Chapter 1

Modification of Oligomers and Reinforced Polymeric Composites by Carbon Nanotubes and Ultrasonic

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Abstract

In the last two and a half decades nanotechnology has been actively developed all over the world. With respect to traditional and nanomodified polymers and reinforced polymeric composites based on them, modification methods are considered as a basic direction of improving their technological and operational characteristics. This chapter analyzes the physical (in the form of ultrasound) and chemical modification of liquid polymer media and reinforced polymeric composites. The main emphasis is made on the analysis of ultrasonic cavitation processing as the most effective one for solving one of the main technological problems in the production of nanomodified polymer composites. It consists in de-agglomeration and further dispersion of the used nanoparticles in liquid polymer media. The peculiarities of nanocarbon modification of epoxy oligomers and reinforced composites based on them are considered. The results of studies of the microstructure of nanomodified polymeric composite materials are presented. The use of nanomodifiers in the form of carbon nanotubes is described, which can be applied for improving the physicomechanical and performance characteristics of polymers. These nanomodifiers include tensile strength and deformation, fatigue strength, electrical conductivity, and glass transition temperature.

Keywords Reactoplast • Oligomer • Composite • Carbon Nanotube • Modification • Ultrasonic • Production • Properties

1.1. Introduction – Modification as Basic Direction of Improving the Technological and Operational Characteristics of Traditional and Nanomodified Liquid Polymeric Media and Reinforced Polymeric Composites

At present, the modification (physical as ultrasonic (US), chemical and physico-chemical) is the basic direction of improving the technological and operational characteristics of traditional and nanomodified elastomers and reinforced polymer composites (PC) based on them (Harris P.J.F. 2004; Kolosov A. E. 2014a). Of the same importance are the design issues of the technological process of producing traditional and nanomodified polymer composites (NMPC) (Kolosov A. E. 2015a). In this case, the use of US modification and intensification is the main method of increasing the productivity of the process and improving the performance characteristics of such materials (Kolosov A.E. et al. 2012a; Kolosov A.E. 2014b).

PC containing carbon nanomaterials (CNM), in particular, carbon nanotubes (CNT), have been researched since the end of the 1990s, when these materials became available in relatively large quantities (Harris P.J.F. 2004). Such studies are much rarer than those dedicated to the use of fullerene. However, interesting practical results have been obtained (Aldoshin S.M. 2008). Many processing and operational characteristics of elastomers and liquid polymers can be increased considerably (sometimes several times) by modifying them with small amounts of nanoparticles, e.g., fullerenes, nanotubes, nanowires, inorganic nanoparticles, etc. (Karpacheva G.P. 2000; Wang C. et al. 2004; Badamshina E.R. and Gafurova M.P. 2008; Luzgarev S. et al. 2013; Kondrashov S.V. et al. 2013). For this, effective methods for dispersing CNT in organic solvents and liquid polymeric media are required.

A number of works have been devoted to the preparation, enhancement of operational properties and the use of reactoplastic NMPC materials. In particular, the prospects for development and practical application of nanotechnology, including for production of NMPC, were analyzed in terms of the achievements of modern science and technology (Kolosov A. E. 2015b). Effective technical means (methods and devices) designed to produce reactoplastic NMPC that provide increased strength and service life for structures based on them were analyzed (Kolosov A. E. 2016a). Effective methods for dispersing carbon nanotubes in organic solvents and liquid polymeric media were analyzed (Kolosov A. E. 2016b).

Features and problems of producing reactoplastic NMPC were considered using modification of epoxide oligomers with carbon nanotubes as an example (Kolosov A.E. 2016c). The characteristics of reactoplastic NMPC were analyzed using structural carbon-fiber prepregs as examples (Kolosov A.E. 2017).

The results obtained both in the above mentioned and in other works provide prerequisites for further studies on the improvement of effective methods for the modification of traditional and nanomodified liquid polymer media and reinforced PC based on them. The above mentioned aspects are briefly reflected in this chapter.

