Properties of MWNT-Containing Polymer Composite Materials Depending on Their Structure

Ilya Mazov, Vladimir Kuznetsov, Anatoly Romanenko and Valentin Suslyaev

1. Introduction

Carbon nanotubes (CNTs) are tubular structures composed of curved graphene sheets with diameter up to several tens of nanometers with typical length up to several micrometers. Single- and doublewall CNTs have diameters from 1.2 to ca. 3 nm and are usually packed in relatively dense structures (“ropes”). Multiwall carbon nanotubes can contain up to tens of concentrically aligned tubules and have diameter from 3-4 to tens of nanometers. Carbon nanotubes, both single- and multiwall, show outstanding mechanical and electrical properties [1, 2]. Nowadays CNTs are regarded as one of the key materials for development of various nanotechnology applications – new materials, sensors, actuators, field emitters etc. [3, 4, 5, 6]. In the last decade great effort was done in this field by many research groups, investigating structural, physical, mechanical, and electrical properties of CNTs.

Among all types of nanotubes single-wall nanotubes (SWNTs) were widely recognized as most perspective in regard of their predicted properties. Depending on chirality and diameter SWNTs can show significantly different electronic structure thus revealing metallic or semiconducting properties [7, 8]. Mechanical properties of SWNTs were investigated both theoretically and experimentally and were shown to outstand all other construction materials such as steel, carbon fibers etc [9].

Extremely remarkable properties of SWNTs are strongly limited in usage by their high cost and low yield of production methods. Commonly used methods of SWNT synthesis include arc discharge [10], laser evaporation of carbon targets [11], or catalytic decomposition of gaseous carbonaceous species (carbon monoxide [12], alcohols [13], various hydrocarbons [14]) by CVD technique [15]. As-produced SWNTs need purification from amorphous carbon and other graphene-like species (fullerenes, multiwall CNTs etc.) which is usually performed by...
strong oxidative media and/or by selective surfactants (followed by ultra-centrifugation etc.). Involvement of such complex techniques results in high cost of resulting material, especially in the case of production of CNTs with tailored mechanical and electronic properties. According to market analysis the average price of highly purified SWNTs (90-99 wt. %) lays in range 200-600 $ per gram depending on purity, chirality and surface composition. Note that high amounts of SWNTs are still less available.

Multiwall carbon nanotubes (MWNTs) were firstly described in 1953 and now are one of the most common and widely used nanotubes allotrope. Multiwall nanotubes are composed with several concentrically aligned tubular graphene sheets, with typical diameter in range 8-30 nm. Physical and mechanical properties of MWNTs are significantly lower than that for SWNTs but still are higher than properties of commonly used construction materials and reinforcement additives.

Multiwall carbon nanotubes can be synthesized in the same way as SWNTs by arc discharge, graphite evaporation by laser irradiation or by catalytic decomposition of gaseous carbon-containing species \[16\] by CVD. The last one is the most perspective due to possibility to regulate CNT diameter and length; due to high yield and high selectivity of the process less or even no purification by aggressive oxidation is needed to achieve MWNT with high purity (higher than 90 wt. %) \[17\]. CVD process has high scaling potential, e.g. by realization of the fluidized bed technique \[18, 19, 20\].

In the last few years significant progress was achieved in the scaling of synthesis of MWNTs by catalytic CVD route. Several companies have demonstrated large-scale facilities for the process, for example, Bayer AG (Germany), Nanocyl (Belgium), Arkema (France), Hyperion Catalyst (USA), Cheap Tubes Inc. (China). Development of the large-scale synthesis route for MWNTs with high purity and relatively low defectiveness allowed to significantly lower market price for such product which is in range 1-15 $ per one gram depending on purity, mean diameter and surface functionalization.

Relatively high availability of MWNTs and their remarkable properties result in great interest of their usage in various nanotechnology applications. At the present time high amount of research work was done in the field of MWNT investigation and application. Multiwall carbon nanotubes can be used as components of composite materials with polymer, metal or ceramic matrices \[21\]; as chemical sensors \[22, 23\]; as components of catalytic systems \[24, 25\]; as electromagnetic shielding materials \[26\]; for biomedical applications such as selective drug delivery \[27, 28\] etc.

One of the most perspective approaches of usage of MWNT’s superior properties is development of new multi-functional composite materials with improved and tailorable properties. Such composites can be used in various applications, for example as construction materials \[29\], anti-static coatings \[30\], low-weight electromagnetic shielding \[31\], conductive polymers \[32\] etc. Polymer matrices are mostly used for development of such composite due to their light weight, low price, good processability and controllable chemical, physical and mechanical properties as well as good scaling perspectives.
To date several tens of polymer matrices were investigated for the synthesis of MWNT-and SWNT-loaded polymeric composites. These are epoxy resins [33], polyurethanes [34], polyolefines [35, 36], polymethylmethacrylate [37], polystyrene [31], and others.

Systematic investigation of properties of novel multifunctional composite materials, containing carbon nanotubes is of essential importance to understand and improve their properties.

It is known [24, 38] that CNTs of same type but produced by different vendors often show significant difference in chemical and physical properties depending on their diameter, length, defectiveness, agglomeration state, surface chemistry etc. Variation in properties of the filler may result in non-linear changes in properties of resulting composite. Thus investigation of properties of CNT-containing composites depending on properties of incorporated nanotubes and polymer host matrix is an important task.

In this chapter we describe an attempt to systematic investigation of structural, physical-chemical, and electrophysical and electromagnetic properties of thermoplastic composite materials, comprising multiwall carbon nanotubes with different mean diameters and morphology.

2. MWNT-containing polymer composites

2.1. Approaches to synthesis, main problems

As it was mentioned above, CNT (and, first of all, MWNT)-containing polymer-based composite materials attract great interest in the last decade. Great work was done in this field and tens of various host matrices were investigated. Several main problems in the area of design and preparation of nanotube-filled composite materials can be outlined according to literature analysis.

1. As-synthesized carbon nanotubes are usually arranged either in dense aligned arrays (“ropes”) or tangled “furballs”, composed of several tens of closely matted CNTs. First type is more typical for SWNTs, and the second one is most typical for CVD-produced MWNTs. Dense entangled MWNT arrays should be destructed during composite synthesis in order to achieve maximum dispersion state of nanotubes and subsequent maximum increase in properties of the composite. Also in this case it is possible to reach electrical percolation threshold at relatively low concentration of the filler due to intensive linking of high-dispersed nanotubes between each other. See review [39] for details of dispersion of MWNTs in various liquids using different technique.

2. Carbon nanotube fillers in the polymer matrix (and, in common sense, in all types of composite materials) can act as reinforcement matrix in several ways.

