shaped, 1 mm thick and had 30 mm in diameter.

The content of MWCNTs in PP/MWCNT compositions and OC in PP/OC compositions varied in the range of (0.5÷3) vol. %, and the ratio of MWCNTs and OC in PP/MWCNT/OC composites was 1:1.

For the preparing of polymer blends based on PP and CPA and the polymer concentrates filled with MWCNTs the Haake MiniLab II, MicroRheology Compounder (Thermo Scientific, Germany) was used. The screws in this mini-extruder are located horizontally and the volume of the mixing zone is 7 cm³ (Fig. 2.4). The concentrate was mixed at the temperature of 200 °C during 7 min at the screw speed rotation of 90 rpm. The blend of the concentrate and pure

polymer was mixed in the extruder with the same parameters during 7 min. The ratio between the blend components are given in Chapter 4.

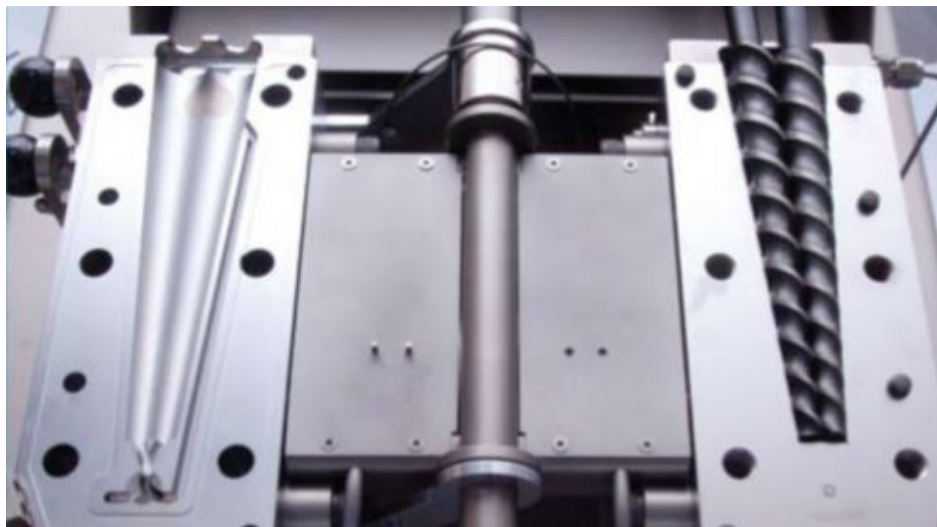


Fig. 2.3. Mixing zone and screws of the Micro 15 DSM XPlore

In order to form PP/MWCNT/Ni composites a laboratory mini-extruder Haake Minilabe II was used. In the case of the binary filler, MWCNTs, Ni particles and polymer were placed into the extruder simultaneously. The components were mixed at the temperature of 200 °C during 7 min at the screw speed rotation of 90 rpm. The MWCNT concentration varied in the range of (0.1÷3) vol. %. In the PP/Ni nanocomposites the content of Ni was in the range of (1÷7) vol. % and in the composites with the combined PP/MWCNT/Ni filler Ni content was constant and equal to 2.5 vol. %.

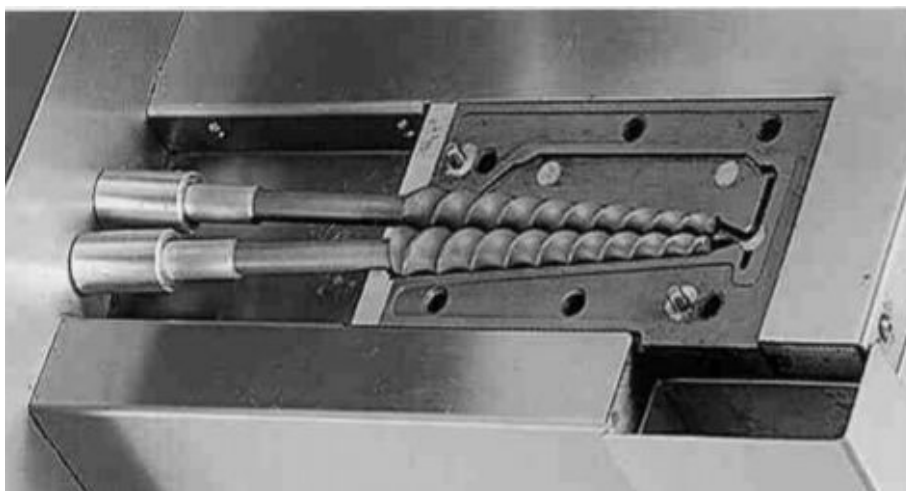


Fig. 2.4. Mixing zone and screws of Haake MiniLab II miniextruder.

Both for polymer blends, as well as for the composites with Ni/MWCNT binary filler, the extruded material was reduced to powder and placed into the steel mold, heated up to 180 °C and compression moulded during 5 min at 12 MPa, with the following cooling down to room temperature.

2.3. Methods for the research of the structure and properties of electro-conductive polymer composites.

2.3.1. *Methods of the electrical measurements.*

2.3.1.1. *Direct current (DC) conductivity.*

The DC conductivity measurements were performed with the use of Radiotechnika E6-13A teraohmmeter (Riga Latvia) by the two-electrode scheme at the voltage of 100 V. During measurements the disc-shaped samples were fixed between two steel polished electrodes. The conductivity value σ (Sm/cm) was calculated by the following equation:

$$\sigma = \frac{1}{R} \cdot \frac{l}{S}, \quad (2.3)$$

where R (Ohm) is a sample resistance, measured by the teraohmmeter, l (cm) is a sample thickness and S (cm²) is the sample area.

2.3.2.1 *A Broadband Dielectric relaxation Spectroscopy.*

A broadband dielectric relaxation spectroscopy (DRS) was performed with the use of the frequency analyzer Novocontrol Concept 40 α -analyzer and Broadband Dielectric Converter (BDC Novocontrol) in the frequency range ($10^{-2} \div 10^6$) Hz. During the investigations of the temperature dependences of the dielectric characteristic, the sample heating and cooling processes were controlled by the Novocontrol Quatro Cryosystem at the temperature range of (-50÷200) °C and with a linear heating rate of 3°C/min. The samples were disc-shaped, 1 mm thick and 30 mm in diameter. The experimental parameters were controlled and regulated via Novocontrol WinDETA software.

The principle of dielectric and impedance measurements is that the studied cell can be compared with the capacitor, which is a sample, fixed between two electrodes. The voltage U_0 , applied to the sample at the fixed frequency $\omega/2\pi$ results in the appearance of the current I_0 with the same frequency. The phase displacement between the voltage and current can be described with the φ angle (Fig. 2.5).

The relation between U_0 , I_0 and φ depend on the electrical properties (dielectric permittivity and conductivity) and on the geometry of the composite:

$$U(t) = U_0 \sin(\omega t) \quad (2.4)$$

$$I(t) = I_0 \sin(\omega t + \varphi) \quad (2.5)$$

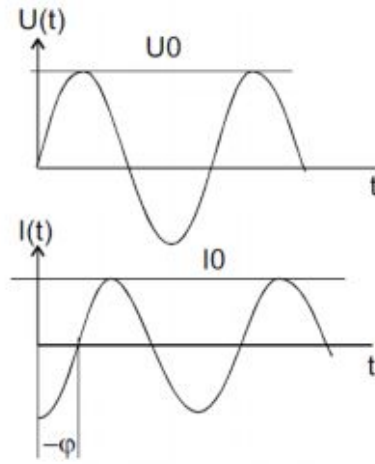


Fig. 2.5. The amplitude and relation between U_0 , I_0 in the sample.

In order to calculate the dielectric parameters, the device software uses the following equations:

$$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = \frac{-i}{\omega Z^*(\omega) C_0} \quad (2.6)$$

$$Z^* = Z' + iZ'' = \frac{U^*}{I^*} \quad (2.7)$$

$$I^* = I' + iI'' \quad (2.8)$$

$$U^* = U_0 \quad (2.9)$$

$$\operatorname{tg}(\varphi) = \frac{I''}{I'} \quad (2.10)$$

where ε' and ε'' are active and reactive components of the complex dielectric permittivity ε^* , relatively, C_0 is the cell capacity without the sample, Z^* is the complex impedance, Z' and Z'' are real and imaginary parts of the impedance, respectively, and $\tan \varphi$ is the phase displacement.

2.3.2 Microscopy.

2.3.2.1. Scanning electron microscopy.

In order to study the morphology of the samples the scanning electron microscopy method (SEM) was used. Having been preliminary frozen in the liquid nitrogen, the braking surface was covered with the Au/Pd layer, about 10 nm thick. The observations were carried out via S800 SEM HITACHI scanning microscope at the accelerating voltage of 15 kV.

2.3.2.2. Transmission electron microscopy (TEM).

TEM investigations were carried out on the cut of the composite, about 60 nm thick. The cut was performed at room temperature with the use of ultramicrotome and ultrasonic diamond knife. The observations were made via PHILIPS CM120 transmission electron microscope at accelerating voltage of 80 kV.

2.3.2.3. Optical microscopy.

Optical microscopy of the segregated systems was performed on the modified optical interference microscope PZO (Warsaw, Poland) in the transmission regime. The thickness of the composite films was up to 200 μm . The results of the optical microscopy were registered in the real-time regime by the Fujifilm FX8000 camera characterized by 18x of the optical zoom.

Optical microscopy of the filled polymer blends was performed on the Carl Zeiss Primo Star microscopy (Germany) in the transmission regime. During the analysis of the obtained results the pictures were treated with the use of Photoshop CS2 ver. 8 software.

2.3.3 The methods for the research of mechanical properties of the composites.

2.3.3.1. The research of the mechanical properties by static method.

The static investigations of the mechanical properties of the polymer blends were performed via the TMA Q40 thermo-mechanical analysis device in the weighting/compression regime. The experimental data enabled to determine the Young's modulus G as the slope of the weighting/compression line at low weightings (0÷1.5) MPa with the using of the following equation:

$$G = \frac{\Delta s}{\Delta C} , \quad (2.11)$$

where Δs and ΔC are the change of weighting and compression, respectively.

2.3.3.2. Thermomechanical analysis.

Thermomechanical properties of the segregated polymer systems were studied with the use of the original equipment in the penetration regime. A sample, 1 mm high and not less than 6 mm in diameter was located on the metal experimental table and pressed via the weighting of $P=0.5$ MPa with the use of plate metal indenter, 3 mm in diameter. The material deformation was registered by high-precision induction sensor, from which the analogous signal was recoded into digital data via analogous-digital device and assayed by the special software. The experiments were performed in the temperature range of (25÷200) °C with a linear heating rate of 3 °C/min. The relative deformation ε (%) was determined from the following relation:

$$L = \frac{\Delta L}{L_0} \cdot 100\% , \quad (2.12)$$

where ΔL (μm) – is the sample deformation at the moment of the study and L_0 is the initial sample width.

The structural transition temperature can be defined as the intersection of two tangents to the temperature dependences of the relative deformation before and after the structure transition.

2.3.3.3. Dynamic mechanical analysis.

Dynamic Mechanical Analysis (DMA) was performed with the use of TA Instruments DMA 9080 equipment in the “three-point bend” regime. The amplitude and frequency of the forced oscillations were 20 μm and 1 Hz, respectively. The temperature range of the investigations was $(-50\div 150)^\circ\text{C}$, and the linear heating rate was $4^\circ\text{C}/\text{min}$. The samples were rectangle shaped, 30 mm long, 0.8 mm thick and 6 mm wide.

The relaxation transition temperature was determined as the maximum of the temperature dependence of the mechanical losses modulus for one frequency.

2.3.4. Differential scanning calorimetry.

Thermo-physical properties of the samples were studied by the Differential Scanning Calorimetry (DSC) method with the use of 2920 MDSC TA Instruments calorimeter in the helium atmosphere in the temperature range of $(-50\div 200)^\circ\text{C}$ with a heating rate of $10^\circ\text{C}/\text{min}$. During the investigation the samples with a mass of $(0.008\div 0.012)$ g had been placed into the aluminium capsule, which were closed hermetically.

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Chapter 3

Structure and properties of conductive segregated polymer composites filled with carbon nanotubes

Introduction

3.1. Electrical conductivity and dielectric properties of segregated polymer systems.

3.1.1. *DC conductivity of composites.*

3.1.2. *Structure of composites.*

3.1.3. *Temperature dependence of conductivity.*

3.1.4. *Dielectric properties.*

3.2. Thermo-mechanical behavior of segregated polymer composites.

Conclusions

Introduction

Carbon nanotubes are of great interest as the conductive filler for polymer composites [1, 2]. Besides of high conductivity they demonstrate many unique properties such as thermal, optical and mechanical ones [3, 4]. Both thermoplastics and thermosets can serve as a polymer matrix while the electrical characteristics of composites depend on spatial distribution of nanoparticles. The value of percolation threshold (i. e. critical concentration of filler that corresponds to the sharp growth of conductivity) strongly depends on the polymer nature and on the processing method of introduction of the nanotubes into the polymer matrix. This is caused by experimental difficulties to separate the curled and tangled long nanotubes and, as a result, leads to the aggregates formation. Experimental values of percolation threshold vary in a wide range of $\varphi_c = 0.0025\text{--}7.5\%$ [5–10]. The attained low values of φ_c are attractive because the conductive composites can be obtained at very low content of nanotubes. Such low values of percolation threshold are caused by high ratio length/diameter of nanotubes, which can be equal to 100–1000 and provides the presence of contacts between individual nanotubes even for very low content in the polymer matrix. So-called segregated systems differ from the conventional filled composites by structuration of filler, namely the filler creates ordered structure in a form of nanotube framework within the polymer matrix.

First such a type of systems was studied in detail by A. Malliaris and D. T. Turner [11] and by Kusy [12]. First the formation of conductive phase and detailed analysis of the percolation effects in segregated polymer systems which were formed by hot compacting of metal-polymer powder were carried out by A. Malliaris and D. T. Turner [11] (Fig. 3.1). The following model demonstrating the conductive phase structure formation in segregated polymer composites filled with metal particles. Small filler particles having size d are assumed to form “shells” around randomly distributed large polymer particles with size D in the initial mechanical mixture ($D \gg d$) [13]. With the φ increasing, the filler particles fill up the boundary between the polymer particles. At the concentration of the

filler $\varphi = \varphi_c$ conductive cluster appears. Further increase of filler content results in the increase of the number of layers n of metallic particles on the kernel surface.

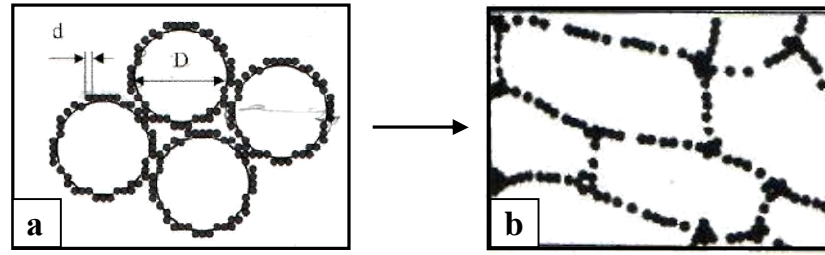


Fig. 3.1. A schematic representation of the assumed distribution of the polymer and metal particles (with D and d size, respectively) in the segregated polymer composites [11].

Considerably lower value of φ_c comparatively with usual filled polymers can be attained due to this effect [13–18]. Such an ordered distribution of filler is also realized, for example, in polymer blends when the filler is localized in one polymer phase or on the interface [19, 20] and in the latex-based composites [21, 22].

The compacting method (pressing of mechanical mixture of the polymer and filler powders) under conditions that the size of polymer particles D greatly exceeds the size of filler particles d , $D \gg d$, is one of simple and effective methods to form the segregated systems [8–12, 23].

Previous studies show that this method enables to obtain the conductive composites based on PE filled with multiwalled carbon nanotubes having ultralow value of the percolation threshold, $\varphi_c = 0.04$ vol.% [18]. This effect was attained owing to both high ratio length/diameter of nanotubes and ordered distribution of the filler within the polymer matrix. Having such interesting properties these systems require the detailed investigations of their electrical, dielectric and mechanical characteristics.

3.1 Electrical conductivity and dielectric properties of segregated systems.

3.1.1. DC conductivity of composites.

The concentration dependence of DC conductivity σ_{DC} of the PVC/MWCNT composites is represented in Fig. 3.2. One can see that for the concentration of

nanotubes higher than 0.04 vol.% the conductivity sharply increases by several orders of magnitude. The conductivity of two-phase conductive-nonconductive systems σ in the region above the percolation threshold $\varphi > \varphi_c$ can be described by the equation:

$$\sigma = \sigma_0 (\varphi - \varphi_c)^t \quad (3.1)$$

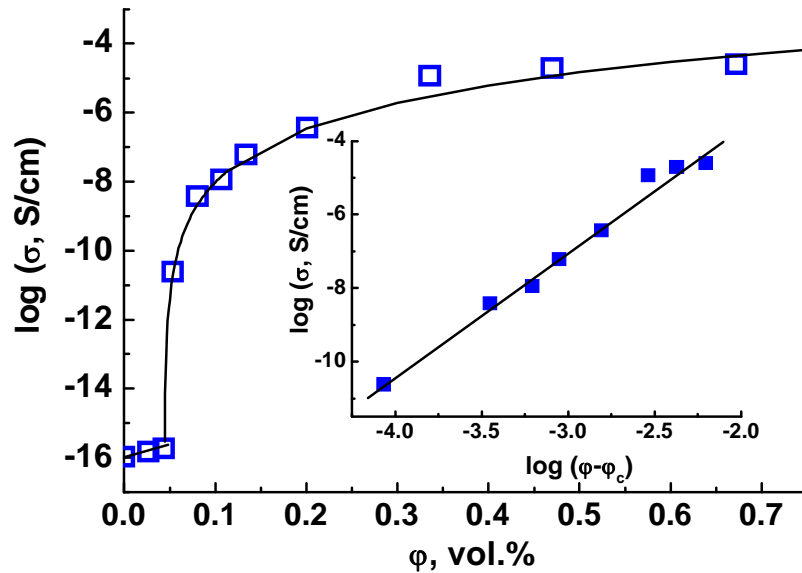


Fig. 3.2. Dependence of DC conductivity σ_{DC} on filler content for PVC/MWCNT composites. The fitting of parameters of eq. (3.1) by scaling relation $\log \sigma \propto \log(\varphi - \varphi_c)$ is given in the insertion.

Insertion to Fig. 3.2 presents the scaling relation $\log \sigma \sim \log(\varphi - \varphi_c)$ to fit the values of t and σ_0 . Such a fitting gives the values of percolation threshold $\varphi_c = 0.045$ vol. %, critical exponent $t = 3.5$ and pre-exponential factor $\sigma_0 = 2.3 \cdot 10^3$ S/cm. The value of the critical exponent t is noticeably higher than its theoretical value $t=2$. This effect can be explained by non-statistical ordered distribution of the conductive phase in the polymer matrix since value $t=2$ is provided by random (statistical) distribution of conductive particles in non-conductive medium [24]. The anomalous value of t was also noticed by Feller [25]. Reached very low value of percolation threshold coincides with results obtained in the previous work [17]. Thus, the segregated state of carbon nanotubes in the PVC/MWCNT composites enables to obtain also the conductive system at minimal content of nanotubes.

The electrical properties of segregated systems based on polypropylene (PP) and carbon nanotubes were also investigated (Fig. 3.3). The calculation of the percolation parameters for composites PP/MWCNT by scaling dependence $\log \sigma \sim \log (\varphi - \varphi_c)$ (insertion Fig. 3.3) gives the following values: $\varphi_c = 0.04$ vol. %, $t = 2.4$, $\sigma_0 = 6$ S/cm.

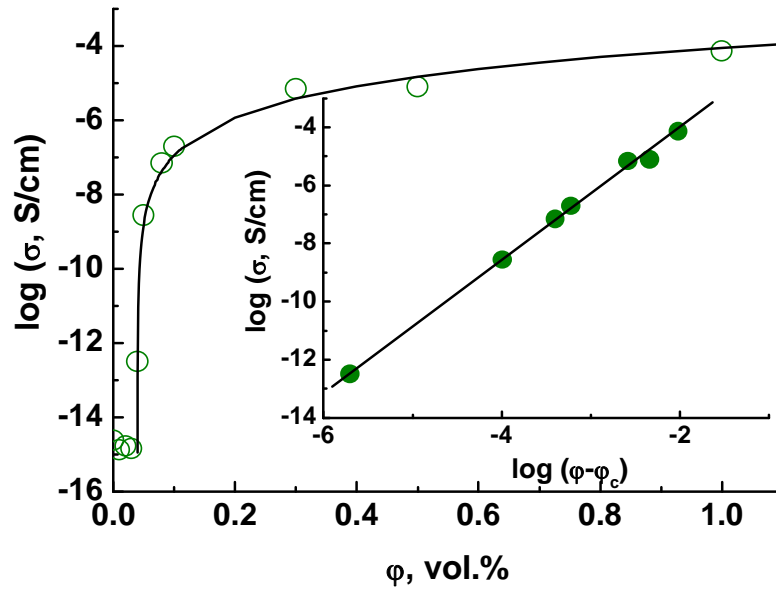


Fig. 3.3. Dependence of DC conductivity σ_{DC} on filler content for PP/MWCNT composites. The fitting of parameters of eq. (3.1) by scaling relation $\log \sigma \propto \log (\varphi - \varphi_c)$ is given in the insertion.

One can notice that for both systems PVC/MWCNT and PP/MWCNT a low value of percolation threshold was achieved. Thus segregated distribution of the filler in composites enables to obtain the conductive system at lower MWCNTs contents. The results show that percolation behavior does not depend on the type of polymer matrix but is determined by the ratio of particle sizes of filler and matrix powder. The values of percolation threshold for both systems are almost identical.

3.1.2. Structure of composites.

Structure model showing the evolution of structure of the PVC/MWCNT composite in a process of its forming is represented in Fig. 3.4. On the first stage the mechanical mixture of polymer/MWCNT contains rather agglomerated nanotubes in the space between polymer particles (Fig. 3.4-a). Then it is necessary to cover the surface of polymer particles with smooth layer of filler without

agglomerates of the filler particles (Fig. 3.4-b). In this case one can expect to obtain the conductive composite with low value of the percolation threshold. On the last stage the mechanical mixture has to be compacted (to be pressed), at higher temperature, which leads to the deformation of polymer particles and the creation of solid polymer matrix.

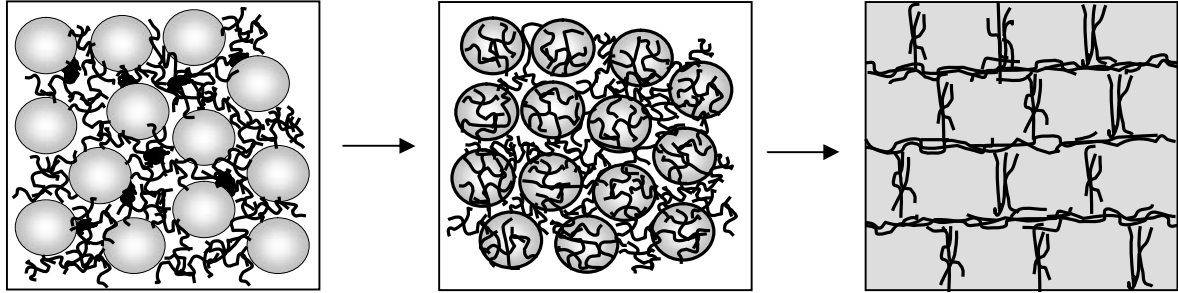


Fig. 3.4. A model of evolution of the PVC/MWNT structure along a process of its forming by hot compacting method.

The filler having such a segregated structure creates continuous nanotube framework inside the polymer matrix with location of the filler on the boundaries between polymer grains (Fig. 3.4-c). Optical microscope images of the segregated PVC/MWCNT structure are presented in Fig. 3.5.

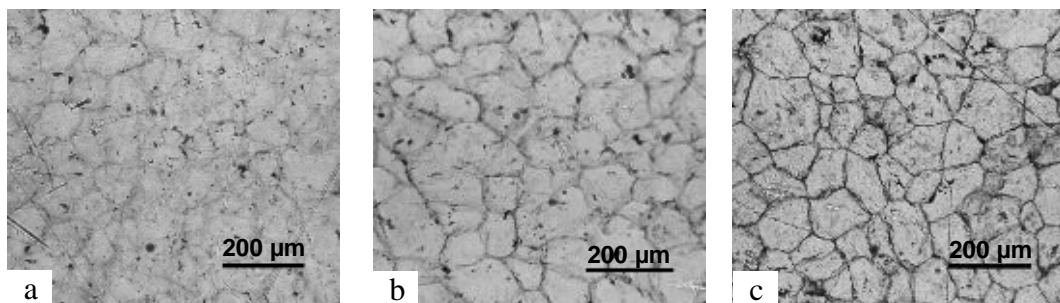


Fig. 3.5. Optical microscope images of segregated PVC/MWCNT composites with the MWCNT content below (0.02%), close (0.04%) and above (0.07%) percolation threshold.

