

Rheological and electrical percolation thresholds of multi-walled carbon nanotube/in-situ polymerised Nylon12 nanocomposites

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Published in Micro & Nano Letters; Received on 31st January 2018; Revised on 18th June 2018; Accepted on 10th July 2018

In this work, in-situ polymerisation of laurolactam in the presence of multi-walled carbon nanotube (MWCNT) was performed toward MWCNT/Nylon12 nanocomposite. Different levels of MWCNT (0.1, 0.3, 0.7, 1.2 and 3.5 wt%) were introduced to the monomer in the presence of 2 wt% toluene diisocyanate and 1 wt% sodium caprolactam as an activator and catalyst, respectively. The test results indicated that by increasing the amount of MWCNT, the conductivity of the nanocomposite increased up to that level at which it could serve as an electrically conductive material at room temperature. The melt rheological measurements showed a transition from liquid-like to solid-like state. The rheological results obtained within the linear viscoelastic region demonstrated that the rheological percolation threshold happened at 0.1 wt% multi-walled nanotube (MWNT), whereas the electrical percolation threshold appeared at 1.2 wt% MWCNT. A homogeneous dispersion of MWCNT into the Nylon12 matrix with a high aspect ratio of MWNT was achieved at a low percolation threshold. This mainly could be attributed to the fact that a denser MWCNT network was required for electrical conductivity, while a less dense MWCNT network sufficiently impeded Nylon12 chain mobility related to the rheological percolation threshold.

1. Introduction: Although multi-walled carbon nanotubes (MWCNTs) have been reported to possess inherent modulus up to 1 TPa, only a very small fraction of their stiffness and strength is translated into the host polymeric matrix through twisting and curling of the nanotubes [1]. On the other hand, MWCNTs with good electronic properties were successfully incorporated into polymer-based composites to improve their electrical conductivity [2]. Conductivity is achieved through the formation of a percolating network of MWCNT particles in the matrix, ‘percolation threshold’ which establishes a conductive pathway throughout the matrix in which electrons can be transferred.

In recent years, polymer nanocomposites have engrossed many researchers in both industry and academia. These efforts have been led to achieving various great properties of nanocomposites in comparison with conventional ones [3–7]. Polymer nanocomposites have been obtained using different preparation methods such as melt mixing, solution mixing and in-situ polymerisation to get the intercalated or exfoliated structures in homo-polymers [8].

To maximise the effect of MWCNTs reinforcement on the properties of a polymer, they must be well dispersed in the matrix [9–12]. Strong van der Waals force between the carbon nanotubes makes the distribution of these nanofillers a challenging issue [13]. Usually, for MWCNT/polymer nanocomposites, both electrical and rheological percolation thresholds are observed. The values relating to these percolations are usually different, which indicates the different nature of the behaviour reinforced by the MWCNT. In order to maintain the mechanical, physical and rheological properties of the polymer, undoubtedly, a lower percolation threshold is desirable. Also, the economical competitiveness in the case of expensive conductive fillers such as MWCNTs is an important parameter [14].

Since the rheological behaviour of these nanocomposites differs significantly after the percolation threshold, it is essential to specify the percolation threshold [15]. Bai *et al.* [16] examined the effect of the carbon nanotubes on the rheological properties of the polymeric matrix during the laser sintering of Nylon12 polypropylene/MWNT nanocomposites were investigated by Kharchenko *et al.* [17]. It was reported that by increasing the shear rate, electrical conductivity and also the viscosity of the samples decreased considerably.

Coagulation method was used by Du *et al.* [2, 18] to prepared poly(methyl methacrylate)/single-walled nanotube nanocomposites. The dispersion of nanotubes at different length scales was analysed. The study resulted in lower rheological percolation threshold than electrical conductivity. The same results were obtained for other polymers filled with carbon nanotubes, such as polyethylene [19] polypropylene [17, 20], polyamide [21], polystyrene [22], poly(methyl methacrylate) [18] and many other polymers [23].

Giannelis *et al.* [24, 25] were the first one investigated the rheological properties of in-situ polymerised nanocomposites. According to this research, the flow behaviour of poly(ϵ -caprolactone) (PCL) and polyamide-6 (PA-6) nanocomposites changed greatly from that of the neat matrices. The morphological control of conductive networks in poly(L-lactide) (PLLA)/poly(ϵ -caprolactone)/MWCNTs nanocomposites was done by Zhang *et al.* [26–28]. Chen *et al.* [29] used graphene oxide (GO) sheets to retard the aggregation of MWCNTs in a biodegradable PCL matrix.