The first, incorporated nanotubes with high mechanical properties and high electrical conductivity, may act in the same way as macroscopic fillers (carbon fiber, glass wool etc.) providing stress transfer from the low-strength matrix in the case of mechanical load or charge transfer through continuous linked conductive network in the case of electrical load [40, 41].
The second, CNT filler is providing nucleation sites for the growth of polymer nanosized crystallites. Introduction of high amount of nanotubes with high surface chemical potential results in significant reduction of the grain size of resulting composite \([42, 43]\) thus leading to increase of its mechanical properties.

Thus it is of crucial importance to obtain high dispersion degree of nanotube filler in the bulk volume of the polymer matrix and provide intensive interaction between CNTs and polymer. These two tasks should be resolved during composite synthesis in order to obtain material with increased properties. This can be done in several ways depending on the type of the polymer used as matrix material.

All polymer materials can be roughly divided in two parts – thermoplastic and thermoreactive polymers. Both types were used for synthesis of MWNT-containing composites with certain success.

*Thermoreactive* matrices, such as epoxy resins and polyurethanes, were one of the first used for preparation of MWNT-loaded composites. The main route of preparation of such type of materials involves mixing of carbon filler with resin or with chosen intermediate solvent (acetone, dimethylformamide etc. \([44]\)) which is later mixed with the resin. The mixing process is often assisted with ultrasonic treatment which results in higher dispersion degree of the nanotube filler in the matrix \([45]\). Obtained mixture is molded to form necessary shape and cured. The technique described is quite experimentally simple and scalable. However, due to high viscosity of epoxy resin it is hard to disperse entangled nanotubes uniformly in whole volume of the polymer. In the case of usage of intermediate solvents such as acetone, the last must be evaporated before curing process. Carbon nanotubes tend to spontaneous agglomeration while staying in suspension, thus destroying achieved dispersive state and resulting in lowering of composite’s properties as compared with theoretically predicted.

Several special procedures can improve the process, such as chemical surface functionalization \([46, 47]\) or usage of short aligned CNT arrays as starting material \([48, 49]\), allowing to obtain good distribution of CNTs with low electrical percolation threshold and increased mechanical properties.

*Thermoplastic* polymers can be used as matrix materials for design and synthesis of nanotube-filled composites. These matrices can be processed by variety of techniques, such as solution casting, extrusion, pressure molding, hot pressing etc. Processing methods can be divided in two main parts – *temperature-assisted* and *solution-assisted* technique.

Twin-screw extrusion, pressure molding, hot pressing, liquid casting and similar methods can be described as *temperature-assisted*. The main step of these techniques involves melting of mixture of the polymer matrix material and CNT filler with subsequent processing of the melt blend \([50]\). Such approaches are relatively cheap, scalable and experimentally simple, but still have several disadvantages.

Usually the polymer blend has high viscosity in molten state thus preventing disaggregation of entangled agglomerates of CNTs. Usage of ultrasonic treatment is this case is complicated.
by high temperatures and closed volume of experimental setup. Moreover, increase of CNT loading results in further sharp increase of viscosity of polymer-nanotube blend, preventing achieving high dispersion of incorporated nanotubes.

These problems can be partially solved by using of additional mixing procedure, such as mechanical activation of the solid polymer powder with CNTs, or using of high CNT shear flow mixers for the molten mixture providing high dispersion degree. However, these procedures can result in breaking of nanotubes, especially in the case of multiwall CNTs with defective walls, with corresponding CNT shortening and decrease in mechanical and electrophysical properties of the composite.

**Solution-assisted** technique of preparation of nanotube-filled polymer composites includes dissolving of polymer material in appropriate solvent, mixing of the resulting solution with CNTs and subsequent evaporation of the solvent with formation of the polymer-nanotube film [50]. High disaggregation state of CNTs can be achieved by using ultrasonication and/or high-intensive mixing [51] of the nanotube-polymer suspension due to reasonably low viscosity of the solution. Thin films can be produced by this technique, allowing one to design functionally grade materials, electrostatic coatings, polarizing films etc.

However, this technique has some disadvantages – it is hard to obtain massive samples by solution casting and also special precautions must be applied in order to avoid CNT agglomeration during drying of the composite film (for example, surface functionalization, shortening of nanotubes etc. [52, 53]).

There are some specific methods of synthesis of CNT-loaded composite materials, which cannot be ascribed to abovementioned types, for example *in situ* polymerization and coagulation precipitation techniques. The first one includes deposition of the catalyst on the surface of CNTs with further polymerization [54] or radical polymerization of the monomer (e.g. polystyrene, polymethylmethacrylate) in presence of carbon nanotubes or other nano-sized fillers or monomers [57, 55, 56, 57]. High dispersion degree of nanotubes can be achieved by such methods, with following processing using conventional techniques, mentioned above.

The second method of CNT/polymer composite synthesis, coagulation precipitation, was firstly developed by Du et al. [58] for SWNT/PMMA composites. The coagulation precipitation (CP) technique involves dissolution of the polymer in appropriate solvent, mixing of this solution with carbon nanotubes (or other filler materials). The resulting slurry is mixed with the second solution in which the first solvent is soluble, but the polymer is not. As a result the polymer/CNT mixture immediately precipitates, forming disperse composite material which can be later processed in usual ways.

Coagulation precipitation technique has several remarkable advantages as compared with abovementioned methods. By right choice of the first solvent it is possible to obtain both dissolution of the polymer and good wetting of nanotubes. For example, in the case of MWNT/PMMA or MWNT/PS composites dimethylformamide of N-methylpyrrolidone can be used for this task. These solvents are known to provide very stable CNT suspensions [59].
and can dissolve corresponding polymers in high concentrations. The second solvent for this system is water.

High CNT dispersion state is produced by ultrasonic treatment of the polymer-solvent mixture and is quite stable during minutes. It is of crucial importance that such high dispersion can be “frozen” on the second step by mixing with the second solvent, thus there is no reason to obtain super-stable CNT suspension.

The precipitation of polymer starts immediately after mixing with the second solvent and this process proceeds at high rate, producing small particles. Dispersed carbon nanotubes act as nucleation sites allowing reaching intimate interaction between polymer and individual CNTs.

CP technique still has certain inconveniences – for example, lack of scalability potential. Solution pair should be chosen carefully, providing both mutual solubility, and partial solubility of the polymer matrix material.

In the present chapter we describe preparation of MWNT-containing composite materials using coagulation precipitation technique and polymethylmethacrylate (PMMA) and polystyrene (PS) as matrices. All these polymers are thermoplastics and can be processed using common pressing and extrusion techniques.

2.2. Experimental: Synthesis of MWNTs and MWNT-loaded composites

Multiwall carbon nanotubes were synthesized in-lab by ethylene decomposition over bimetallic FeCo catalyst in hot-wall CVD reactor at 680 °C. Details of preparation technique can be found elsewhere [60]. As-prepared MWNTs were additionally purified by reflux in HCl (15 wt. %) during 3 hours, washed with distilled water and dried in air at 80 °C for 24 hours.

Preparation of MWNT-loaded composites was performed using coagulation precipitation technique.