1.2 Physical Modification of Liquid Polymeric Media and Reinforced Polymeric Composites: Methods and Means

1.2.1 Physical Modification of Liquid Polymeric Media by Ultrasonic

As the main method of physical modification of liquid polymer media and reinforced PC based on them, US low-frequency cavitation is currently used. At the same time, the achievement of the necessary positive result from the cavitation effect can be achieved by varying the parameters of the cavitation treatment (frequency, amplitude, intensity, pressure, temperature, volume of the liquid medium being treated).

On the other hand, the hardening value depends on the particular type of oligomer to be processed and can be up to 40-50% for traditional thermosets, or several times (depending on the type of nanomodifier) for nanomodified reactoplastics (Kolosov A.E. 2014c; Kolosov A.E. 2016c). The effect of low-frequency US treatment regimes on reactoplastic PC material (PCM) operating properties was analyzed. An example was provided of effective US treatment by the technology developed compared with known methods (Kolosov A.E. 2014c).

The analysis of the specific features of the realization of US modification of liquid media indicates that it is promising to carry out such a modification of liquid epoxy oligomers (EO) and epoxy compositions (EC) used in the molding of reactoplastic PC materials. Moreover, such a modification is effective both in the low-frequency and mid-frequency US ranges.

The effect of heterofrequency US treatment on reactoplastic PCM operating properties was analyzed. Conformity is established for effective process parameters of heterofrequency US cavitation in liquid EC, and this makes it possible to select effective energy saving processing base parameters for preparing epoxy polymers (EP) based upon them (Kolosov A.E. 2014d).

The use of excessive pressure in the US treatment of liquid polymeric media, for example during the molding of epoxy sleeves with shape memory effect, is an important factor in increasing the intensity and shortening the processing time, as well as the cumulative production time of the finished product. The effect of low-frequency US treatment regime and excess pressure on reactoplastic PCM (unfilled and filled with short-fiber fillers) is analyzed. Optimum process parameters are established for US treatment of liquid epoxy composites (Kolosov A. E. 2014e).

These effective parameters, as a rule, are set experimentally in each specific case. The found optimal parameters of US cavitation processing lead to an increase in the physico-mechanical properties of solidified oligomers (Harris P.J.F. 2004; Karimov A.A. et al. 1989).

1.2.2 Ultrasonic Modification of Reinforced Polymeric Composites

Effective US modification of reinforced polymeric composites allows to achieve several results at once. Firstly, it is US activation of the surface and structure of the fibrous filler to improve its wettability EC. Secondly, it is degassing the structure of the filler just before it is impregnated. Thirdly, this is an increase in the productivity of the impregnation process and the dosed application of the EC by increasing the speed of pulling the filler while preserving the properties of the final composite.

Finally, the use of ultrasound is an effective method of stabilizing the content of epoxy binder in impregnated woven filler, with variation in the speed of its stretching during the dosing process.

It has been experimentally established that as a result of the application of effective US treatment regimes in the impregnation of oriented fibrous fillers, the total height of the EC lift (the productivity of US impregnation) in the impregnation of fibrous fillers with previously voiced EC increases by (2.5 - 3) times (Kolosov A.E. et al. 1989a). In addition, US treatment allows to increase the deformation-strength and adhesion characteristics of materials, to lower the level of residual stresses, to increase the durability, and, moreover, to significantly shorten the hardening time (Kolosov A. E. et al. 1990).

Technological bases of impregnation of fibrous fillers and dosed application of epoxy binders on them with application of ultrasound are developed. Improved high-performance designs of impregnation and dosing unit on serial impregnating and drying equipment. It is established that the use of the developed energy-saving and environmentally safe technical means makes it possible to use highly viscous and highly concentrated impregnating compounds. In addition, quality is increased and the productivity of the impregnation process is increased, and uniform impregnated composite material is obtained practically without air inclusions.

It is these factors that determine the choice of US as the dominant method of physical modification of fibrous PCM at the main stages of their production.