The percolation threshold of polyamide 12-MWCNT nanocomposite has not been studied previously, the aim of this Letter is to obtain and compare both electrical and rheological percolation thresholds. In this research, Nylon12-MWCNT nanocomposites were synthesised through in-situ polymerisation of laurolactam by introducing different levels of MWCNT (0.1, 0.3, 0.7, 1.2 and 3.5 wt%) in the presence of toluene diisocyanate (TDI) (2 wt%) and sodium caprolactam (NaCL) (1 wt%). Then, the related tests were carried out in order to calculate the rheological and electrical percolation thresholds.

2. Experimental: MWCNTs with a length and outer diameter (OD) ranging from 10–30 μm and 20–30 nm, respectively, were supplied from Nanosany Co. and used as received without any further treatment. Laurolactam was used as the monomer in this Letter which was supplied by Evonik Co., Germany. TDI, used as an activator, was obtained from Karoon Co., Iran. The catalyst, NaCL, was obtained from Karangin Co.

The process was similar to the one used for the in-situ anionic polymerisation of ϵ -caprolactam in the presence of MWCNT

[30–32]. The in-situ polymerisation process allowed using TDI and NaCL as activator and catalyst, respectively. In the first step, the monomer was dried at 80°C in a vacuum oven for 24 h. After that, a specified amount of monomer was molten on a hot plate at 190°C. MWCNT was weighed and added to '50 ml glassware' containing molten monomer at 180°C, under N₂ atmosphere. Then it was stirred with the speed of 500 rpm for 24 h, using a shaft, in order to obtain a homogeneous dispersion. The long dispersion time and high shear allowed the nanotubes to better intercalate within the polymeric chains which have been formed simultaneously. After that, the polymerisation was taken place in a Haak internal mixer with a capacity of 75 cm³. In this part, the master batch of MWCNT and lauro lactam was fed into the internal mixer and then NaCL was added to the mixer at a temperature of 200°C. TDI was then introduced to the mixture. After about 2 min the polymerisation was completed. At the end of the polymerisation, the polymer was washed with toluene as solvent at 120°C and vacuum dried at 80°C for 24 h in order to remove the residual monomer.

2.1. Rheological properties: Frequency sweep mode was conducted on a RADII instrument at 230°C to investigate the melt rheology in the linear viscoelastic region. The tests were performed in the frequency range of 0.01–600 rad/s. Sample discs with a diameter of 25 mm and thickness of 2 mm were prepared by hot pressing at 220°C. To maintain a linear response, strain amplitude of 1% was used to obtain reasonable signal intensities at elevated temperature or low frequency.

2.2. Electrical measurements: The electrical measurements were carried out at room temperature with a Keithley 610C solid state electrometer on the composite. This instrument is used for the conductivities of <10⁻⁶ S/cm. BK PRECISION 5491A Multimeter was used for higher conductivities. Samples were prepared under the same conditions as those for the parallel plate rheological measurements.

2.3. Morphological study: Morphological analysis was performed by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods. The SEM micrographs of the gold-coated fractured surfaces (broken in the liquid nitrogen) of the MWCNT/Nylon12 nanocomposite were analysed using (TESCAN, VEGAII, XMU, Czech Republic) operating at an accelerating voltage of 20 kV. The samples for TEM prepared using a Leica Ultra microtome UC7 at -80°C to obtain thin cuts. The samples were characterised with Zeiss Libra 120 microscope (Zeiss, Germany) operating at an accelerating voltage of 300 kV.

3. Result and discussion

3.1. Characterisation of the grafted MWCNT after polymerisation: In order to investigate the grafting of nanotubes, first the polymeric matrix of the synthesised samples was dissolved in the mixture of dichloromethane-formic acid with the volume fraction of 1/1, then the nanotubes were extracted from the obtained solution by centrifuging the solution and drying the nanotubes at 100°C in an oven for 24 h, finally FTIR and TGA tests were done. According to Fig. 1, the related peak to amide groups was appeared on nanotubes after polymerisation also the degradation peak for Nylon12 was clearly appeared at about 460°C in the TGA diagram of grafted MWCNT, which proved the grafting of nanotubes by polymeric chains (Fig. 2). Also, TEM analysis for grafted and pure MWCNT is shown in Fig. 3. It is clear that the OD of the MWCNTs has been increased from about 20 to about 66 nm. This figure confirms again the existence of polymeric chains on the MWCNT surface.