MWNT/PMMA and MWNT/PS composites were synthesized in similar way as follows. Polymer powder (PMMA, m.w. ~ 100000; Polystyrene, m.w. ~ 120000) was dissolved in dimethylformamide with concentration 0.1 g/ml. Calculated amount of air-dried MWNTs was loaded in water-cooled glass reactor and poured with polymer/DMF solution (40 ml) diluted with pure DMF (40 ml).

Resulting mixture was sonicated by Ti horn ultrasonicator (output power 8.5 W/cm²) during 15 minutes under constant water cooling (the temperature of mixture was not higher than 50 °C). Resulting slurry was poured in ~ 1.5 liters of distilled water (t = 60-70 °C) under vigorous stirring immediately after US treatment. Precipitation of the polymer-MWNT composite proceeds immediately, resulting in formation of spongy-like deposit, which was left to stay overnight to complete coagulation.

The precipitate was filtered using Buchner funnel, washed with water (3×500 ml) and dried in air at 60 °C overnight. Residual water was removed by drying in vacuum (10⁻² torr) at 60 °C for 2 hours.
Composite powder can be processed using common technique. In our case hot pressing was chosen as one of the most simple ways to make polymer films. Powder was placed between two polished steel plates, which were heated up to melting temperature of the polymer and pressed with hydraulic press with pressure ca. 400 kg/cm². Copper ring with 0.5 mm thickness was used as spaces. Produced composite films were Ø 60×0.5 mm³ in dimensions.

*Scanning and transmission electron microscopy* was used for investigation of the structure of composite powder and films (JSM6460LV and JEM 2010 electron microscopes were used). Powder samples were placed on the conductive carbon adhesive tape, films were cut in plates with size ca. 8×3×0.5 mm³, which were broken and glued to the copper stand with breaks upwards using silver glue. In order to avoid surface charging during SEM investigations all samples were additionally covered with 5-10 nm gold layer.

*Electrophysical properties* of composite films were investigated using four-probe technique with silver wires connected to sample surface with silver glue.

*Electromagnetic response properties* of free-standing polymer composite films were investigated in frequency range 0.01-12 GHz, 26-37 GHz. Array of experimental setups was used: quasi-optical setup based on panoramic meter KSwN R2-65 (Russia), Mach-Zehnder interferometer based on backward wave oscillator (Russia), HP Agilent PNA 8363B network analyzer (Agilent, USA) with multimode resonators (for dielectric permittivity spectra), and R2M-04 reflectance/transmission meter (Mikran, Russia). For ε spectra measurement samples were cut in pieces with size 0.5×2.5×30 mm³ and placed in antinode of electric field parallel to electric field lines. Transmission coefficient was measured using polyfoam gasket, samples were cut in rings with an outer diameter Ø16.5 mm and inner diameter Ø6.95 mm and glued to the gasket. The measuring setup was calibrated using pure polyfoam gasket covered with glue.

### 2.3. Properties of pure MWNTs

Macro-scale properties of MWNTs and MWNT-based composites depend strongly on their nanoscale parameters, such as diameter, particle size distribution, morphology of agglomerates. In this work we have investigated three types of MWNTs differing in main diameter (and diameter distribution), defectiveness and morphology of agglomerates. On Figure 1 TEM data and diameter distribution for all types of MWNTs is shown.

Mean diameter of MWNT (as obtained by statistical analysis of TEM images) makes the value of ~7-9 nm for MWNT⁸, ~10-12 nm for MWNT¹², and ~22-24 nm for MWNT²². From TEM images one can roughly evaluate defectiveness of MWNT (amount of amorphous species on the surface of CNT, opened walls etc.) which is increasing with decreasing of their mean diameter.

According to SEM data the morphology of MWNT secondary agglomerates varies, changing from rope-like structure for “thin” tubes (MWNT⁸, MWNT¹²) to tangled furball-like structure for “thick” tubes (MWNT²²). On figure 2 SEM images of typical MWNT agglomerates are presented.
Entangled nanotubes, which are forming “furball” structure, are hard to disperse in liquid media. MWNTs of all types tend to agglomerate in liquid dispersion, thus it is necessary to achieve certain conditions, allowing to “freeze” dispersed state of nanotubes. In our case usage of the coagulation precipitation technique allows to do this, as coagulation proceeds almost immediately after sonication and dispergation.

### 2.4. PMMA and PS composites – Influence of matrix type

Polymethylmethacrylate (PMMA) and polystyrene (PS) both are cheap, large-scale and easily processable polymer matrices, which are often used as model systems for synthesis of polymer composites. Polymers with similar average molecular weight were used for
synthesis of composites, both PMMA and PS are soluble in DMF and precipitate using water as secondary solvent.

Principal physical-chemical properties of polymethylmethacrylate and polystyrene polymers are quite similar (see Table 1 for details) [61].

From the Table 1 it can be clearly seen that PMMA and PS have very similar physical and chemical properties and the main difference is their surface composition and polarity of the surface [62, 63]. Carboxylic functions are present in PMMA structure thus resulting in increased oxygen content and increased polarity of the surface. Polystyrene has no oxygen-containing groups, showing lower polarity and surface tension [64].

| Polymer | Formula | Surface free energy | Surface oxygen (XPS) | Polarity$^1$ | Density, g/cm$^3$ | Thermal conductivity, W/m×K | Dielectric constant, $\varepsilon\prime@1\text{MHz}@25^\circ\text{C}$ |
|---------|---------|---------------------|----------------------|--------------|------------------|-------------------------------|-------------------------------------------------|
| PMMA    | ![PMMA structure] | 41.2 mJ/m$^2$ [65] | 38.6 at. % [66] | 0.28         | 1.17             | 0.19                          | 2.80 [68]                                       |
| PS      | ![PS structure]  | 40.1 mJ/m$^2$      | 0 at. %              | 0.17         | 1.04             | 0.22                          | 2.55                                           |

Table 1. Physical-chemical properties of polymethylmethacrylate (PMMA) and polystyrene (PS).

Thus investigation of these model polymer systems allows one to reveal basic principles of the influence of the matrix type on the properties of MWNT-loaded composites.

Transmission electron microscopy analysis of MWNT/PMMA and MWNT/PS composites was performed to investigate internal structure of materials. Corresponding micrographs are shown on figure 3. Interaction of carbon nanotubes with polymer matrix results in surface wetting of MWNTs with polymer, which depends strongly both on the surface composition of CNTs and on surface properties of the polymer. As-prepared nanotubes have low amount of polar (oxygen-containing) groups, thus surface is mostly hydrophobic. Chemical functionalization (e.g. oxidation) can modify surface composition of the materials, making it hydrophilic. According to our previous study [69], as-prepared CNTs have ca. 0.3-0.5 oxygen-containing groups per nm$^2$, so their surface is mostly hydrophobic, but still can show several hydrophilic behavior.