1.2.3 Technical Means for Ultrasonic Modification

Existing technical means for US modification of liquid, in particular, polymer media, and reinforcing fillers on their basis can be conditionally divided into US concentrators - speed transformers and radiating plates. The first type of US equipment is used primarily for processing liquid polymer media, including when nanomodifiers are incorporated into them. The second type of US technical means is used primarily for processing the impregnated woven fibrous fillers. For both types of

US technical means, it is necessary to determine the effective design and technological parameters (Kolosov A.E. 2012b).

The first type of radiators has been studied quite fully, while a number of problems arise in calculating the second type of US technical means. When using powerful emitters used in various technological processes, first of all, it is necessary to control the level of intensity. Otherwise, such undesirable changes as mechanical destruction, chemical reactions, etc. can occur in the liquid medium being treated. In addition, the level of intensity and frequency of oscillations must meet the sanitary standards and requirements of the technology used. In this regard, it is advisable to analyze the effective technical means of cavitation processing with a radiating plate that generate US vibrations necessary for specific technological processes, as well as corresponding improved methods for calculating these technical means.

The existing unevenness of the unevenness of bending vibrations under the action of an US field along and across the outer surface of the radiating plate makes it difficult to rationally use US transducers in automated technological installations. This is particularly evident in the contact treatment of woven materials of considerable width. As a result, the appearance of defective portions of the resulting final CM is possible.

Analytical peculiarities of US cavitators based on piezoceramic transducers with a radiative plate, which experiences bending vibrations, are analyzed. The acoustic dimensions of components of a sectional piezoelectric transducer used in the production process of contact US treatment of a dry 1120-mm wide cloth impregnated with a polymeric binder, are calculated (Kolosov A.E. et al. 2013).

The approaches developed by the authors to determine the effective design and technological parameters make it possible to eliminate the nonuniformity of the above bending vibrations (Kolosov A.E. et al. 2013; Kolosov A.E. et al. 2012b). The implementation of the developed approaches allows to obtain practically defect-free traditional PC and NMPC.

1.2.4 Process Design for the Production of Traditional and Nanomodified Composites with Ultrasonic Modification

The complexity of solving the problem of designing a technology and equipment for the production of reactoplastic PCM is due to the need to investigate a set of issues. These issues are aimed at identifying and studying the interrelations between the structural, mechanical and geometric parameters of products, on the one hand, and the technological factors of their production, on the other. The subject of researching the technology of manufacturing products from PCM is the patterns that establish not only the interrelations, but also the mutual influence of technological factors. The latter determine in certain pre-defined production conditions the production of the required performance characteristics of manufactured products from PCM within the limits of design deviations.

Thus, for example, the kinetic equations of longitudinal and transverse impregnation of oriented fibrous fillers with polymeric binders make it possible to predict the speed of broaching the fibrous filler through the impregnating bath, and also to design its dimensions (Kolosov A. E. 1988a). The study of the influence of technological impregnation regimes on the strength of impregnated and cured fibrous fillers makes it possible to design the optimum force of impregnated fibrous fillers during winding (Kolosov A. E. et al. 1988b; Kolosov A. E. and Repelis I. A. 1989b).

To minimize material and time costs, it is necessary to use effective techniques for modeling the design and technological parameters of technology and equipment (tools) for the production of reactoplastic PCMs. This should be done taking into account the specifics of the objects being modeled, in particular, by adapting the perspective methodology of structural-parametric modeling (SPM) to solving specific problems (Kolosov A.E. et al. 2015a). The principle of the system approach assumes the analysis of the investigated object simultaneously and as a set of certain interrelated elements, and as a potential component of the higher hierarchical level. Therefore, it seems expedient to separate the investigated structural scheme of the impregnation and dosing application of the polymer binder onto a long fibrous filler using ultrasound into separate structured blocks.

These blocks represent the corresponding base processes and in this case include: 1) US treatment unit for EO and preparation of impregnating composition (EC); 2) a block of "free" impregnation of oriented fiber filler with liquid EC; 3) block of dosed application of liquid EC to impregnated fibrous filler. In the future, only the above enlarged blocks and their constituent structural elements are analyzed, as well as the interrelations between them, within the framework of the synthesis.

