

**A promising approach to low electrical percolation threshold in PMMA nanocomposites by using MWCNT-PEO predispersions**

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## Abstract

Electrical conductive poly(methyl methacrylate) (PMMA) nanocomposites with low percolation threshold are not easy to be obtained. Here, we show that miscible blending with poly(ethylene oxide) (PEO) can be exploited as an efficient approach to achieve very low electrical percolation threshold in PMMA/multi-walled carbon nanotubes (MWCNTs) nanocomposites. PMMA/PEO-MWCNTs nanocomposites were prepared by a two steps solution casting method involving pre-blending of MWCNTs with PEO and then blending of PEO-MWCNTs with PMMA. The electrical percolation threshold (EPT) value was determined to be  $\sim 0.07$  wt% which is significantly smaller than most of reported EPT values in the literature for PMMA/CNT composites. The very low electrical percolation threshold was attributed to the effectual role of PEO in self-assembly of secondary structures of nanotubes into an electrically conductive network. This was further confirmed by transmission electron microscopy and by comparing the obtained EPT value with the prediction of the excluded volume model in which statistical percolation threshold is defined based on uniform distribution of high-aspect ratio sticks in a matrix. Moreover, based on light transmission and linear viscoelastic rheological measurements, optical and rheological percolation thresholds were calculated to be 0.005 wt% and 2.53 wt%, respectively.

**Keywords:** Electrical Percolation; Rheological Percolation; Poly(methyl methacrylate); Multi-walled Carbon Nanotube; Poly(ethylene oxide); Miscible Blends

## Introduction

Nowadays, nanostructured materials based on carbon nanotubes (CNTs) have paved the way to fabricate advanced semi-conductive and conductive polymer nanocomposites (CPCs). They have also opened the door for manifestation of novel multifunctional materials [1–4]. However, suitable dispersion and homogenous distribution of CNTs into polymer matrices have been mentioned as the major challenges [5,6]. It is well realized that the high aspect ratio of CNTs and the strong intermolecular Van der Waals (VdW) forces between nanotube walls as well as weak interactions between CNTs and the polymer matrix lead to re-agglomeration of CNTs [7–9]. Improved dispersion state of CNTs redounds to outstanding mechanical, electrical and thermal properties at very low loadings. Hence, covalent and non-covalent functionalizations have been employed as suitable strategies to improve quality of dispersion and CNT processability into polymer matrices. Accordingly, considerable number of research work focused on different types of functionalization, which have been comprehensively reviewed by Sahoo et al. [10], Grady [11], and Hirsch and Vostrowsky [12,13].

To describe the nanotube network formation in the host polymer, percolation concept is used [14]. In order to justify economic aspects plus maintaining the mechanical, physical and rheological properties of polymers a low percolation threshold is desired [15]. The low percolation threshold is directly correlated with the way of CNT assembling in a host polymer [16]. Depending on the particular assembling, different types of percolation threshold including optical percolation threshold (OPT), rheological percolation threshold (RPT), and electrical percolation threshold (EPT) have been defined [17–21]. A low electrical percolation threshold is supported by good dispersion (individualization) of CNTs and the formation of a suitable network structure including some secondary agglomeration in the polymer matrix [22,23]. Therefore, any dispersion method that assists CNTs to establish networks at lower CNT concentration can be considered as a suitable choice.

Convenient strategies such as alignment of CNTs in polymer matrix, incorporating secondary filler into the nanocomposite, and using the double percolation concept have been proposed to obtain suitable network structures and low percolation threshold in CPCs. Well alignment of CNTs not only leads to lower electrical percolation threshold, but also provide an opportunity to fabricate anisotropic nanocomposite with tailored properties [24,25]. In the case of secondary filler concept,

significant reductions in percolation threshold and synergistic effects are observed due to either a supporting dispersion action of a second nonconductive filler or an arrangement of a second conductive nanofiller within gaps of the network of the first [26–29]. The strategy of double percolation is considered also as a very suitable way to decrease percolation threshold in polymer matrix. Here, CNTs selectively localize in one continuous component or at a continuous interface of an immiscible polymer blend. This is especially effective in co-continuous blends and conductive paths can be formed at significantly lower CNT contents [30,31]. However, this concept requires accurate control on preparation of the blends as well as deep understanding of interaction of CNTs with the polymer components. Furthermore, the final morphology of the blend should be thermodynamically and kinetically stable which may be a challenge in co-continuous immiscible polymer blends [32].

Poly(methyl methacrylate) (PMMA) is an amorphous polymer with good mechanical properties [33]. Incorporation of CNTs into PMMA as a model glassy polymer has been well studied in the literature. It is well demonstrated that PMMA/CNT nanocomposites can be used in applications such as gas sensors [34], nanocomposite foams [35], electromagnetic interference shielding (EMI) [36], electromagnetic shielding (EMS) and bone cements [37]. Different approaches such as applying treatment on CNT surface, solution and melt mixing, coagulation method and in-situ polymerization have been used to disperse CNTs into this polymer matrix and to achieve a low electrical percolation threshold.

In the literature, however, investigations on the miscible polymer blends containing CNTs are rare [38, 39]. To the best of our knowledge, there is no report on the dispersion of CNTs in miscible polymer blends based on the pre-dispersion of nanotubes in one miscible component. Accordingly, the motivation behind our study is to reach very low electrical percolation in PMMA/MWCNT nanocomposites by using PEO polymer as the component thermodynamically miscible with PMMA. To do so, MWCNTs were uniformly dispersed in PEO and then the PEO-MWCNTs nanocomposite mixed with PMMA via solvent casting method. The obtained PMMA/PEO-MWCNT nanocomposites were characterized with complementary techniques.

## Experimental

Multi-walled carbon nanotubes (MWCNTs) (Nanocyl<sup>®</sup>-7000) were obtained from Nanocyl<sup>™</sup>, Belgium. According to the supplier, the nanotubes synthesized via the catalytic carbon vapor deposition (CCVD) method having an average length of 1.3  $\mu\text{m}$ , average diameter of 9.5 nm, purity of 90% and surface area of 250-300  $\text{m}^2/\text{g}$  [40]. PEO ( $M_v = 10^5$  g/mol,  $T_g = -67^\circ\text{C}$ ,  $T_m = 65^\circ\text{C}$ , density = 1.13  $\text{g}/\text{cm}^3$ ) and PMMA ( $M_w = 93000$  g/mol, density = 1.19  $\text{g}/\text{cm}^3$ ) were obtained from Sigma-Aldrich and Altuglas<sup>®</sup> Arkema, respectively. Polysorbate (Tween 80) used as a non-ionic surfactant and N, N-dimethylformamide (DMF) as solvent were supplied by Merck.