It shows the evolution of the composite structure along the increase of MWNT concentration from 0.02 vol. % which is below percolation threshold φ_c (Fig. 3.5-a) through 0.04 vol. % (close to φ_c) (Fig. 3.5-b) to 0.07% (above φ_c) (Fig. 3.5-c). One can see more pronounced boundaries between polymer grains, blackened by the nanotubes, with increase of the MWCNT content which reflects a creation of the nanotube framework.

In such a system two specific values of the filler concentration exist: the average concentration φ which is related to whole composite volume, and the local concentration φ_{loc} which implies the filler concentration in the walls of the framework, where $\varphi_{loc} > \varphi$. The models describing the dependence of the percolation threshold on parameters of the skeleton structure have been developed [12–17], and in the case of composites containing nanotubes the model predicts low values of percolation threshold φ_c [18]. Some regularities of the framework formation were ascertained.

The properties of segregated system depend on the filler particle size, their conductivity, the value of contact resistance, the type of filler packing inside the conductive network, a number of contacts between particles and others. Usually it is very difficult to determine the parameters which were mentioned above. Thus the most convenient to describe such systems is a model that relates the system properties and geometric parameters of the network [24]. Models that describe the dependence of percolation threshold on the parameters of the conductive networks have been represented in [11, 23, 24, 26,]. The first geometric model that describes the segregated system was proposed by A. Malliaris and D. T. Turner [11]. This model enabled to calculate the two critical volume concentrations of the filler V_A and V_B which define the beginning and the end of the interval where conductivity is changed dramatically (equation 3.2). The first critical volume concentration V_A derived from the assumption that the initial sharp rise in conductivity occurs due to formation of monolayer of the filler around each particle of polymer matrix. The other critical volume concentration V_B was determined from the assumption that conductivity rising stopped when around of the polymer matrix particles was formed a double layer of filler.

$$V_B = \frac{100}{1 + (\phi/4)(R_p/R_f)}, \quad V_A = 0.5 p_c V_B, \quad (3.2)$$

where R_p – the radius of the polymer particles, R_f – radius of filler particles, p_c – critical probability, ϕ – a factor which depends on the type of filler particles packing in the conductive network. A. Milliaris and D. T. Turner [11] suggest the

following values ϕ for different types of packing, namely: for hexagonal – = 1.11, square – = 1.27 and triangle – = 1.38.

Applying of this model to the composites PE/Ni with the ratio of R_p/R_f in the range from 30 to 7,5, the authors found a significant discrepancy between the experimental and theoretical values of V_A [26]. Experimental values were 3 times higher than the theoretical one which was calculated using equation (3.2). This difference was due to non-uniform covering of the surface of polymer matrix particles by the filler. Thus R. P. Kusy et al. [23] proposed to improve this model, using the assumption that the filler particles tend to accumulate in a void between the particles of polymer and random single or double layer of filler around polymer particles can not be formed. Therefore, in equation 3.2 was introduced factor χ_c that determined which part the surface of polymer matrix is coated by the particles of filler.

$$V_A = \frac{100}{1 + (\phi / 4\chi_c)(R_p / R_f)}, \quad (3.3)$$

where χ_c – a critical portion of the surface of the polymer matrix coated by the particles of the filler.

To achieve a more exact match between experimental and theoretical values, I. J. Youngs [27] proposed a model which provided that during formation of the composites the polymer particles changed their shape from spherical to quadratic one. In addition, it was assumed that in the composites the voids between the polymer particles were absent, and the maximum conductivity is achieved when all of the conductive particles touch each other. According to this model the critical volume concentration can be calculated by the following equation:

$$V_B = \frac{2,99 \cdot (R_f / R_p)}{1 + 2,99 \cdot (R_f / R_p)}, \quad (3.4)$$

Current models which connect percolation threshold with parameters of conductive networks were presented in [14, 28]. In particular, Ye. P Mamunya et al. [14] have presented a model in which a following ratio takes place:

$$\varphi_{cs} = \varphi_c \left[1 - (1 - nd/D)^3 \right], \quad (3.5)$$

where φ_{cs} – percolation threshold of the system, φ_c – concentration of the system with homogeneous distribution of filler particles, n – number of filler layers in the conducting network, d and D – the size of the particles of the filler and the polymer, respectively.

The model mentioned above was slightly improved by N. Lebovka et al. [28] As a result, was offered the following dependence:

$$x_* = p_*(\lambda, n) \left\{ 1 - [1 + n/\lambda]^{-d} \right\}, \quad (3.6)$$

where d – the parameter that characterizes the spatial dimension of the conductive network and has values 2 or 3, λ - the ratio of polymer particle sizes and filler, $p_*(\lambda, n)$ – volume content of the particles in the channels between the particles of polymer.

The value of percolation threshold for investigated segregated systems PVC/MWCNT and PP/MWCNT can be theoretically estimated using equation (3.7) that was proposed by N. Lebovka et al. [28]:

$$\varphi_c^s \approx \left[1 - (1 + n/\lambda)^{-3} \right] \varphi_c^r \quad (3.7)$$

where φ_c^s – percolation threshold for systems with uniformly distributed filler, λ – the ratio of polymer particle of and filler sizes, n – number of the filler particles on the surface of the polymer, d and D – the size of the filler and polymer particles, respectively.

The value of φ_c^r equals to $\varphi_c^r \approx 1/a$ [18] and a is defined as the ratio of length and diameter of the nanotube. Assuming that the nanotubes form one conductive layer around the polymer particles $n \sim 1$, and substituted values in equation (3.7) one can obtained the following equation:

$$\varphi_c^s \approx 3n/(a\lambda), \quad (3.8)$$

The length of nanotubes is $d \approx 10 \mu\text{m}$, the value $a = 1000$, average particle size of PVC $D_{PVC} = 100 \mu\text{m}$ and of PP $D_{PP} = 200 \mu\text{m}$, thus $\lambda_{PVC} = D_{PVC} / d = 10$ and $\lambda_{PP} = D_{PP} / d = 20$. Introducing of the values of n , a , λ in equation (3.8) we obtained the theoretical percolation thresholds for the investigated segregated systems. For

PVC/MWCNT theoretical value $\varphi_c=0.0003$ and for PP/MWCNT $\varphi_c=0.00015$. Obtained theoretical results have good correlation with experimental, namely for PVC/MWCNT $\varphi_c=0.00045$, and for PP/MWCNT $\varphi_c=0.00040$.

3.1.3. Temperature dependence of conductivity.

Temperature dependencies of conductivity of the PVC/MWNT composites are shown in Fig. 3.6. The increase of filler content changes the form of the curves. In pure PVC and composite with 0.04% MWNT the conductivity increases with rise of temperature (curves 1 and 2). Such a character of the temperature dependencies can be attributed both to ionic and electronic type of conductivity.

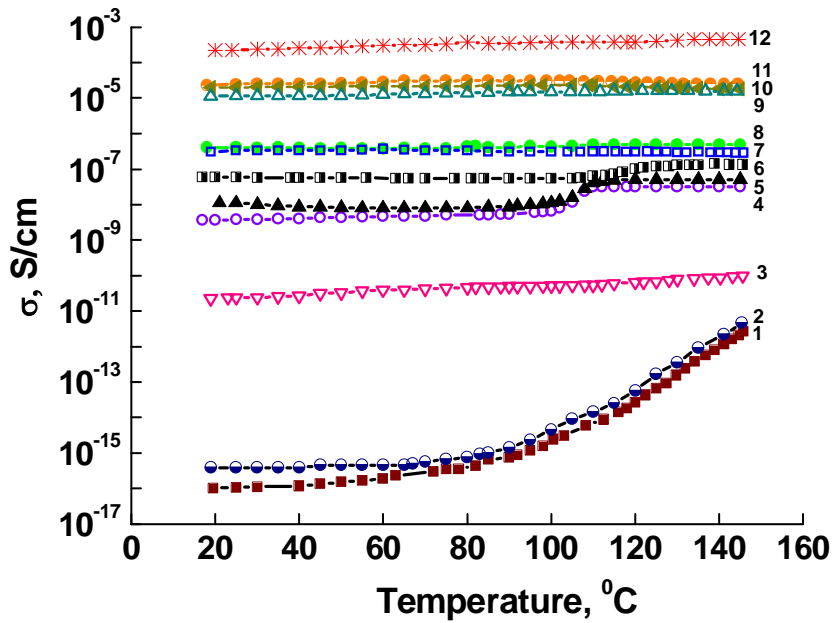


Fig. 3.6. Temperature dependencies of DC conductivity for PVC composites with different content of filler. Content of MWNT in the composites (vol. %): 1 – 0, 2 – 0.044, 3 – 0.054, 4 – 0.08, 5 – 0.107, 6 – 0.134, 7 – 0.201, 8 – 0.268, 9 – 0.336, 10 – 0.470, 11 – 0.672, 12 – 100.

Thus, the authors [29, 30] claim the electronic type of conductivity in PVC whereas in Refs. [31, 32] the conductivity of PVC was related to the movement of ions. The temperature dependence is found to be composed of two linear regions with a bend at temperature of glass transition. The transition from glassy state to high-elastic state leads to stronger dependence of conductivity on temperature

that can be related to heightened molecular mobility which influences on charge transport. These dependencies are represented by Arrhenius plot in Fig. 3.7

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right), \quad (3.9)$$

where E_a is an activation energy, k is a Boltzmann constant. Calculation of the activation energy values for the both parts of curve gives the E_a values in the temperature regions higher and lower of T_g respectively: 23.0 and 2.1 kcal/mol for the pure PVC and 19.0 and 0.9 kcal/mol for the PVC/MWCNT composite with 0.04% MWCNT.

Crossing glass-transition temperature the value of activation energy sharply increases as the result of rise of the charge carrier mobility at the temperatures higher than T_g . Similar values of the activation energy for high temperature region were found in PVC for the cases when charge transport was realized both electronic [29] and ionic [31] types of conductivity. The influence of temperature (temperature higher or lower than T_g) on the value of the activation energy enables to include the segmental mobility in the charge transport process [32]. This approach takes into consideration the change of viscosity of the polymer matrix under temperature influence what, in turn, modifies the mobility of charge carriers [32]. Even insignificant excess of the filler concentration over percolation threshold leads to the change of the conductivity character. Thus at MWNT content equal to 0.054 vol. % the conductivity increases notably and the dependence of σ on temperature becomes negligible (Fig. 3.6, curve 3). It indicates a conversion from conductivity through the matrix to conductivity through the filler phase. Further growth of the filler content causes the increase of the conductivity value and it becomes independent on temperature in the region of 20–150 °C (curves 4–11).

The measurements of the nanotube conductivity demonstrate the independence of σ on temperature (curve 12), accordingly the temperature dependence of the conductivity of PVC/MWCNT composites has the same character since it is provided by electronic conductivity of the filler phase.

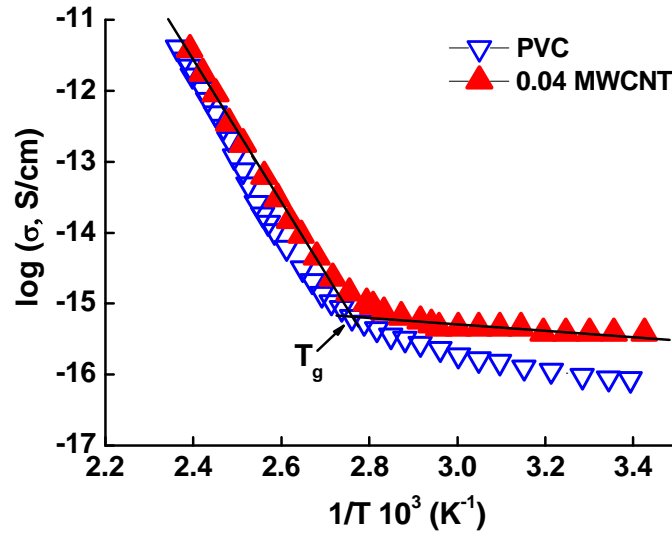


Fig. 3.7. Arrhenius plots for the conductivity of the pure PVC and composite with 0.04 vol. % of MWCNT.

3.1.4. *Dielectric properties.*

Fig. 3.8 represents dielectric constant ε' , dielectric losses ε'' and AC conductivity σ_{AC} versus frequency. The values of both ε' and ε'' of the composites with the MWCNT content 0–0.04 vol. % (i.e. lower than percolation threshold) are close and independent on frequency. The values of ε' and ε'' increase and reveal a negative slope if the filler content exceeds the percolation threshold which is especially noticeable in the range of low frequencies (10^{-1} – 10^2 Hz). The frequency dependence of dielectric parameters in two-phase conductive-insulating system in the range of percolation threshold can be considered with two models, such as intercluster polarization (IP) that implies polarization effects between clusters inside percolation system or anomalous diffusion (AD) within cluster [33–35]. The IP model predicts the power-law dependence of ε' and σ_{AC} on the frequency that may be written as follows:

$$\varepsilon'(\omega) \propto \omega^{-y}, \quad (3.10)$$

$$\sigma(\omega) \propto \omega^x, \quad (3.11)$$

Where x and y – are critical exponents, ε' – dielectric constant, σ – conductivity.

Critical exponents x and y have to satisfy the following conditions:

$$x + y = 1. \quad (3.12)$$

For the theory of intercluster polarization:

$$x = t / (t + s), \quad (3.13)$$

$$y = s / (t + s), \quad (3.14)$$

where t – critical exponent of DC conductivity σ_{DC} , s – critical exponent of ε' .

For the theory of anomalous diffusion:

$$x = t / \nu(2 + \theta), \quad (3.15)$$

$$y = (2\nu - \beta) / \nu(2 + \theta), \quad (3.16)$$

where θ – critical exponent which determined the process of diffusion in percolation clusters, $\theta = (t - \beta) / \nu$.

In the case of three-dimensional lattice percolation the critical exponents t and s are: $t \approx 2$, $s \approx 0.8$ [24] what gives the values of x and y calculated from the intercluster polarization IP theory equal to 0.72 and 0.28, respectively. From the anomalous diffusion AD model the values of x and y are equal to 0.58 and 0.42, respectively, for three dimensions.

For the conductive PVC/MWCNT composites with MWCNTs content in the range of percolation threshold 0.08–0.13 vol. % the average value of y (which was calculated as a slope of the ε' curve in the 10^{-1} – 10^2 Hz frequency range, Fig.3.8) is found to be 0.18, which is lower than the theoretically predicted value.

For higher concentration of the filler in the composites (in the range of 0.20–0.67 vol. %) the values of ε' grow drastically. The reason of such an effect can be an electrode polarization that leads to a separation of charges which gives an additional contribution to the polarization. It occurs for moderately to highly conductive systems and results in extremely high values of the real and imaginary part of the complex dielectric permittivity [33]. In fact Fig. 3.8 demonstrates a presence of very high ε' values equal to 10^5 – 10^6 and ε'' values equal to 10^8 in the range of low frequencies 10^{-1} – 10^0 Hz for the samples with filler concentration above 0.20 vol. %.

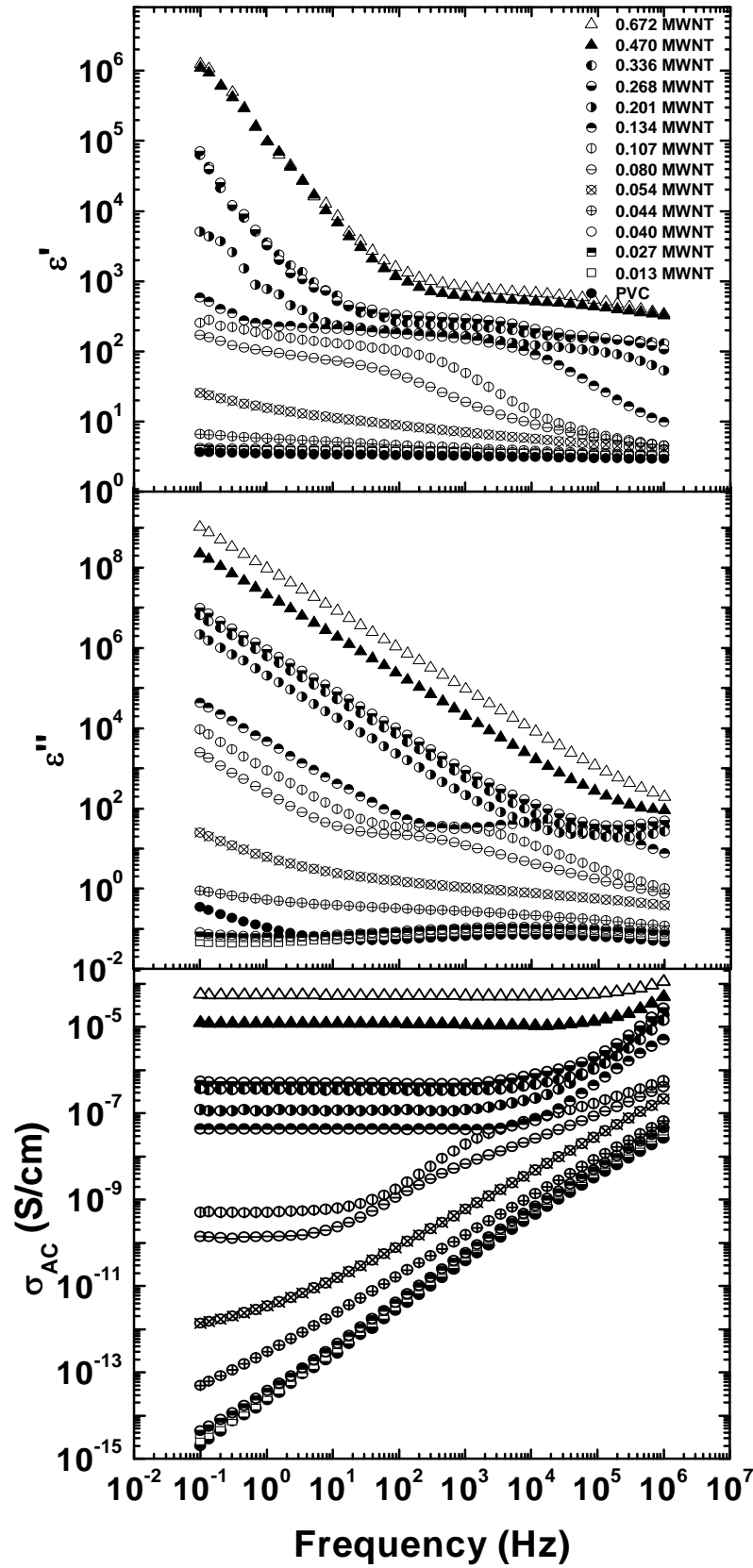


Fig. 3.8. Frequency dependencies of dielectric constant ϵ' , dielectric losses ϵ'' and AC conductivity σ_{AC} for the PVC composites with different MWCNT content.

Plot of conductivity versus frequency in a double logarithmic scale (Fig. 3.8) shows two cases of the frequency dependence of AC conductivity σ_{AC} : (a) below percolation threshold the values of σ_{AC} of the composites are overlapping and the curves have average slope close to 1, which indicates the highly insulating material [37]; (b) above φ_c the conductivity is constant at low frequency due to the contribution of DC conductivity. The slope of curves σ_{AC} for the concentrations in the range of percolation threshold at higher frequencies is about 0.91 (experimental value of x), that exceeds the theoretically predicted value of critical exponent $x = 0.72$. As far as the experimentally measured values $x + y = 0.91 + 0.18 = 1.09 (\approx 1)$, one can consider that the general scaling relation (3.12) is fulfilled satisfactory.

Thus, the experimental results are closer to the IP model than to the AD model. Note, that in Ref. [33–35] the similar results are obtained, the critical exponents x and y do not agree separately with the theoretical predictions but the general scaling law (3.12) is satisfactorily fulfilled. For PE/MWCNT composites the authors [38] have found an agreement of the experimental values of critical exponents with the theoretical prediction by power law relations Eqs. (3.10)–(3.12).

The presence of percolation behavior of the ε' concentration dependencies in PC/MWCNT and PP/MWCNT composites has already been observed [39, 40]. In our study the dielectric constant and dielectric losses for the PVC/MWCNT and PP/MWCNT composites demonstrate percolation behavior as well. The concentration dependence of ε' and $\tan \delta = \varepsilon'' / \varepsilon'$ is shown in Fig. 3.9.

Above percolation threshold $\varphi_c (PVC) = 0.045$ vol. % and $\varphi_c (PP) = 0.04$ vol. % the values of ε' and $\tan \delta$ dramatically increase by many orders of magnitude. For the PP/MWCNT the values of $\tan \delta$ were found to be higher than that for PVC/MWCNT composites. Such an effect can be caused by the presence of ionic conductivity in PVC which compensates the electronic conductivity of MWCNTs thus decreasing the $\tan \delta$ values.

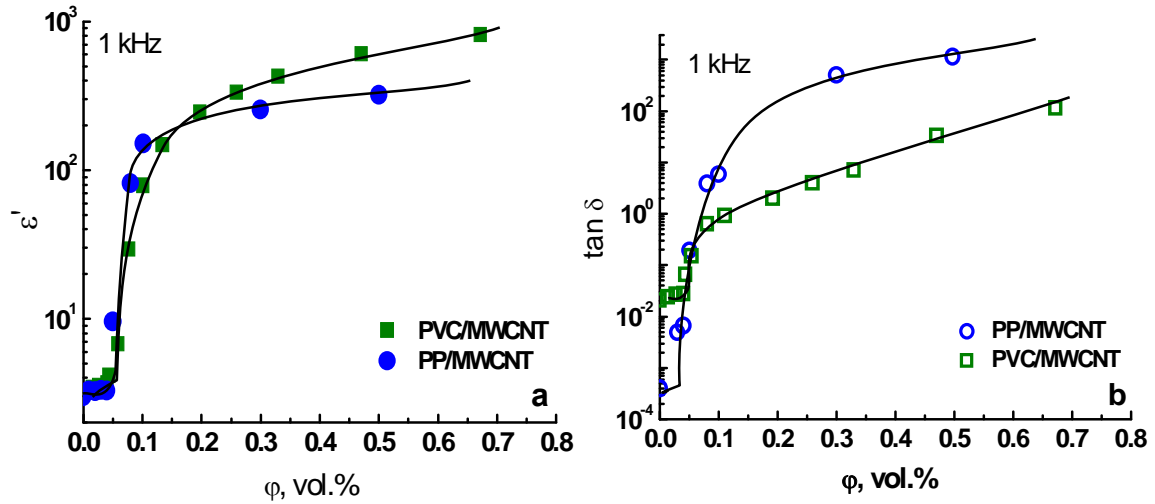


Fig. 3.9. Percolation behavior of the dielectric parameters ϵ' (a) and $\tan \delta$ (b) of the PVC/MWCNT and PP/MWCNT composites at 1 kHz.

It is seen that the values of $\tan \delta$ are significantly higher for lower frequencies (Fig 3.10). Since $\tan \delta$ indicates a part of the electromagnetic energy which is dissipated in a composite, the polymer/MWCNT composites can be considered as the potential protective shielding materials for electromagnetic irradiation (EMI). Thus, it is necessary to provide the high values of electromagnetic losses in the wide range of frequencies including those above $>10^5$ Hz. As it follows from this plot, in order to increase the conductivity and to reach higher values of $\tan \delta$ at high frequency it is necessary to increase the MWCNTs concentration in the polymer matrix.

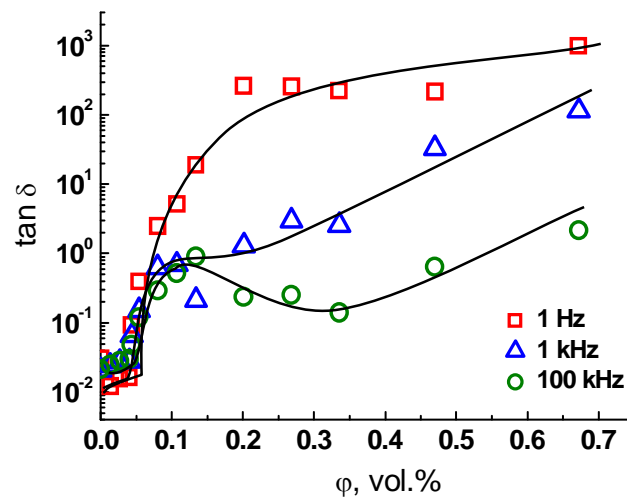


Fig. 3.10. Percolation behavior of $\tan \delta$ of the PVC/MWCNT composites at different frequencies.

A very low concentration of MWCNTs in the composites and a specific type of their distribution as the nanotube framework remains most part of the polymer in the neat state within framework. Consequently, one could expect the dielectric properties of PVC/MWCNT and PP/MWCNT composites close to those ones in the unfilled PVC or PP. However, the experimental data reveal very high contribution of conductive phase in the dielectric response. We can assume that majority of nanotubes creating the framework takes part in conductivity due to their high local concentration φ_{loc} in the walls of the framework whereas in usual statistical conductive clusters only small part of particles creates a conductive skeleton [41], and the rest ones are dead ends and non-conductive side branches.