It should be noted that research and modeling of the entire technological cycle for obtaining high-strength and defect-free traditional PC and NMPC and the entire complex of equipment realizing it is an extremely difficult task, has not yet been solved.

1.3 Modification of Oligomers and Reinforced Polymeric Composites by Carbon Nanotubes

1.3.1 Bulk Content of a Nanofiller in a Polymer Composite

Even small additions of CNT (1 - 2%, sometimes 0.1 - 0.3%) can increase by several times the elasticity modulus and tensile strength of a reactoplastic polymer (Coleman J.N. at al. 2006). The thermal and electrical conductivity of the polymer is sharply increased at the same time. CNT additives can also expand the operating temperature range of nanomodified PC (NMPC) by increasing the glass-transition temperature (Aldoshin S.M. 2008).

The conditions required to produce NMPC are a small size and CNM particle distribution as uniform as possible in the polymeric matrix. The tendency of CNM to aggregate hinders the preparation of stable CNT dispersions in water and organic solvents (including polymers). Therefore, effective methods for facilitating aggregate disintegration are being actively pursued (Atovmyan E.G. et al. 2005). These include chemical modification of CNM by low-molecular-mass compounds and polymers to form covalent bonds between the modifier and nanotube and non-covalent modification of CNM by both low-molecular-mass and polymeric surfactants (SA).

Polymethylmethacrylate was used as an example to show (Aldoshin S.M. 2008) that small additives (10^{-2} – 10^{-3} wt.%) of carboxylated multi-walled CNT (MWNT) to the starting reaction mixture can increase the dynamic elasticity modulus of the polymers by 1.5 - 2 times. The yield (change of sample linear dimension) of the polymers decreases by ~3 times on passing the glass-transition temperature. The effect reaches a maximum at MWNT concentrations of ~ 0.05 wt.%.

Thus, a serious scientific effort to study and design new NMPC with improved operational characteristics as compared with the starting polymers was undertaken. This helped to extend the service life (and decrease the materials consumption, mass, and dimensions) of parts prepared from NMPC (Aldoshin S.M. 2008).

1.3.2 Chemical Modification of CNT

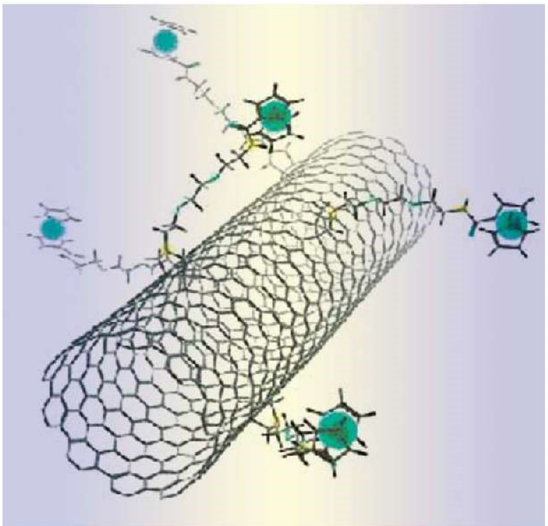
Practical application of CNT is hindered by their insolubility (in particular, in aqueous media) and tendency to aggregate and form linkages, channels, etc. (Priluts'ka S.V. et al. 2009). Aggregates form because of the hydrophobicity of the CNT and the action of intratubular forces, e.g., Van-Der-Waals and electrostatic interactions.

Various chemical modification methods (oxidation, non-covalent and covalent functionalization) and USation are used to improve the properties of colloidal CNT dispersions (Smart S.K. et al. 2006; Hirsch 2002). For example, oxidation of CNT by various acids forms CNT with carbonyls and/or carboxylic acids on the CNT ends and walls (Prylutska S.V. et al. 2008). However, such modification can alter the CNT properties. Ultrasonication of their aqueous suspensions, a commonly employed method for altering CNT solubility, is used for accelerated dispersion of CNT (Andrews R. et al. 2002).