Nanocomposite films were prepared by two steps solution casting method (Fig. 1). First, non-covalent functionalization was used to disperse MWCNTs in PEO. MWCNTs were mixed in deionized water with the aid of Tween 80. Different ratios of Tween 80-to-MWCNTs of 1 to 15 were investigated and optimum ratio was found at 10. To disperse the nanotubes, ultrasonication was applied by a probe sonicator (Lapsonic<sup>®</sup> P, 50% intensity, 3 min). Then the dispersed nanotubes were added to PEO solution (2.5% w/w) in deionized water. The PEO-MWCNTs solution was again ultrasonicated for 6 min and then mixed by magnetic stirring for 4 h. Evaporation casting was used to fabricate PEO-MWCNTs nanocomposites at  $55^\circ\text{C}$ . In the second step, completely dried PEO-MWCNTs nanocomposite were added to PMMA solution in DMF (10 w/w) at  $55^\circ\text{C}$ , mixed together and ultrasonication was applied for 3 min. The final PMMA/PEO-MWCNTs nanocomposite samples were prepared by evaporation casting method at  $55^\circ\text{C}$ . Different samples with nanotube concentrations including 0.01, 0.03, 0.07, 0.1, 0.3, 0.5, 1 and 3 wt% were prepared. The composition of PMMA/PEO was 80/20 (w/w) in all samples and weight percent of the CNTs in the nanocomposites was calculated based on total weight of PMMA/PEO blend.

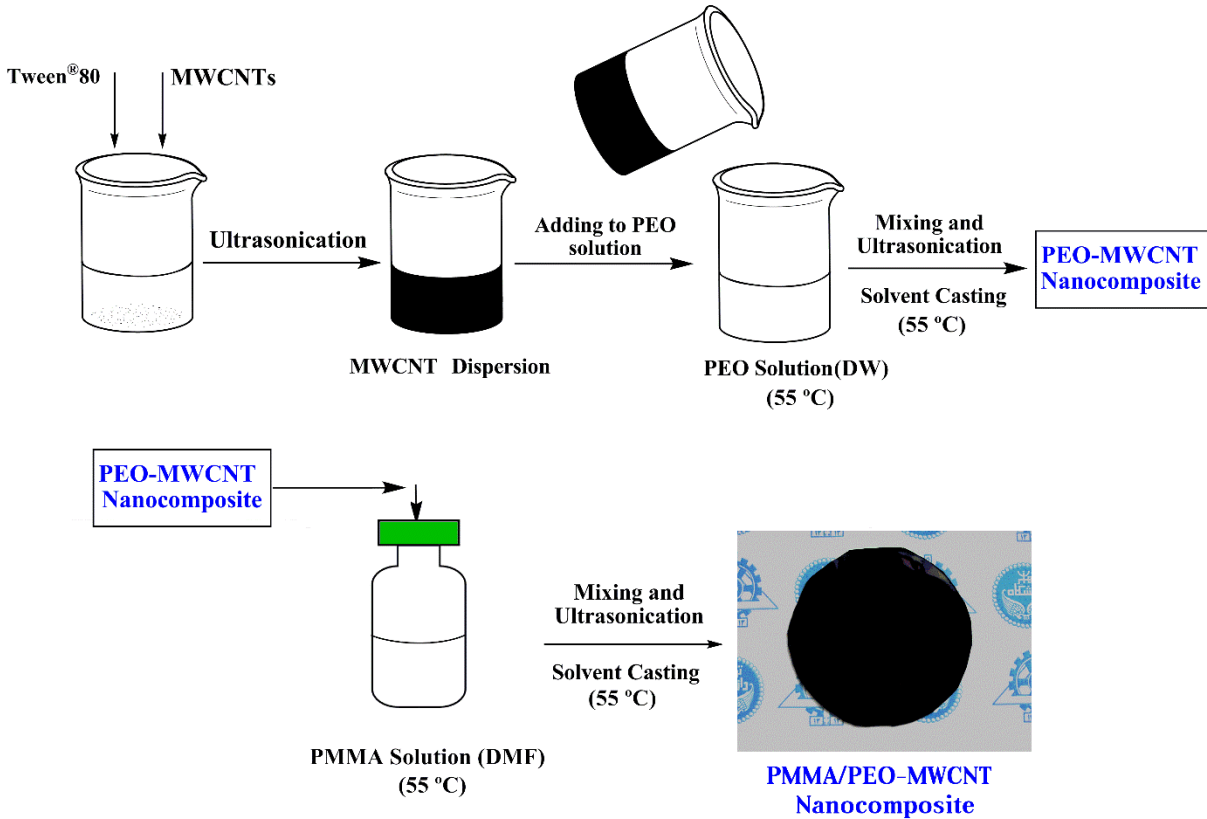


Fig. 1. A schematic representation of fabricating PMMA/PEO-MWCNTs nanocomposites.

## Characterization

### 1. Electrical Measurement

The electrical volume resistivity of the nanocomposite strips was determined according to the ASTM D4496 and ASTM D 257 standards. The resistivity measurements on the nanocomposite films with resistance  $> 10^7$  Ohm were performed by using a Keithley 8009 Resistivity Test Fixture. For nanocomposites with resistance  $< 10^7$  Ohm, the cast samples were cut to strips (5 mm  $\times$  30 mm  $\times$  0.25 mm) and electrical resistance were measured by a 4-point test fixture using a Keithley electrometer 6517A or a Keithley multimeter DMM2000 (Keithley Instruments Inc., Cleveland, USA). Electrical conductivity ( $\sigma$ ) of samples was calculated from electrical volume resistance ( $\rho$ ) by following equation:

$$\sigma(S/cm) = \frac{1}{\rho(\Omega cm)} \quad (1)$$

## ***2. Optical Microscopy***

In order to visualize the nanotube dispersion state in a microscopic scale, optical microscopy (OP) micrographs were obtained from the cast nanocomposite films by means of an Olympus BH2 microscope in transmission mode equipped with a digital camera model DP71. Thin films with 10  $\mu\text{m}$  in thickness were cut from samples embedded in epoxy resin by using a Leica microtome RM2265.

