MULTI-WALL CARBON NANOTUBE DISPERSION IN PMMA MATRIX STUDIED THROUGH RHEOLOGY

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Abstract

Polymeric matrix with carbon based nanoparticle nanocomposites based on Poly(methyl methacrylate)/Multi-wall carbon nanotubes (MWCNT) were prepared by solution/precipitation method. In the course of procedure dispersions of MWCNT in PMMA methyl ethyl ketone solution were sonicated followed by dispersions precipitation pouring into non-solvent, water. Both types of CNT materials were used such as pure MWCNT and the same MWCNT after their adequate surface treatment with help of oxidation/grafting of binding element/radical polymerization. The aim of treatment was to covalently attach organic material onto surface of CNT to process their better dispersion in polymeric matrix leading to more effective CNT reinforcement effect. The state of CNT dispersion was characterized through rheology measurements with help of parameters like elasticity and viscosity of the melt. Also the effect of sonication onto pure PMMA matrix was analyzed.

Introduction

Carbon nanotubes (CNT) can be considered as very promising filler for polymeric matrixes. It is mainly due to their very high Young modulus reaching values of about 1TPa together with very high aspect ratio up to $10^3$–$10^5$, the promising is also their excellent electrical and thermal conductivity. Although they have been already practically used, substantial technological problems remain. At first, it is very problematic to disperse CNT in a polymeric matrix due to their insolubility in organic materials and also due to strong tendency to agglomerate. Thus, it is very difficult to de-agglomerate the bundles or ropes (in the case of MWCNT4 or SWCNT5, respectively) using conventional methods of melt processing. Practically, in the nanocomposites prepared by convectional melt mixing methods agglomerates of nanotubes of micrometric size or larger can be observed in the matrix, e.g. PP (ref.4), PMMA (ref.5), HDPE (ref.7,8) or PA6 (ref.9). The aggregates of CNT considerably reduce the aspect ratio of the tubes, and thus the reinforcing effect. Also load transfer can be limited because of the bundles of nanotubes; when some of the tubes are not bonded to the matrix, they slip within the bundles, and it is easier for them to slide out of the bundle than to break. Another critical point referring to polymeric/CNT composites seems to be the issue of a good adhesion between a polymeric matrix and CNT surface. Generally, their good compatibility is not expected although some experimental works disprove this14,15. Therefore the development and innovation of CNT/polymeric nanocomposites preparation methods is still a current issue. Commonly used methods, such as mixing in the polymeric melt, are being replaced by more efficient methods using e.g. ultrasound as a stirring element. Other efficient way to improve CNT dispersion in the polymeric matrix and to increase transfer of tension through polymer/CNT interface is chemical functionalization of CNT when covalent bond of organic molecules or polymeric fragments on CNT surface is being created. Probably the most progressive method seems to be the process of CNT oxidation16,17 leading to creation of carboxyl and hydroxyls groups which become a binding element for different polymeric molecules18–22. The state of CNT dispersion in polymeric matrix and interaction between CNT and polymer matrix can be powerfully analyzed thought rheology measurements23–25. It is relatively easy and prompt indirect method.