$^1$ Polarity calculated according to surface tension values, measured by sessile drop technique.
It is reasonable to suggest that hydrophilic surface would have higher affinity to polar polymer matrices, and pristine nanotubes would be better wetted by low-polar polymers.

Such behavior was observed for both compared MWNT/PMMA and MWNT/PS samples. As it can be seen from Figure 3, the surface of CNTs is covered with polymer. In the case of PMMA as a matrix, nanotubes are not fully covered with polymer. Both covered and naked surface areas are observed (marked with arrows on Fig. 3 A, B) for PMMA-treated composite. It is important to note that observed contact angles between nanotube surface and PMMA layer are still lower than 35°.

The possible reason for partial surface coverage with PMMA is certain irregularity of the functional composition of MWNT surface, for example, PMMA-covered areas are observed due to higher polarity of that nanotube part (e.g. due to partial oxidation), providing better wetting and lowering of the contact angle.

In contrast, PS-covered composite sample reveal significantly different structure where the surface of MWNTs is completely covered with thin continuous layer of the polymer (with thickness up to several nanometers). In the case of low CNT loading in composite one can observe disaggregated nanotubes, completely wrapped and wetted by PS (fig. 3, D). For
higher nanotube content polystyrene “drops” are observed settled on the surface of nanotubes covered still with undestructured PS layer. As soon as polystyrene shows lower polarity as compared with PMMA and moreover has aromatic rings in structure, which have high affinity to the conjugated π-system of pristine (low-oxidized) nanotube, the wetting is more ease and coverage is higher in this case.

The contact angle between PS drops and CNT surface is in range 22-25° indicating high wetting ability of PS towards untreated surface of nanotubes.

Interfacial interaction between polymer matrix and incorporated nanotubes significantly affects structural and physical properties of composite films. Formation of dispersed nanotube array or network in the volume of the polymer matrix is essential to drastical change of material properties. Carbon nanotubes tend to agglomerate during synthesis of composites, thus decreasing dispersion degree.

Formation of CNT agglomerates in composite powder was observed for both PMMA- and PS-based materials using transmission electron microscopy. TEM micrographs of different nanotubes agglomerates are shown on Figure 4.

![TEM images of agglomerated nanotubes in composite powders. A, B – MWNT22/PMMA (5 wt. %), C, D – MWNT22/PS (10 wt. %).](image_url)
Two types of nanotube agglomerates can be distinguished in polymer-based composite materials. These agglomerates have been identified as “primary” and “secondary”, according to their origin. Primary agglomerates are formed mainly during synthesis of carbon nanotubes themselves and can be avoided in growth-aligned nanotube arrays [70]. These aggregates must be destroyed during composite synthesis by ultrasonic treatment, high-shear flow mixing etc. Destruction of such particles is necessary to achieve high dispersion degree and, for example, correspondingly low percolation threshold for composites. Nevertheless, for CVD-grown nanotubes these aggregates are hard to destroy and they are still occurring in composites, covered with polymer layer. Such aggregates are typical for systems with low wetting of CNTs with polymer, e.g. for MWNT-PMMA (fig. 3-A & 4-A).

Agglomerates of secondary type are formed during the process of composite synthesis due to re-aggregation of dispersed nanotubes in solution due to van der Walls forces. In this case individual nanotubes are separated from each other in solution and linked by the polymer particle in solid composite (fig. 4-B&D). Strong wetting of carbon nanotubes with polymer assists destruction of primary agglomerates with subsequent formation of secondary-type agglomerates. Such phenomenon is observed for PS-based composites and is clearly seen on TEM micrographs – even for high MWNT loading (up to 10 wt. %) almost none primary agglomerates were observed. MWNTs are dispersed and separated from each other, forming secondary agglomerates, clued by polymer particles (fig. 4-C&D).

Investigation of composite films using scanning electron microscopy (SEM) was performed in order to elucidate influence of CNT-polymer interface on structural properties of composites. Corresponding SEM images of fresh breaks of composite films with different MWNT loading are shown on fig. 5.

For both types of polymer matrices separated nanotubes can be clearly seen on the surface of film breaks.

Difference in polymer-nanotube interface properties results in significant changes of the dispersion state of nanotubes in PMMA- and PS-based composites. For PMMA-based samples only single nanotubes can be seen for samples with 1 wt. % of nanotubes (fig. 5-A). Increase of MWNT content to 4 wt. % results in more uniform and dense dispersion of nanotubes in the volume of the polymer (fig. 5-C). Nevertheless, low-filled areas can be observed indicating relatively low dispersion degree of nanotubes. Certain amount of MWNTs can still occur in the agglomerated form, preventing formation of highly-disaggregated nanotube “network” in the polymer matrix.

Such phenomenon can be observed for the highest investigated MWNT loading in the composite (10 wt. %, fig. 5-E). Dense and uniform nanotube array can be clearly seen on the surface of composite film break. Note that the length of MWNT residues on the surface of the film is 1-2 µm, moreover, the surface of nanotubes is not covered with the polymer. This may be attributed to stretching of CNTs from the volume of the polymer during breakage of the film, which can be easily assumed taking into consideration low wetting ability of PMMA towards hydrophobic surface of untreated carbon nanotubes.
Polystyrene-based composite materials show opposite phenomenon of high wetting and high dispersion degree even at low MWNT loadings. Nanotubes in all MWNT/PS composite film samples are well-dispersed and covered with polymer layer. Uniform CNT distribution can be observed for samples with both low and high nanotube loading. According to SEM data nanotubes are randomly and evenly distributed on whole breakage area, which can be clearly seen on fig. 5-B, D, F.

Note that protruding parts of MWNT for PS-based composites are shorter as compared with similar PMMA-based samples and are wrapped with polymer layer. Such phenomenon can be attributed to higher wetting of CNTs with polystyrene and higher adhesion of filler to the material of the polymer matrix.

Thereby according to TEM and SEM data significant difference in wetting ability of investigated polymers towards MWNTs results in drastic changes of structural properties of composite powders and films. Highly-wetting aromatic polystyrene matrix allows one to reach higher dispersion degree at lower filler concentrations as compared with more polar polymethylmethacrylate due to mainly hydrophobic surface character of untreated nanotubes.

Area of application of novel materials is strongly dependent on their physical properties. As it was shown above, MWNT-based composites are perspective as tailorable materials for electrical and electromagnetic applications. Structure and dispersion state of nanotubes in composite, as well as their interconnections (i.e. formation of connected array of CNTs) strongly affect physical properties of composite materials. It is well known that introduction of continuous carbon nanotubes in the dielectric polymer matrix allows to increase conductivity of the resulting composite by several orders of magnitude. Conductive composite materials can be characterized by the percolation threshold which for multiwall carbon nanotubes lays in range from ca. 0.005 wt. % [71] to 3-4 wt. % [72] depending on the electrophysical properties of initial nanotubes and peculiarities of the composites’ preparation (alignment and dispersion of nanotubes etc.).