## ***3. Transmission electron microscopy (TEM)***

In order to gain more insight into the nanocomposite morphology and dispersion state of MWCNTs within the blend matrix, transmission electron microscopy (TEM) was performed with a TEM LIBRA 200MC (Carl Zeiss SMT, Germany) using an operating voltage of 200 kV. Samples were cut into ultrathin sections (60 nm in thickness) with a Leica UC7 ultramicrotome at -80  $^{\circ}\text{C}$  using a diamond knife.

## ***4. Differential scanning calorimetry (DSC)***

Thermal properties of the nanocomposites were investigated by DSC Q2000 V24.11 Build 124 instrument in nitrogen cell at a heating rate of 10  $^{\circ}\text{C}/\text{min}^{-1}$ . The weight of the samples varied from 5 to 7 mg. The samples were heated from room temperature to 150  $^{\circ}\text{C}$  (run 1) and maintained there for 10 min to remove their thermal history. The samples were cooled to -100  $^{\circ}\text{C}$  before a second heating run from -100  $^{\circ}\text{C}$  to 150  $^{\circ}\text{C}$  (run 2).

## ***5. Rheological measurements***

Rheological measurements in the molten state were carried out using dynamic oscillatory rheometry with a strain controlled rheometer (TA instrument, USA) under dry nitrogen condition. A dynamic frequency sweep analysis in the range of 100-0.1 rad/s was performed at 155  $^{\circ}\text{C}$  within the linear viscoelastic strain range (which was determined prior to measurements) at constant strain amplitude of 10% using parallel plate geometry with a diameter of 25 mm.

In order to confirm that thermal degradation did not occur during the rheological measurements, each frequency sweep cycle was followed by another cycle in which the variation of frequency was applied inversely, i.e. from 0.01 to 100 rad/s.

## 6. Optical measurements (UV-Vis)

The optical percolation threshold was determined according to Kara et al. [21]. Thin films of nanocomposite samples (10 mm × 30 mm × 50 μm) were prepared according to method proposed by Park et al. [41] and then placed in a UV-Vis spectrophotometer (Perkin-Elmer UV/SVI Spectrophotometer). The transmitted light intensity was measured at 400 nm wavelength at room temperature. All measurements were done on three zones of each sample and their average was considered.

## Results and discussion

Electrical conductivity of the nanocomposite blends increases drastically with increasing MWCNT content (Fig. 2). Specifically, the electrical conductivity increase by about 8 orders of magnitude with the addition of 0.1 wt.% of MWCNT. The rapid increase in the electrical conductivity between 0.07 and 0.1 wt.% can be attributed to the transition from insulator to conductor corresponds to the formation of network-like structure of CNT clusters in the blend matrix. This three-dimensional network provides conductive paths for electrons to transit within the insulating PMMA/PEO blend. The electrical conductivity of the nanocomposites,  $\sigma_{DC}$  can be treated by percolation equation [42] below and above the electrical percolation threshold (EPT),  $\varphi_{c,\sigma}$ :

$$\sigma_{DC} = \sigma_0 \left( \frac{\varphi_{c,\sigma} - \varphi}{\varphi_{c,\sigma}} \right)^{-a_\sigma} \quad \text{for } \varphi < \varphi_{c,\sigma} \quad (2-a)$$

$$\sigma_{DC} = k \left( \frac{\varphi - \varphi_{c,\sigma}}{1 - \varphi_{c,\sigma}} \right)^{\beta_\sigma} \approx k (\varphi - \varphi_{c,\sigma})^\gamma \quad \text{for } \varphi > \varphi_{c,\sigma} \quad (2-b)$$

where,  $\sigma_0$  is the electrical conductivity of the matrix,  $\varphi$  is the weight or volume fraction of MWCNTs, and  $a$  and  $\beta$  are critical exponents. Percolation equation is described based on volume fraction of randomly distributed filler in matrix. The volume fraction of nanotubes was calculated by applying  $\rho_{\text{matrix}}=1.17 \text{ g/cm}^3$  for 80/20 blend and  $\rho_{\text{CNTs}}=2.1 \text{ g/cm}^3$ .



Electrical percolation in the nanocomposites occurs when the MWCNT concentration is  $\varphi_{c,\sigma} = 0.039$  vol% (0.0712 wt.%) and  $\beta = 1.725$  (Fig. 2). The very low  $\varphi_{c,\sigma}$  can be ascribed to the high aspect ratio ( $L/D = 137$ ) of the MWCNT and the effectual role of PEO in dispersing MWCNTs. This implies that by replacing a part of PMMA with PEO, formation of electrical network occurs at considerably lower MWCNT concentration. Moreover, the exponent  $\beta$  is in agreement with the transport mechanism in three dimensions network ( $\beta = 2$ ).

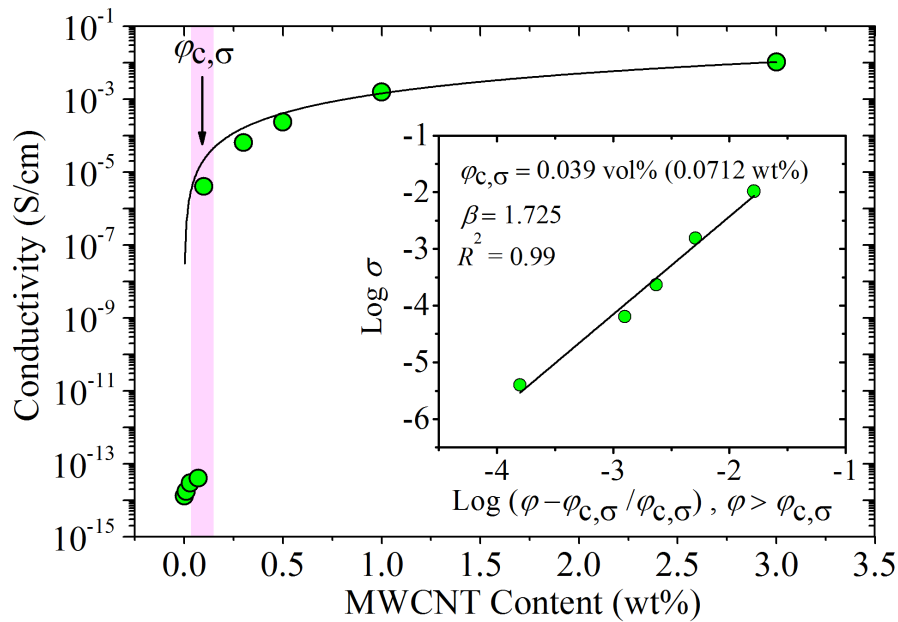


Fig. 2. The conductivity values of PMMA/PEO-MWCNT nanocomposites versus MWCNT content. The inset curve represents the log-log plot for DC conductivity vs.  $(\varphi - \varphi_{c,\sigma} / 1 - \varphi_{c,\sigma})$  for nanocomposites. The best fit on percolation equation gives values  $\varphi_{c,\sigma} = 0.0712$  wt% and  $\beta = 1.725$ .