3.2. Thermo-mechanical behavior of segregated polymer composites.

Thermomechanical analysis (TMA) enables to follow the change of physical polymer state during the temperature change. Depending on temperature the thermomechanical curve reflects three regions of the polymer mechanical deformation. They correspond to the glassy, high-elastic and viscous-flow state of polymer with the values of transition temperature between those states [42]. Transition temperatures for the PVC/MWCNT composites are shown in Fig. 3.11: T_g is a glass-transition temperature and above this temperature, at T_e , the polymer transforms to the high-elastic state which can also be characterized by the value of the equilibrium high-elastic deformation L_e [43]. Further increase of the temperature leads to a polymer transition to viscous-flow (plastic) state at temperature T_p .

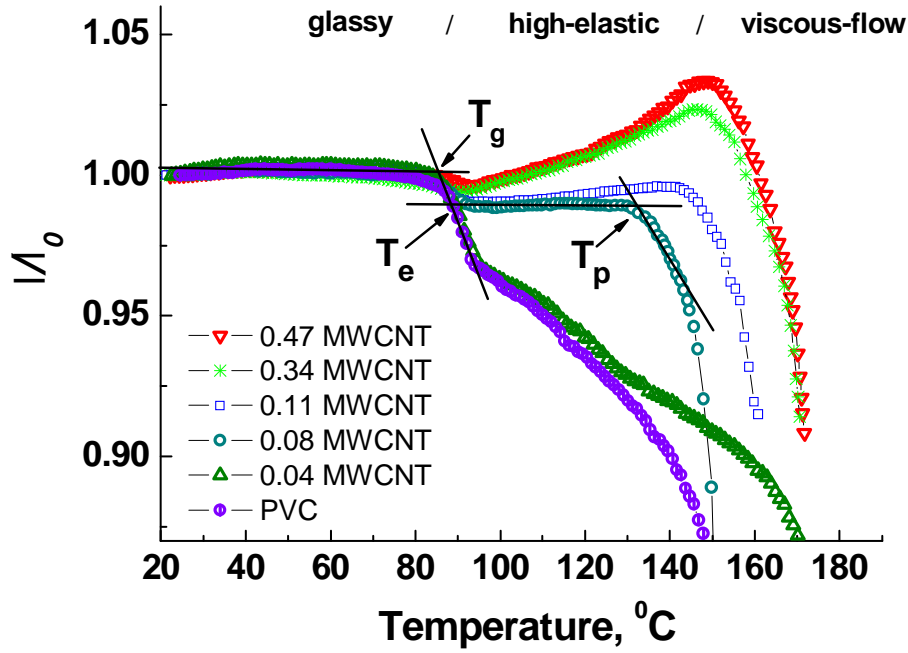


Fig. 3.11. Thermomechanical curves of the PVC/MWCNT composites with different content of filler.

The experimental thermomechanical curves of the PVC/MWCNT composites with different content of nanotubes are also presented in Fig. 3.11 where l (μm) – the thickness of the sample at investigated temperature, l_0 (μm) – the initial sample thickness.

A sharp change of the deformation is observed on all TMA curves as a result of transition from glassy to high-elastic state. The biggest values of deformation revealed pure PVC and PVC composite with 0.04% MWCNT. These values of high-elastic deformation L_e were calculated from the relation:

$$L_e = \frac{\Delta l}{l_0}, \quad (3.17)$$

where $\Delta l = l - l_0$ (μm) is the sample deformation. This deformation decreases with the increase of the filler concentration and is associated with value of high-elastic deformation L_e , which enables to calculate the equilibrium high-elastic module E_e [44]:

$$E_e = \frac{P}{L_e}, \quad (3.18)$$

where P (MPa) is the applied pressure on the sample, L_e (%) is the relative value of high-elastic deformation at T_e . For all examined composites the values of E_e and T_e are listed in the table 3.1.

One can see, that the values of T_e are constant whereas the values of E_e dramatically increase when the filler concentrations are higher than 0.04 vol. % i.e. above percolation threshold. This fact indicates the formation of the hard nanotube framework which influences the mechanical properties of the composite. The pronounced region of high-elastic state (high-elasticity plateau) appears when the concentration of MWCNTs is higher than 0.04 vol. %. In pure PVC and composite with 0.04 vol. % MWCNT the region of high-elasticity is smoothed because of the contribution of the plastic deformation at temperatures close to T_e .

Table 3.1. TMA and DSC data for the PVC/MWCNT composites.

| φ , vol. % | T_g (TMA), °C | T_g (DSC), °C | T_e , °C | T_p , °C | E_e , MPa |
|--------------------|-----------------|-----------------|------------|------------|-------------|
| 0 | 87 | 84.1 | 93 | - | 29.2 |
| 0.04 | 86 | - | 95 | - | 28.2 |
| 0.08 | 85 | 84.9 | 93 | 131 | 80.8 |
| 0.11 | 85 | 85.2 | 92 | 146 | 731 |
| 0.34 | 86 | 84.6 | 91 | 148 | 137.1 |
| 0.47 | 87 | 85.4 | 93 | 150 | 154.2 |

The presence of high-elasticity plateau is inherent to the volume structured polymers [42] whereas PVC is a linear polymer. Hence, an appearance of this region on TMA curve is caused by forming of the spatial macroscopic filler framework with period, which equals to the size of the polymer particles (Fig 3.5). Such a framework formed with nanotubes results in appearance of high-elastic state of PVC composites in a presence of physical interaction between filler and polymer matrix. Similar behavior of thermomechanical curves was observed for the PE/MWCNT systems at high concentration of filler [38]. The authors explain a

presence of the high-elasticity region in the TMA curve by creation of the network in the polymer matrix and blocking of mobility of the PE macromolecules.

It is necessary to note, that with growth of the filler concentration the extension of the high-elasticity plateau increases i.e. value of T_p is shifted to high temperatures (see table 3.1). It indicates the increase of framework rigidity, what restrains the transition of composite in viscous-flow state and leads to the increase of E_e values. Relaxation of internal stresses at $T > T_e$ (which can exist in polymer at temperature below T_g) leads to distortion of the high-elastic plateau. At filler concentration higher than 0.1% the high-elasticity plateau changes its form i.e. gains a typical view for the systems with relaxation of the internal stresses when the L_e value decreases with the increase of temperature [42]. The curves reflect more pronounced effect in the composites with higher content of nanotubes. During hot compacting the spherical polymer particles are deformed together with framework and create a compact matrix at applied pressure. Then this deformation is freezing at cooling of the sample below T_g . Heating above T_g enables the relaxation of stresses in the framework and, as a result, the inverse deformation which is accompanied by the expansion of the sample. Note, that during the measurement a pressure on the sample (1 MPa) is much lower than the pressure applied to the sample during hot compacting and cooling (about 20 MPa). The upper curves in Fig. 3.11 demonstrate that the more rigid framework with filling is formed, the higher inverse deformation is achieved. The Table 3.1 data show that glass-transition temperature T_g obtained both via TMA and DSC methods remains constant with increase of the filler concentration. The boundary layer with properties different from those for pure polymer exists nearby the surface of filler and thus it can shift the value of glass-transition temperature T_g (to increase or to decrease depending on the interaction energy polymer-filler) [45, 46]. The model of segregated system [14] stipulates that filling of composite leads to the increase of the number of the filler layers in the walls of the conductive framework (where the local concentration of filler is maximal) whereas the main part of polymer is unfilled. Hence, the boundary layer with different value of T_g is localized near the walls of framework while basic part of

polymer, which is distributed between walls of framework exists in the unperturbed state.

Consequently influence of the framework on T_g values is minimal. On the other hand, DSC results show a slight trend to T_g increase, what correlates with influence of the filler framework on mechanical properties of the composites. Thus, the thermomechanical study evinces the creation of the rigid coherent MWCNTs framework in the PVC matrix above percolation threshold and simultaneously with appearance of electro-conductivity. Growth of MWCNTs content leads to the increase of the conductivity and the rigidity of the framework.

Conclusions

In the segregated systems PVC/MWCNT and PP/MWCNT which processed by hot compacting method the MWCNTs create the conductive skeleton at the value of the ultralow percolation threshold $\varphi_c = 0.045$ vol. % and $\varphi_c = 0.04$ vol. %, respectively. The obtained ultralow value of percolation threshold is caused by both high aspect ratio of MWCNTs and existence of segregated structure.

Pure PVC and PVC composite with the MWCNTs content below φ_c demonstrate strong temperature dependence of σ in the range $T > T_g$, what can be caused by increasing of the charge carrier mobility and its dependence on viscosity of a medium. The increase of the nanotube content higher than that at percolation threshold leads to the appearance of electronic conductivity through the filler phase which is independent whatever on the temperature. Frequency dependence of the dielectric parameters ε' , ε'' and conductivity σ_{AC} demonstrates different behavior below and above percolation threshold. Below φ_c the values ε' and ε'' are independent on frequency while σ_{AC} curves have a slope close to 1 that clearly indicates the insulating properties. Above φ_c , when the composites become conductive, the polarization gives a contribution to the complex dielectric permittivity, what is resulted in the increasing of ε' and ε'' with the frequency decrease. Simultaneously the conductivity increases and gives higher contribution in the dielectric parameters. The experimental values of critical exponents $x = 0.91$ and $y = 0.18$ satisfactorily obey the general scaling relation $x + y = 1$ and are

confined with an approach of the intercluster polarization (IP) model. At fixed frequency the values of the dielectric parameters ε' and $\tan \delta$ reveal the percolation behavior as well.

Thermomechanical properties of composites correlate with electrical and dielectric properties. Forming of the filler framework in the composites at MWCNT content above percolation threshold leads to creation of the high-elasticity plateau on the TMA curves. It is caused by the restrictive influence of skeleton on transition of polymer to the viscous-flow (plastic) state. Growth of the elastic module E_e values indicates the increase of the framework hardness in the composites with high values of MWCNTs.

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Chapter 4

Specificities of the conducting phase formation in polymer blends

Introduction

- 4.1. Spatial distribution of the MWCNTs in heterogeneous polymer matrix.
 - 4.1.1. *Thermodynamic factor.*
 - 4.1.2. *Kinetic factor.*
 - 4.1.3. *Processing factor.*
- 4.2. Electrical properties of the composites.
- 4.3. Structure of nanocomposites.
- 4.4. The temperature dependence of conductivity in CPA and polymer blends CPA/PP filled with MWCNT.
- 4.5. Mechanical properties of the composites (stress-contraction test).
- 4.6. Dynamic mechanical analysis of the conductive polymer blends.

Conclusions

Introduction

Conductive polymer composites (CPC) filled with conductive fillers are of great interest because of their wide range of application. Carbon nanotubes (CNT) were found to be one of the promising conductive filler, which initially attracted the researchers' attention [1, 2]. Besides, it turned out that high conductivity of the CNT is one of their unique properties, such as thermal, optical and mechanical ones [3, 4]. Nowadays the investigations of CPC filled with carbon nanotubes are mainly focused on the decreasing of the percolation threshold value and improving the processability. The electrical properties of the CPC filled with carbon nanotubes and their percolation behaviour depend on many factors, particularly, on a kind of polymer matrix, type of CNT, spatial distribution of nanotubes, interfacial interaction polymer–filler, etc.

Experimental values of percolation threshold of CPC depending on the different parameters vary in a wide range, $\varphi_c = (0.0025 \div 10) \%$ [5-10]. The attained low values of φ_c are attractive because the conductive composites can be obtained at very low content of nanotubes. Such low values of percolation threshold are caused by high ratio length/diameter of nanotubes, which can be equal to $(100 \div 1000)$ and provide the presence of contacts between individual nanotubes even at their small content in polymer matrix. However, the attainment of low φ_c values is impeded by experimental difficulties of separation of the curled and tangled long nanotubes and, as a result, leads to a presence of aggregates, which heightens the percolation threshold.

One of the ways to reduce the percolation threshold in the composite is to induce inhomogeneous distribution of the filler in polymer matrix [11, 12]. Introduction of the CNT into binary polymer blends can significantly decreases the value of the percolation threshold due to double percolation effect in heterogeneous matrix [11, 13-15]. Such an effect is caused by the formation of a co-continuous phase morphology of two polymers, where the conductive filler is localized in one polymer phase or on the interface [12, 16]. In [11, 13] the authors reported about low percolation threshold in PVDF/PA6/CNT and PA6/PP/CNT composites in which conductive nanotubes were selectively located in the PA6

phase and conductive PA6/CNT domains were dispersed in the PVDF or PP phase. The effect of double percolation in conductive polymer blends filled with carbon black was also investigated and reported in [17-19].

On the other hand, the polymer blend-composites are of interest due to the possibility to obtain the materials with combination of properties of both blended components. Co-continuous structure of polymer blends can give the maximum contribution of the mechanical modulus from each component simultaneously [20]. The deep interest of PA/PP polymer blends is caused by rather good mechanical properties of PA and easy processability of PP. On the other hand, heterogeneous system with immiscible components has reduced mechanical characteristics due to the presence of the boundary between two components with low adhesion to each other. Incorporation of the carbon nanotubes, which have the high elastic modulus, into the polymer blends can improve significantly the mechanical properties of the obtained composites. L. Zhang et al. have reported that in PA6/PP/MWCNT composites the MWCNTs were preferentially located in the PA 6 phase and a small amount of MWCNTs were located in the interface between the polymers [21]. MWCNTs, localized in the interface, have bridged two phases, what is important for the load transfer through the polymer matrix and growth of such characteristics as the complex viscosity, storage modulus and loss modulus of the blends [13]. Similar effect was reported for PC/CNT/PE polymer blends where MWCNT bridged the PC and PE phases [15].

The results of the study of the polymer blends structure based on polypropylene and low-melting co-polyamide filled with carbon nanotubes will be presented in this Chapter. The influence of spatial distribution of the conductive filler on electrical and mechanical characteristics of polymer composites will be also discussed.

4.1. Spatial distribution of the CNT in heterogeneous polymer matrix.

In the described investigation polypropylene (PP) and co-polyamide (CPA) with low melting temperature $T_m = 125\text{ }^{\circ}\text{C}$ were used as the polymer components

of composites. The multiwalled carbon nanotubes (MWCNTs) were used as conductive filler.

The filled blends were processed in two ways. In one case the MWCNTs was introduced into polymer component with lower viscosity (CPA), then the CPA-4% MWCNT concentrate was diluted by pure PP, and the composite PP/CPA-MWCNT was obtained. In the second case, on the contrary, the concentrate PP-3% MWCNT was diluted by pure CPA in order to obtain the composite CPA/PP-MWCNT. Such diluting of concentrates with pure polymer matrix leads to the change of polymer components ratio along with the change of the filler content. The content of composites is given in Table 4.1. For CPA/PP-MWCNT composites was used the concentrate filled with 3 vol. % of MWCNTs because at such nanotubes content in the composites PP/MWCNT the highest level of conductivity has been achieved. In the case of CPA/MWCNT composites the highest level of conductivity has been achieved at 4 vol. %.

Table 4.1. The content of composites PP/CPA-CNT and CPA/PP-CNT depending on filler content ϕ_{MWCNT} .

| PP/CPA-MWCNT | $\phi_{MWCNT},$ % | PP, vol. % | CPA, vol. % |
|----------------------------------|----------------------|------------|-------------|
| Symbols in the Figs. 4.1 and 4.2 | | | |
| - | 4 | 0 | 96 |
| c | 3 | 25 | 72 |
| - | 2 | 50 | 48 |
| b | 1.5 | 62.5 | 36 |
| - | 1 | 75 | 24 |
| a | 0.5 | 87.5 | 12 |
| - | 0 | 100 | 0 |
| CPA/PP-MWCNT | | | |
| Symbols in the Figs. 4.1 and 4.2 | | | |
| - | 3 | 97 | 0 |
| - | 2.5 | 80.8 | 16.7 |
| f | 2 | 65 | 33 |
| e | 1.5 | 48.5 | 50 |
| d | 1 | 32 | 67 |
| - | 0 | 0 | 100 |

Binary polymer blend of the incompatible polymers creates the heterogeneous structure of matrix. When a filler is introduced in polymer blend, three cases of filler spatial distribution can take place. First, the filler can be distributed randomly within polymer blend. Second, it can occupy one of the polymer components. Third, it can be localized on the boundary between polymer components.

The type of the filled blend morphology depends on the following factors:

- *thermodynamic factor* (relationship between the interface surface tension polymer1-filler γ_{fp1} , polymer2-filler γ_{fp2} , and polymer-polymer γ_{p1p2});
- *kinetic factor* (relationship between viscosities of polymer components η_{p1} and η_{p2} at the temperature of processing);
- *processing factor* (methods of the filler introduction into the complex polymer matrix, it can enhance or depress the influence of thermodynamic and kinetic factors).

4.1.1. Thermodynamic factor.

The behaviour of the filler particles around the boundary of two polymer melts is defined by the value of the wetting coefficient ω [22]:

$$\omega = \frac{\gamma_{fp1} - \gamma_{fp2}}{\gamma_{p1p2}}, \quad (4.1)$$

where γ_{fp1} , γ_{fp2} , γ_{p1p2} are the interfacial tension between filler and polymer 1, between filler and polymer 2 and between polymer 1 and polymer 2, respectively. If the wetting coefficient is higher than 1 ($\omega > 1$) or less than -1 ($\omega < -1$) the filler is localized in polymer 2 or in polymer 1, respectively. If the value of wetting coefficient lies between -1 and 1, the filler is localized at the interface between the two polymers.

The interfacial tension can be evaluated from the surface energies of the components from the Fowkes equation [23]:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1 \cdot \gamma_2}. \quad (4.2)$$

Generally, the surface tension includes non-polar, dispersive part γ^d and polar part γ^p :

$$\gamma = \gamma^d + \gamma^p. \quad (4.3)$$

The equation (4.2) gives the adequate results for non-polar and weakly polar polymers. However, if the polar part is essential, it is necessary to use a harmonic-mean equation (4.4) or a geometric-mean equation (4.5):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \right), \quad (4.4)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\sqrt{\gamma_1^d \gamma_2^d} + \sqrt{\gamma_1^p \gamma_2^p}), \quad (4.5)$$

where γ_1 and γ_2 are the surface tensions of the components 1 and 2, respectively; γ_1^d, γ_2^d are the dispersive parts (γ_1^p, γ_2^p are the polar parts) of the surface tension of components 1 and 2, respectively.

The surface tension values (dispersive and polar parts) of PP at 20 °C were taken from [23, 24], and for nanotubes they were evaluated from [25]. Since we do not have the experimental results of surface tensions for CPA, these values were calculated in accordance with the fraction of the individual polyamides in the copolyamide. The ratio of polyamide ingredients in CPA is PA6/PA6.6/PA6.10=70/6/24. Then the values of γ (γ^d and γ^p) were calculated as:

$$\gamma_{CPA} = 0.7\gamma_{PA6} + 0.06\gamma_{PA6.6} + 0.24\gamma_{PA6.10}. \quad (4.6)$$

The values of γ (γ^d and γ^p) for polyamides were reported in [24, 26]. Surface tensions of the composite components at the processing temperature (200 °C) were calculated as

$$\gamma_{T2} = \gamma_{T1} - \partial\gamma / \partial T \cdot (T_2 - T_1), \quad (4.7)$$

where $T_1=20$ °C, $T_2=200$ °C. The values of temperature coefficients $\partial\gamma/\partial T$ were taken from [24, 26, 12]. The calculated values of interfacial energy γ_{12} for the components of composites evaluated by the eq. (4.5) were equal to 10.3 mJ/m², 19.4 mJ/m² and 4.3 mJ/m² for the PP-MWCPA, PP-MWCNT and CPA-MWCNT interfacial tension, respectively. The values of calculated parameters of the surface tension are given in the Table 4.2.

Table 4.2. Surface tensions of polymers and carbon nanotubes at 20 °C and 200 °C.

| Material | γ , mJ/m ² | | γ^d , mJ/m ² | | γ^p , mJ/m ² | | $d\gamma/dT$, mJ/(m ² ·°C) |
|----------|------------------------------|--------|--------------------------------|--------|--------------------------------|--------|--|
| | 20 °C | 200 °C | 20 °C | 200 °C | 20 °C | 200 °C | |
| PA 6 | 52 | – | 37.4 | – | 14.6 | – | – |
| PA 6.6 | 46.5 | – | 32.5 | – | 14.0 | – | – |
| PA 6.10 | 40.7 | – | 36 | – | 4.7 | – | – |
| CPA | 49 | 37.3 | 36.8 | 27.7 | 12.2 | 9.6 | 0.065 |
| PP | 30.1 | 19.7 | 30.1 | 19.7 | 0.0 | 0.0 | 0.058 |
| MWCNTs | 45.3 | 31.8 | 18.6 | 13.0 | 26.7 | 18.8 | 0.075 |

The calculations according to eq. (4.1) have shown that wetting coefficient is higher than 1 ($\omega=1.5$), what indicates that the filler is localized in co-polyamide under impact of thermodynamic factor.

4.1.2. Kinetic factor.

If polymer components have different values of melt viscosities ($\eta_{p1} \gg \eta_{p2}$), then it is necessary to consider the influence of the kinetic factor. In this case, during mixing process, the filler is localized in one of polymer components, which has lower viscosity, but only on conditions that processing and thermodynamic factors are the same for both polymer components. The viscosities of PP and CPA are strongly different. Thus, for PP and CPA the $MFI_{190/2.16}$ values are equal to 0.5 g/10 min and 11.8 g/10 min, respectively, i.e. CPA is less viscous. Therefore, the kinetic factor intensifies the influence of thermodynamic factor in polymer blend PP/CPA-CNT.

4.1.3. Processing factor.

The processing factor depends on the conditions of the filler introduction into polymer matrix. The filled blends were processed in two stages by diluting of filled polymer component 1 with pure polymer component 2. Since the MWCNTs is primary introduced in the defined polymer with thermodynamic or kinetic

parameters which provide higher or lower interaction with filler, the processing factor could intensify or weaken the influence of kinetic and thermodynamic factors.

4.2. Electrical properties of the composites.

In order to determine the relationship between the morphology and the electrical properties, the direct current (DC) conductivity σ_{DC} of the CPA/MWCNT, PP/CPA-MWCNT and PP/MWCNT, CPA/PP-MWCNT composites as a function of the carbon nanotubes content was investigated.

Polymer blends filled with carbon nanotubes, prepared by two-stage method (a filled polymer concentrate was diluted by another pure polymer), revealed similar regularities. The filled polymer composites CPA/MWCNT reveal the percolation threshold at $\varphi_c=1.4$ vol. %. If one dilutes the concentrate of CPA-4 vol. % MWCNT by pure PP, the value of percolation threshold of polymer blend is reduced to $\varphi_c=0.7$ vol. % (Fig. 4.1-a). In this case the significant reduction of percolation threshold was achieved by the ordered distribution of the filler in one polymer phase due to mutually action of three factors – thermodynamic, kinetic and processing, which affect in the same “direction” and contribute to such morphology. MWCNTs were previously introduced into CPA matrix, which is less viscous than PP, and carbon nanotubes are stayed in the CPA phase due to higher interaction of CPA-MWCNT than PP-MWCNT.

In order to demonstrate the influence of the filler distribution on electrical characteristics, the composites based on PP/MWCNT masterbatch diluted by pure CPA were also prepared. The opposite polymer blend CPA/PP-MWCNT prepared by diluting of the concentrate PP - 3 vol. % of MWCNTs with pure polymer reveals the increase of percolation threshold ($\varphi_c=1.4$ vol. %) in comparison with the filled PP/MWCNT composite with $\varphi_c=0.7$ vol. % (Fig. 4.1-b). In this case the nanotubes migrate from the PP phase to the CPA phase during mixing in the extruder, and the filler is re-localized between PP and CPA phases.