Electrical conductivity measurements reveal significant difference between PMMA- and PS-based composites with similar MWNT loading. Conductivity data for PMMA-based composites with different types of MWNTs is shown on figure 6.

Electrical percolation threshold for PMMA-based composites was estimated as ~ 1-2 wt. %, reaching maximum value of \(10^{1-2}\) S/m for 3-5 wt. % of CNT content.

PS-based composite materials show surprisingly low electrical conductivity. Significant conductivity (~ 4.5×10^4 S/cm) was observed for composite sample with 10.0 wt. % loading of CNTs, all other samples show electrical resistivity higher than 10⁹ Ohm/cm which was the sensitivity threshold for the setup used for measurements.

As it was shown by electron microscopy investigations, PS-based composites reveal higher wetting and higher dispersion degree of nanotubes in the volume of the polymer as compared with PMMA-based materials. Unusually high percolation threshold and low
conductivity value can be explained taking into consideration insulation of conductive nanotubes with wrapped polystyrene layer. In this case perfectly dispersed three-dimensional nanotube network in the bulk volume of the polymer is formed by insulating objects, preventing current flow through composite even at high CNT loadings.

Figure 5. SEM images of MWNT/PMMA (left column) and MWNT/PS (right column) composite films. A, B – 1 wt. %, C, D – 4 wt. %, E, F – 10 wt. %.

In the case of poorly-wetted PMMA-based composites the surface of nanotubes is not completely insulated, thus allowing reaching of electrical saturation at relatively low CNT
loadings. Moreover, destruction of primary agglomerates of nanotubes, observed for PS and not for PMMA-based samples, results in diminishing of electrical contacts between nanotubes due to their insulation. Residual CNT agglomerates in the case of PMMA-based composites facilitate formation of conductive paths in the volume of the polymer matrix. As a result overall electrical conductivity of MWNT/PMMA materials is higher as compared with PS-based samples.

Figure 6. Electrical conductivity of MWNT/PMMA composites with various types of nanotubes versus filler concentration.

Electromagnetic response properties of composite materials play significant role in their application area. Incorporation of conductive media, such as carbon nanotubes, affects strongly the way of interaction of certain material with electromagnetic irradiation (EMI). Conjugated π-system, occurring in carbon nanotubes, allows both to dissipate and reflect electromagnetic wave, thus providing two possible mechanisms of EM response – reflectance and absorbance.

Electromagnetic response properties of MWNT-containing composites were investigated in broadband region (2-36 GHz) and was found to be strongly dependent on MWNT type and diameter as well as on polymer matrix type.
Influence of structural properties of MWNTs on EM shielding properties of composites was investigated for MWNT/PMMA materials due to their high electrical conductivity. Structure of initial CNT affects electrical and electromagnetic properties of CNT-based composites. We have investigated EM response properties of MWNT-based composites in frequency range 3-11 GHz (complex dielectric permittivity for MWNT/PMMA samples). Transmission ($T$) and reflection ($R$) coefficients can be easily calculated using following equations. Absorption coefficient of the EM radiation in the sample can be calculated as

$$A = 1 - R - T$$

where $\rho = \frac{Z - 1}{Z + 1}$, $Z = \sqrt{\frac{\mu^*}{\varepsilon^*}}$ is wave impedance, and $k = \frac{2\pi f \sqrt{\varepsilon^* \mu^*}}{c}$ is the wavenumber, $f$ is the frequency of the EM wave, $c$ is the speed of light, $d$ is the thickness of the sample, $\varepsilon^* = \varepsilon' - i\varepsilon''$ and $\mu^* = \mu' - i\mu''$ are complex permittivity and magnetic permeability of the investigated material correspondingly. Dielectric losses ($\varepsilon'$ and $\varepsilon''$) are measured experimentally, and $\mu' = 1$, $\mu'' = 0$ (no magnetic losses are observed in the sample). Observed values of $\varepsilon'$ and $\varepsilon''$ are growing with increase of the CNT loading in the composite and lay in range 20-70 for MWNT$^{22}$/PMMA and 5-40 for MWNT$^{12}$ and MWNT$^8$/PMMA composites.

On the figure 7 data on measured transmission and reflections coefficients are shown.

Increase of the conductivity of the composites with MWNT loading in all samples leads to growth of $R$ and diminishing of $T$ parameters. For example for the MWNT$^9$/PMMA composite one can see higher $R$ and lower $T$ values for the sample with 3 wt.% of MWNT whereas for the sample with 5 wt. % these values are lower and higher, correspondingly, correlating with its conductivity. It should be mentioned that even composites with the lowest electrical conductivity (with CNT loading 0.5-2 wt.%) show high values of the $R$, which may be due to formation of isolated conductive MWNT structures in the volume of the polymer that cannot be registered by macroscopic measurements of the electrical conductivity but still can interact with electromagnetic field. Polarization of such isolated structures gives contribution in EM response of non-conductive materials with subsequent growth of the permittivity.

Note that transmission and reflection coefficients do not depend directly on the electrical conductivity for different MWNT types. The highest values of $R$ are observed for the samples MWNT$^{22}$/PMMA which show the lowest conductivity among other composites. This phenomenon may be described taking into account significant difference between number of individual nanotubes of each type incorporated into polymer matrix. Relationship between CNT number can be roughly estimated as relationship between $r_{0j}^2 - r_{ij}^2$, where $r_{0j}$ is the outer diameter of CNT type $j$, $r_{ij}$ is the inner diameter of CNT type $j$.

Simple math gives rough approximate of relationship between CNT number in the composite with the same weight loading as $N(MWNT^{22}):N(MWNT^{22}):N(MWNT^8) = 8:4:1$. 
Thus it is possible to propose that despite of the lower macroscopic electrical conductivity, composite materials comprising MWNT with lower diameter possess higher amount of polarizable species, giving higher values of dielectric permittivity and reflection coefficient.

All samples with low CNT content (0.5 wt. %) are almost transparent in all frequency range. Increase of MWNT loading leads to reduction of transmission coefficient. Transmission is strongly affected by MWNT type and is changing unidirectionally with the dependence of permittivity – the lowest transmission is observed for MWNT22-containing composites which have higher ε value as compared with MWNT12/PMMA, MWNT8/PMMA and composites.

For both matrices percolation-like concentration dependence can be observed with sharp decrease of EM transmission coefficient (and corresponding increase of EM shielding of composites) after 1-2 wt. % of MWNTs in materials.

Nevertheless, the most significant difference for investigated matrices is that in case of PS matrix EM shielding is provided mainly by absorption, growing with increase of MWNT loading, and for the case of PMMA matrix main part of EM shielding is constituted by EM reflectance. Principal changes in mechanisms of EM attenuation in polymer composites filled with same type MWNTs can be explained taking into consideration abovementioned differences in their structural and electrophysical properties.

PMMA-based composites show high electrical conductivity and relatively low percolation threshold therefore above percolation threshold such materials interact with incident EM radiation as typical conductor, reflecting most part of electromagnetic wave.