Different values of EPT have been reported for PMMA/CNT nanocomposites (Table S1). The discrepancy between the reported EPTs is not surprising, because EPT is affected by various parameters e.g. the dispersion method and parameters pertaining to nanocomposite fabrication. For instance, parameters such as solvent nature, casting temperature and nanocomposite components profoundly influence the quality and the way of network assembling of CNTs within the matrix in nanocomposites prepared by solution method. Reported ranges for PMMA-MWCNT nanocomposites in the literature are  $\varphi_{c,\sigma} \sim 0.03$ -10 wt% and  $\beta \sim 2.1$ -3.66 [33,43–57], and for PMMA-SWCNT nanocomposites,  $\varphi_{c,\sigma} \sim 0.03$ -1 wt% and  $\beta \sim 1.3$ -2.3 [25,55,58–65]. Compared to

the published data, the obtained EPT in the current work is much lower than most of the reported EPT values and very close to the lowest one (Table S1). Therefore, introducing a secondary miscible polymer with PMMA can be considered as an appropriate approach for formation of conductive paths in the insulating PMMA matrix and consequently obtaining a very low EPT.

According to the excluded volume analysis proposed by Celzard et al. [66], percolation threshold greatly depends on the aspect ratio of the filler. The statistical percolation threshold in a system containing randomly oriented long sticks with a known aspect ratio,  $L/D$  can be estimated from the following equation [14]:

$$\left(\frac{L}{D}\right)p_c \cong 0.5 \quad (3)$$

where,  $p_c$  is EPT by weight. By taking  $D=9.5 \text{ nm}$  and  $L=1.3 \mu\text{m}$ ,  $p_c=0.365 \text{ wt\%}$  is calculated. This calculated value is considerably higher than the EPT measured for the PMMA/PEO-MWCNT nanocomposite. The large deviation of the experimentally determined EPT from the prediction of the excluded volume theory (0.071 versus 0.365) strongly suggests that the main assumption of the excluded volume theory, i.e. the random dispersion of the nanotubes in the matrix does not hold in the current systems. In other words, the non-uniform dispersion of MWCNTs in the PMMA/PEO blend and formation of secondary structures might be responsible for achieving the very low EPT. This discrepancy has been also noticed by other authors. For instance, Martin et al. [67] and Bauhofer and Kovacs [14] postulated that the excluded volume theory does not take into account Brownian motions of particles during the network formation as well as particle-particle and particle-matrix interactions. They attributed the lower EPT compared to the value calculated by excluded volume to the kinetic percolation threshold in which particles have a freedom to move through the matrix and re-agglomerate.

In order to get more insight about the dispersion state of nanotubes in the PMMA/PEO matrix, optical and TEM micrographs of the nanocomposite containing 1 wt% nanotubes were investigated. The optical micrographs of the nanocomposite (Fig. 3) indicate the non-homogeneous dispersion and the presence of nanotube clusters within the PMMA/PEO matrix. Secondary structures of MWCNTs in the matrix can mainly be attributed to the presence of PEO

polymer in the nanocomposite system and to the strong intermolecular van der Waals interactions between the nanotubes.

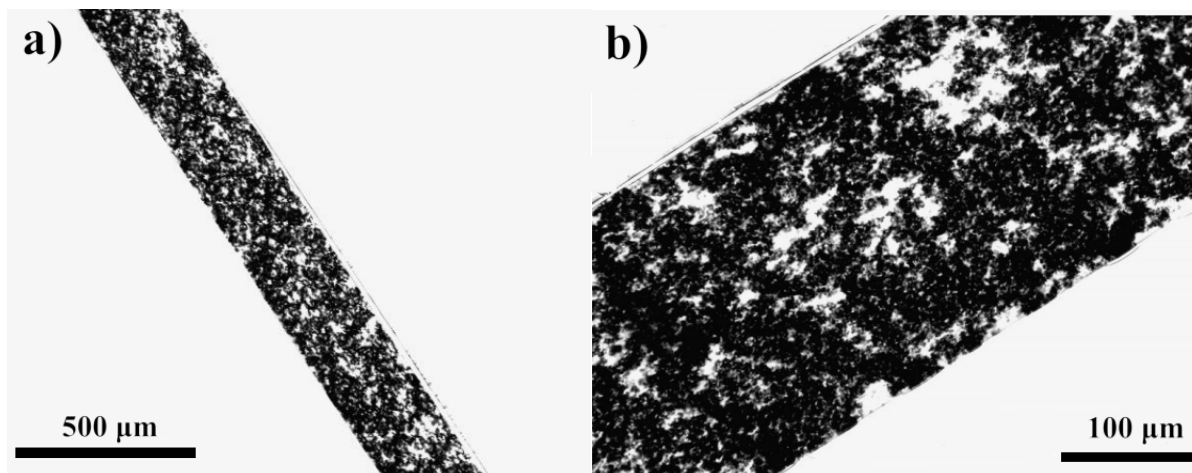


Fig. 3. Optical micrographs of PMMA/PEO-MWCNTs nanocomposite sample containing 1 wt% MWCNTs.

Moreover, TEM micrographs confirm that locally dispersed micro-clusters of MWCNTs with a size of  $\sim 1 \mu\text{m}$  are present in the PMMA/PEO matrix (Fig. 4). More importantly, the clusters seem to be composed of individual nanotubes that have been assembled during fabrication of the nanocomposite film and therefore can be considered as secondary structures, i.e. secondary agglomerates. We presume that this particular structure is related to the solvent nature, casting temperature, and the PMMA/PEO blend morphology during nanocomposite preparation and solvent casting. PMMA and PEO form a miscible polymer blend at PEO concentration lower than 30% by weight [68]. The DSC measurements on the examined samples show that the neat blend and the nanocomposites possess a broad glass transition suggesting that PMMA and PEO form a miscible blend even at the presence of high loadings of MWCNTs (Fig. 5).