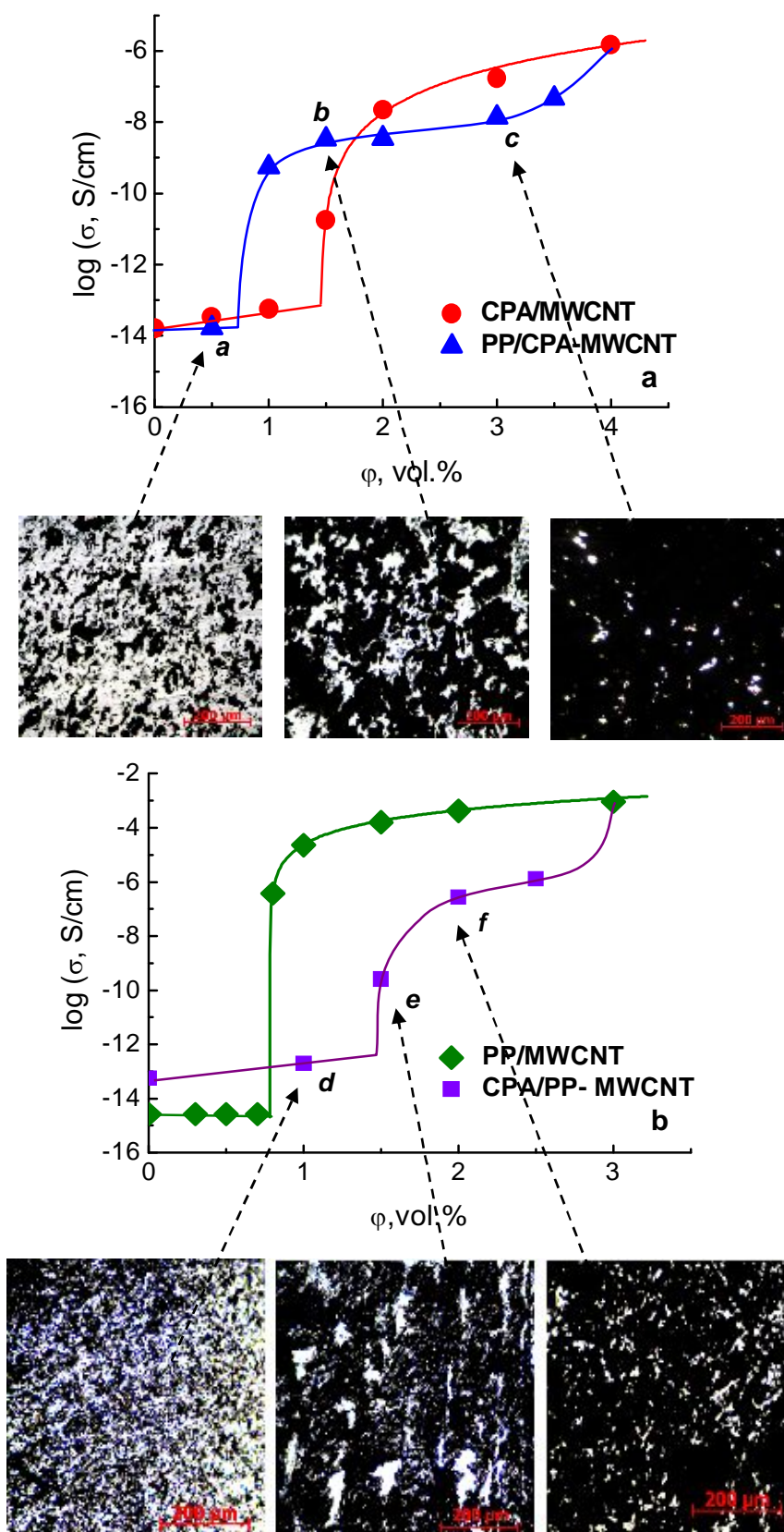


Fig. 4.1. Dependence of conductivity on filler content for the filled polymers and polymer blends CPA/CNT and PP/CPA-MWCNT (a), PP-MWCNT and CPA/PP-MWCNT (b).

It is necessary to notice that for PP/MWCNT composites the percolation threshold $\varphi_c=0.7$ vol. % was found to be lower than that for CPA/MWCNT $\varphi_c=1.4$ vol. %. Such difference in the percolation threshold values is the result of different level of interaction between the carbon nanotubes and polymer matrices. The mentioned above analysis of thermodynamic factor have shown that CPA has higher interaction with MWCNTs than with PP. Around the carbon nanotubes can form the thin layer of CPA which prevents the formation of the contacts between carbon nanotubes, thus, increasing the value of percolation threshold and decreasing the level of conductivity of CPA/MWCNT composites.

4.3. Structure of nanocomposites.

Such a behaviour of percolation curves is caused by the change in the nanocomposites structure during melt mixing. The changes of the structure after diluting of CPA-4 %MWCNT concentrate with pure PP and PP-3%MWCNT concentrate with pure CPA are shown in Fig. 4.2 (a–c) and 4.2 (d–f), respectively. The increase of pure polymer part in the filled polymer blend leads to the decrease of the filler fraction together with the content of the filler-containing polymer component (see Table 4.1). The adding of small amounts of pure PP to CPA-4%MWCNT leads to PP localization in a form of separated inclusions (Fig. 4.2-c). Then, the filler-containing component CPA-CNT and the pure polymer create co-continuous structure (Fig. 4.2-b). Such a structure corresponds to a plateau on the percolation curve (Fig. 4.1-a, points "c" and "b"). High amounts of PP destroy conductive network created by CPA filled with MWCNTs, and the CPA-MWCNT phase exists in the form of separated conductive inclusions in PP. This structure is non-conductive below the percolation threshold (Fig. 4.1-a, point "a"). The value of percolation threshold ($\varphi_c=0.7$ vol. %) corresponds to the ratio PP/CPA-CNT = 85/15, i.e., the CPA-MWCNT phase maintains its continuity and, consequently, its conductivity up to rather low volume content (15 vol. %). The presence of conductivity at such low content of concentrate illustrates the concept of double percolation which claims the conductivity availability, first, in the presence of filler-containing polymer phase continuity, and, second, at filler

network continuity within this polymer component. For the PP/CPA-MWCNT blends, the percolation threshold value is defined by the creation/destruction of the polymer network, where the filler is maintained within CPA and provides the conductivity of this filler-containing phase.

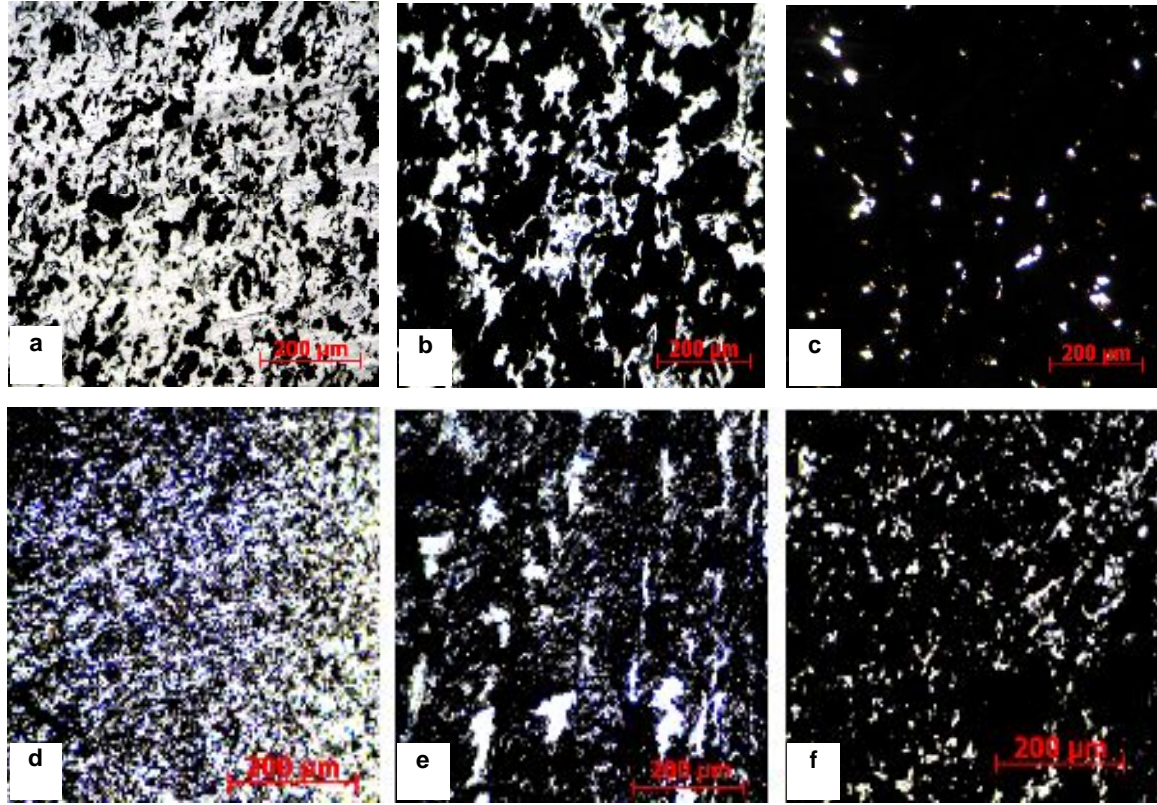


Fig. 4.2. Optical microscope images of the structure of PP/CPA-MWCNT (a–c) and CPA/PP-MWCNT (e–f) filled polymer blends. The symbols (a–c) and (d–f) indicate the points, corresponding to the composites structure, shown on the percolation curves of the polymer blends in Fig. 4.1.

For the other CPA/PP-MWCNT blends obtained by diluting of PP-3%MWCNT concentrate with pure CPA, the transfer of MWCNTs from PP to CPA occurred in accordance with thermodynamic and kinetic factors. As a consequence, during mixing the filler is distributed in both of polymer components and, finally, if the mixing process is long enough, MWCNTs completely moves into CPA. In Fig. 4.2-f, one can see the structure of the filled blend at CPA/PP-MWCNT ratio of 33/67 (point "f" in Fig. 4.1-b, Table 4.1), when the polymer blend is conductive Here one can see small pure inclusions of CPA. At CPA/PP-MWCNT ratio of 50/50, the conductivity of the blend begins to decrease

(point "e" in Fig. 4.1-b). The value of percolation threshold ($\phi_c=1.4$ vol.%) corresponds to a CPA/PP-MWCNT ratio of 52/48 (i.e., the structure in Fig. 4.2-e is close to non-conductive state). Nanotubes are mostly distributed in both polymer components, and some pure inclusions of PP phase without nanotubes are obviously present.

Based on the double percolation concept, it can be concluded that in this case, filler network is destroyed due to MWCNTs transition from PP into CPA, whereas co-continuous polymer network (polymer ratio CPA/PP is close to 50/50) retains to be intact. Further diluting of PP-3 vol. % MWCNT concentrate results in the morphology with uniformly distributed small inclusions of CPA-MWCNT phase among half pure PP inclusions of PP phase (Fig. 4.2-d). Such a morphology of the composite corresponds to the point "d" in Fig. 4.1-b, which lies below the percolation threshold.

Thus, one can conclude that the processing factor (the order of filler introduction in polymer blend) plays a key role in the structure of the filled polymer blends. The processing factor interacts with thermodynamic and kinetic factors, while increasing their impact in one case and impeding their influence in another one.

One can conclude that:

| Polymer composites : PP/CPA-MWCNT | Polymer composites : CPA/PP-MWCNT |
|--|--|
| MWCNTs are previously introduced in CPA and diluted by pure PP. | MWCNTs are previously introduced in PP and diluted by pure CPA. |
| CPA is <i>less viscous</i> than PP therefore carbon nanotubes are absorbed in CPA component during mixing. | CPA is <i>less viscous</i> than PP therefore carbon nanotubes are migrated to CPA component during mixing. |
| MWCNT localized in co-polyamide under impact of thermodynamic factor | MWCNT migrate to co-polyamide under impact of thermodynamic factor |
| <i>Processing, kinetic and thermodynamic</i> factors affect in the same direction, | <i>Processing</i> factor affects in opposite direction to <i>kinetic</i> and <i>thermodynamic</i> factors. |
| MWCNT are localized in percolating CPA phase, $\phi_c=0.7$ vol. %. | MWCNT are distributed in whole polymer matrix, $\phi_c=1.4$ vol. %. |

4.4. The temperature dependence of conductivity in CPA and polymer blends CPA/PP filled with MWCNT.

In order to understand the mechanism of charge transport in the nanocomposites the temperature dependence of conductivity was investigated. The conductivity of the dry CPA, CPA/MWCNT and PP/CPA-MWCNT composites as a function of temperature was measured. Fig. 4.3 shows the dependence of the direct current conductivity σ_{DC} on the temperature for the pure CPA and polymer composites based on CPA filled with different amount of MWCNTs.

For pure CPA (green curve) the conductivity grows with the temperature increase, what indicates the ionic type of conductivity. D. A. Seanor [27] suggested that in dry polyamide 66 the different types of conduction mechanisms take place, and charge transport depends on temperature. In PA 66 at the temperatures below 80 °C electrons and positive holes are created in the amide linkages, and conductivity mechanism is electronic one. With the temperature increase the conductivity of nylon 66 is mostly PROTONIC –ionic- because of self-ionization of the amide groups.

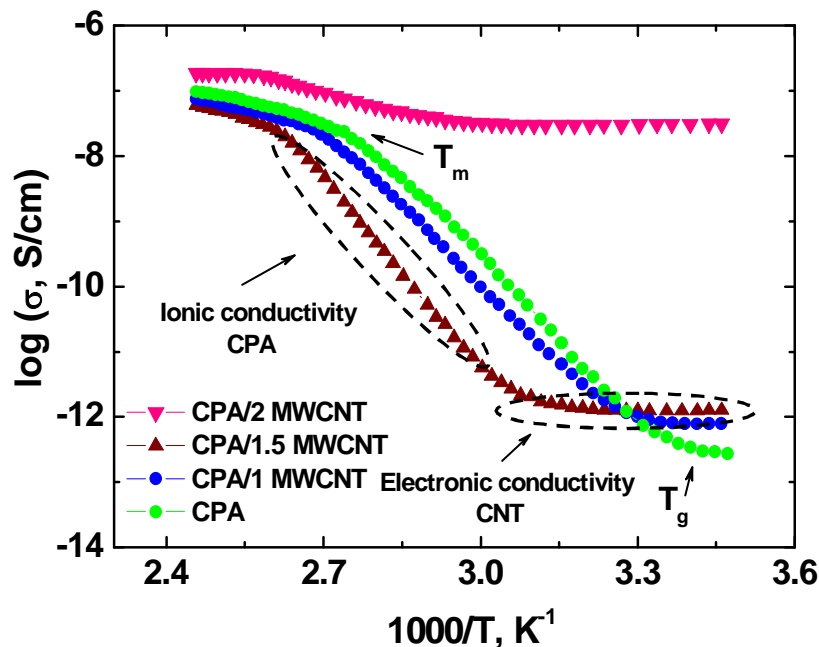


Fig. 4.3. The dependence of σ_{DC} on the temperature for pure CPA and composites filled with different concentration of CNT.

At lower temperatures in nylon 66 electronic charge transfer is realized through hydrogen bonds (Fig. 4.4). In this case the charge mobility does not depend on the rotation of the amide groups [28]. Nevertheless, at lower temperatures molecular rotation cannot assist in the creation of charge carriers, thus, the electronic conduction is low.

With the temperature increase the conductivity mechanism is modified from electronic to ionic one because of the changes of charge carrier mobilities and recombination rates. At high temperatures molecular motion becomes intensive, and the hydrogen-bonded network destroys, thus, the probability of recombination increases, and the electronic contribution discontinues. Due to this, ionic mobility becomes greater, and the probability of ion recombination is reduced [29].

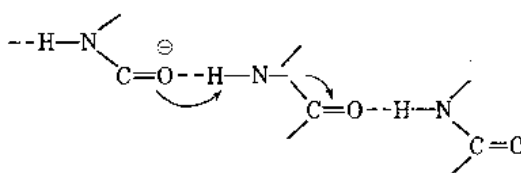
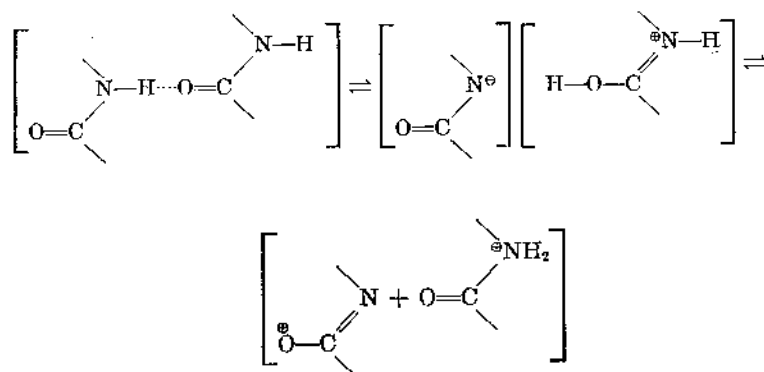


Fig. 4.4. Electronic charge transfer in PA 66 realized through hydrogen bonds [28].

The ionic conductivity is controlled by self-ionization and proton mobility. In the mechanism of self-ionization of the amide groups, two amide links in neighboring chains are disproportionate, what results in the following process [28]:



Later a proton alone or a proton and an electron are transferred. The mobility of the proton is determined by the local mobility of the polymer segments.

For the investigated pure CPA the conductivity above the temperature, which is associated with glass transition T_g increases significantly (Fig. 4.3). Such

a behaviour suggests that above T_g in CPA the ionic conductivity appears which is governed by the motion of the polymeric chains. It has been found that the temperature dependence of the CPA/MWCNT composites depends on MWCNT content and demonstrates different behavior below and above the percolation threshold. For the composites filled with MWCNTs the curves on the plot can be characterized by two regions. The first one is localized at lower temperatures and associated with electronic conductivity of MWCNTs and the second one is localized at higher temperatures and associated with the ionic conductivity of CPA. We can also note that presence of carbon nanotubes in the composites with the concentrations lower than percolation threshold results in the increase of T_g values (Fig. 4.3). For the composite with 2 vol. % of MWCNTs (above percolation threshold) it is difficult to analyze the value of T_g because of electronic conductivity of CNT which predominates the ionic conductivity of CPA in the wide temperature range.

For the PP/CPA-MWCNT nanocomposites the change of DC conductivity is starting at the temperature close to the melting point of CPA, $T_m=125\text{ }^{\circ}\text{C}$ (DSC) when the conductive phase of concentrate CPA-4%MWCNT is completely in melted state (Fig. 4.5).

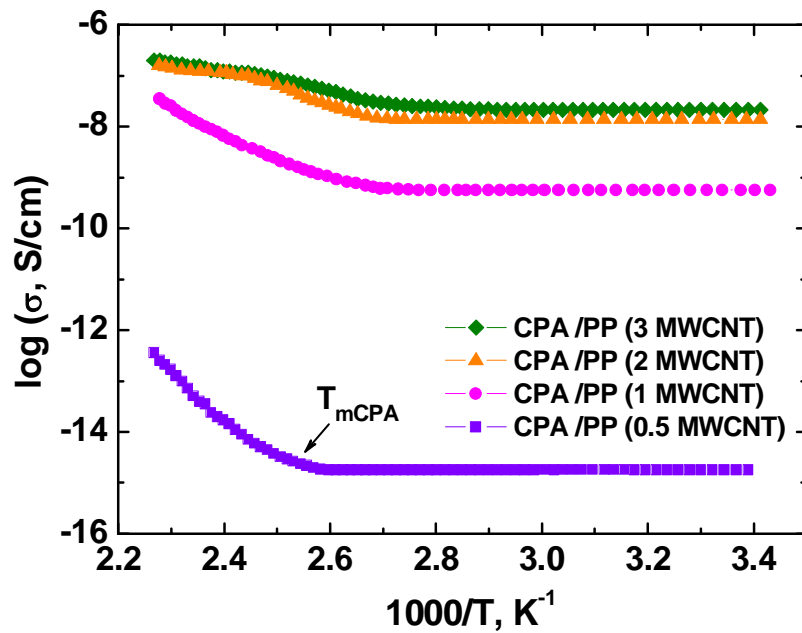


Fig. 4.5. The dependence of σ_{DC} on the temperature for polymer blends which were obtained by the dilution of concentrate CPA-4%CNT with pure PP.

The influence of MWCNTs on the morphology and crystallization of CPA was analyzed by DSC method. The DSC results are summarized in Table 4.4. As it follows from the table, the degree of crystallinity χ_c increases with the growth of the MWCNTs content in the nanocomposites. The addition of nucleation centers, such as carbon nanotubes, leads to an increase of the crystallinity degree [30]. For the investigated samples such an effect was found only for the composites with low filler content. For the system with the concentration of MWCNTs be equal to 4 vol. % the degree of crystallinity decreases compared to the composites with low nanotubes content (see Table 4.3). At high MWCNTs content the polymer cannot crystallize as good as at low filler content because of high nanotube density which restricts the motion of CPA chains and can block the formation of the crystallites during crystallization.

The results, listed in Table 4.3 can also indicate the growth of the glass transition temperature as the content of MWCNT increases. Such an effect can be caused by the strong polymer-filler interaction in the amorphous phase of CPA and by the formation of an immobilized interfacial layer around carbon nanotubes [30]. Nevertheless, at high filler content (4 vol. %) the T_g value is close to that of pure polymer matrix. This behavior can be interpreted by the increase of the system free volume at high filler content. With the increase of free volume the molecular mobility of the polymer chains increases, what results in the cooperative motion of the polymer chains at lower temperature [30].

The presence of strong polymer-filler interaction which influence on the percolation threshold value and maximal level of conductivity of CPA/MWCNT composites can be analyzed by the heat capacity step of glass transition ΔC_p . The heat capacity in Table 4.3 grows up as the content of MWCNTs increases. The degree of crystallinity for these composites increases, and it means that a part of the amorphous phase decreases. That is why the heat capacity step of the glass transition also should decrease. But for our systems we can notice the opposite effect. Such result can be interpreted in terms of formation of the immobilized portion of the polymer around the MWCNTs with partially or completely suppressed mobility caused by interaction of the polar polymer chains with the surface of carbon nanotubes.

Table 4.3. Glass transition temperature (T_g), Heat capacity step (ΔC_p), degree of criatallinity χ_c , % of the CPA/MWCNTs composites.

| Composition | χ_c , % | T_g , °C | ΔC_p , J/g/°C |
|--------------|--------------|------------|-----------------------|
| CPA | 20.5 | 14.3 | 0.23 |
| CPA/ 1 MWCNT | 23.2 | 16.7 | 0.25 |
| CPA/ 2 MWCNT | 28.8 | 18.1 | 0.28 |
| CPA/ 4 MWCNT | 22.1 | 15.2 | 0.24 |

The DSC results indicate that presence of low content of MWCNTs in CPA matrix influence on the morphology of the investigated composites. Also it was found strong polymer-filler interaction in the amorphous phase of CPA and as the result the formation of an immobilized interfacial layer of polymer around carbon nanotubes which influences on the percolation threshold value and level of conductivity.

4.5. Mechanical properties of the composites.

The static Young's modulus G was calculated as a slope of stress-contraction curves:

$$G = \Delta s / \Delta c, \quad (4.8)$$

where Δs is the change of stress and Δc is the respective change of contraction. Stress-contraction tests were carried out using thermomechanical analyzer TMA Q400EM (TA Instruments) at 40 °C in the range of applied force (0÷1) N.

As one can see in the Fig. 4.6, these dependencies are linear in the range of applied stresses, what proves the elastic behavior of the composites studied at low stresses

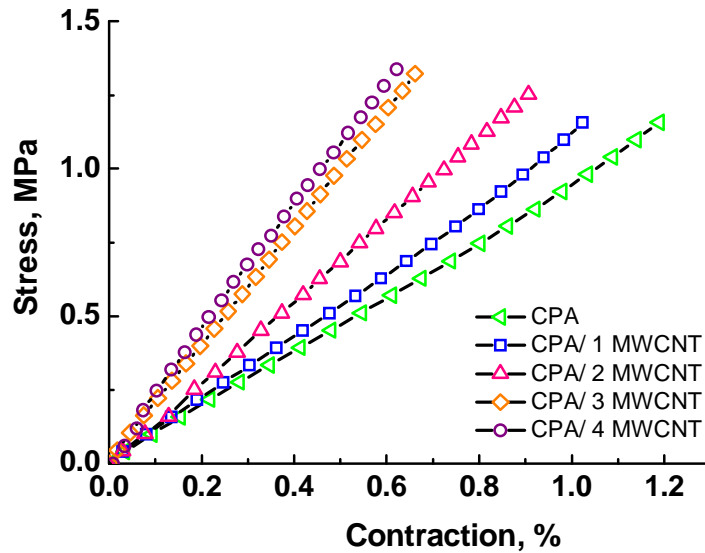


Fig. 4.6. Stress-contraction curves for the CPA/MWCNT composites.

The values of G versus MWCNTs content for CPA/MWCNT and PP/MWCNT composites are shown in Fig. 4.7-a and reveal the monotonic rise with the increase of MWCNT fraction. A high value of CNT modulus (G values reported in [31, 32] are equal to $(0.3 \div 1.5)$ TPa) provides essential rise of composite modulus even at low content of CNT, for instance, in the range of $(0.01 \div 0.04)$. Actually, the increase of G is 88 % and 57 % for the CPA/MWCNT and PP/MWCNT composites, respectively at 3 vol. % of filler content. A similar behaviour of Young's modulus (obtained in tensile test) of the composites based on polyamide and polycarbonate reported in [14, 33], where the rise of G was approximately linear in the range $(0 \div 4)$ % of MWCNTs but at higher content of MWCNTs the G values increased more slowly. In our case one can also suspect the similar shape of the curve at higher MWCNTs content. It is necessary to note, that Young's modulus of such two-phase systems with random distribution of the filler is not sensitive to the percolation transition, which is exhibited on the conductivity curves (see Fig. 4.1).