Sharp increase in EM absorbance for PMMA-based composites at MWNT loading lower than 2 wt. % may be attributed to absence of reflectance allowing propagation of incident EM wave through the sample and its interaction with conjugated π-system of incorporated carbon nanotubes.

The value of EM absorbance reaches saturation for MWNT loadings higher than 2 wt. %, corresponding to electrical percolation threshold value. This phenomenon indicates formation of interconnected array (or cluster) of carbon nanotubes in the volume of the polymer, providing conductive paths for electrical current, decreasing electrical resistivity of the composite with subsequent increase in EM reflectance. Further increase of EM reflectance with growing MWNT loading is caused by formation of new conductive paths in linked nanotube network, increasing its electrical conductivity and reflective properties, however not affecting or diminishing absorption of EM radiation.

Polystyrene-based composites with same MWNTs as filler show surprisingly high shielding efficiency, as they are almost insulating at low nanotube loadings. In contrast to PMMA-based materials main part of shielding efficiency of PS-based composites is provided by absorption, growing with increase of MWNT concentration, especially for higher frequencies. At the same time reflection of EM radiation is increasing slowly, showing similar behavior as compared with EM absorbance for MWNT/PMMA composites.
Internal structure of composite materials and interaction between MWNTs and polystyrene matrix show i) strong wetting of MWNT surface with polymer, providing certain insulation of nanotubes from each other; ii) high dispersion degree of MWNT without primary agglomerates; iii) random uniform distribution state of individual nanotubes in the volume of the polymer even for high filler concentrations. All these factors affect changes in EMI shielding mechanism of MWNT/PS composites as compared with relatively poorly-dispersed highly-conductive PMMA-based materials.
Low-conductive PS composites possess correspondingly low EMI reflectance from the surface, allowing electromagnetic radiation to propagate in-depth of the sample. The characteristic wavelength for the EM radiation in microwave region is 1-10 mm, which is higher than the size of the individual nanotube and MWNT agglomerate and is comparable with the macroscopic size of the composite sample. Thus incident EM wave may interact with whole volume of the composite sample and this interaction is strongly facilitated due to the absence of surface conductivity and reflectance due to skin-effects.

Propagating EM wave interacts with individual nanotubes uniformly dispersed in the volume of the composite with corresponding attenuation. High dispersion degree of MWNTs in polymer results in uniform density of attenuating particles, providing correspondingly high “extinction coefficient” of composite material.

3. Conclusion

Properties of multiwall carbon nanotubes and MWNT-containing composite materials are strongly dependent on their structure and morphology and on the type of polymer matrix.
Variations of mean diameter distribution and morphology of agglomerates results in significant changes of their dispersive and electrical properties, affecting electromagnetic response of composites.

MWNT-filled composites with PMMA matrix show higher EM reflectance, higher electrical conductivity with low percolation threshold due to relatively low wetting of hydrophobic MWNTs with polar PMMA molecules and corresponding low dispersion degree of individual nanotubes.

In contrast for low-polar polystyrene matrix high wetting was observed resulting in formation of uniformly dispersed array of PS-covered MWNTs in the matrix. Coverage of MWNT surface with polystyrene results in insulation of nanotubes, thus resulting in high electrical resistivity with high percolation threshold. High shielding efficiency was observed for such composites, provided mainly by absorbance of EM radiation with low-conductive media.

Thus variation of main properties of polymer matrices and incorporated nanotubes allows to obtain composite materials with predictable tailorable properties, which may be used in various applications.

Author details

Ilya Mazov  
Boreskov Institute of Catalysis, Novosibirsk, Russia  
National Research Technical University “MISIS”, Moscow, Russia

Vladimir Kuznetsov  
Boreskov Institute of Catalysis, Novosibirsk, Russia

Anatoly Romanenko  
Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

Valentin Suslyaev  
National Research Tomsk State University, Tomsk, Russia

Acknowledgement

This work was partially supported by RFBR grant #11-03-00351, ISTC project B-1708, and RNP projects #2.1.1/10256, #16.740.11.0016 & #16.740.11.0146.

4. References

[1] J.-P. Salvetat, J.-M. Bonard, N.H. Thomson, A.J. Kulik, L. Forro, W. Benoit, L. Zuppiroli, Mechanical properties of carbon nanotubes, Appl. Phys. A 69, 255–260 (1999)

[2] M. Terrones, Science And Technology Of The Twenty-First Century: Synthesis, Properties, And Applications Of Carbon Nanotubes, Annu. Rev. Mater.Res. (2003) 33 419–501

[3] P.M. Ajayan, O.Z. Zhou, Applications of Carbon Nanotubes in M. S. Dresselhaus, G. Dresselhaus, Ph. Avouris (Eds.): Carbon Nanotubes, Topics Appl. Phys. 80, 391–425 (2001)
[4] D. Srivastava, C. Wei, K. Cho, Nanomechanics of carbon nanotubes and composites, Appl. Mech. Rev. 56 (2003) 215-230
[5] J.R. Stetter, G.J. Maclay Carbon nanotubes and sensors: a review, Advanced Micro and Nanosystems, Vol. 1, edited by: H. Baltes, O. Brand, G.K. Fedder, C. Hierold, J. Korvink, O. Tabata 357-382 (2004)
[6] J. Wang, Carbon-Nanotube Based Electrochemical Biosensors: A Review, Electroanalysis 17 (2005) 7-14
[7] J.W.G. Wilder, L.C. Venema, A.G. Rinzler, R.E. Smalley, C. Dekker Electronic structure of atomically resolved carbon nanotubes Nature 391 (1998) 59-62
[8] Q. Liu, W. Ren, Z.-G. Chen, L. Yin, F. Li, H. Cong, H.-M. Cheng, Semiconducting properties of cup-stacked carbon nanotubes, Carbon 47 (2009) 731-736
[9] R.S. Ruoff, D. Qian, W.K. Liu Mechanical properties of carbon nanotubes: theoretical predictions and experimental measurements C.R. Physique 4 (2003) 993–1008
[10] T. W. Ebbesen, P. M. Ajayan, Large scale synthesis of carbon nanotubes, Nature, 358, 220 (1992).