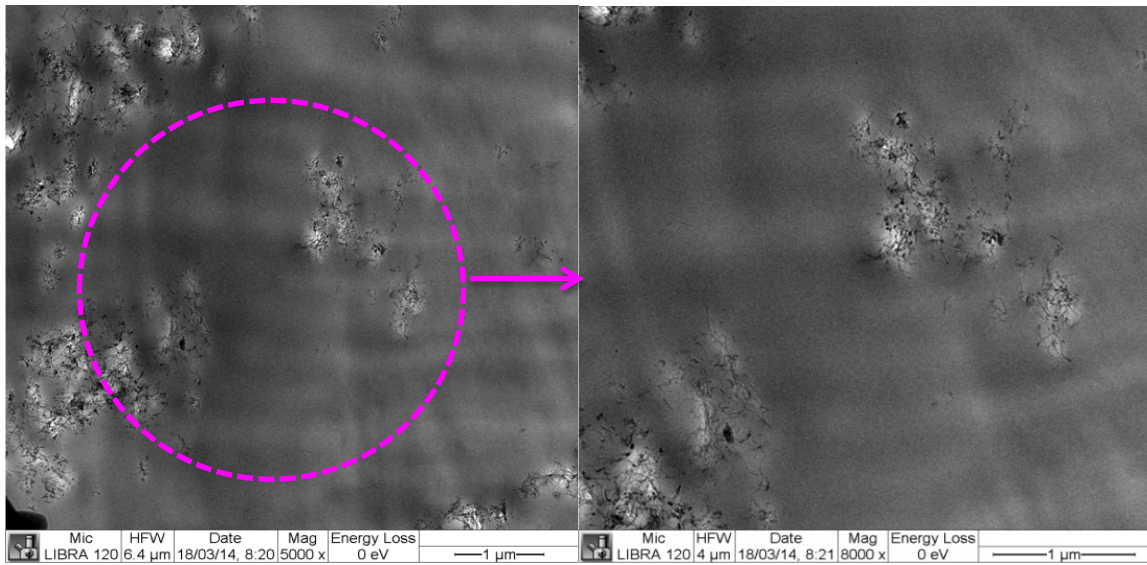


Fig. 4. TEM micrographs of PMMA/PEO-MWCNT nanocomposite containing 1 wt% MWCNT

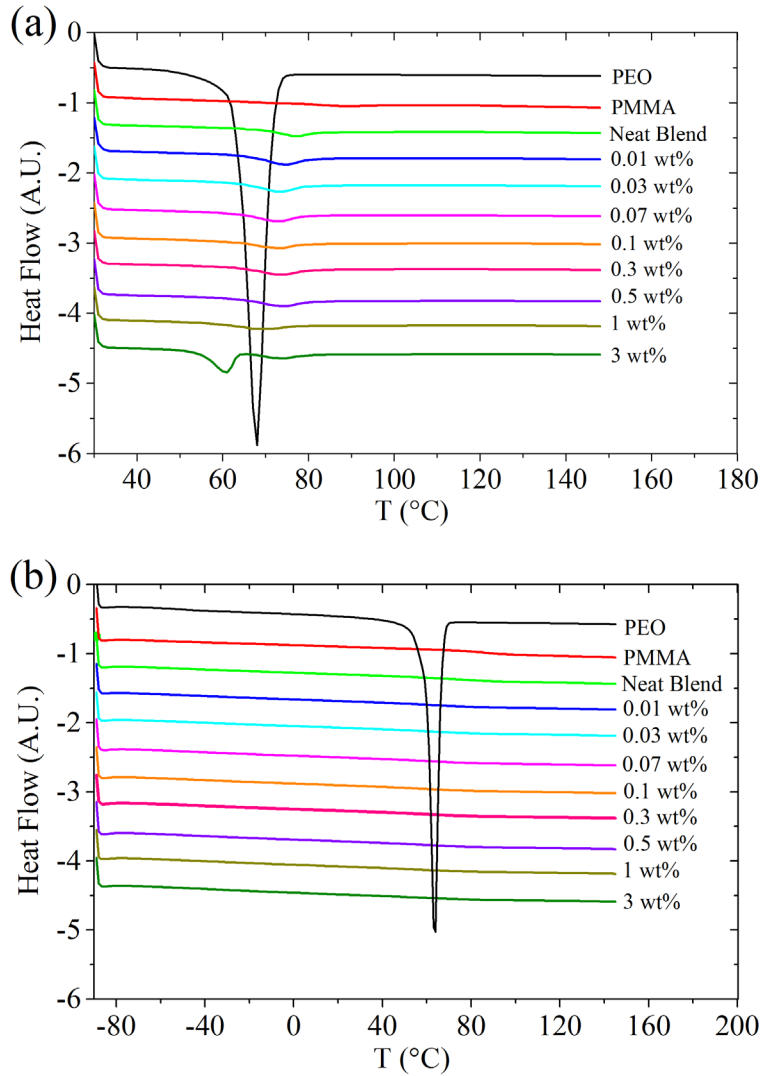


Fig. 5. DSC thermograms of PMMA, PEO, PMMA/PEO and the nanocomposites obtained from first (a) and second heating (b) runs.

The specific structure of nanotube networks influences the transparency of the PMMA/PEO blend. Since, PMMA/PEO blend form a transparent blend due to miscibility of PMMA and PEO and on the other side CNTs impede light transmission, investigation of the optical properties is a good idea to get more information about nanotube network within matrix. Generally, scattered light intensity,  $I_{sc}$  increases drastically upon incorporation of MWCNTs into transparent polymer matrix (Fig. 6). The neat PMMA/PEO blend shows the lowest  $I_{sc}$  denoting transparency of this sample, however the nanocomposite containing 0.01 wt% MWCNTs transmits only 35% of the incident light. Moreover, no light transmission is observed above 0.3 wt% of MWCNT. This suggest

formation of assemblies (Fig. 7) that are big enough to scatter the light, i.e. with sizes larger than the wavelength of the visible light at 400 nm [69].