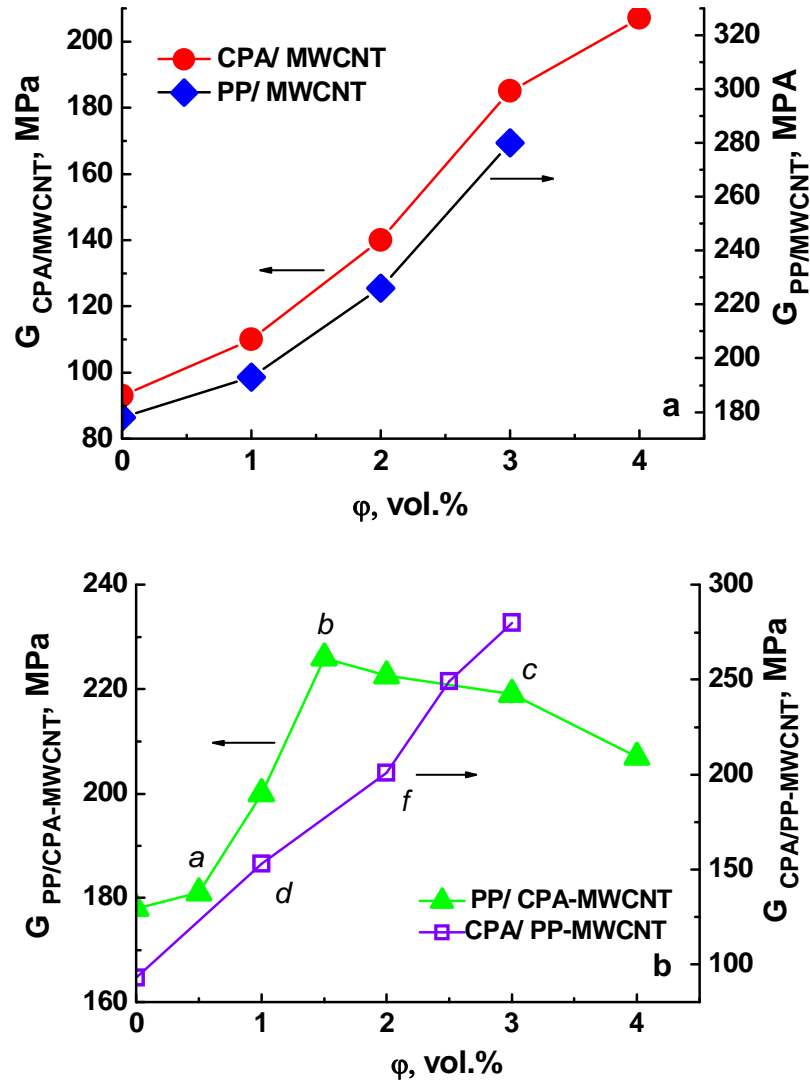


Fig. 4.7. Young's moduli G versus MWCNT content for CPA/MWCNT, PP/MWCNT composites (a) and for PP/CPA-MWCNT, CPA/PP-MWCNT composites (b). The symbols a–f near the points coincide with those for the conductivity curves in Fig. 4.1.

The stress-contraction curve for PP/CPA-MWCNT polymer blend processed by diluting of the CPA-4%MWCNT concentrate with pure PP is shown in Fig. 4.7-b. One can see, that the change of the composite during diluting from CPA-4%MWCNT concentrate, along the points "c" and "b", leads to the rise of G . It caused by increase of the part of the PP, which modulus is higher in comparison with CPA (see Table 4.1) and by presence of the CPA-4%MWCNT concentrate filled with MWCNT. Thus, the part of CPA in the concentrate is 96 % and in the points "c" and "b" is 72 % and 36 % respectively (see Table 4.1). Further diluting

of the concentrate causes the sharp decrease of G -values in the range of (0.5÷1.5) vol. % MWCNT (from the point "b" to the point "a") what coincides with the range of percolation transition in PP/CPA-MWCNT composite (see Fig. 4.1-a).

A similar behaviour of electrical and mechanical properties can be explained by the changes of the composite structure described above. In the range of MWCNT content (1.5÷3) vol. %, there are two co-continuous polymer phases, pure PP and filled CPA-MWCNT, which provide the existence of plateau of the conductivity and inclined the plateau of the G -modulus. P. Pötschke and D. R. Paul [20] claimed that co-continuous structure results in the maximum simultaneous contribution of each component into the mechanical modulus [20]. As the PP content increases, the continuous CPA-MWCNT phase is destroyed, and the system loses both conductivity and high values of G (transition from point "b" to point "a" in Figs. 4.1-a and 4.7-b) in accordance with the conception of double percolation.

For the opposite blend CPA/PP-MWCNT the Young's modulus changes linearly versus CNT content. Such a character of the dependence proves that at the diluting of PP-MWCNT concentrate with pure CPA, nanotubes occupy both of components moving from PP to CPA and their distribution is similar to that in the individual polymer PP or CPA. In this case Young's modulus is not sensitive to the percolation transition in MWCNTs network unlike the PP/CPA-MWCNT composite, where percolation network is created by CPA-MWCNT conductive phase.

Fig. 4.8 exhibits the combined curves both for the filled polymer blend and the individual one, namely PP/CPA-MWCNT, CPA/MWCNT in Fig. 4.8-a and CPA/PP-CNT, PP/CNT in Fig. 4.8-b. One can see that in the first case the modulus values of the filled blend are higher than those of the filled CPA (Fig. 4.8-a).

In the opposite case, the values of Young's modulus for the filled CPA/PP-CNT blend lie lower than for the filled PP (Fig. 4.8-b). Hence, filled polymer blend PP/CPA-MWCNT demonstrates better mechanical and conductive properties than the respective filled individual polymer (Figs. 4.1-a and 4.8-a), whereas the CPA/PP-MWCNT composite shows worse mechanical and conductive characteristics in comparison with the filled polymer PP/MWCNT (Figs. 4.1-b and

4.8-b). This implies that both mechanical and electrical properties are defined by the spatial distribution of the conductive filler in a polymer blend.

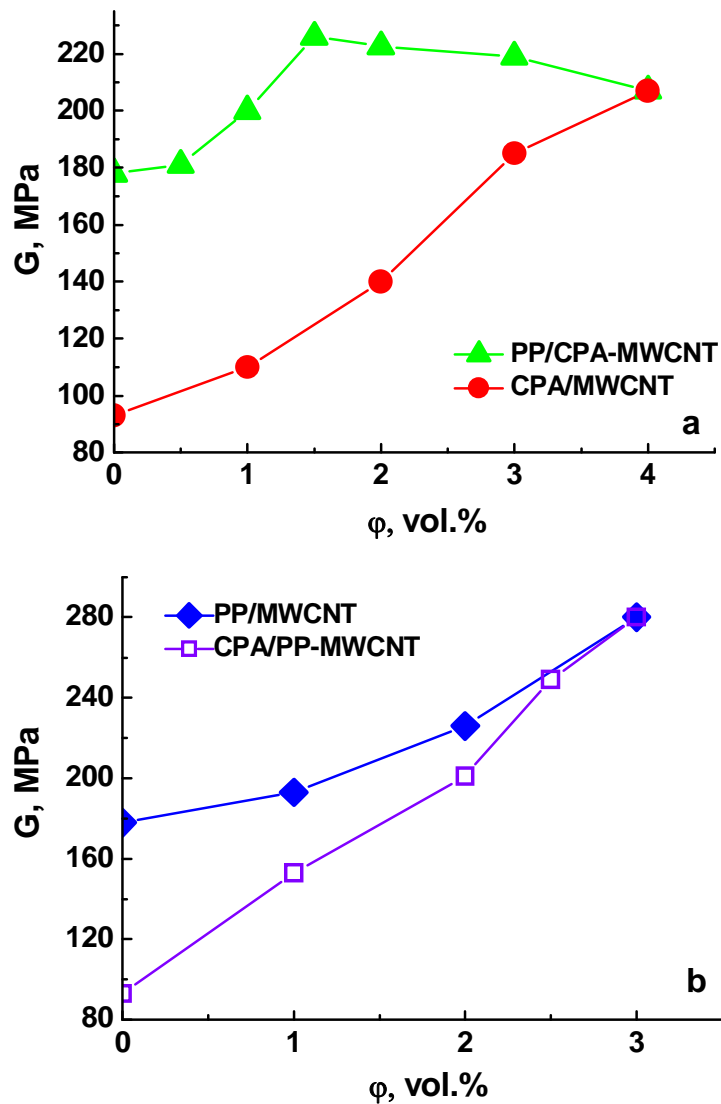


Fig. 4.8. Combined curves for the filled polymer blend and individual polymer, namely PP/CPA-MWCNT, CPA/MWCNT (a) and CPA/PP-MWCNT, PP/MWCNT (b).

4.6. Dynamic mechanical analysis of the conductive polymer blends.

Dynamic mechanical analysis (DMA) makes it possible to receive different physical parameters, which are important characteristics of the material properties. Parameters obtained from DMA, namely, elastic modulus E' , loss

modulus E'' and $\tan \delta$ of mechanical losses are useful characteristics of the material at the applied stress and temperature. DMA also enables to study the relaxation transitions in composites, which are caused by the presence of different levels of molecular mobility in the polymers. The relaxation transitions correspond to the relaxation processes and characterized by the required temperature. There are two main mechanical relaxation processes in polymers: segmental relaxation and polymer chains relaxation. As the relaxation processes are related to the mobility of the polymer chains and segments, the analyzing of relaxation transitions can detect the influence of the fillers on the molecular mobility in the polymer, and determine the degree of interaction between the filler and polymer matrix and between polymer matrices.

In general, on the DMA curves for PA6 three relaxation peaks are observed [34]. The most intense of them is α -relaxation, localized in the temperature range $(20 \div 90)^\circ\text{C}$ and associated with the mobility of polymer chains in amorphous part of polymer (i.e., glass transition). β -relaxation being determined in the temperature range $(-70 \div -40)^\circ\text{C}$ is related to the mobility of polar groups that are not hydrogen bonded and of polymer–water complex units. γ -relaxation associated to the motion of polar groups of PA6 and the motion of methylene groups and localized in the temperature range $(-140 \div -120)^\circ\text{C}$. In general, at DMA curves for pure PP (in general) there are also three areas of relaxation: -80°C (γ -relaxation), 8°C (β -relaxation), 100°C (α -relaxation). β -relaxation is associated with the glass transition of PP, while α -relaxation refers to the transitions in the crystalline phase [35].

Fig. 4.9 shows the dependence of the $\tan \delta$ on the temperature for pure CPA. In the studied temperature range $(-50 \div 140)^\circ\text{C}$ for pure CPA one can clearly distinguish only one large relaxation maximum, localized at 31°C , which is associated with the α -relaxation of CPA. Such low value of T_g is connected with the fact that in our work we have used the co-polyamide with the ratio between the components $\text{PA6} : \text{PA6.6} : \text{PA6.10} = 70 : 6 : 24$. On the DMA curve for pure PP (Fig. 4.9) in the investigated temperature range one can observe the presence of β -relaxation peak with a maximum at 14°C as well as the relaxation peak at

average temperature 80 °C, which can be associated with the process of α -relaxation.

Fig. 4.10 presents DMA curves for polymer blend CPA/PP with the ratio of components equal to 24/76 and polymer composite PP/CPA-MWCNT with the same ratio of polymer components filled with 1 vol. % of nanotubes. As one can see from the curve for the CPA/PP, the temperature maximum of β -relaxation peak of PP coincides with the temperature peak position of β -relaxation of pure PP, which is presented in Fig. 4.9.

The lack of influence of one polymer component on the glass transition of another polymer component in the polymer blend indicates the lack of interaction between them and shows their incompatibility. For the polymer blend CPA/PP one can observe that the relaxation maxima of PP and CPA (at 14 °C and 80 °C, respectively) do not change their localization. Therewith the α -relaxation peak of CPA shifts to the high temperature region (from 31 °C – in the pure CPA to 46 °C – in the polymer blend). The intensity of this peak decreases from 0.21 to 0.10. The decrease of the intensity of α_{CPA} -relaxation in CPA/PP blend (the ratio of the components is 24/76) in the whole temperature range can be caused by the small values of the $\tan \delta$ for pure PP.

On the $\tan \delta$ curves for the polymer blend filled with 1 vol. % of MWCNTs the α_{CPA} -relaxation peak is shifted to the higher temperatures and its intensity is decreased. E. Logakis et al. [36] also observed a significant intensity decrease of the mechanical α -relaxation of PA6 at the presence of MWCNTs (Fig. 4.10). This behavior can be explained by the assumption that nanotubes decrease the chain mobility of polyamide. The shift to higher temperature of merely CPA relaxation peak indicates that the nanotubes are localized exclusively in the phase of the CPA and do not affect the relaxation processes in PP.

Table 4.4 shows the values of elasticity modulus E' for pure polymers, polymer blends and filled polymer blends in the glassy (–40 °C) and rubbery (50 °C) states. As one can see from the table, polymer blends filled with MWCNTs show higher mechanical properties compared with the unfilled blends. This effect is caused by the contribution of MWCNTs in the resulting elasticity modulus of composites.

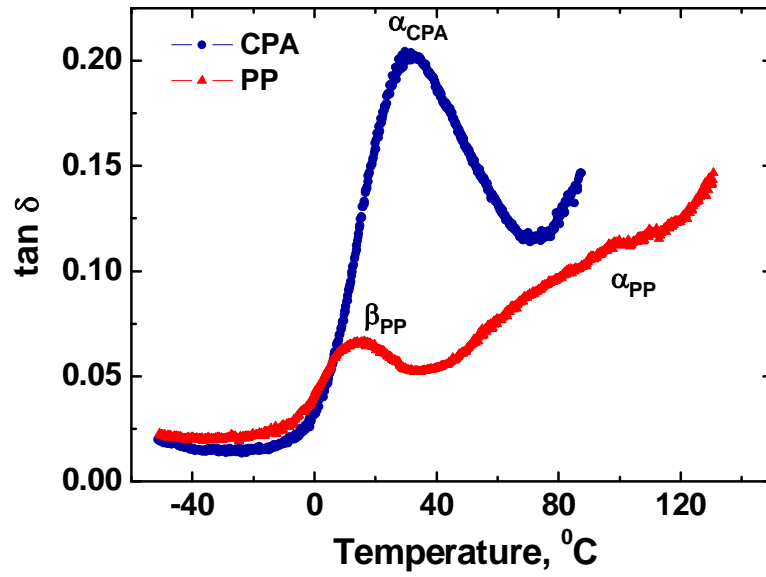


Fig. 4.9. The $\tan \delta$ curves for pure CPA and PP at 1 Hz.

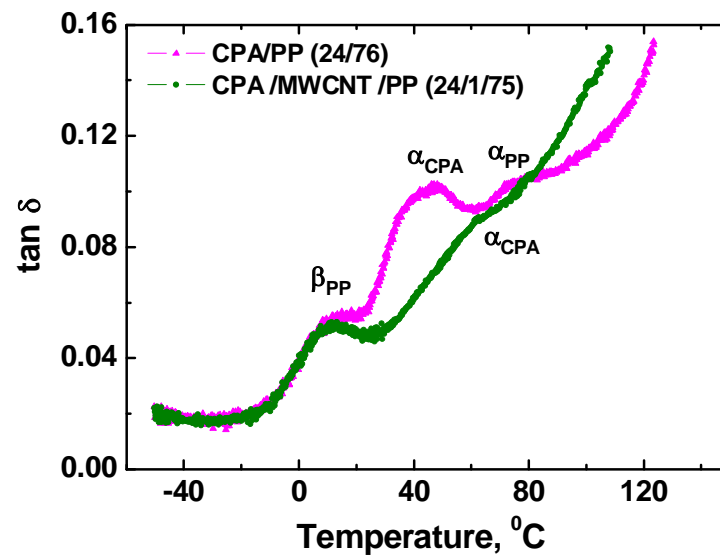


Fig. 4.10. The $\tan \delta$ curves at 1 Hz for polymer blend CPA/PP with the ratio of components (24/76) and for the same blend filled with 1 vol. % of MWCNTs.

The higher value of elastic modulus was found for the composite with concentration of MWCNTs equal to 1 vol. % (Fig. 4.11) (see Table. 4.4), which correlated with the data obtained by the static method, where the highest Young's modulus was determined for the composite with the nanotubes content, which is equal to 1.5 vol.% (Fig. 4.7-b). This effect for the composites with such components ratio can be explained by the presence of MWCNTs in the interphase

region, when one nanotube can occupy two phases of polymer blend ("bridging"-effect).

Table 4.4. DMA data: values storage modulus E' in the glassy and in the rubbery states for pure PP, CPA and filled polymer blends.

| Sample | E' in glassy state (-40 °C), GPa | E' in rubbery state (60 °C), GPa |
|----------------------------|---------------------------------------|---------------------------------------|
| PP | 4.5 | 1.4 |
| CPA | 2.5 | 0.4 |
| PP/CPA (76/24) | 4.1 | 1.0 |
| PP/CPA/MWCNT (24/75/1) | 4.7 | 1.6 |
| PP/CPA (63/37) | 3.7 | 0.7 |
| PP/CPA/MWCNT (62.5/36/1.5) | 4.1 | 1.5 |
| PP/CPA (51/49) | 2.6 | 0.5 |
| PP/CPA/MWCNT (50/48/2) | 4.1 | 1.2 |

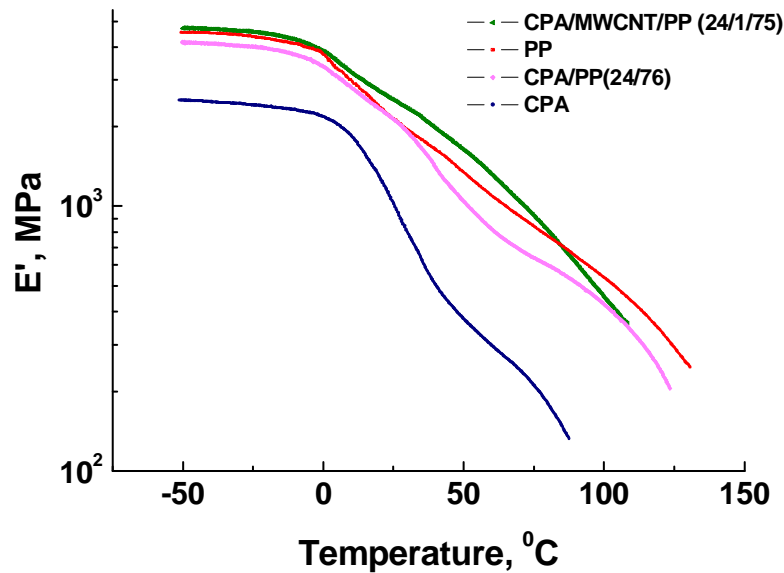


Fig. 4.11. The E' curves at 1 Hz for PP, CPA, polymer blend CPA/PP with the ratio of components (24/76) and for the same blend filled with 1 vol. % of MWCNTs.

L. Zhang et al. [21] showed that in PA6/PP/MWCNT composites, nanotubes were mainly localized in the PA6 phase, and only a small amount was localized in

the interphase of polymer blend. MWCNTs localized at the boundary between two phases can belong simultaneously to each polymer of the mixture, while forming the "bridges" between them, and, thus, improving the mechanical properties of the composite. The presence of such bridges in the polymer blends increases their viscosity and mechanical modules [13]. A similar effect was found for the PC/PE/MWCNT blends, which is connected with the way of the filler introduction into the polymer blend [15].

Conclusions

The morphology of the filled polymer blends and their conductivity are defined by three factors, namely thermodynamic, kinetic and processing ones. The influence of thermodynamic factor depends on the ratio of the surface parameters of the polymer components and the filler. The kinetic factor is related to viscosities of the polymer components. At melt processing a filler moves to the polymer component with lower viscosity. The processing factor means the order of the filler introduction into the polymer blend. All factors can supplement or counteract with each other.

The polymer blends based on PP and CPA and filled with carbon nanotubes obey to the revealed regularities. Electrical properties and, in particular, percolation behaviour, strongly depend on the spatial distribution of MWCNTs in the polymer matrix. For the PP/CPA-MWCNT polymer blend processed by diluting of the CPA-4%MWCNT concentrate with pure PP, the value of percolation threshold is defined by creation/destruction of the conductive network of CPA-MWCNT and is lower in comparison with the percolation threshold for the individual filled CPA. In the opposite blend CPA/PP-MWCNT the distribution of the filler is quite different, and the value of percolation threshold is connected with the creation/destruction of the conductive network, created by nanotubes. These two cases obey the double percolation conception.

The dependence of Young's modulus on the filler content in the individual polymer is not sensitive to the creation of the conductive network of MWCNTs and

to the existence of the percolation threshold. In the polymer blend PP/CPA-MWCNT, where conductive network is created by the filled phase of CPA, the behaviour of electrical and mechanical properties are of similar character and reveal the percolation behaviour. The opposite blend CPA/PP-MWCNT shows a similar dependence to that for the filled individual polymer with the lack of the percolation threshold. Hence, mechanical characteristics of the filled polymer blends strongly depend on the spatial distribution of the filler.

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Chapter 5

Specificities of the conducting phase formation in polymer composites with combined filler

Introduction

5.1. Investigation of the structure and the properties of polymer nanocomposites filled with carbon nanotubes and organo-modified clay.

5.1.1. *Thermal analysis of crystallization and melting behaviour of the composites.*

5.1.2. *The morphology of composites filled with organo-clay, carbon nanotubes and combination of two fillers.*

5.1.3. *Dynamic mechanical properties.*

5.1.4. *Dielectrical properties of composites based on PP filled with organo-clay.*

5.1.5. *Electrical properties of the composites.*

Conclusions

5.2. Investigation of the structure and the properties of polymer composites filled with nanometals and carbon nanotubes.

5.2.1. *Electrical properties of the polymer nanocomposites, filled with carbon nanotubes and nickel nanoparticles.*

5.2.2. *Thermal analysis of the melting and crystallization of composites filled with nickel and carbon nanotubes.*

Conclusions

Introduction

In recent years, nanoparticles of different dimensions are frequently used together to prepare multi-component polymer nanocomposites, to study the synergistic effects of different nanofillers [1]. Due to this the application of combined fillers such as carbon black – CNTs [2], carbon black – carbon fiber [3], clay – carbon black [4, 5, 6] and nanometals – CNTs [7, 8] became a new scientific trend. One can suppose that the combination of two fillers results in a significant improvement of the polymer composite characteristics due to mutual influence of the nanoparticles and integration of their properties. Such a combination can provoke the amplification of the effect of the basic filler or influences significantly the structure and the properties of the composite due to synergism. Interaction between two types of the nanoparticles will be also considered as a new factor influencing the structure and the properties of the polymer composites in addition to the interaction between the nanoparticles and the matrix.

5.1. Investigation of the structure and properties of polymer nanocomposites filled with carbon nanotubes and organo-modified clay.

Up to now there are only a few papers in which the authors report about the use of clay combined with CNTs for the improvement of the conductivity and mechanical properties of the investigated composites [1, 9, 10]. These works were generally focused on the distribution of carbon fillers in the epoxy matrix in the presence of clay. In epoxy-based composites, it can provide a better distribution of carbon nanoparticles can be achieved due to low viscosity of the epoxy and possibility of ultrasonication of the polymer-filler mixture. Therefore, it seems to be an accurate perspective to use a combined filler in order to obtain some new properties of composites, based on thermoplastic, in particular, polypropylene (PP).

PP is one of the most widely used polymers, being applied for different purposes and, especially, it is good as construction material. PP is usually filled

with different nanoparticles to obtain defined electrical and mechanical properties [11]. In order to improve mechanical properties of the PP, organo-modified clay (OC) is widely used. It was found, that the introduction of OC into PP had increased the thermostability of composites [12, 13]. The results, published in [14, 15, 16] have shown, that in the composites PP/clay the introduction of the filler into the PP matrix results in the increase of elastic modulus and rigidity of the nanocomposites. Moreover, numerous reports were devoted to the investigation of mechanical and electrical properties of polymer composites based on PP filled with CNTs [17-19]. It was found, that the composites based on PP and CNTs revealed the presence of CNTs agglomerates, what resulted in large value of percolation threshold [18]. The integration of the CNTs into agglomerates is entailed by a strong interaction between the nanotubes due to Van der Waals forces, weak interaction between the PP and the carbon nanotubes and high viscosity of the matrix.

The presence of clay nanoparticles in the PP/CNT composites could increase the spatial distribution of the CNTs and improve the electrical properties of the material. We suspect that due to filler-filler interaction, one type of nanoparticles will improve the dispersion and distribution of another one. The results presented below are devoted to the study of the morphology, electrical, dynamo-mechanical and thermal properties of composites based on PP with different amount of CNTs and organo-modified clay. The advantages of the combined usage of CNTs and clay for the preparation of conductive polymer composites will be shown in this chapter.

5.1.1. Thermal analysis of crystallization and melting behaviour of the composites.

The influence of MWCNTs, OC, and their combination, on the thermal properties and crystallization of PP was analyzed by DSC method. Fig. 5.1-a shows crystallization thermograms for PP/OC composites with different concentrations of the filler. Addition of small amounts of organo-clay provides the increase of crystallization temperature T_c from 113 °C, for the pure PP, up to 121 °C, for the

composite with 0.5 vol. % of OC. Such an effect can be explained by the following conception. Clay layers act as nucleation agents and make easier the process of crystallization. However, further increase of OC content in the composite (up to 3 vol. % of OC) results in slight decrease of crystallization temperature T_c to 119 °C. Nevertheless, T_c of such composition is still higher than that of pure PP. A similar dependence of the PP crystallization temperature on organo-clay content was reported in [20, 21] and can be associated with the plasticizing effect of organic modifier, which is present in organo-clay. Moreover, at high content of OC, the platelets of the filler can block the formation of the crystallites during crystallization process. One can see that crystallization peaks of PP/OC composites are more broad, compared to pure PP. Such an effect characterizes more broad crystallite size distribution in the presence of OC.