A unique method for chemical modification of CNT is non-covalent functionalization, i.e., formation of CNT complexes with organic molecules through non-covalent bonds (van-der-Waals or π-π-stacking interactions). Various polymers and biological macromolecules such as peptides and nucleic acids act as such organic molecules (Andrews R. et al. 2002). An advantage of this method is that the electronic structure of the CNT surface is preserved (Priluts'ka S.V. et al. 2009).

Covalent functionalization of CNT involves covalent attachment of molecules, e.g., peptides, organic acids, polyamines, and poly-L-lysine, to CNT walls in order to improve their solubility (Fig. 1.1). This is achieved via 1,3-dipolar cycloaddition, amination, or esterification of COOH groups after CNT are purified of side products (amorphous C and the metal particles used to grow the CNT (Priluts'ka S.V. et al. 2009).

Fig. 1.1 Diagram of single-walled CNT functionalized by organic compounds (Priluts'ka S.V. et al. 2009)



An important advantage of both covalent and non-covalent functionalization is that more stable colloidal dispersions based on these CNT can be prepared and new nanomaterials can be formed from them.

1.3.3 Preparation of Carbon Nano Materials Dispersions in Organic Solvents and Rubber

Recently, carbon materials have been investigated mainly using low-frequency US (US) treatment of the reaction mixture. This enhances disintegration of carbon material aggregates and forms surface defects on them (Luzgarev S. et al. 2013).
This increases the chemical reactivity of the CNM surface (Luzgarev S.V. and Denisov V.Ya. 2005). As a rule, US baths, immersed and flow US dispersers, and high-speed mechanical dispersers (simultaneously with US devices) arc used for low-frequcncy US treatment. However, the poor mechanical characteristics of the starting NMPC limit their scope of application (Badamshina E.R. et al. 2010).

The possibility of producing stable dispersions of carbon materials in organic solvents and high-molecular-mass polydimethylsiloxane (PDMS) rubber SKT was studied (Luzgarev S. et al. 2013). The organic solvents toluene and benzene were used to prepare the dispersions. Optical microscopy found that the maximum particle sizes were small (30 - 40 μm) if an immersion US disperser (operating frequency 22 kHz) was used.

Dispersion carried out in an US bath (operating frequency 25 kHz) formed large particles (80 - 100 μm). Carbon material of PUM grade could not be dispersed using this method.

A high-speed electromechanical disperser did not give high degrees of dispersion. The particle sizes of the carbon materials were 300 - 400 μm. Furthermore, dispersions prepared using US tended to aggregate rapidly (1.5 - 4 min) and form flakes that subsequently settled regardless of the carbon-material concentration and used organic solvent. However, aggregated dispersions prepared using an immersed US disperser were easily restored by repeated treatment in an US bath.

1.4 Preparation and Study of Epoxide Nanocomposites

Recent research identified CNT as the most promising platform for designing materials with fundamentally new properties (Vorob'eva E.A. et al. 2011). CNT differ from other nanofillers (ultradispersed particles, organic clays) by an atomically smooth surface. This stretches matrix-polymer macromolecules on the surface and forms a densely packed polymeric-matrix-CNT interfacial layer.

An increased fracture strength e_f of NMPC filled with CNT compared with the starting matrix polymer or increased plasticity of nanocomposites (Vorob'eva E.A. et al. 2011), e.g., epoxypolymer-CNT nanocomposites (Khabashesku V.N. et al. 2007) and others, were reported several times. Increased plasticity for this class of NMPC is rather general in nature.

This effect is very important from a practical viewpoint because the main deficiency of PC is their brittleness. The ε_f value decreases as the filler content increases. Therefore, it is important to estimate theoretically the effect of increasing the plasticity of reactoplastic-polymer-CNT nanocomposites. This can produce NMPC with a unique set of operational properties, i.e., a simultaneous increase of stiffness, strength, and plasticity. However, uneven filling of the polymer matrix by CNT increases the NMPC brittleness. Individual nanotubes are broken at relatively low loadings (Wagner H.D. et al. 1998).