3.2. Effect of MWCNT loading on storage and loss moduli: Higher *G'* values at lower frequencies are related to the more elastic

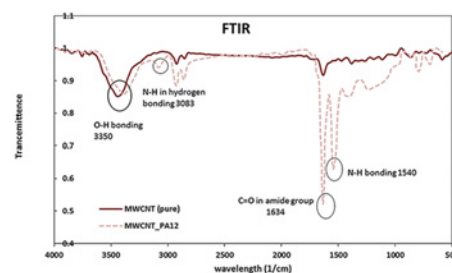


Fig. 1 FTIR results of grafted and pure MWCNT, after and before polymerisation

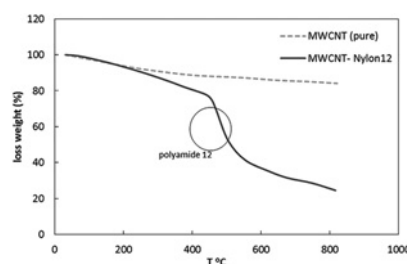


Fig. 2 TGA results of grafted and pure MWCNT, after and before polymerisation

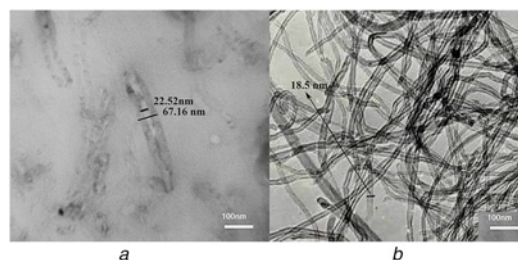


Fig. 3 TEM analysis for
a Grafted and
b Pure MWCNTs

structure which inhibits the molecular mobility by either chain length in the case of high molecular weights or by structural properties in the particle network formation in well dispersed polymeric nanocomposite systems. Similar to the increased *G'* values, this extra elasticity sometimes reveals in the appearance of a terminal zone in the low frequency region where *G'* is approximately frequency independent to a solid like behaviour. The effect of MWCNT wt% on the storage and loss modulus for synthesised Nylon12-MWCNT nanocomposite samples are shown in Figs. 4 and 5, respectively.

The rheological behaviour of Nylon12 is sensitive to the MWCNT loading at lower frequencies. *G'* gradually increased with MWCNT loading of nanotubes the storage modulus increased tenfold in comparison with the pure Nylon12. Moreover, increasing MWCNT loading in Nylon12 reduced the frequency dependency. The different rheological behaviour of the polymers which is manifested by introducing the MWCNT is related to the better interaction of the Nylon12 chains with the nanotubes according to the polar nature of Nylon12 chains and the presence of acidic components on the MWCNT surface. This interaction makes the nanotubes to be dispersed better [14]. The Nylon12-MWCNT nanocomposite showed an increase in *G'* and *G''* in comparison with the pure Nylon12 sample. With the increase in MWCNT loading *G'* and *G''* were also increased slightly, however, this was minimal and not to the extent of the increase of the PA12 MWCNT 0.1 to Nylon12. It was observed that the effect of MWCNT on the matrix rheology was still noticeable even although in the very low MWCNT loadings. The increasing in *G'* means a

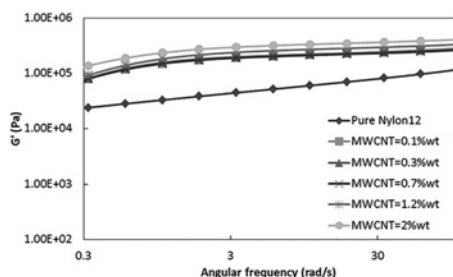


Fig. 4 Effect of MWCNT wt% on the storage modulus of the synthesised Nylon12-MWCNT nanocomposites

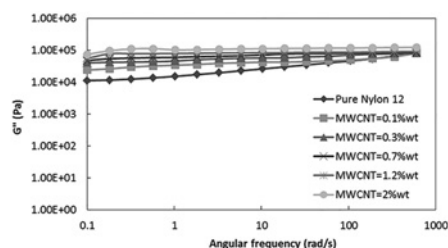


Fig. 5 Effect of MWCNT wt% on the loss modulus of the synthesised Nylon12-MWCNT nanocomposites

more elastic structure which indicates the restriction of polymer chain motion due to the MWCNT nanofillers. It is known that for linear mono dispersed polymer melts where polymer chains are fully relaxed there is an approximate power law relation of $G' \sim \omega^2$ and $G'' \sim \omega$ [33]. When the frequency is low there is enough time for the molecular relaxation process which makes the measurement of G' and G'' more sensitive. Table 1 shows the slope of G' and G'' in the low frequency region for Nylon12 and Nylon12/MWCNT nanocomposites.