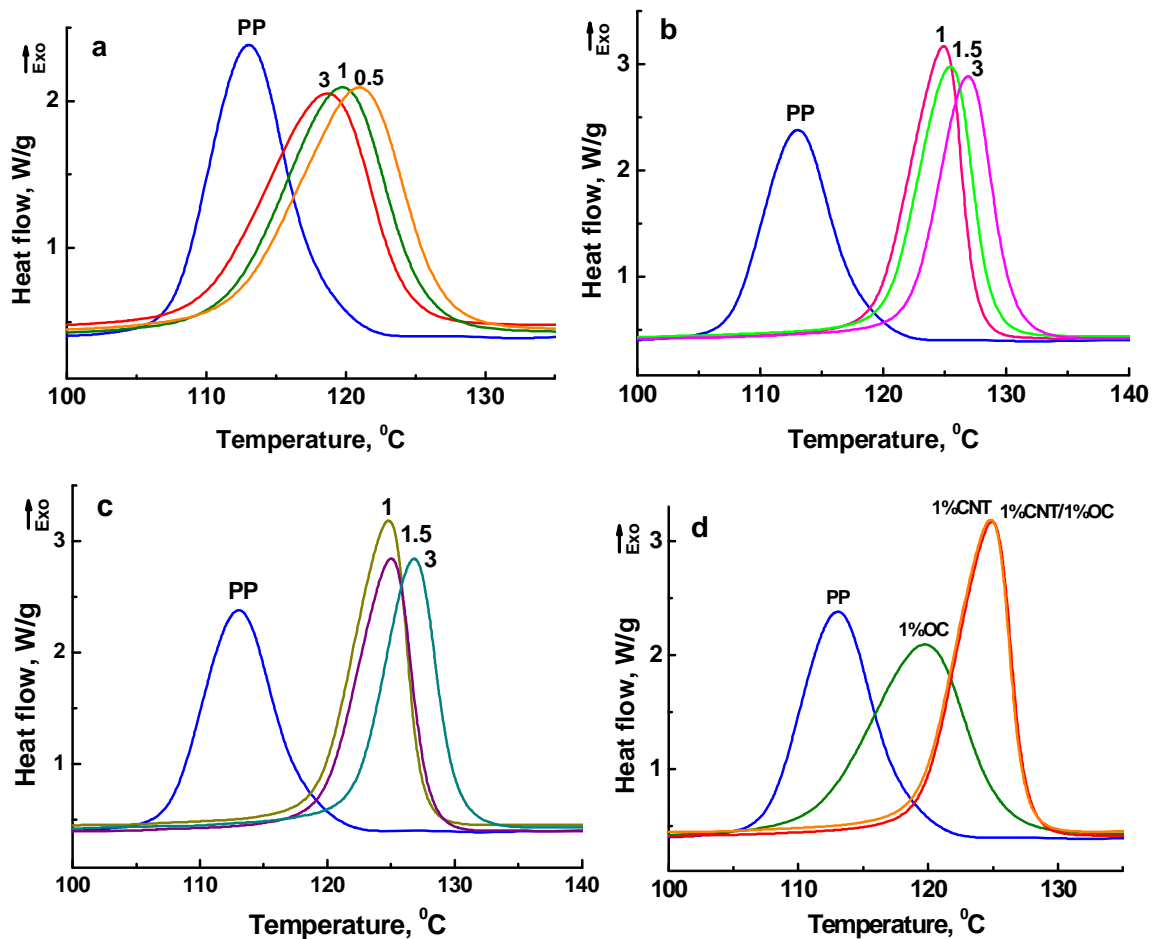


Fig. 5.1. DSC crystallization thermograms of PP and PP/OC (a), PP/MWCNT (b), PP/MWCNT/OC (c) composites and all these composites filled with 1 vol. % of the filler (d). The numbers near the curves indicate the content of the fillers in the polymer matrix.

The thermograms for PP/MWCNT composites are shown in Fig. 5.1-b. The addition of nanotubes into the polymer matrix provides the abrupt shift of the crystallization peak from 113 °C for pure PP to 127 °C for the composite with 3 vol. % of MWCNTs. In contrast to PP/OC composites, crystallization temperature of PP/MWCNT composites grows gradually with the increase of the nanotube content (Fig. 5.1-b). Such a shift of T_c was reported for different polymer matrices filled with carbon nanotubes and indicates that carbon nanotubes act as nucleating agents [17]. CNT surface helps to decrease the energy barrier of nucleation in the process of crystallization due to interactions between CNTs and PP macromolecules [11]. One can see that crystallization peaks of PP/MWCNT composites are more narrow, compared to pure PP. Such an effect characterizes more narrow distribution of crystallite size in the presence of CNTs [22].

Crystallization behavior of PP/MWCNT/OC composites was found to be identical to that of PP/MWCNT composites (Fig. 5.1-c). Such a dependence of the crystallization temperature on the filler content demonstrates that the influence of OC on PP crystallization in the presence of MWCNTs is negligible as compared to PP/OC composites.

The degree of crystallinity in all the composites was determined from DSC melting thermograms using the following equation [23]:

$$X_c (\%) = \frac{\Delta H_m (m_c / m_p)}{\Delta H_0} 100\% , \quad (5.1)$$

where ΔH_0 is the theoretical enthalpy for 100 % crystalline PP ($\Delta H_0 = 207.1$ J/g [23]), ΔH_m is melting enthalpy of the composite, m_c is weight of the sample, and m_p is the weight of PP in the sample.

Table 5.1 shows that both of the fillers affect crystallization of the PP matrix. Introduction of OC into PP leads to the abrupt increase of crystallinity X_c and crystallization temperature T_c . The reason is the effect of OC on nucleation which promotes the crystallization process. The growth of OC content in PP increases crystallinity X_c , whereas the value of T_c decreases. The decrease of T_c value can be a result of the plasticization effect of the OC organic modifier on PP chains, therefore more mobile plasticized chains crystallize at lower temperature.

Otherwise, T_c decrease can be explained by the assumption that in the composites with higher OC content the platelets of the filler limit the growth of the crystallites.

Table 5.1. Degree of crystallinity (X_c), crystallization temperature (T_c), melting temperature (T_m), supercooling temperature (ΔT) for pure PP matrix and filled composites.

| Sample | X_c , % | T_c , °C | T_m , °C | $\Delta T = T_m - T_c$, °C |
|---------------------|-----------|------------|------------|-----------------------------|
| PP | 35.5 | 113.0 | 164.3 | 51.3 |
| | | | | |
| PP/0.5 OC | 40.5 | 121.0 | 166 | 45 |
| PP/1 OC | 40.1 | 119.7 | 166 | 46.3 |
| PP/1.5 OC | 43.6 | 119.0 | 165.3 | 46.3 |
| PP/3 OC | 44.2 | 118.7 | 165 | 46.3 |
| | | | | |
| PP/1 MWCNT | 38.6 | 124.9 | 162 | 37.1 |
| PP/1.5 MWCNT | 38.2 | 125.5 | 162.4 | 36.9 |
| PP/3 MWCNT | 38.2 | 126.9 | 162 | 35.1 |
| | | | | |
| PP/1 MWCNT/1 OC | 38.5 | 124.8 | 162 | 37.2 |
| PP/1.5 MWCNT/1.5 OC | 37.0 | 125.0 | 161.7 | 36.7 |
| PP/3 MWCNT/ 3 OC | 38.4 | 126.8 | 161.5 | 34.7 |

Adding of MWCNTs to PP results in less increase of X_c and higher jump of T_c in comparison with PP/OC composite. Further growth of the filler content in the polymer matrix results in the increase of T_c value, but crystallinity changes are negligible in contrast to the OC-containing materials. The effect of combined MWCNT/OC filler is identical to the effect of individual MWCNTs (Fig. 5.1-d), i.e. the presence of MWCNTs shields the influence of OC on crystallization in PP. Thus, one can conclude that CNTs have greater influence on the crystallization process of PP matrix in comparison with OC filler.

Incorporation of OC into PP slightly increases the melting point T_m , from 164.3 °C in PP to 166 °C in PP/0.5 OC and 165 °C in PP/3 OC, what is in a good correspondence with the behaviour of T_c . Therewith, T_m of the materials containing MWCNTs and MWCNT/OC, slightly decreases first to 162 °C. A further

increase of the filler content makes T_m constant and independent on filler concentration, which is in contrast to behaviour of T_c .

It seems to be interesting to study the behaviour of the supercooling temperature $\Delta T = T_m - T_c$, which can be related to two factors. The first factor is caused by kinetics of crystallization, i.e., the ratio of crystallization and cooling rates. Since cooling rate is identical for all the composites, changes in ΔT can be determined by the rate of crystallization. The second factor can be related to the number of crystallization centres or to the content of the filler particles, which are nucleating agents. The presence of fillers both accelerates the crystallization process and increases the number of crystallization centres, as far as the values of ΔT are lower, and the degree of crystallinity is higher for the filled systems than for pure PP. In turn, the supercooling temperature and the degree of crystallinity are higher for PP/OC composite than for PP/MWCNT and PP/MWCNT/OC composites. It means that the crystallization process of PP/OC is longer, however the number of crystallization centres is larger, what results in higher degree of material crystallinity. For PP/MWCNT and PP/MWCNT/OC composites, the values of ΔT decrease, while the values of X_c are invariable, with growth of MWCNTs content. It indicates on reduction of the crystallization process, whereas the nucleating effect of MWCNTs is constant.

5.1.2. *The morphology of composites filled with organo-clay, carbon nanotubes and combination of two fillers.*

While analyzing the systems, filled with OC, one has to mention, that dependently on the types of polymer matrix, clay, organic modifier and the method of composite preparing, one can obtain two types of polymer nanocomposites, i. e. the composites with intercalated and exfoliated structures [24, 25]. Intercalated structure of the nanocomposite is created in the case, when polymer chains are localized in the interlayer galleries of the clay. This interaction results in the creation of the structure in which silicate plates are separated from each other by the polymer chains and organic component. In such systems the distance between the silicate plates do not exceed 20–30 Å [26, 27, 28]. In the case

when the plates of the clay are separated from each other and distributed in the whole polymer matrix, they say about the exfoliated composite structure, in which the average distance between the plates is about 80–100 Å [28]. The most interesting is the exfoliated structure, as it is characterized by the best interaction between the polymer and its filler, what results in the significant changes of the mechanical and physical properties [26].

The pictures, obtained by the scanning electronic microscope (SEM) reveal the presence OC aggregates with average size of 7–10 μm (Fig. 5.2 a) as well as intercalated and (individual) exfoliated silicate plates (Fig. 5.2 b). L. Százdi et al. reported, that in the PP/OC both intercalated and exfoliated structures were equally observed in the sample [29].

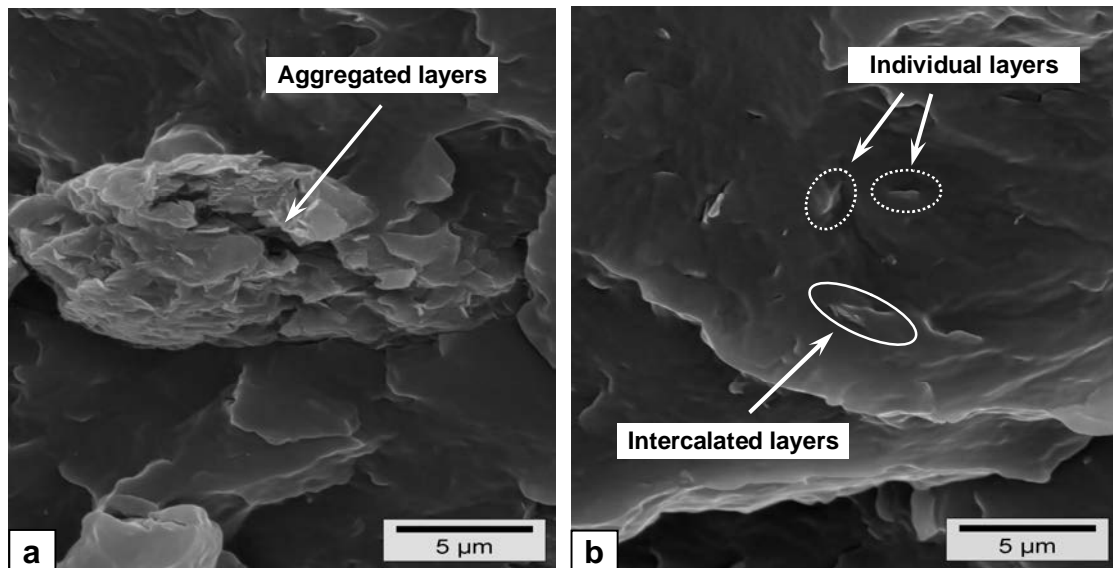


Fig. 5.2. The SEM images of PP/OC composites, filled with 1% of OC.

The SEM images for PP/MWCNT composites reveal the presence of the large CNT aggregates (Fig. 5.3 a) with the sizes at about (0.5-3) μm (the average value is 1.5 μm). The introduction of the clay into the PP/MWCNT composites provokes the better MWCNTs dispersion in the polymer matrix. On the image of PP/CNT/OC (Fig. 5.3 b) one can clearly see the individual nanotubes, uniformly distributed in PP. Thus, while analyzing the SEM images, one can conclude, that the presence of OC in the PP/MWCNT composites can improve the dispersion of nanotubes in the polymer matrix.

The distribution of the organo-clay and carbon nanotubes in PP matrix was also studied via the transmission electron microscopy (Fig. 5.4). The obtained results do not indicate the presence of great aggregates of MWCNTs and OC in polymer matrix, what correlates with the SEM data. Really, the sizes of the MWCNTs aggregates do not exceed $0.7\ \mu\text{m}$ (Fig. 5.4). From the TEM images we can also see the interaction between surfaces of clay and carbon nanotubes.

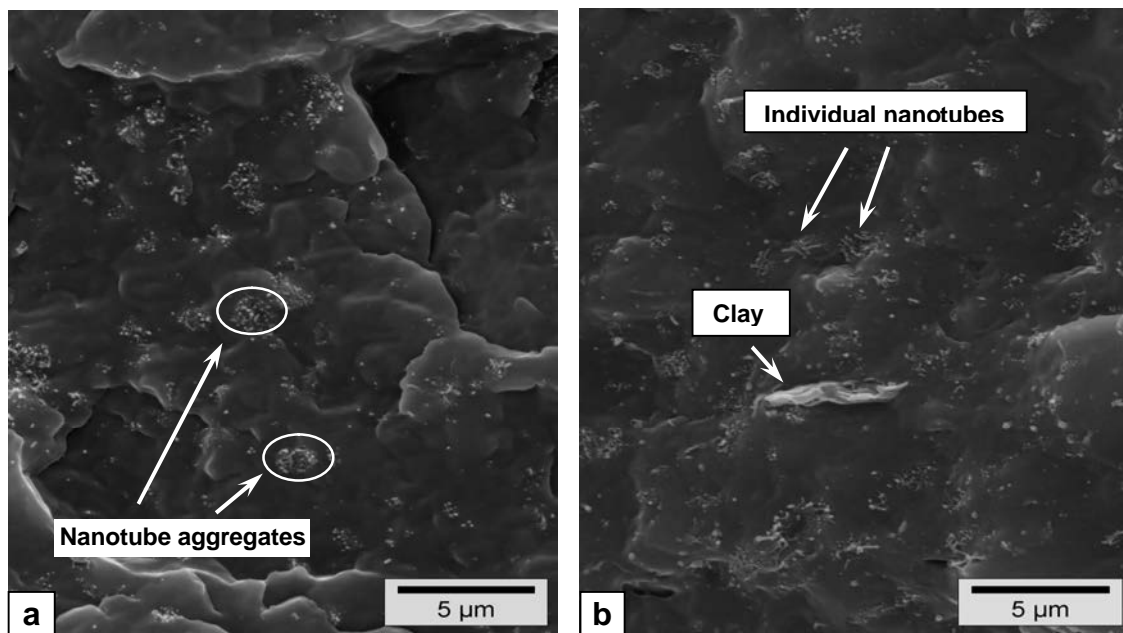


Fig. 5.3. The SEM images of 1 vol. % MWCNT aggregates composites (a) and individually distributed nanotubes at the presence of organo-modified clay (b).

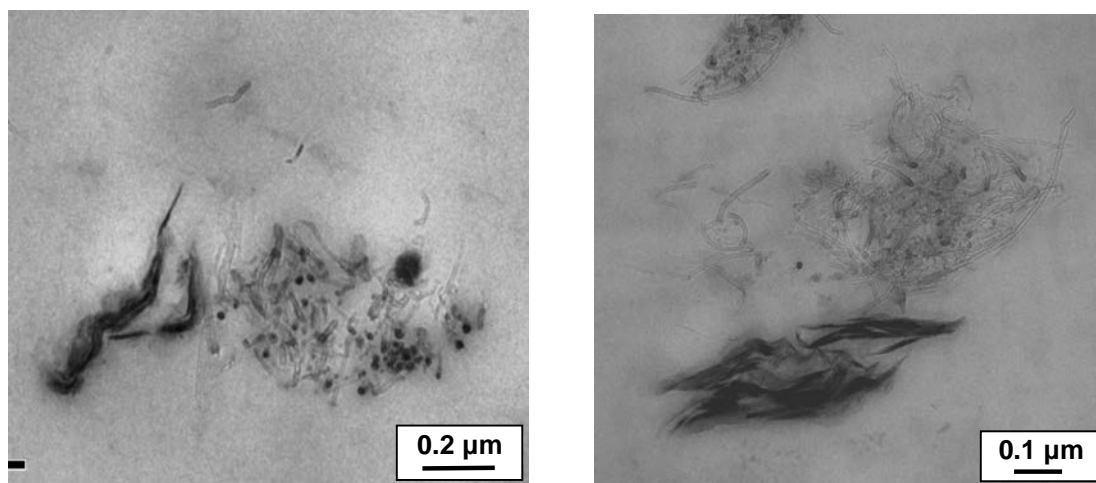


Fig. 5.4. The transmission electron microscopy (TEM) microimages of the PP/MWCNT/OC filled with two fillers (1 vol. % of CNT and 1 vol. % of OC).

L.Liu et al. [9] have also reported about interaction between single-wall carbon nanotubes and clay in epoxy matrix. This CNT-clay interaction was visualized using partially polarized light in an optical microscope. The authors have found that all the clay aggregates were surrounded by CNTs, and have suggested that there was strong affinity between these two particles.

5.1.3. *Dynamic mechanical properties.*

The experimental results of the PP/OC, PP/MWCNT and PP/MWCNT/OC composites obtained by dynamic mechanical analysis are presented in Fig. 5.5. J. I. Velasco et al. [23] have observed two relaxation peaks around 10 °C and 100 °C on dynamic loss modulus curve of pure PP, which were related to β - and α -relaxations, respectively. The dominant relaxation appeared around 10°C was related to the glass-rubber transition (β -relaxation) of the amorphous phase of PP. The weak peak existing at higher temperatures corresponds to the α -relaxation. There are different interpretations of the nature of mechanical α -relaxation in PP. It may be caused by molecular mobility of the polymer chains on the lamellar surface or by relaxation of the intracrystalline amorphous chains of PP [24]. D. Bikiaris et al. [30] have stated that α -relaxation is related to the crystalline polymer regions and the softening point of PP. In [31] the authors explain existence of α -relaxation by the lamellar slip and rotation in the crystalline phase. There were reported different values of the α -relaxation temperature T_a in PP matrix. J. I. Velasco et al. [23] have found that $T_a = 52$ °C, whereas K. S. Santos et al. [24] have observed T_a peak about 86 °C (it is necessary to note that the value of T_a depends on the frequency at which the experiment was done).

The DMA thermograms (Fig. 5.5, plots a, c, e) show that the OC, MWCNTs and combination of both fillers do not influence the glass transition in PP. Maximum of the relaxation peaks are localized near 11 °C for all the composites and pure PP. However, it was found that filler significantly influenced on the α -relaxation process, which depends on the type of the filler. The temperatures of α -relaxation T_a are presented in the Table 5.2. The increase of the OC content in the

PP/OC composite decreases intensity of the α -peak (from 0.10 to 0.09) and leads

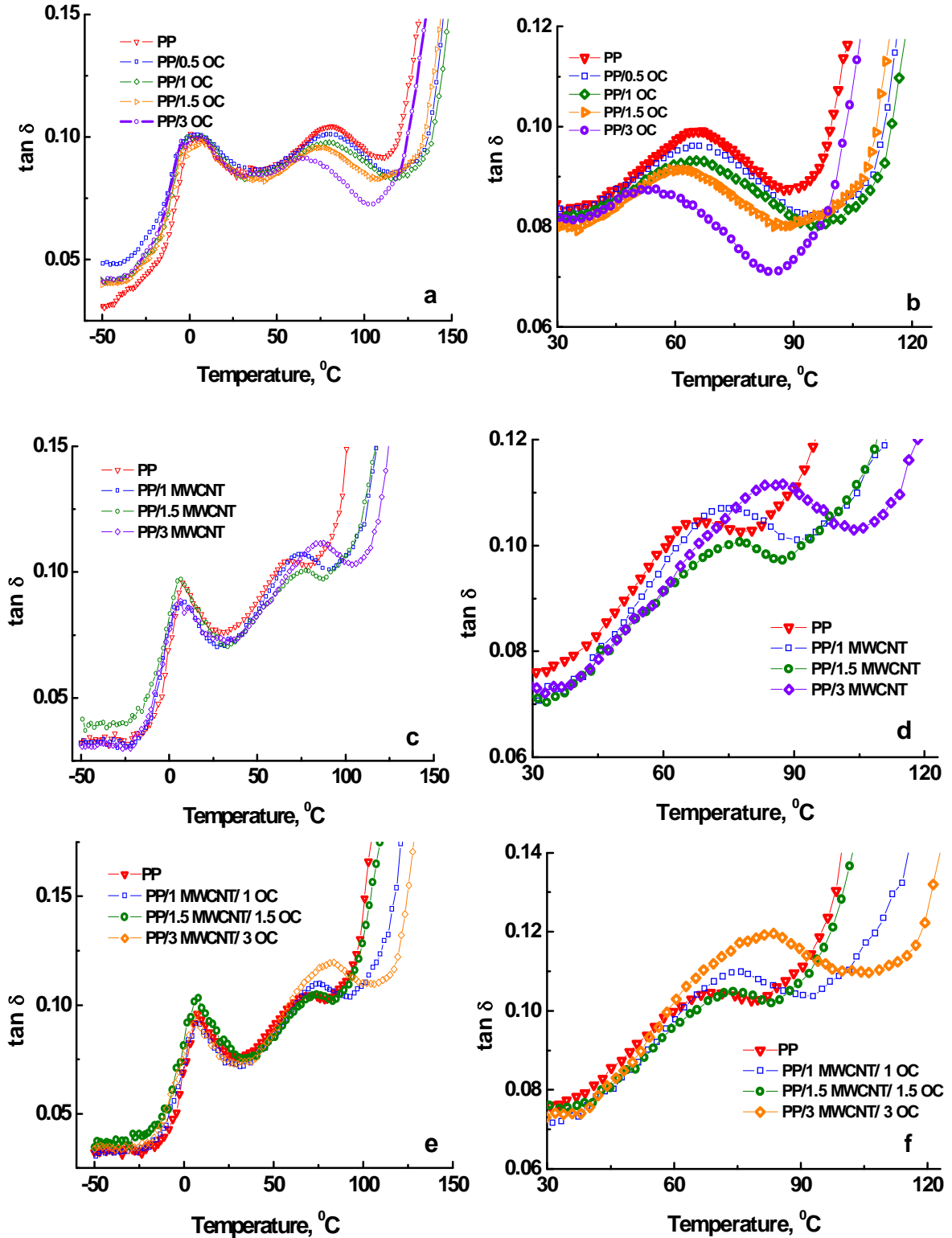


Fig. 5.5. DMA curves at 1 Hz of the PP/OC (a, b), PP/MWCNT (c, d) and PP/OC/MWCNT (e, f) composites in the temperature range $-50 \div 150$ $^{\circ}\text{C}$ (a, c, e) and in the α -relaxation area (b, d, f).

to the relaxation maximum shift towards the lower temperatures (Fig. 5.5-b). This shift with increasing of OC content can be caused by plasticizing effect of organic modifier which is present in organo-clay and facilitate the relaxation process. The organo-modified clay contains 30 wt. % of organic part. Such an effect can be also caused by the decrease of the crystallite size. The presence of the OC in the composites can decrease the size and quality of the crystallites, thus the T_a value can shift to lower temperatures. However, an opposite effect on the α -relaxation process can be observed in the case of MWCNTs (Fig. 5.5-d).

The maximum of the α -relaxation peak shifts towards higher temperatures and the amplitude increases (from 0.10 to 0.11) with the growth of the content of nanotubes in PP/MWCNT composites (Fig. 5.5-d). The influence of the combination of fillers on the relaxation processes in PP is similar to that observed for PP/MWCNT composites (Fig. 5.5-f).