[11] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tománek, J.E. Fischer, R.E. Smalley Crystalline Ropes of Metallic Carbon Nanotubes, Science 273 (1996) 483-487
[12] B. Kitiyanan, W.E. Alvarez, J.H. Harwell, D.E. Resasco, Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co–Mo catalysts, Chemical Physics Letters 317 (2000) 497–503
[13] Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy, Chemical Physics Letters 385 (2004) 298–303
[14] G. Zhang, D. Mann, L. Zhang, A. Javey, Y. Li, E. Yenilmez, Q. Wang, J.P. McVittie Y. Nishi, J. Gibbons, H. Dai Ultra-high-yield growth of vertical single-walled carbon nanotubes: Hidden roles of hydrogen and oxygen PNAS 102 (2005) 16141–16145
[15] M. Kumar, Y. Ando, Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production Journal of Nanoscience and Nanotechnology 10 (2010) 3739–3758
[16] Y. Li, X.B. Zhang, X.Y. Tao, J.M. Xu, W.Z. Huang, J.H. Luo, Z.Q. Luo, T. Li, F. Liu, Y. Bao, H.J. Geise, Mass production of high-quality multi-walled carbon nanotube bundles on a Ni/Mo/MgO catalyst, Carbon 43 (2005) 295–301
[17] K.B. Hong, A.A.B. Ismail, M.E. Mahayuddin, A.R. Mohamed, S.H.S. Zeiri, Production of High Purity Multi-Walled Carbon Nanotubes from Catalytic Decomposition of Methane Journal of Natural Gas Chemistry 15 (2006) 266-270
[18] D. Venegoni, Ph. Serp, R. Feurer, Y. Kihn, C. Vahlas, Ph. Kalck, Parametric study for the growth of carbon nanotubes by catalytic chemical vapor deposition in a fluidized bed reactor, Carbon 40 (2002) 1799–1807
[19] M. Corrias, B. Caussat, A. Ayral, J. Durand, Y. Kihn, Ph. Kalck, Ph. Serp, Carbon nanotubes produced by fluidized bed catalytic CVD: first approach of the process, Chemical Engineering Science 58 (2003) 4475 – 4482
[20] S.W. Jeong, S.Y. Son, D.H. Lee, Synthesis of multi-walled carbon nanotubes using Co–Fe–Mo/Al2O3 catalytic powders in a fluidized bed reactor, Advanced Powder Technology 21 (2010) 93–99
[21] J. Wang, H. Kou, X. Liu, Y. Pan, J. Guo, Reinforcement of mullite matrix with multi-walled carbon nanotubes, Ceramics International 33 (2007) 719–722
[22] Y.-T. Jang, S.-I. Moon, J.-H. Ahn, Y.-H. Lee, B.-K. Ju A simple approach in fabricating chemical sensor using laterally grown multi-walled carbon nanotubes, Sensors and Actuators B: Chemical 99 (2004) 118–122
[23] N. Sinha, J. Ma, J.T.W. Yeow, Carbon Nanotube-Based Sensors, Journal of Nanoscience and Nanotechnology 6 (2006) 573–590
[24] N. Maksimova, G. Mestl, R. Schlogl Catalytic activity of carbon nanotubes and other carbon materials for oxidative dehydrogenation of ethylbenzene to styrene, Studies in Surface Science and Catalysis, G.F. Froment and K.C. Waugh (Editors) 133 (2001) 383–389
[25] M.S. Saha, R. Li, X. Sun, High loading and monodispersed Pt nanoparticles on multiwalled carbon nanotubes for high performance proton exchange membrane fuel cells, Journal of Power Sources 177 (2008) 314–322
[26] M.H. Al-Saleh, U. Sundararaj, Electromagnetic interference shielding mechanisms of CNT/polymer composites, Carbon 47 (2009) 1738-1746
[27] T.A. Hilder, J.M. Hill Carbon nanotubes as drug delivery nanocapsules, Current Applied Physics 8 (2008) 258–261
[28] C. Tripisciano, K. Kraemer, A. Taylor, E. Borowiak-Palen Single-wall carbon nanotubes based anticancer drug delivery system, Chemical Physics Letters 478 (2009) 200–205
[29] Makar, J. & Beaudoin, J. Carbon nanotubes and their application in the construction industry. Nanotechnology 331-341 (2003)
[30] M. Sangermano, S. Pegel, P. Potschke, B. Voit Antistatic Epoxy Coatings With Carbon Nanotubes Obtained by Cationic Photopolymerization, Macromol. Rapid Commun. 29 (2008) 396–400
[31] Y. Yang, M.C. Gupta, K.L. Dudley, R.W. Lawrence A Comparative Study of EMI Shielding Properties of Carbon Nanofiber and Multi-Walled Carbon Nanotube Filled Polymer Composites Journal of Nanoscience and Nanotechnology 5 (2005) 927-931
[32] X. Zhang, J. Zhang, Z. Liu, Conducting polymer/carbon nanotube composite films made by in situ electropolymerization using an ionic surfactant as the supporting electrolyte, Carbon 43 (2005) 2186–2191
[33] Sun, L. and Sue, H.-J. (2010) Epoxy/Carbon Nanotube Nanocomposites, in Epoxy Polymers: New Materials and Innovations (eds J.-P. Pascualt and R. J. J. Williams), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany
[34] S. Shang, W. Zeng, X. Tao, High stretchable MWNTs/polyurethane conductive nanocomposites J. Mater. Chem., 21 (2011) 7274-7280
[35] Y. Zou, Y. Feng, L. Wang, X. Liu, Processing and properties of MWNT/HDPE composites, Carbon 42 (2004) 271–277
[36] W. Tang, M.H. Santare, S.G. Advani, Melt processing and mechanical property characterization of multi-walled carbon nanotube /high density polyethylene (MWNT/HDPE) composite films, Carbon 41 (2003) 2779–2785
[37] S. Shang, L. Li, X. Yang, Y. Wei Polymethylmethacrylate-carbon nanotubes composites prepared by microemulsion polymerization for gas sensor, Composites Science and Technology 69 (2009) 1156–1159
[38] J.H. Lehman, M. Terrones, E. Mansfield, K.E. Hurst, V. Meunier, Evaluating the characteristics of multiwall carbon nanotubes, Carbon 49 (2011) 2581–2602
[39] J. Hilding, E.A. Grulke, Z.G. Zhang, F. Lockwood, Dispersion of Carbon Nanotubes in Liquids, Journal Of Dispersion Science And Technology 24 (2003) 1-41
[40] L.S. Schadler, S.C. Giannaris, P.M. Ajayan, Load transfer in carbon nanotube epoxy composites, Appl. Phys. Lett. 73, 3842 (1998)
[41] L.R. Xu, S. Sengupta, Interfacial stress transfer and property mismatch in discontinuous nanofiber/nanotube composite materials, J. Nanosci Nanotechnol. 4 (2005) 620-626
[42] K.T. Kim, J. Eckert, S.B. Menzel, T. Gemming, S.H. Hong, Grain refinement assisted strengthening of carbon nanotube reinforced copper matrix nanocomposites Appl. Phys. Lett. 92, 121901 (2008)
[43] X. Zeng, G. Zhou, Q. Xu, Y. Xiong, C. Luo, J. Wu, A new technique for dispersion of carbon nanotube in a metal melt, Materials Science and Engineering: A 527 (2010) 5335–5340
[44] K. Q. Xiao, L.C. Zhang, Effective separation and alignment of long entangled carbon nanotubes in epoxy, Journal of Materials Science 40 (2005) 6513–6516
[45] S. Bal, S.S. Samal Carbon nanotube reinforced polymer composites–A state of the art, Bull.Mater. Sci. 30 (2007) 379–386
[46] Y.J. Kim, T.S. Shin, H.D. Choi, J.H. Kwon, Y.-C. Chung, H.G. Yoon Electrical conductivity of chemically modified multiwalled carbon nanotube/epoxy composites, Carbon 43 (2005) 23–30
[47] R.E. Gorga, K.K.S. Lau, K.K. Gleason, R.E. Cohen, The Importance of Interfacial Design at the Carbon Nanotube/Polymer Composite Interface, Journal of Applied Polymer Science, 102 (2006) 1413–1418
[48] Z. Yang, Z. Cao, H. Sun, Y. Li Composite Films Based on Aligned Carbon Nanotube Arrays and a Poly(N-Isopropyl Acrylamide) Hydrogel, Adv. Mater. 2008, 20, 2201–2205
[49] E.J. Garcia, A.J. Hart, B.L. Wardle, A.H. Slocum, Fabrication and Nano-compression Testing of Aligned Carbon-Nanotube–Polymer Nanocomposites, Adv. Mater. 2007, 19, 2151–2156
[50] W. Yuan, J. Che, M.B. Chan-Park A Novel Polyimide Dispersing Matrix for Highly Electrically Conductive Solution-Cast Carbon Nanotube-Based Composite, Chem. Mater. 23 (2011) 4149–4157
[51] P. Ciselli, R. Zhang, Z. Wang, C.T. Reynolds, M. Baxendale, T. Peijs, Oriented UHMW-PE/CNT composite tapes by a solution casting-drawing process using mixed-solvents European Polymer Journal 45 (2009) 2741–2748
[52] N.G. Sahoo, Y.C. Jung, H.J. Yoo, J.W. Cho, Effect of Functionalized Carbon Nanotubes on Molecular Interaction and Properties of Polyurethane Composites, Macromol. Chem. Phys. 207 (2006) 1773–1780
[53] K. Zhang, J.Y.Lim, B.J.Park, H.J. Jin, H.J. Choi Carboxylic Acid Functionalized Multi-Walled Carbon Nanotube-Adsorption onto Poly(methyl methacrylate) Microspheres Journal of Nanoscience and Nanotechnology 9 (2009) 1058-1061
[54] L. Cui, N.H. Tarté, S.I. Woo, Synthesis and Characterization of PMMA/MWNT Nanocomposites Prepared by in Situ Polymerization with Ni(acac)2 Catalyst, Macromolecules 2009, 42, 8649–8654
[55] H.-J. Jin, H.J. Choi, S.H. Yoon, S.J. Myung, S.E. Shim, Carbon Nanotube-Adsorbed Polystyrene and Poly(methyl methacrylate) Microspheres Chem. Mater. 2005, 17, 4034-4037
[56] D. Wang, J. Zhu, Q. Yao, C.A. Wilkie, A Comparison of Various Methods for the Preparation of Polystyrene and Poly(methyl methacrylate) Clay Nanocomposites, Chem. Mater. 2002, 14, 3837-3843