Kara et al. [21] showed that the relation between  $I_{sc}$  and nanotubes content can be treated as an exponential relationship and the site percolation theory is a good representative for calculating a particular percolation threshold called the OPT. By taking the  $I_{sc}$  as an increasing property upon addition of MWCNTs, percolation equation can be re-written as:

$$\frac{I_{sc}(\phi)}{I_0} = \left( \frac{\varphi_{c,op} - \varphi}{\varphi_{c,op}} \right)^{-a_{op}} \quad \text{for } \varphi < \varphi_{c,isc} \quad (4-a)$$

$$I_{sc}(\phi) = m \left( \frac{\varphi - \varphi_{c,isc}}{1 - \varphi_{c,isc}} \right)^{\beta_{op}} \approx m (\varphi - \varphi_{c,isc})^\alpha \quad \text{for } \varphi > \varphi_{c,isc} \quad (4-b)$$

where,  $\varphi_{c,isc}$  is the EPT. Best fit on optical data using equation (3-b) indicates that optical percolation does occur at MWCNT concentration of 0.005 wt% and  $\beta$  exponent takes value of 0.127 (Fig. 6). Again, the very low OPT might suggest formation of particular secondary structures of carbon nanotubes which impede transmission of light through nanocomposite (Fig. 7). Kara et al. calculated the  $\varphi_{c,isc}=0.13$  wt% and  $\beta=0.32$  for the nanocomposites in which MWCNTs had been uniformly dispersed in the PS matrix.

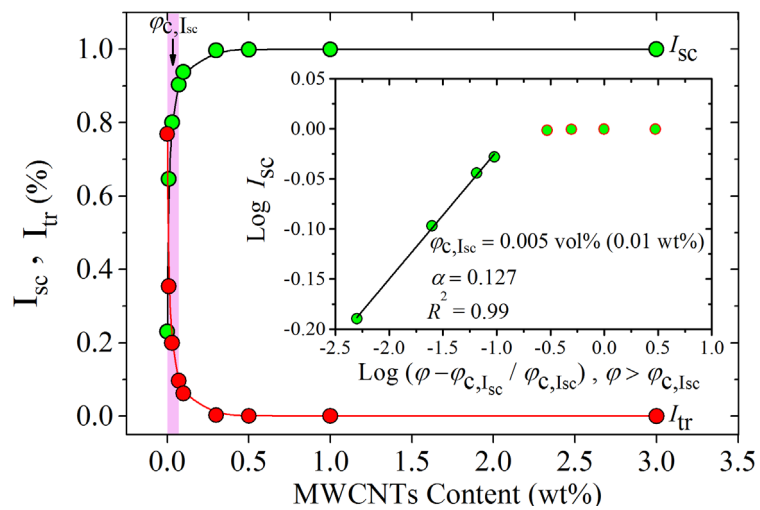
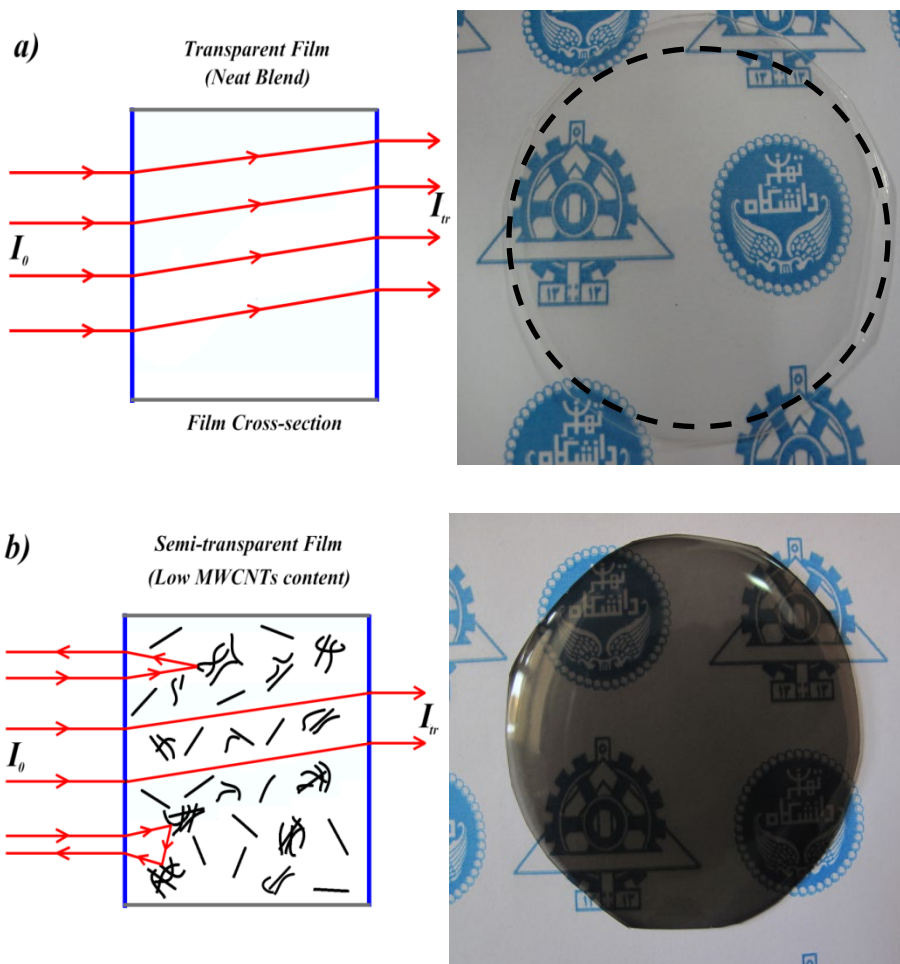


Fig. 6. Evaluation of  $I_{sc}$  and  $I_{tr}$  as a function of MWCNT content at wavelength of 400 nm. The inset curve represents the plot for logarithmic curve of  $I_{sc}$  versus  $(\varphi - \varphi_{c,isc} / 1 - \varphi_{c,isc})$  for all nanocomposites. The best fit on percolation equation gives  $\varphi_{c,isc} = 0.005 \text{ wt\%}$  and  $\beta = 0.32$ .