The relationship between T_c and T_a in the filled systems is shown in Fig. 5.6. It shows that fillers influence dramatically the thermal and mechanical properties of the polymer matrix, and the character of such influence depends on the type of the filler. As it follows from the plot, the PP/MWCNT and PP/MWCNT/OC composites exhibit comparable dependences of T_a versus T_c in contrast to PP/OC composite, which demonstrates noticeably different behaviour. The similarity of curves for PP/MWCNT and PP/MWCNT/OC systems can be explained in assumption of stronger OC interaction with MWCNTs in comparison with PP matrix.

The described effects of the filler influence on the relaxation processes can be explained by a weak filler interaction with the polymer chains. Therefore, this interaction does not affect the β -relaxation process. At the same time, the structure of the polycrystalline phase, especially its amorphous part, significantly depends on the filler, which extrinsically affects the crystallization processes. The interaction between amorphous part of the crystalline phase of PP and CNTs was showed in [11]. Furthermore, formation of special kind of morphology around carbon nanotubes in various semicrystalline polymers known, as the trans-crystalline structure has been reported earlier [17, 32]. Indeed, MWCNTs and

combination of the fillers (MWCNT/OC) cause the increase of α -relaxation temperature, which correlates with T_c (DSC) increase for these composites. Whereas increase of the OC content in the polymer matrix shifts the crystallization point T_c , as well as α -relaxation peak, towards lower values. Thus, filler exerts significant influence on formation of the crystalline phases during crystallization process, whereas its effect on molecular mobility in amorphous phase of the polymer (β -relaxation) is negligible.

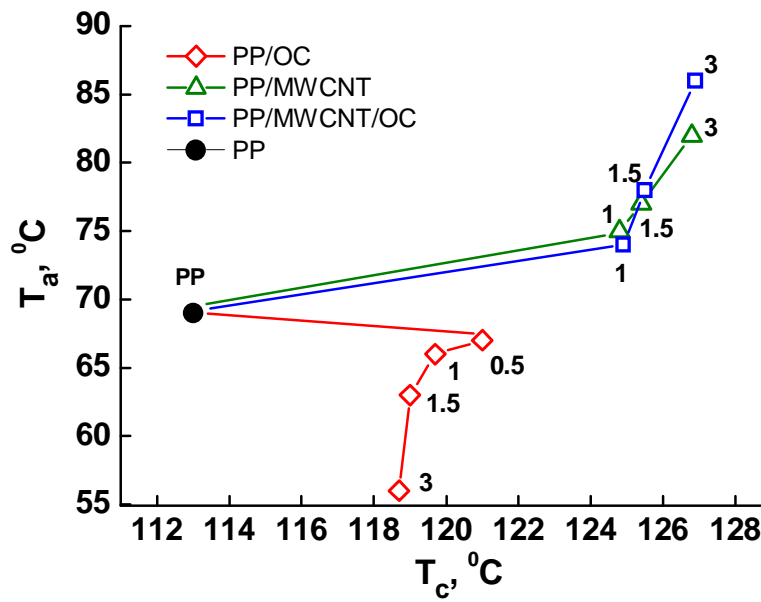


Fig. 5.6. T_g versus T_c for the filled systems and pure PP. The numbers near points indicate the content of fillers in the polymer matrix.

Here two important points should be noted. First, the influence of OC on crystallization and α -relaxation is rather complicated. Thus, the increase of OC content in the polymer matrix decreases the intensity of α -relaxation peak due to decrease of the content of the amorphous part, related to the lamellar crystalline phase, caused by increase of crystallinity X_c . Moreover, T_c and T_g decrease, what indicates easier mobility of the molecular chains probably, caused by the plasticizing effect of organic modifier in OC. K. Wang et al. [21] have mentioned that plasticizing function of the organically modified clay promoted mobility of the polymer chains. On the other hand, the decrease of T_c value can be caused by platelets of the clay which can block the formation of the crystallites during

crystallization process. And T_α reduction can be the result of the decrease of the size and quality of the crystallites.

The higher temperature shifts of T_c and T_α in PP/MWCNT and PP/MWCNT/OC composites are identical. This effect proves the assumption that MWCNTs weaken the influence of OC on crystallization process and evidences stronger OC interaction with MWCNTs in comparison with polymer matrix. The shift to higher temperatures of the α -relaxation peak for PP/MWCNT and PP/MWCNT/OC composites can be due to increase of the crystallite sizes.

The dependence of the storage modulus E' on the OC content in PP/OC composites is shown in Fig. 5.7. In the temperature range of β -relaxation ($0 \div 20^\circ\text{C}$), the sudden decrease of E' value is observed, what is typical for glass-rubber transition. In the α -relaxation region the storage modulus change with temperature is not so extreme.

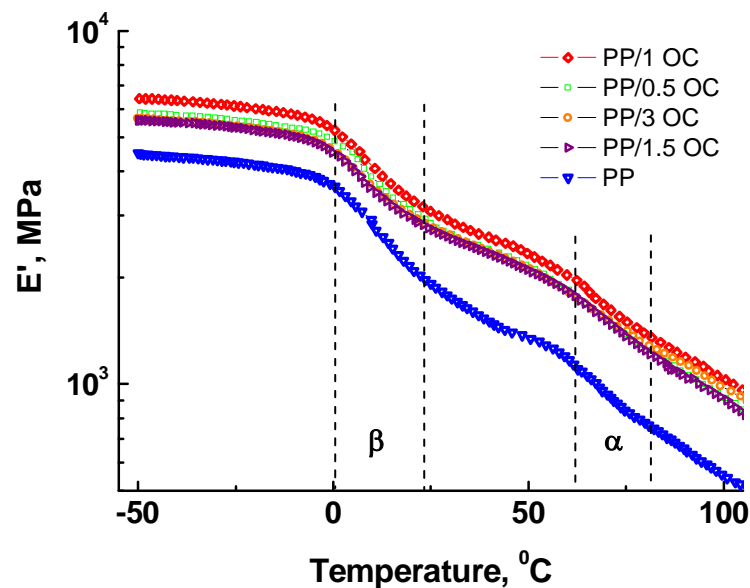


Fig. 5.7. Dynamic mechanical spectra (storage modulus) of the PP/OC composites, taken at 1 Hz. The temperature ranges of β - and α -relaxations are indicated.

Incorporation of OC into PP matrix increases the storage modulus of the PP/OC composites in the whole temperature range from -50°C up to 150°C , what indicates about the reinforcement effect. The storage modulus curves of the filled composites are shifted parallelly to the PP curve. The values of storage modulus in the glassy (at -40°C) and rubbery (at 50°C) states of the composites with

different filler contents are listed in the Table 5.2. One can see, that both dependences of the E' and T_c on the OC content for PP/OC composites demonstrate the identical behaviour. At small OC content E' and T_c values increase, however, further rise of OC content in composites (up to 3 vol.% of OC) results in slight decrease of E' and T_c . Such coordinated behaviour of T_c and E' depending on the OC content proves the plasticization effect.

The introduction of MWCNTs in the composite results in the increase of the storage modulus increases in the whole temperature range, what indicates the reinforcement effect. However, E' value increases more sharply in the PP matrix filled with OC compared to PP/MWCNT composites. The similar effect of the filler content on the storage modulus was found for PP/MWCNT/OC composites. The mechanical properties of the polymer composites improved in the presence of nanotubes the polymer matrix [17, 33]. Long nanotubes favour the load transfer between two phases and, consequently, lead to better mechanical properties of the composites [34].

It is necessary to note that composites filled with OC/MWCNTs exhibited the increase of the storage modulus compared to those containing only MWCNTs. It also can be argued as a confirmation of the hypothesis of interaction between two fillers. A similar effect was found in the epoxy/CB/clay systems, where the authors reported that high values of the storage modulus were caused by the interaction between clay and CB, which resulted in better dispersion of the fillers [4]. These data are in a good agreement with T_α values and, correspondingly, with T_c . Hence, one can conclude that storage modulus and, consequently, mechanical properties of material depend on the structure of the crystalline phase.

We should mention that not only content of the filler influences E' value. This parameter depends on the degree of crystallinity X_c as well. Since the values of X_c for PP/OC are higher than those for PP/MWCNT and PP/MWCNT/OC composites, the corresponding values of E' are higher as well (table 5.2).

Table 5.2. DMA data: values of α -relaxation peak T_α and storage modulus E' in the glassy and in the rubbery states for pure PP matrix and filled composites.

| Sample | T_α , °C | E' in the glassy state (at -40°C), (GPa) | E' in the rubbery state (at 50°C), (GPa) | X_c , % (DSC) |
|---------------------|-----------------|--|--|-----------------|
| PP | 69 | 4.2 | 1.3 | 35.5 |
| | | | | |
| PP/0.5 OC | 67 | 5.8 | 2.2 | 40.5 |
| PP/1 OC | 66 | 6.3 | 2.3 | 40.1 |
| PP/1.5 OC | 63 | 5.5 | 2.1 | 43.6 |
| PP/3 OC | 56 | 5.6 | 2.1 | 44.2 |
| | | | | |
| PP/1 MWCNT | 74 | 4.5 | 1.5 | 38.6 |
| PP/1.5 MWCNT | 78 | 4.9 | 1.7 | 38.2 |
| PP/3 MWCNT | 86 | 4.9 | 1.8 | 38.2 |
| | | | | |
| PP/1 MWCNT/1 OC | 75 | 4.8 | 1.8 | 38.5 |
| PP/1.5 MWCNT/1.5 OC | 75 | 5.0 | 1.8 | 37.0 |
| PP/3 MWCNT/ 3 OC | 82 | 5.6 | 2.1 | 38.4 |

5.1.4. Dielectrical properties of the composites based on PP filled with organo-clay.

In the filled systems one of the methods of the molecular mobility investigations is dielectric relaxation spectrometry method [35]. The molecular mobility, in turn, depends on the dispersion of the filler in the polymer matrix and polymer-filler interaction. Owing to the large surface area of nanofillers, the polymer composites are characterized by the presence of interphase regions, which properties affect significantly the physical characteristics of the nanocomposites. In order to study the influence of organo-clay (OC) on the PP matrix, the broadband dielectric spectroscopy method was applied. We should take into account that dielectric response in semicrystalline polymers can originate from the relaxation processes both in amorphous and in crystal phase. In the unfilled semicrystalline polymers, one can discriminate three following relaxation processes [36]:

- local motions in the glassy state (γ -relaxation). It appears around $-100\text{ }^{\circ}\text{C}$;
- glass-rubber transition (T_g or β -relaxation) of the amorphous phase. It appears around $(0\div 10)\text{ }^{\circ}\text{C}$, the corresponding activation energy is about 200 kJ/ mole ;
- pre-melting or crystalline transition (T_c or α -relaxation), which is attributed to the crystalline-amorphous interface or to the crystalline defects. This process can be observed around $(40\div 90)\text{ }^{\circ}\text{C}$.

F. Kremer et al. [37] have also reported that α -relaxation process is attributed to the molecular dynamics of the amorphous phase which is confined between the crystalline lamella or on the lamella surface. The α -process is assigned to the crystalline lamella where a rotational-translation of chain segments was assumed to be assisted by a chain twisting.

In the case of polymer composites, which include at least two components (polymer and filler), a new relaxation process, called Maxwell-Wagner-Sillars relaxation or interphase one, can appear on the dielectric relaxation spectra. This relaxation is connected with the charge accumulation on the boundary of two different materials, e.g. polymer and filler [37].

In Fig. 5.8 one can see the dependence of the loss tangent $\tan \delta$ on the temperature at frequency being equal to 1 kHz for pure PP and composites with different contents of OC. For pure PP the relaxation transitions are not intensive, whereas the introduction of a small amount of the filler changes the relaxation character significantly. In Fig. 5.8 for the filled composites one can clearly notice two relaxation transitions at about $10\text{ }^{\circ}\text{C}$ and at high temperature range. The dependence $\tan \delta = f(T)$ obtained via dielectric spectroscopy method has a good correlation with the results obtained by the DMA method, which will be presented further.

On the temperature dependence of the dielectric losses $\tan \delta$, the position of the relaxation peaks, corresponding to the glass transition almost does not depend on the filler content. At the same time, the latter value influences significantly the relaxation transition connected with the crystalline phase.

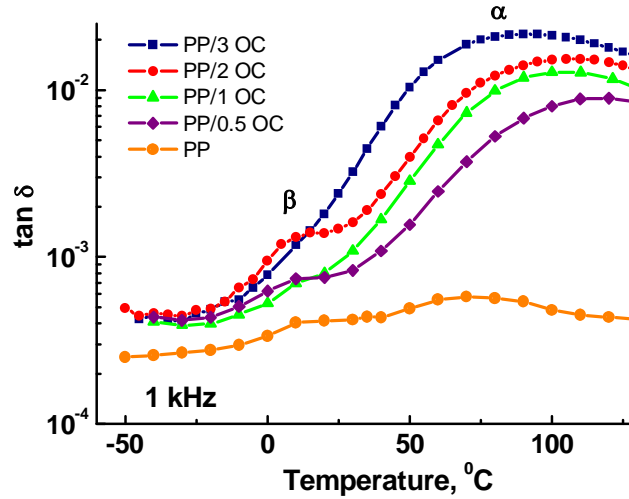


Fig. 5.8. The dependence $\tan \delta$ of dielectric losses on the temperature for different concentrations of OC at 1 kHz.

The maximum of the α -relaxation peaks on the dielectric relaxation curves shifts towards the lower temperature range as OC content increases. This tendency may be explained by the plastification effect, which facilitates the movement of segments or chains of polymer under applied electric field. It has been found that opposite to the DMA data it was found that for the dielectric measurements reveal that at filler content increase $\tan \delta$ value increases as well. It can be connected with more complicated nature of the α -relaxation peak. M. Ambid et al. [38] have explain the appearance of the α -relaxation peak in the PP filled with clay by the movement of the segments on the crystalline surface or by the presence of the clay clusters. The α -relaxation peak can be a result of two processes: relaxation, corresponding to crystalline phase and interphase polarization. The Maxwell-Vagner-Sillars polarization results in the charge accumulation on the polymer/filler boundary, what increases the α -relaxation peak intensity when the OC content increases.

For the PP/MWCNT and PP/MWCNT/OC composites it was difficult to separate the relaxation processes due to influence of conductivity on the ϵ' and ϵ'' values.

5.1.5. Electrical properties of the composites.

Fig. 5.9 demonstrates percolation behaviour of DC conductivity σ_{DC} versus content of carbon nanotubes for PP/MWCNT (curve 1) and PP/MWCNT/OC

(curve 2) composites. The electrical conductivity of conductive-nonconductive systems above the percolation threshold can be described by the classical scaling relation:

$$\sigma = \sigma_0 (\varphi - \varphi_c)^t \quad (5.2)$$

where σ_0 is the adjustable parameter, t is the critical exponent, φ is the volume content of conductive filler, and φ_c is the percolation threshold.

Insertion in Fig. 5.9 presents the scaling $\log \sigma$ versus $\log (\varphi - \varphi_c)$ relation, which was used for the determination of the values of φ_c , t and σ_0 . Such fitting of the experimental data for PP/MWCNT composites gives the percolation threshold $\varphi_c = 0.95$ vol. %, critical exponent $t = 4.1$ and preexponential factor $\sigma_0 = 1.5 \cdot 10^3$ S/cm (line 1). Adding of organo-clay into PP/MWCNT composites (with MWCNT:OC ratio of 1:1) promotes the decrease of the percolation threshold to the value of $\varphi_c = 0.68$ vol. % of MWCNTs (line 2). Fitting of the scaling parameters for PP/MWCNT/OC composites results in the critical exponent $t = 4.2$ and preexponential factor $\sigma_0 = 5.5 \cdot 10^3$ S/cm. The value σ_0 corresponds to the conductivity of pure CNTs.

The critical exponent t values, obtained for PP/MWCNT and PP/MWCNT/OC composites, are noticeably higher than the theoretical universal value for the three-dimension systems, which is equal to $t \approx 2$. The models for non universal critical exponent t were described by many authors. They take into account several factors, which can influence t values. First, it is a wide distribution of electric conductances of bonds between conductive clusters in the percolation network, or wide distribution of intercluster tunnelling contacts. Second, it is the shape of the conducting filler (such as rods, plates, etc.) [39]. D. S. McLachlan et al. [40] have reported about high non universal value of $t = 4.12$ in Fe_3O_4 -based systems was reported. The authors had suggested that high value of t was caused by combination of the wide range of tunnelling and point contact resistances between angular Fe_3O_4 grains.

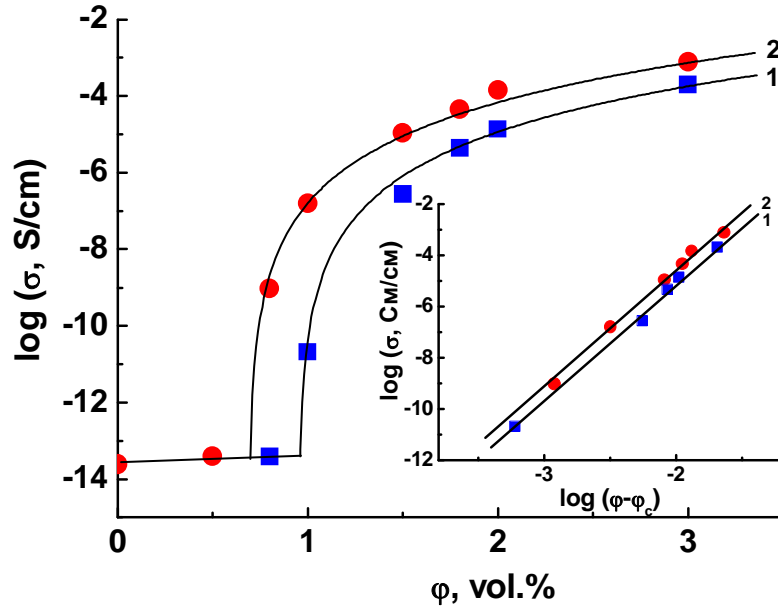


Fig. 5.9. The dependence of the electrical conductivity on the content of carbon nanotubes for PP/MWCNT (1) and PP/MWCNT/OC (2) composites with MWCNT:OC ratio equal to 1:1 (points are the experimental results, curves are calculated according to Eq. (5.2)). Fitting of the parameters of the equation (5.2) by the scaling relation $\log \sigma \sim \log (\phi - \phi_c)$ is given in the insertion.

Also, high t value can indicate nonstatistical distribution of the filler in the polymer matrix or can be explained by the cluster-cluster aggregation [41]. In particular, in the polymer composites filled with conductive filler, the interparticle electrical contacts can be realized due to tunnelling [42]. A polymer can form a thin layer around nanofillers, which prevents the formation of the physical contacts and increases distances between them. I. Balberg has reported that wide distribution of the inter-particle distances results in high non-universal t values [43].

In the PP/MWCNT composites, conductive network consists of the aggregates of nanotubes. In such a network, the charge transport can be realized through tunnelling between MWCNT aggregates or through the individual nanotube bridges, which connect agglomerates. A high value of the critical exponent $t = 4.1$, obtained for this system, can be caused by the aggregation of nanotubes what leads to wide distribution of inter-particle distances. OC affects dramatically the state of the network of conductive nanotubes what can influence the mechanism of charge transport. The addition of OC makes better dispersion of

nanotubes and results in conductive network formed by individual carbon nanotubes. Nevertheless, in PP/MWCNT/OC composites, the value of critical exponent was found to be the same, i. e. $t=4.2$, what evidences that even such a distribution of nanotubes is nonstatistical and is caused by interaction between the fillers. It is necessary to note that high values of the critical exponent were also found for the systems with carbon nanotubes [44, 45] and different conductive fillers [46, 47].

The addition of organo-clay to the PP/MWCNT composites provides one order of magnitude increase of the conductivity value for the samples with high concentration of nanotubes and few orders of magnitude conductivity increase for the samples with concentration of nanotubes close to the percolation threshold (Fig. 5.9). The increase of conductivity can be explained by the assumption that due to filler-filler interaction, OC untangles the nanotube aggregates, prevents their re-agglomeration during melt mixing and increases the number of interparticle contacts in the conductive network.

The similar percolation phenomenon was identified in the case of nanoparticles based on polyamide 6 filled with CB and clay [6]. It has been observed that percolation threshold shifts to lower volume fraction of CB in the presence of OC. Organo-clay was used as a dispersion control agent which induces self-assembling of CB network at low CB content. Such an effect was reported by Feller et al. [5] in conductive polymer composites (CPC) based on different thermoplastics filled with CB and montmorillonite. Lowering of the percolation threshold was explained by formation of a percolation pathway of clay platelets with adsorbed CB aggregates. The influence of clay on the electrical properties of SWCNTs/epoxy composites was also reported by L. Liu and J.C. Grunlan [9]. It was shown that percolation threshold was 0.05 wt. % of SWCNTs for the composites without clay, while adding of clay reduced this value to 0.01 wt. %. Two possible explanations of this phenomenon were proposed by the authors. First, addition of clay increases viscosity of composites, thus preventing migration and re-aggregation of nanotubes. Second, the nanotubes interact with clay stronger than with epoxy.

It is also necessary to note that addition of the organo-clay into the PP/MWCNT composites does not influence the change of morphology of the polymer matrix (DSC data). On the other hand, the addition of the OC influences the electrical properties of PP/MWCNT composites (Fig. 5.9), rising the values of σ_{DC} . Disentanglement of the carbon nanotubes (and thus changing of their spatial distribution) under the action of the OC does not affect the thermal characteristics of the composites. At the same time, it significantly influences the value of electrical conductivity, which depends on the mutual location of the conducting particles and on the presence of contacts between them, which forms the conducting network. This explains the duality of OC influence on the thermal and electrical properties of the composites, which include carbon nanotubes.

Conclusions

An introduction of organo-clay, MWCNTs or combination of the fillers into PP matrix strongly affected its thermal, electrical and mechanical properties. It reflects the influence of fillers on matrix crystallization and their distribution in the polymer matrix. Addition of OC into PP/MWCNTs composites (with MWCNTs:OC ratio of 1:1) impacts the dispersion of carbon nanotubes in the polymer matrix. SEM microscopy showed that in this case the morphology of MWCNTs changed dramatically from the randomly distributed aggregates to a network consisting from individual nanotubes. Organo-clay untangles the nanotube aggregates and improves their distribution. This promotes the decrease of the percolation threshold values from $\varphi_c = 0.95$ vol. % (for PP/MWCNTs composite) to $\varphi_c = 0.68$ vol. % (for PP/MWCNTs/OC composite) and provides the increase of the conductivity value by $(1 \div 4)$ orders of magnitude.

It was found that the presence of the fillers did not affect the glass transition of PP matrix. However, DMA results showed the significant influence of the fillers on α -relaxation peaks of the composites attributed to the relaxation in the crystalline phase of PP. This effect is caused by a change in crystallization conditions in the presence of the fillers, what results in the change of crystallization temperature T_c and degree of crystallinity X_c . A good correlation

was observed between changes in α -relaxation maximum temperature T_α , crystallinity degree X_c and crystallization temperature T_c . The influences of both MWCNTs and MWCNTs/OC combination on mechanical relaxation processes in PP are similar. It indicates that MWCNTs shield the effect of OC on the crystallization process. It can be assumed, that OC interaction with nanotubes is stronger than with PP. Due to this peculiarity, OC changes the spatial distribution of MWCNTs filler and influences the electrical properties of the material.

5.2. Investigation of structure and properties of polymer composites filled with nanometals and carbon nanotubes.

Lately the composition materials based on the polymers and filled with metal nanoparticles are of great interest for different science and technology branches. These systems are very attractive because of their specific properties, typical both for polymer and for conducting filler [48]. The research of such polymer-metal composites, which are used as conductive adhesive with silver, iron and nickel fillers (as conductive components) has shown the following tendency. The contact effects are insignificant in the composites with silver filler, whereas in the case of nickel filler the conductivity appears only at high Ni concentration, what indicates about the great value of contact resistance between the Ni particles [49]. The formation of the composites with the metal fillers is a very complicated process, as for the high level of conductivity it is needed to get a large content of particles, which can create a conductive network. For instance, H. P. Wu et al. have determined the percolation threshold ($\phi_c=13$ vol.%) for the system, based on the epoxy resin, filled with silver nanoparticles [50]. The percolation threshold of the polymer composites filled with metal particles can be reduced using immiscible polymer blends. A. Rybak et al. [51] have shown that by the appropriate use of the immiscible polymer blends the percolation threshold can be decreased even twice, from 17.4 vol.% of Ag for individual components (HDPE–Ag, PBT–Ag) to 8.2 vol.% for the HDPE/PBT–Ag blend. Such effect was observed due to creation of co-continuous structure with localization of the filler

in the polymer phase with lower viscosity, as it was evidenced by the microscopic investigations.