Low-frequency US treatment is one of the most effective methods for distributing CNT evenly in a polymer matrix. CNT are effectively distributed in an acelone: EtOH mixture (9:1) at ~50°C for an US irradiation lime of ~10 min (Brent C.J. et al. 2011). The following conclusions were drawn based on the experimental results (Tkachev G. and Zolotukhin I.V. 2007). Preliminary activation (in particular, US) of the polymer matrix in a mixture of organic solvents is required to create CNT modified composites.

The optimum CNT concentrations in the composite (determined experimentally) lies in a certain range, e.g., 0.4 - 0.8 wt.%. As a rule, increasing the CNT content above 1 mass% decreases considerably the strength of the final NMPC. The operational characteristics of composites based on epoxide diane oligomer ED-20 could be increased considerably (by 1.5 – 2.0 times) by using CNT as the filler.

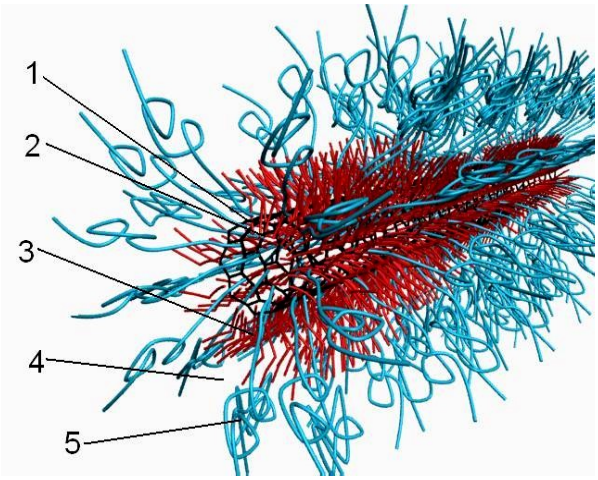
Il was reported that a material that became only stronger with regular loads was fabricated (Brent C.J. et al. 2011). The created nanocomposite consisted of a forest of vertical MWNT, the gaps among which were filled with PDMS. Cyclic loading of this material did not generate mechanical fatigue, like for traditional composites, but strengthened the NMPC. Compression of a sample at a frequency of five times per second for a week increased the sample stiffness by 12%.

1.4.1 Features of Nanocarbon Modification of Epoxide Oligomers

Effects of employed nanodisperse fillers on the physico-mechanical properties of the filled polymers must be analyzed during development of an actual NMPC industrial process. The properties of the final PC with nano-sized fillers (as compared with micro-sized fillers) are difficult to predict (Kolosov A.E. 2015c) because several factors related to adhesion and cohesion mechanisms and aspects of NMPC destruction must be considered. A potential destruction mechanism of the disperse-filled polymer matrix that occurs most often in construction PC was discussed before (Blokhin A.N. 2012). Disperse inclusions present an actual barrier to the advancing crack front in a stress-strained NMPC. The front lengthens as it winds its way between each pair of neighboring disperse nanoparticles.

According to the Lang model, lengthening of the crack front can contribute considerably to the destruction energy of a brittle composite, e.g., one based on an EP (Blokhin A.N. 2012). The size of the disperse particles also affects crack propagation. Larger particles cause larger stressed zones (within a particle and around it) and; therefore, more destructive deformation energy is accumulated due to the effect of the particle (Blokhin A.N. 2012). External stresses applied to the material should not exceed the strength limit (for brittle materials) or the flowability limit (for plastic materials). With this condition, the critical sizes of inclusions d_{cr} at which the material can stratify along matrix-filler interfaces can be estimated. The orienting effect of a disperse filler on the polymer binder (PB) is important. Shrinkage on the microscale that is observed during NMPC forming also causes spatial orientation (Fig. 1.2).