[57] T. Wang, S. Shi, F. Yang, L. M. Zhou, S. Kuroda, Poly(methyl methacrylate)/polystyrene composite latex particles with a novel core/shell morphology, J Mater Sci (2010) 45:3392–3395

[58] F. Du, J.E. Fischer, K.I. Winne, Coagulation Method for Preparing Single-Walled Carbon Nanotube/Poly(methyl methacrylate) Composites and Their Modulus, Electrical Conductivity, and Thermal Stability, Journal of Polymer Science: Part B: Polymer Physics 41 (2003) 3333–3338

[59] T. Gabor, D. Aranyi, K. Papp, F.H. Karman, E. Kalman, Dispersibility of Carbon Nanotubes, Materials Science Forum 161 (2007) 537-538

[60] A. Usoifteva, V. Kuznetsov, N. Rudina, E. Moroz, M. Haluska, S. Roth, Influence of catalysts’ ctivation on their activity and selectivity in carbon nanotubes synthesis, Phys. Stat. Sol. 11 (2007) 3920–3924.

[61] M. Sikka, N.N. Pellegrini, E.A. Schmitt, K.I. Winey, Modifying a Polystyrene/Poly(methyl methacrylate) Interface with Poly(styrene-co-methyl methacrylate) Random Copolymers, Macromolecules 30 (1997) 445–455

[62] S. Varennes, H. P. Schreiber, On Origins of Time-Dependence in Contact Angle Measurements, The Journal of Adhesion, 76:293-306, 2001

[63] Y. Li, Y. Yang, F. Yu, L. Dong, Surface and Interface Morphology of Polystyrene/Poly (methyl methacrylate) Thin-Film Blends and Bilayers, Journal of Polymer Science: Part B: Polymer Physics, Vol. 44, 9–21 (2006)

[64] Y.T. Sung, W.J. Seo, Y.H. Kim, H.S. Lee, W.N. Kim Evaluation of interfacial tension for poly(methyl methacrylate) and polystyrene by rheological measurements and interaction parameter of the two polymers, Korea-Australia Rheology Journal 16 (2004) 135-140

[65] Tanaka K, Takahara A, Kajiyama T. Macromolecules 1996;29:3232-9.

[66] C. Ton-That, A.G. Shard, D.O.H. Teare, R.H. Bradley, XPS and AFM surface studies of solvent-cast PS/PMMA blends, Polymer 42 (2001) 1121-1129

[67] S. Wu, Polar and Nonpolar Interactions in Adhesion, J. Adhesion, 1973. Vol. 5, pp. 39-55

[68] P.K.C. Pillai, P. Khurana, A. Tripathi, Dielectric studies of poly(methyl methacrylate) /polystyrene double layer system Journal of Materials Science Letters 5 (1986) 629 – 632

[69] I. Mazov, V.L. Kuznetsov, I.A. Simonova, A.I. Stadnichenko, A.V. Ishchenko, A.I. Romanenko, E.N. Tkachev, O.B. Anikeeva “Oxidation behavior of multiwall carbon nanotubes with different diameters and morphology”, Applied Surface Science, 258, 17 (2012) 6272–6280

[70] L. Ci, J. Suhr, V. Pushparaj, X. Zhang, P. M. Ajayan, Continuous Carbon Nanotube Reinforced Composites, Nano Letters 8 (2008) 2762-2766

[71] A. Moisala, Q. Li, I.A. Kinloch, A.H. Windle, Thermal and electrical conductivity of single- and multi-walled carbon nanotube-epoxy composites, Compos. Sci. Technol., 66, 10 (2006), pp 1285-1288

[72] W.K. Park, J.H. Kim Effect of Carbon Nanotube Pre-treatment on Dispersion and Electrical Properties of Melt Mixed Multi-Walled Carbon Nanotubes / Poly(methyl methacrylate) Composites, Macromolecular Research, Vol. 13, No. 3, pp 206-211 (2005)