On the other hand, the introduction of the carbon nanotubes into the polymer matrix, even at their low content, results in conductive properties of the polymer composites. Usually the threshold value φ_c of the thermoplastic matrixes at melt-mixing reaches (1.0÷1.5) vol. % [40], whereas at special conditions of composite formation, the minimal value of the percolation threshold φ_c can reach (0.002–0.005) vol. % [52, 53]. The structure of the conductive phase, which is created by the carbon nanotubes is characterized by the branchy conductive lattice, what results in the low percolation threshold value. At the same time, low concentration of the conductive filler leads to the low value of the specific conductivity of the composition.

Electric conductive fillers, such as carbon nanotubes and nanometals, can also be used for the formation of the materials, applicable for the electromagnetic shielding. In such composition materials one of the most important characteristic is concentration of the conductive filler, at which the electro-magnetic radiation is absorbed effectively due to the proper conductance value of the material. Thus, the combination of carbon nanotubes and metal filler is an effective way to obtain the compositions with low percolation threshold and high electric conductivity. In the case of metal content beyond the percolation threshold, adding of nanotubes can provoke the appearance of conductance due to conductive lattice, formed by separate nanotubes being connected by metal nanoparticles (so-called “bridging-effect”) [8]. In the case of such formation of the compositions, one can obtain a high conductivity at low value of percolation threshold.

5.2.1. Electrical properties of the polymer nanocomposites, filled with carbon nanotubes and nickel nanoparticles.

The electric conductivity for the PP compositions with nickel nanoparticles, carbon nanotubes and combination of these two fillers – Ni/MWCNT are presented in Fig. 5.10. The experimental data were calculated in accordance with the percolation equation (5.2). For all the composites PP/MWCNT/Ni the

concentration of Ni nanoparticles was constant and equal to 2.5 vol.%, what is lower than the percolation threshold for the PP/Ni composites (which exceeds 7.5 vol.% in PP/Ni system). At the same time, the MWCNTs concentration varied from 0.1 vol. % to 3 vol. %. The measuring of the electroconductivity of the composites PP/MWCNT at direct current (DC) has shown the presence of the percolation threshold $\varphi_c = 0.7$ vol. % (Fig. 5.10, curve 2), whereas PP/Ni composites were non-conducting for all the values of Ni concentrations – up to 3 vol. % (Fig. 5.10, line 3). Such a low conductivity of PP/Ni composites can be explained by the spherical shape of Ni nanoparticles and polymer-metal interaction, what makes it difficult to form the conducting framework. A composite with binary filler Ni/MWCNT revealed the significant difference of the electrical characteristics in comparison with PP/MWCNT composites (Fig. 5.10, curve 1).

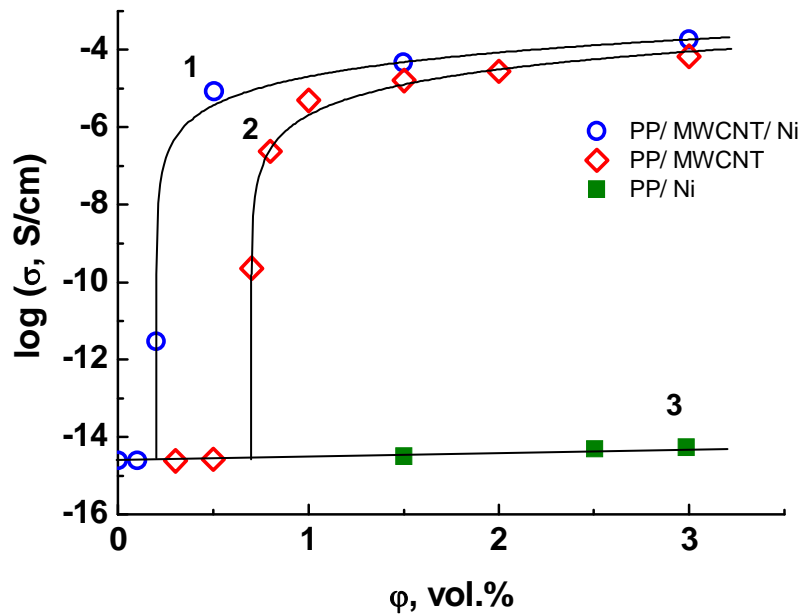


Fig. 5.10. The dependence of the electroconductivity on the filler content for the compositions of PP with different combinations of the fillers: Ni/MWCNT (1); carbon nanotubes (2); nanonickel (3). The content of Ni in the composites with combined filler was 2.5 vol. %.

In this case the percolation threshold value in PP/MWCNT/Ni composites decreases sharply and becomes to be equal to 0.2 vol. % of CNT (Fig. 5.10, curve 1), i.e. more than 3 times lower in comparison with PP/MWCNT. Such a percolation threshold shift towards lower values of MWCNT concentration can be

explained by a high anisotropy of the nanotube sizes and by the existence of the “bridging”-effect.

Long carbon nanotubes connect Ni particles or their aggregates and, thus, the number of electroconductive chains in composition materials increases. It is obvious, that in this case electric conductivity is provided by the lower content of nanotubes, what results in the percolation threshold decrease. It should also be noted, that the conductivity of the PP/MWCNT/Ni exceeds that of PP/MWCNT 4 and 2 times in the case of 1.5 vol. % and 3 vol % of nanotube concentration value, respectively.

The percolation behaviour of the obtained system with combined filler can be characterized in two ways. If one assumes, that in the composite with 2.5 vol. % of Ni and 0.2 vol. % of MWCNTs, Ni particles are conductive phase, one can conclude, that addition of insignificant amount of MWCNTs (0.2 vol. %) shifts the percolation threshold of the PP/Ni significantly. If one supposes, that percolation threshold for the PP/Ni composites is 7.5 vol. % (as it follows from the measurements, in the case of 7.5 vol. % of Ni PP/Ni composite is not conductive yet), then while adding of 0.2 vol. % of MWCNTs into PP/Ni composite with 2.5 vol. % of Ni, one can achieve the decrease of the percolation threshold by 3 times. In the case, when CNT is considered to be a conductive phase, then the adding of Ni particles (2.5 vol. %) into PP/MWCNT composite results in the decrease of the percolation threshold by 3.5 times from 0.7 vol. % to 0.2 vol. % of MWCNTs.

The presence of the percolation behavior of the ε' concentration dependencies in PP/MWCNT and PP/MWCNT/Ni composites has already been observed (Fig. 5.11). For the PP/MWCNT/Ni the values of ε' were found to be higher than that for PP/MWCNT composites while for the PP/Ni composites the value of ε' was low even at 5 vol. % of Ni. Such an effect is caused by the presence of Ni nanoparticles in conductive network, which influence the permittivity of the composite.

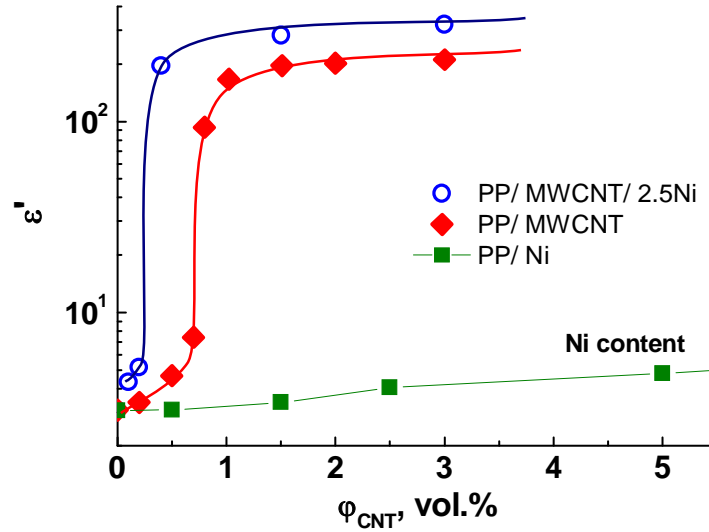


Fig. 5.11. The permittivity ϵ' of the PP composites filled with Ni nanoparticles, MWCNTs and combination of two fillers – Ni/MWCNT.

Fig. 5.12 shows the model of the conductive phase structure as the combination of spherical particles (nanometal, carbon-black) with elongated nanotubes. Such a model has been reported by P. C. Ma et al. [2]. As it has been mentioned earlier, the improvement of the electrical characteristics of a composite with a combined filler can be caused by the so-called “bridging”-effect. It means, that one of the fillers creates conducting bridges between the particles of the another one, and thereby they create a conductive structure.

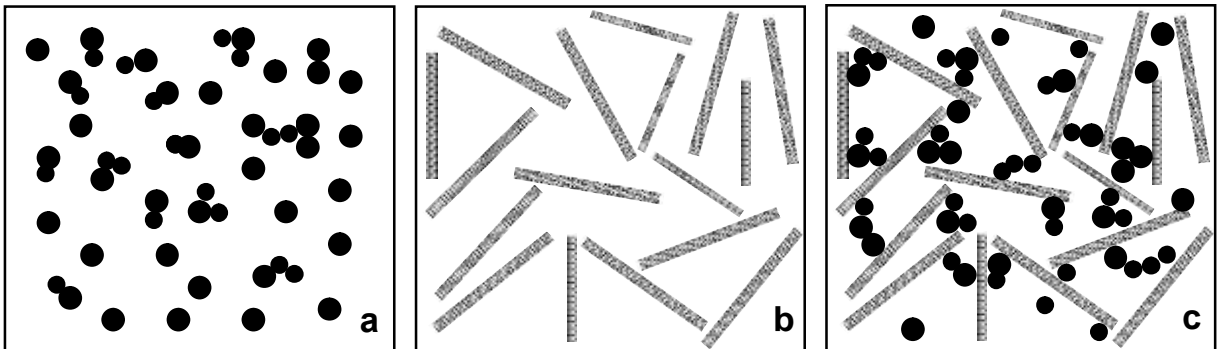


Fig. 5.12. A schematic model of the combined filler in polymer matrix: a) Ni particles; b) carbon nanotubes; c) combined filler [2].

The existence of a “bridging”-effect, at which nanotubes act as conductive bridges between the nickel nanoparticles in conducting cluster, can be proved by the electron microscopy images (Fig. 5.13). One can see the presence of nickel

aggregates in the polymer matrix, which are distributed between the nanotube aggregates and contact with them (Fig. 5.13, c).

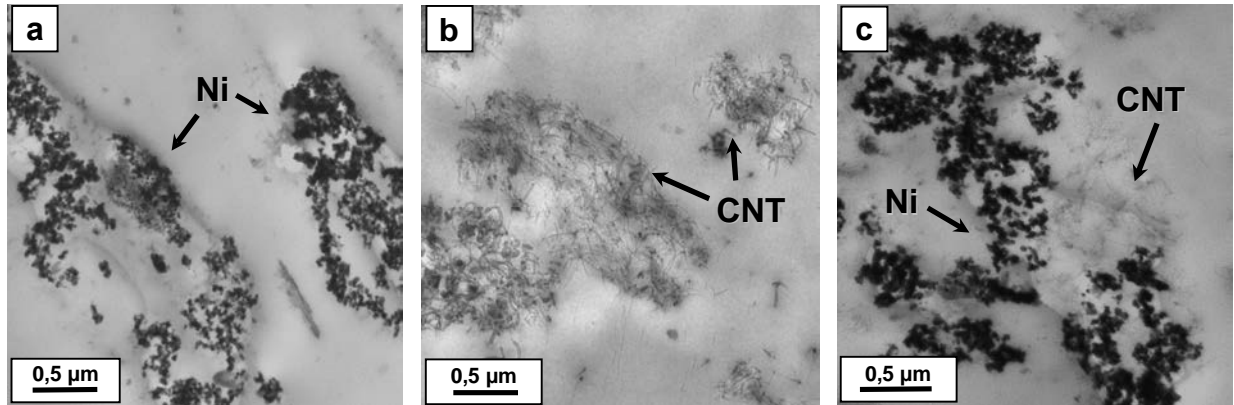


Fig. 5.13. TEM images of the following structures: a) PP/Ni composite, filled with 2.5 vol. % of Ni; b) PP/MWCNT, filled with 0.5 vol. % of MWCNTs; c) PP/MWCNT/Ni filled with combined filler 0.5 MWCNT/2.5 Ni.

5.2.2. Thermal analysis of the melting and crystallization of composites filled with nickel and carbon nanotubes.

One more possible reason for the percolation threshold decrease in PP/MWCNT/Ni composites can be the influence of the nickel nanoparticles on the formation of the morphological structure in polymer matrix. This influence can change the space distribution of nanotubes, while increasing their local concentration in some regions, what promotes the formation of the conducting cluster.

The influences of nanofiller on the formation of the composite structures was studied by Differential Scanning Calorimetry (DSC) and made it possible to determine melting and crystallization temperature. As one can see in Fig. 5.14, the crystallization temperature T_c of all the composites are shifted towards higher temperatures in comparison with pure PP, what demonstrates the role of the filler surface as crystallization center.

Due to this peculiarity the crystallization process at cooling of the melt begins earlier (at higher temperatures) in the filled systems, than in the unfilled PP. The data of the melting and crystallization temperatures are listed in the Table 5.3.

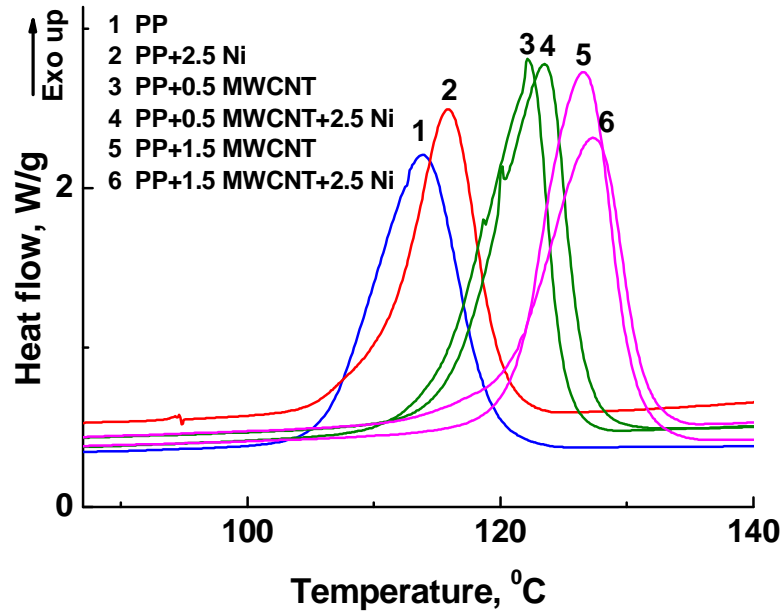


Fig. 5.14. The crystallization maxima of the PP/MWCNT, PP/Ni, PP/MWCNT/Ni composites and pure PP.

From these data one can conclude, that the introduction of nanotubes into PP does not change significantly the melting temperature T_m , whereas one can observe a noticeable difference of crystallization temperature T_c of the pure PP and filled systems. It means that in comparison with melting, crystallization is more sensitive process to the presence of the introductions, which influence the formation of the crystal structure. The same effect was reported by M.-K. Seo et al. [22].

The behaviour of the supercooling temperature $\Delta T = T_m - T_c$ was found to be rather interesting. This temperature is caused by the kinetics of the crystallization, i.e. the ratio of crystallization and cooling rates at DSC measurement process. As the cooling rate is equal for all the composites, then ΔT is defined by the crystallization rate. The presence of the fillers accelerates the crystallization process, then ΔT value is lower for the filled systems in comparison with pure PP. For PP/MWCNT and PP/MWCNT/Ni ΔT decreases by 7 °C with MWCNT content increase (from 0.5 vol. % to 1.5 vol. %), what indicates about the acceleration of the nucleation at the presence of the MWCNTs at crystallization process. The main feature is the crystallization and supercooling temperatures are almost identical for PP/MWCNT and PP/MWCNT/Ni systems with equal

nanotube content. It means that the presence of the nanonickel filler does not influence the crystallization process in the polymer matrix, which includes nanotubes.

Table 5.3. Melting and crystallization temperatures and crystallinity for PP/Ni, PP/MWCNT and PP/MWCNT/Ni composites.

| Composition | T_c , °C | T_m , °C | $\Delta T = T_m - T_c$, °C | χ , % |
|-----------------|------------|------------|-----------------------------|------------|
| PP | 113.9 | 166.7 | 52.8 | 41.66 |
| PP/2.5Ni | 115.9 | 160.3 | 44.4 | 49.28 |
| PP/0.5CNT | 123.5 | 167.0 | 43.5 | 47.25 |
| PP/0.5CNT/2.5Ni | 122.1 | 166.9 | 44.8 | 48.22 |
| PP/1.5CNT | 126.6 | 163.4 | 36.8 | 43.38 |
| PP/1.5CNT/2.5Ni | 127.3 | 164.5 | 37.2 | 45.16 |

Thus, the processes of structure formation in PP/MWCNT system in the presence of Ni nanoparticles do not change the space distribution of the nanotubes and in PP/MWCNT conductive compositions the effect of decrease of percolation threshold via nanonickel fillers is caused exclusively by “bridging”-effect.

Conclusions

The addition of a small amount of Ni nanoparticles promotes significantly the electrical properties of ternary PP/MWCNT/Ni nanocomposites. The conductivity of the PP/MWCNT/Ni exceeds that of PP/MWCNT 4 and 2 times in the case of 1.5 vol. % and 3 vol % of nanotube concentration value, respectively, and the percolation threshold of the composites shifts from 0.7 vol. % to 0.2 vol. %. The metal nanoparticles act as bridges among MWCNTs, thus facilitating the formation of conductive paths in the PP/MWCNT/ hybrid composites. The DSC results shows that structure formation in PP/MWCNT

system in the presence of Ni nanoparticles do not change the space distribution of the nanotubes. Thus, in PP/MWCNT conductive compositions the effect of decrease of percolation threshold via nanonickel fillers is caused exclusively by "bridging"-effect.

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General conclusions

Owing to the unique mechanical, electrical and thermal properties, carbon nanotubes (CNTs) are very promising nanofiller for creation of the electro-conductive polymer composites. Incorporation of CNTs with their excellent properties into polymer matrix becomes a greatly attractive route for the fabrication of various advanced functional materials. However, all the improvements which can be achieved with the presence of CNTs in a polymer composite greatly depend on the amount of CNTs added into the polymer matrix and mainly on the structure organization of the conductive nanofiller and its interaction with polymer phase.

The structural organization of carbon nanotubes in the composites based on thermoplastic polymers plays one of the crucial roles in the manifestation of specific electrical, mechanical and thermal properties. Thus, one can conclude, that a possibility to control the structure formation of the filler conductive phase becomes especially important when this process determines the electro-physical properties of the polymer composite and enables to create the composites with predefined electro-physical properties.

The three types of polymer systems filled with carbon nanotubes have been investigated, namely: 1) segregated systems with ordered distribution of the nanofiller, which is caused by the processing conditions of processing; 2) conductive polymer blends, where the creation of conductive phase of carbon nanotubes depends on the conditions of formation of the composite and on the degree of the interaction between CNTs and polymer components; 3) composites with binary fillers where carbon nanotubes have been combined with organo-modified clay in one case and with metal nanoparticles in another one. All these systems are connected by the fact that the structural organization of conducting nanofiller, the spatial distribution of the particles and the degree of filler interaction with the polymer matrix determine their electrical and mechanical properties, despite their different conditions of processing, the composition and structure. However, each system is characterized by its own specific conditions of the formation of conducting phase, different conditions of interaction between

polymer matrix and nanofiller, and by the rate of influence of nanofillers on structuring in the polymer phase. All three systems are also characterized by different levels of structural organization of conductive phase, which affects the electrical percolation characteristics, dielectric parameters, thermal properties and mechanical characteristics of the composites.

The study of the segregated systems has shown that in PVC/CNT and PP/CNT composites, which were processed by hot compacting method, CNTs create a conductive skeleton at the value of the ultralow percolation threshold $\varphi_c = 0.045$ vol. % and $\varphi_c = 0.040$ vol. %, respectively. The obtained ultralow values of percolation threshold have caused by both high aspect ratio of CNT and existence of segregated structure in a form of conductive skeleton of nanofiller on the boundaries between compacted polymer grains. The results have also shown that percolation behavior does not depend on the type of polymer matrix but is determined by the size ratio of the filler particles and polymer powder grains. Thermomechanical properties of composites correlate with electrical properties. Forming of the filler framework in the composites at CNT content above percolation threshold causes the restrictive influence of skeleton on transition of the polymer to the viscous-flow (plastic) state. Growth of the elastic module E_e values with higher values of CNT content indicates the increase of the framework hardness in the composite and its influence on the elastic properties of a segregated system.

In polymer blends based on PP and CPA and filled with carbon nanotubes the electrical properties and, in particular, percolation behaviour strongly depends on the spatial distribution of CNTs in binary polymer matrix. For the PP/CPA-CNT polymer blend processed by diluting of the CPA-4%CNT concentrate with pure PP, the value of percolation threshold is reduced to $\varphi_c=0.7$ vol. % in comparison to the filled polymer composites CPA/CNT with the value of $\varphi_c=1.4$ vol. %. In the opposite blend CPA/PP-CNT the distribution of the filler is quite different, whereas the nanofiller is distributed randomly through the composite. In the first case CNTs remain in CPA component and create interpenetrating conductive-nonconductive (CPA-CNT)-(PP) network. In the opposite case the nanofiller is distributed in both of polymer components randomly. In the first case

the ordered distribution of the filler in one polymer phase was realized due to mutually action of three factors – thermodynamic, kinetic and processing, which affect in the same “direction” and contribute to such morphology. In the opposite system CPA/PP-CNT the thermodynamic and kinetic factors counteract to the processing factor and define such type of spatial distribution of nanofiller. These two cases demonstrate the double percolation conception. The value of φ_c in the first PP/CPA-CNT system is defined by creation/destruction of the conductive network of CPA-CNT phase within the polymer matrix. In the opposite CPA/PP-CNT blend the value of φ_c is connected with the creation/destruction of the conductive network of nanotubes distributed in both of polymer components.

The dependence of Young's modulus on the filler content correlates with percolation behaviour of composites. In the PP/CPA-CNT polymer blend where conductive network is created by the filled phase of CPA-CNT, the behaviour of electrical and mechanical properties are similar because of sensitivity to the creation of the conductive network of CPA-CNT and to the existence of the percolation threshold. The opposite system CPA/PP-CNT shows a similar behaviour of Young's modulus to that for the filled individual polymer.

The literature data testify that the improvement of electrical conductivity of polymer composites is still limited for the moment due to poor dispersion of CNTs and their ability to create aggregates during the introduction into the matrix. These factors diminish the effectiveness of the CNT usage as electro-conductive filler. Thus, the organo-modified clay (OC) has been introduced into PP/CNT composites in order to improve the dispersion of CNTs and to enhance the electrical properties of the composites. It has been shown that such a combination of two types of the nanofillers can provokes the amplification of the effect of the basic filler or influences significantly the structure and the properties of the composite due to synergism. The obtained results have shown that organo-clay untangles the nanotube aggregates and improves their distribution. This promotes the decrease of the percolation threshold values from $\varphi_c = 0.95$ vol. % to $\varphi_c = 0.68$ vol. % for PP/CNT and PP/CNT/OC composites, respectively and provides the increase of the conductivity value by 1–4 orders of magnitude. The

DSC results have shown that CNT, OC, and their combination have crucial influence on the thermal properties and crystallization of PP. Crystallization behavior and degree of crystallinity of PP/CNT/OC composites were found to be identical to those of PP/CNT composites. Such a dependence of the crystallization behavior on the filler content demonstrates that the influence of OC on PP crystallization in the presence of CNTs is negligible as compared to PP/OC composites. It indicates that the presence of CNTs shields the influence of OC on crystallization in PP. This peculiar interaction between clay and CNTs indicates that the nanofillers with different dimensions can considerably cooperate with each other and improve the properties of the composites. In spite of the fact, that the investigation of polymer composites containing both clay and CNTs is still at its primary stage, but it seems to be promising and perspective to assemble two types of nanoparticles in order to avoid the limitation of the usage of individual nanofiller in the composites.

The use of combination of two types of conductive fillers with different nature, as CNT and metal nanoparticles, has also shown perspective results. It has been found that the addition of a small amount of Ni nanoparticles promotes significantly the electrical properties of ternary PP/CNT/Ni nanocomposites. The conductivity of PP/CNT/Ni composite exceeds that of PP/CNT composite, and the values of the percolation thresholds are much lower ($\phi_c=0.2$ vol. % for the ternary PP/CNT/Ni nanocomposite versus 0.7 vol. % for the PP/CNT composite). The metal nanoparticles act as bridges among CNTs facilitating the formation of conductive paths in the PP/CNT/ hybrid composites. The DSC results show that structure formation in PP/CNT system in the presence of Ni nanoparticles do not change the space distribution of the nanotubes. Consequently, the effect of decrease of percolation threshold via adding of nanonickel fillers is caused exclusively by "bridging"-effect. Thus, introduction of differently dimensioned conductive nanofillers into the polymer matrix and the use of nanofillers with different physical characteristics makes it possible to control the electrical properties of the composites and, particularly, the value of the percolation threshold.

A filling of polymer matrix with carbon nanotubes and the possibility to control the conductive phase formation enables to form nanocomposites with a predesigned complex of electro-physical properties. All three studied systems demonstrate the ways of creation of promising materials for the use in various technical areas.