Fig. 1.2 Schematic of polymer-CNT boundary layer morphology (Blokhin A.N. 2012):
1 – CNT; *2* – adsorbed polymer microlayer;
3 – oriented polymer layer;
4 – polymer transition layer;
5 – polymer in bulk phase



The formation in the NMPC bulk of a three-dimensional framework of nanofiller particles alternating with a structured hardened polymer matrix is an important factor. The framework is formed by boundary layers of polymer matrix whereas disperse filler particles are boundary layer carriers. The disperse filler must be evenly distributed in the NMPC in order to form a continuous reinforcing three-dimensional framework of filler particles and structured reactoplastic polymer layers. Thus, the conditions tor producing a positive effect upon filling the highly cross-linked thermoreactive polymer matrix with hard disperse particles are: 1) optimal degree of filling (depends on disperse particle size); 2) particle sizes in the nanometer range; and 3) good adhesion of filler to polymer matrix, preferentially with the ability to form a chemical bond between the filler and matrix.

Research on the influences of the filling parameters and the nature of disperse particles on structural changes in the polymer taking into account features of the reactoplastic NMPC is crucial. Distribution processes of disperse particles in a liquid epoxide binder (EB), the influence of modifying the matrix with carbon nanoparticles, and the development of effective technologies for introducing nanoparticles into the liquid (EB or EO) must be investigated.

Experiments on the incorporation, distribution, and stabilization of a dispersion using multi-walled CNT (MWCNT) (Blokhin A.N. 2012) showed that physic-mechanical characteristics increased insignificantly for low percent MWCNT contents (from 0.01 wt.% to 1 wt.%). The absolute value decreased with increasing percent content of solid phase in the dispersion.

Simple (mechanical) mixing of CNT with EO was ineffective for improving the physico-mechanical characteristics. A large part of the suspension particles were agglomerates consisting of significantly shortened CNT. As a rule, their dimensions were out of the nanoscale range. However, air adsorbed on the surface and within agglomerates was entrained with them into the polymer matrix if they were added. Therefore, agglomerates had to be disintegrated and distributed evenly in the EB bulk for modification of EO with CNT.

Methods for disintegrating and distributing MWCNT in liquid EB were tested (Blokhin A.N. 2012). These included high-energy impact of milling balls and friction between balls and the wall of the milling vessel (in a ball mill); stretching, compressing, and shear forces, elevated temperatures, and static electricity (in a roll mill); and US irradiation. The equivalent particle sizes increased upon treatment in a planetary mill (Fig. 1.3) because of agglomeration and combination into globules. The optimum US irradiation time was ~6 min in a highly viscous medium (Blokhin A.N. 2012).

The physico-mechanical characteristics of the hardened binder were worse by an order of magnitude if surfactant (SA) was added to the composition. Apparently, this was a consequence of blocking nanoparticle active sites. A MWCNT concentration of 0.5 wt.% gave the best physico-mechanical characteristics for functionalized MWCNT. However, the cost of functionalized MWCNT was significantly greater than that of the starting MWCNT.

1.5.3. Electrical Conductivity of Polymer Composite Materials Modified by CNTs

A promising direction of polymeric material science is the creation of PCM that have the necessary functional properties (the so-called functional PCM). One of such important properties is the electrical conductivity of PCMs, which is carried out by modification with CNT. It was found that the conductivity of nanocomposites with CNTs is influenced not only by the type, concentration of CNTs and the composition of the polymer matrix, but also by the technologies for obtaining a nanocomposite. For example, the use of extruders that provide a high level of shear stresses makes it possible to obtain hybrid PCMs, which simultaneously combine high electrical conductivity and high physical and mechanical properties.

It is shown that the use of carbon nanotubes as the main reinforcing filler makes it possible to obtain PCM with a record tensile strength of 3.8 GPa, an elasticity modulus of 293 GPa, and a conductivity of 1230 Sm/cm. (Kondrashov S.V. et al. 2016). It was considered the possibility of giving functional properties to hybrid PCM, in which carbon nanotubes are used along with the basic reinforcing carbon fiber. The authors have used CNTs dispersed in an EC with a three-roll mixer to make a hybrid PCM (Reia da Costa E.F. et al. 2012). For the manufacture of PCM the transfer molding method (RTM) was used.