Experimental

Multi-wall carbon nanotubes, functionalization and PMMA matrix nanocomposite

MWCNTs produced by chemical vapor deposition of acetylene were supplied by Sun Nanotech Co. Ltd., China (diameter 10–30 nm, length 1–10 μm, purity >90 % and volume resistivity 0.12 Ωcm according to the supplier). To complete information about the MWCNTs investigated, we refer to our previous paper26,27, where the results of TEM analysis are presented in detail. Via micrography the diameter of individual nanotubes was determined to be between 10 and 60 nm (100 measurements) with the average diameter and standard deviation of 15±6 nm, and their length from tenths of micron up to 3 μm. The tubes consist of about 15 to 35 rolled layers of graphene, with the interlayer distance of ca 0.35 nm. The functionalization yielding oxidized functional groups covalently detached onto surface of MWCNTs were performed according to
procedures described in previous studies for the mixture of HNO$_3$-H$_2$SO$_4$ (ref.16). The functionalized MWCNTs are denoted in the following as MWCNT (HNO$_3$-H$_2$SO$_4$). The functional groups detached on MWCNT (HNO$_3$-H$_2$SO$_4$) surface act in the next process as binding elements. MWCNT (HNO$_3$-H$_2$SO$_4$) were then functionalized by 4,4′-methylenebis(phenyl isocyanate) (MDI) and methacrylamide (MAAm) to synthesize so called “CNT-mer” (ref.28). In this course active polymerizable vinyl groups on CNT surface is incorporated finally used as an element for growing of PMMA polymer chain during consequential radical solution polymerization. Amount of 0.2 g of MWCNT (HNO$_3$-H$_2$SO$_4$) were added in a 250 ml round-bottomed flask filled with 50 ml of anhydrous dimethylformamide (DMF) and 0.36 g of MDI and stirred mechanically at 80 °C for 4 hours under N$_2$ atmosphere. Finally 0.29 g of MAAm was added and stirred for another 8 hours at RT. Two different MDI and MAAm concentrations were used as in the first case mentioned 0.36 g of MDI and 0.29 g of MAAm and in the second one larger excess of MDI compared to amount of expected functional groups detached onto MWCNT (HNO$_3$-H$_2$SO$_4$) like 3.78 g of MDI and 2.93 g of MAAm. Prepared surface treated filler was then again separated by ultracentrifugation and added to 15 wt.% solution of methylmethacrylate (MMA) in DMF with 1.5 wt.% of AIBN as an initiator of polymerization and the mixture was polymerized at 70 °C for 4 hours, both further denoted as treated CNT filler like CNT/PMMA I and CNT/PMMA II, respectively. Final CNT based filler was again separated by ultracentrifugation and finally mixed into PMMA commercial polymer (DELPET 80N, Asahi Kasei Corporation) by solution method. The CNT dispersion in methylethyl ketone (MEK) with concentration from 0.1, 0.5, 1.0 to 2.0 wt.% of CNT on total concentration in PMMA matrix were prepared by sonication using ultrasonic bath (Bandelin electronic DT 103H) at 70 °C for 4 or 8 hours followed by additional 2 hours using ultrasonic homogenized (Homogenizer UZ Sonopuls HD 2070 kit) at 60 °C. The coagulation was performed by pouring of prepared dispersions into mixer filled by antisolvent – water and prepared composites were vacuum dried at 60 °C till constant weight.

Characterization

MWCNTs (pure) were observed with the help of scanning electron microscope (SEM) Vega LMU, produced by Tescan Ltd. The samples were deposited on carbon targets and covered with a thin Au/Pd layer. For the observations the regime of secondary electrons was chosen. Treated and separated tubes CNT/PMMA I were analyzed via transmission electron microscopy (TEM) using microscope JEOL JEM 1010 at the accelerating voltage of 160 kV. The sample was deposited on 300 mesh copper grid with a carbon film (SPI, USA) from MWCNT dispersion in acetone prepared by ultrasonication, which was deposited on the grid and dried.

Thermogravimetric analyses (TGA) of the nanotube samples like pure CNT, acid treated MWCNT (HNO$_3$-H$_2$SO$_4$), functionalized fillers CNT/PMMA I and CNT/PMMA II, and pure PMMA matrix were carried out using thermogravimeters Setaram Setsyt Evolution 1200 and TA Q500. The samples were examined under inert atmosphere of helium (5.5 purity, SIAD TP); the gas flow was 30 cm$^3$ min$^{-1}$ at the pressure of 101.325 kPa (i.e. 30 scem) for all experiments. A platinum crucible was used for the sample, the weight of which was about 4 mg. The temperature was increased from 25 °C up to 950 °C at the rate of 10 °C/min. CNT/PMMA I and CNT/PMMA II materials were before measurement two times refluxed in excess of MEK and centrifuged to remove residual chemicals and non-bonded organics material to CNT surface. The states of prepared PMMA matrix with dispersed CNT/PMMA I filler and influence of sonication onto rheological parameters of PMMA solution were characterized thought rheology measurements using the Advanced Rheometric Expansion System (ARES 2000) Rheometrics rheometer in terms of complex viscosity and recoverable shear. It should be mentioned that the recoverable shear, $\eta_r$, is the measure of the shear elasticity, which is given by the following equation:

$$\eta_r = \frac{N_1}{2 \tau_w}$$  \hspace{1cm} (1)$$

where $N_1$ is the first normal stress difference and $\tau_w$ is the shear stress. Considering the Cox–Merz rule (ref.29) and the similarity between $N_1/2$ and storage modulus $G'$ (ref.30), Eq. (1) can be rewritten into the following form:

$$\eta_r = \frac{G'}{\eta \omega}$$  \hspace{1cm} (2)$$

where $\eta^*$ is the complex viscosity and $\omega$ is the frequency. In this work, the recoverable shear shown in Figures 4–5 was calculated by using rotational rheometry data according to Eq. (2).