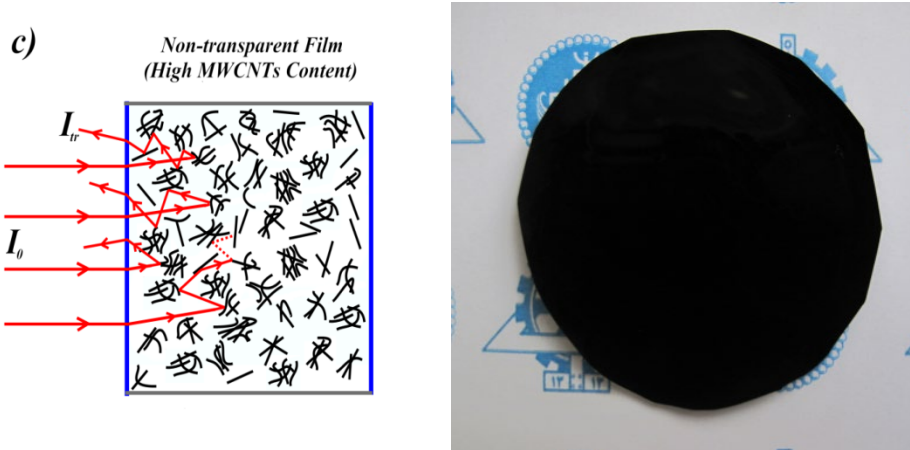


Fig. 7. A simple 2-dimensional schematic that describes how adding MWCNTs create scatter centers and directly affects transparency of the films. a) Neat PMMA/PEO blend, b) nanocomposite blend with at low MWCNT concentration (0.01 wt.%) and c) nanocomposite blend a high concentration of MWCNT (3 wt.%).

It is well comprehended that evaluation of rheological response in the molten state is a valuable method to assess the microstructure of polymer nanocomposites and to gain in-depth knowledge about the quality of the filler network established in the polymer matrix during nanocomposite processing. Figs. 8-a and 8-b represent evaluation of frequency dependency of dynamic storage modulus ( $G'$ ) and loss modulus ( $G''$ ) for the nanocomposite blends at 155 °C. By adding nanotube into the matrix the slopes of terminal zone diminish and both  $G'$  and  $G''$  deviate from terminal behavior. In other words, the terminal behavior disappears gradually by increasing nanotube concentration and a plateau is observed at lower frequencies for the nanocomposite containing 3 wt% MWCNTs. The low frequency plateau suggests microstructural changes and transition from a liquid-like ( $G' < G''$ ) to a solid-like ( $G' > G''$ ) viscoelastic behavior as depicted by Cole-Cole plot (Figure 8-c). This observation directly correlates with the formation of network like structure of MWCNTs in the blend and can be regarded as the RPT [19]. Beyond the RPT, the nanotubes restrain long-range polymer chains motions, resulting in increased relaxation times.



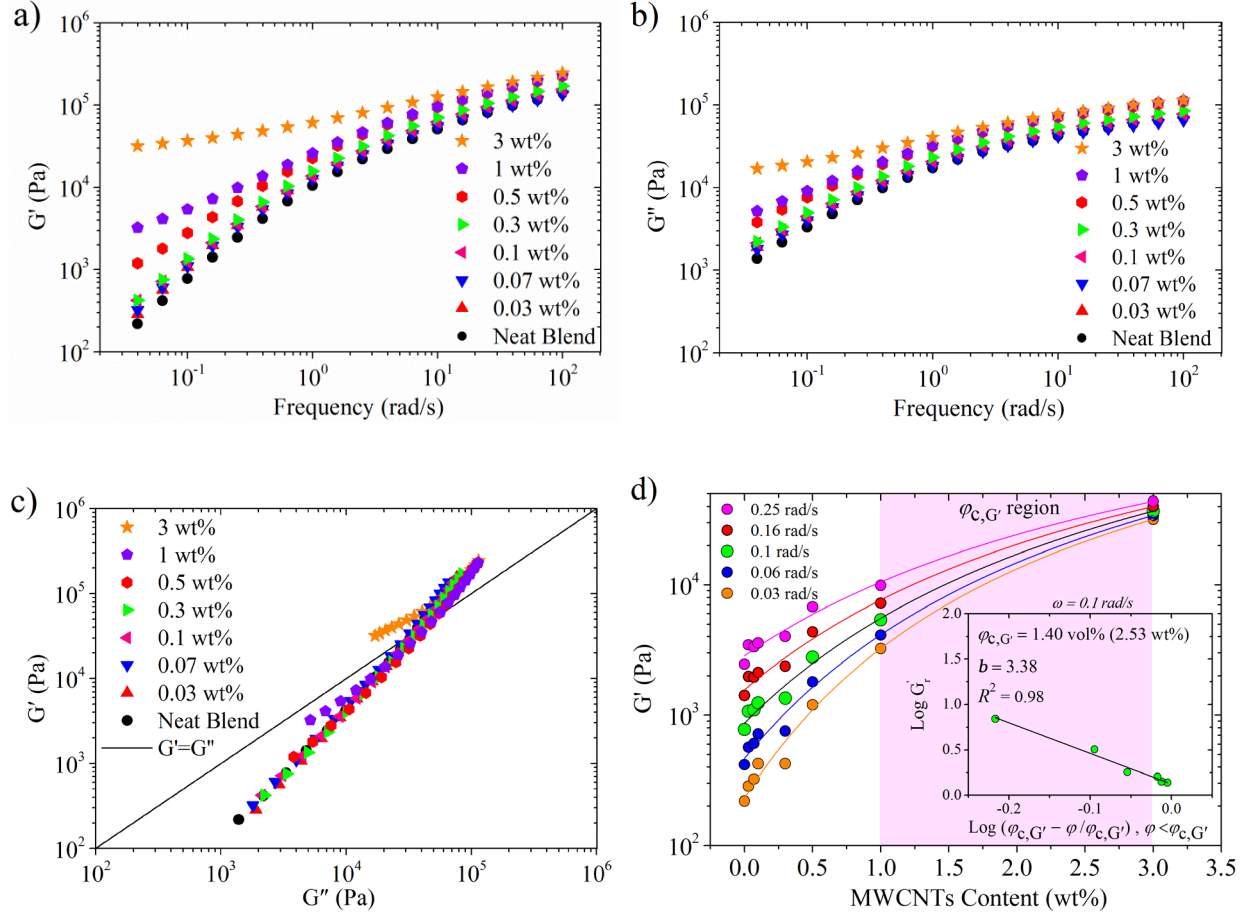


Fig. 8. (a)  $G'$ , (b)  $G''$  as a function of angular frequency ( $\omega$ ) for PMMA/PEO-MWCNTs nanocomposite blends with different MWCNTs contents at 155 °C, (c) Cole-Cole plots ( $G'$  versus  $G''$ ) at 155 °C, (d) Storage modulus versus MWCNTs content at frequency of 0.1 rad/s. The solid line is guide for the eye. The inset is the logarithmic plot for reduced storage modulus vs.  $(\varphi_{c,G'} - \varphi) / \varphi_{c,G'}$  for nanocomposites below 3 wt%. The solid line is the Eq. 6 fit to the data.