The analysis showed that the use of such technology for the production of carbon plastics makes it possible to increase the electrical conductivity in a direction perpendicular to the laying plane by a factor of 2 compared to the initial one - up to 200 Sm/cm. In the case of glass-reinforced plastic, the electrical conductivity increases from $7 \cdot 10^{-8}$ Sm/cm to $5 \cdot 10^{-7}$ Sm/cm. At a distance of 30 cm from the inlet, the electrical conductivity decreased by 50%. The obtained results show that this method is unpromising for giving the PCM functional properties (Reia da Costa E.F. et al. 2012).

Another approach to this problem was demonstrated by the group of authors (Garcia E.J. et al. 2008). According to this investigation, CNTs were grown on alumina fabrics by chemical vapor deposition (CVD), which was then impregnated with an EC, followed by compression at room temperature for 12 hours and final curing at 60 °C. The electrical conductivity of the obtained PCM was 3-5 Sm/cm in the laying plane and 4-3 Sm/cm in the perpendicular direction at a concentration of CNTs: 1-3% (by weight). The authors also noted an increase in the tensile strength at the interlayer shear τ_s in the hybrid PCM (33.8 ± 1.1 MPa) as compared to the control sample (20.1 ± 0.9 MPa) (Garcia E.J. et al. 2008).

A similar approach has been applied by the authors in the work for PCMs based on carbon fibers with the additional use of carbon fiber felt as a substrate for the growth of CNTs (Singh B.P. et al. 2014). After impregnation of the felt with the epoxy composition by hot pressing, a PCM with a high content of CNTs was obtained - up to 18% (by weight). Investigations of mechanical properties showed that the value of the bending strength increased from 85 MPa to 115 MPa. The electrical conductivity increased from 3 Sm/cm to 18 Sm/cm. At the same time, this approach requires careful selection of CVD process parameters, since using this method of growing CNTs on the surface of glass and carbon fibers leads to a drop in their tensile strength (Lubineau G. and Rahaman A. 2012).

1.6 Conclusions

The studies results described in this chapter confirm the effectiveness of physical, chemical and combine physico-chemical modification methods as a basic direction for improving the technological and operational characteristics of traditional and NM liquid polymer media and reinforced PC on their basis. The technology for NMPCs production depends on the type of particle nanomodifiers that are incorporated into the liquid polymer system. The high surface energy of nanoparticles creates certain difficulties for combining them with a liquid polymer matrix. It leads to adhesion and aggregation of particles, that is, formation of fullerites.

Agglomerating of excess of CNTs leads to a sharp decrease in the strength of polymerized samples. Thus we can consider CNT agglomerates as a kind of tension concentrators. Operating properties of produced NMPC can be highly scattered if the dispersion quality is insufficient. Therefore, nanoparticles should be added first to the least viscous binder component (low-viscosity hardener).

Incorporated nanoparticles are very active, they enter into a chemical reaction with other substances quickly and lose their unique properties. Therefore, it is difficult to obtain NMPCs with traditional methods for composites. Various solutions and surfactants are used for dispercing fillers, including methods using ultrasonic cavitation action. Therefore, ultrasonic treatment, as the most effective method which is used in the stages of de-agglomeration, dispersion of nanoparticles in liquid polymer media, and also for further combination of components of traditional (classical) and NMPCs, deserves special attention.

Functionalized with different functional groups, nanomodifiers in the form of CNTs are used to increase the heat resistance of EB used for structural purposes, as well as for the elasticization of heat-resistant binders characterized by small tensile deformation. In this case, the use of functional CNTs as modifiers of heat-resistant EB is a promising direction for future research. The optimal concentration and uniform distribution of CNTs in the polymer binder has a decisive role in the final hardening of NMPCMs.

The analyzed research results for nanocarbon modified EO and the approaches used to solve actual problems could be applied to studies of new types of NMPCMs. In general, the effects of filling parameters and the nature of the disperse particles on structural changes in the polymer considering features of reactoplastic polymeric binders and nanodisperse fillers must be investigated.

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