Results and discussion

SEM analyses in Fig. 1 part a) demonstrates class of used tubes which are organized into bundle of entangled tubes. Their diameters and length were determined together with help of additional TEM analyses to be 15±6 nm and up to 3 μm, respectively. The TEM images of CNT/PMMA I treated filler are shown in Fig. 1 b–c). The TEM micrographs clearly confirm the presence of organics material layer adhering onto the MWCNT surface. Here two different structures can be observed. The first represents core-shell structure of MWCNT with organics material layer on CNT surface, the second represents organics material with shape of lamellas firmly adhered on CNT surface. These materials were not solved/
separated from CNT material during washing procedure so it is considered to be covalently bonded to CNT surface. These organic material originates from oxidized groups (mainly -COOH) coupled with MDI and MAAm finally with detached PMMA macromolecular chains. It is considered that this material should be also partially cross linked when several reaction sites on surface of CNT can be in close vicinity.

Fig. 2 shows TG analyses of pure CNT, acid treated MWCNT (HNO₃-H₂SO₄), functionalized CNT like CNT/PMMA I and CNT/PMMA II, and of pure PMMA matrix. As can be seen, pure MWNT shows hardly any degradation in the used range of heating, here displayed up to 700 °C; only very small mass loss of ca 3 wt.% at the 700 °C was observed. This decomposition is probably caused by amorphous carbon contained in the original material together with decomposition of functional groups like O-C=O or C-O also included in crude material²⁸. On the other hand, oxidized tubes, MWCNT (HNO₃-H₂SO₄), shows higher weight loss achieving at mentioned 700 °C about ca 12 wt.%. This increase is probably due to higher content of functional groups, mainly acidic sites (but also –OH or C=O groups) which should be expected to be introduced during oxidizing process. Traces for CNT/PMMA I and CNT/PMMA II, (line c) and d), respectively) clearly shows two decomposition events. The beginning of the first one for both specimens are located at ca. 300 °C (47.8 wt.% mass loss), next smaller one at ca. 410 °C (11.1 wt.% mass loss for CNT/PMMA I and 26.1 wt.% mass loss for CNT/PMMA II). The first event probably represents decomposition of binding elements like oxidized groups/MDI/MAAm bonded to CNT surface. The second event should represent decomposition of incorporated PMMA chains. There was found relatively high amount of groups/MDI/MAAm detached on surface of CNT, for both specimens nearly the same, but lower amount of PMMA in CNT/PMMA I compared with CNT/PMMA II. It is probably because of higher amount of isocyanate groups free for bonding with MAAm when higher excess of MDI was used leading to
more mono MDI functionalized CNT. Line e) represents decomposition of pure PMMA with initial temperature in range of ca. 365 °C and fully decomposed at 450 °C.

In the first step, the effect of sonication time on the complex viscosity of PMMA has been investigated (see Fig. 3). It is clearly visible that increase in the sonication time leads to decrease in complex viscosity which can be taken as evidence that the PMMA degrades during the sonication process. In the second step, the effect of CNT content in the PMMA melt on its elasticity (recoverable shear) has been investigated (see Fig. 4). Obviously, the increase in the CNT level in the PMMA matrix leads to increase in the PMMA melt elasticity. Finally, the effect of the CNT surface modification, which is described above, on the PMMA melt elasticity has been analyzed through recoverable shear (see Fig. 5). In this case, the surface modified CNT in the PMMA matrix enhances the melt elasticity more than no surface modified CNT which suggest that the suggested CNT surface modification might be good tool to improve the interaction between CNT and PMMA polymer matrix.

Conclusion

Based on the rheological evaluation of the tested polymer samples, it has been found that, firstly, sonication of the PMMA can lead to degradation of PMMA macromolecules. Secondly, the increase of the CNT content in the PMMA/CNT nanocomposite may leads to enhanced melt elasticity and finally, modification of the CNT surface can increase the PMMA/CNT melt elasticity more than no surface modified CNT.

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