In order to quantify the RPT, we use  $G'$  data at lower frequencies (Fig. 8-d). The use of  $G'$  data was based on Kota et al. [70] work in which by comparing normalized log values of various rheological parameters in PS/MWCNT nanocomposites, they concluded that the elastic load transfer is considerably more sensitive to the onset of the RPT than dissipation mechanism caused by viscous response. They suggested that  $G'$  and  $G' / G''$  curves are the most appropriate parameters for quantitative analysis of the RPT. The statistical percolation based on the elastic modulus can be written as:

$$G'_r = \frac{G'}{G'_0} = \left( \frac{\varphi_{c,G'} - \varphi}{\varphi_{c,G'}} \right)^{-a_{G'}} \quad \text{for } \varphi < \varphi_{c,G'} \quad (5-a)$$

$$G' = n \left( \frac{\varphi - \varphi_{c,G'}}{1 - \varphi_{c,G'}} \right)^{\beta_{G'}} \approx n (\varphi - \varphi_{c,G'})^{\beta_{G'}} \quad \text{for } \varphi > \varphi_{c,G'} \quad (5-b)$$

where,  $G'$  is storage modulus of nanocomposites,  $G'_0$  is storage modulus of matrix,  $G'_r$  is reduced storage modulus and  $\varphi_{c,G'}$  is the RPT. The best fit of percolation theory on  $G'$  at 0.1 rad/s versus MWCNTs concentration below percolation region gives values of  $\varphi_{c,G'}=2.53$  wt% and  $a_G=3.38$  (Fig. 8-d inset).

The obtained result for our nanocomposite system is in agreement with other polymeric systems filled with CNTs and other fillers [17,71–74].

It is well understood that rheological and electrical properties of the nanocomposites containing CNTs are extremely governed by CNTs arrangement and their state of dispersion in the polymer matrix. In the literature, the rheological percolation threshold has been frequently reported to be smaller than the electrical percolation threshold [60]. This can be explained by the different nanotube–nanotube distances required for occurring electrical or rheological percolation. When the distance between individual CNTs become smaller than the radius of gyration (10-50 nm) of polymer chains, nanotubes can interlock with polymer chains and consequently the mobility of chains is restricted by the continuous interconnected CNT-polymer network. On the other hand, in the case of electrical percolation phenomenon, the mentioned distance must reach to the vicinity of 5-8 nm to allow nanotubes make transport charges via the tunneling/hopping mechanism.

In some cases, however, the opposite results have been reported. For instance, Grossiord et al. [71] prepared isotactic polypropylene grafted maleic anhydride (iPP-g-MA)/MWCNTs nanocomposites by mixing an aqueous suspension of exfoliated carbon nanotubes (CNTs) and a polymer latex. They reported a RPT smaller than the electrical one. Authors suggested that this phenomenon is related to the intrinsic electrical conductivity of iPP-g-MA, which promotes electron transfer over inter-CNT distances much larger than in insulating polymer matrices. In our systems, the electrical conductivity of PMMA and PEO matrices are in orders of  $10^{-14}$  and  $10^{-12}$  S/cm, respectively. This indicates that these polymers are essentially insulated materials and therefore they are not effective in promoting electron transfer and lowering the EPT. Chapartegui et al. [75] reported similar results for epoxy pre-polymer/MWCNT dispersion. They suggested that due to lack of polymer chains in the thermoset pre-polymer, CNT-polymer interaction and

hindrance of polymer chains are eliminated and consequently the RPT occurs simply when the nanotubes touch physically. However, for occurring the EPT, physical contact is not necessary and charge transport can take place through electron hopping/tunneling.

In the present study, it is found that the RPT (2.53 wt%) is considerably higher than the EPT (0.0712 wt%). The very low EPT is directly related to the formation of conductive clusters during solvent casting process as the presence of PEO in the nanocomposite provide an opportunity for nanotubes to make conductive clusters at very low concentration. The control samples, i.e. PMMA/MWCNT nanocomposites prepared at the same condition showed completely different morphologies and remained non-conductive even at high MWCNT concentrations (Fig. S1). Also, other important factors might be solvent nature and casting temperature. The samples cast at lower temperatures and higher temperatures (Fig. S2) or the ones prepared by acetic acid, toluene, NMP, ethyl acetate and 1,2-Dichlorobenzene as the common solvent of PMMA and PEO showed undesirable morphologies (Figs. S3-S8) According to Kota et al. [70] both EPT and RPT parameters show sensitivity to selection of the solvent. For instance, dimethylformamide influences the electrical conductivity more than elastic response of the nanocomposites [70].

The anomaly difference between EPT and RPT can be also explained by rigid RPT concept proposed by Penu et al. [18]. It seems that electrical bridges are formed by formation of clusters of the nanotubes while the polymer-CNTs interaction would not be enough to affect the elastic properties of the nanocomposites. In other words, the EPT is reached through the formation of first interconnected conductive clusters to carry out charge transfer by means of tunneling/hopping process. With increasing the CNTs concentration in the blend, conductive cluster approaches together and 3 dimensionally interconnected structure of CNTs clusters is formed and subsequently the rheological percolation occurs. This fact is visualized by suggested mechanism presented in Fig. 11. Moreover, Pötschke et al. [76] have shown that RPT depends strongly on measuring temperature. Upon changing the measuring temperature from 170 °C to 280 °C, the RPT shifted from 5 wt% to 0.5 wt% which is lower than the reported EPT value (0.99 wt%). They suggested the temperature dependence RPT cannot be explained by classical solid like to liquid like transition and the existence of a combined nanotube-polymer network might be responsible for this phenomenon [76].

## ***Conclusion***

An effective method is proposed to obtain a low EPT in PMMA nanocomposites containing unmodified MWCNTs. The method involved the pre-blending of MWCNTs with PEO polymer, as a secondary miscible polymer with PMMA. The evaluation of optical, rheological and electrical properties manifested that pre-blending of MWCNTs with PEO polymer directly influences the way of MWCNTs assembling in PMMA polymer. Specific interconnected structure of secondary clusters of MWCNTs within PMMA matrix in the presence of PEO was observed. Significantly low EPT close to 0.07 wt% was found for glassy PMMA/PEO-MWCNTs nanocomposite system. This was explained by the fact that PEO polymer provides an opportunity for nanotubes to assemble conductive network at significantly lower contents.

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