The slopes of the G' and G'' curves for the Nylon12 were smaller than 2 and 1, respectively, which might be affected by the polydispersity of the polymer chain lengths [25]. Compared to Nylon12, The slopes of the G' and G'' curves of the Nylon12-MWCNT nanocomposite were lower, which could be explained by the polymer-nanotube and nanotube-nanotube interactions in the matrix. At lower frequencies, the interaction between MWCNTs and polymeric matrix determines the dynamic modulus of the nanocomposite. While at higher frequencies, due to insufficient time for detecting the behaviour of nanoparticles within the matrix, the polymeric chains interaction determines the dynamic modulus behaviour. Referring to Figs. 4 and 5, it is seen that by increasing the MWCNT content, both the storage and loss moduli increase further at lower frequencies. By increasing the amount of MWCNT, the interaction between the nanoparticles and polymer molecules increases as well. In the molten pure Nylon12, the polymer chains show terminal behaviour. By increasing the MWCNT content, the terminal behaviour will be omitted gradually, and therefore the dependency of G' and G'' to the frequency will be weakened. This non-terminal behaviour not only limits the

Table 1 Slopes of the G' and G'' curves in the low-frequency region for Nylon12-MWCNT nanocomposites

MWCNT	Slope	
	G'	G''
0	0.93	1.01
0.1	0.92	0.97
0.3	0.86	0.64
0.7	0.80	0.54
1.2	0.76	0.53
2	0.65	0.41

relaxation of polymer chains but also affects the chain dynamics or the local motion of the polymer chains in nanocomposites.

3.3. Effect of MWCNT loading on the complex viscosity: The viscosities (η) of the Nylon12 and Nylon12-MWCNT nanocomposites as a function of frequency at 230°C are shown in Fig. 6. It can be seen that, with the increase in frequency, the viscosities of all the samples decrease, showing shear thinning behaviour. This can be explained as the greater the shear rate, the more quickly two molecules move relative to each other, which leads to reduced chain entanglement density [34]. As a result, fewer polymer chains remain in the entanglement state for a sufficiently long time, which causes the drop in viscosity. For the Nylon12-MWCNT nanocomposite, the shear thinning effect was as obvious as Nylon12, which indicated good dispersion of the MWCNTs, as dispersed MWCNTs aligned with the flow direction and caused the viscosity to decrease. Compared to Nylon12, the viscosity of nanocomposites was raised significantly, and this effect was enlarged with an increase in MWCNT loading. Increased viscosity for Nylon12-MWCNT is a common phenomenon for filler reinforced polymers, which can be explained by the interaction between the MWCNTs and Nylon12 hindering the movement of the chains [16].

3.4. Effect of MWCNT loading on the damping factor ($\tan\delta$): Fig. 7 shows the changes of $\tan\delta$ with the frequency for the nanocomposites. As it is clear from this figure, the damping factor is increased specially at low frequencies by increasing the MWCNT content, and the curve is flattening. This behaviour is due to the strong interaction between Nylon12 and MWCNTs. By increasing the MWCNT content, the relaxation movement of the Nylon12 polymer chains is limited. At low frequencies, the pure polymer has a liquid like a behaviour ($G'' \gg G'$), and therefore, $\tan\delta$ is greater. At higher frequencies, due to shorter relaxation times, a solid like behaviour is expected while the damping factor decreases. By introducing MWCNT, the elastic modulus increases, and the behaviour of $\tan\delta$ is similar to its behaviour at higher frequencies.

3.5. Rheological percolation threshold of the synthesised Nylon12-MWCNT nanocomposites: By increasing the MWCNT

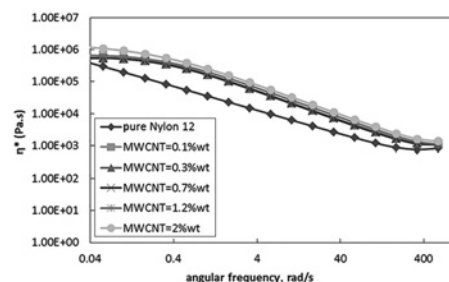


Fig. 6 Effect of MWCNT wt% on the complex viscosity of the synthesised Nylon12-MWCNT nanocomposites

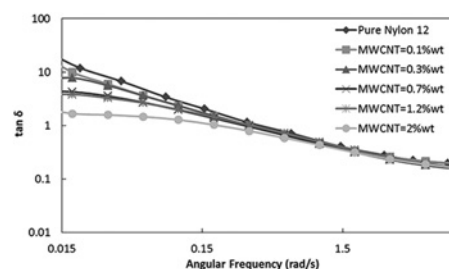


Fig. 7 Changes of $\tan \delta$ with the frequency for synthesised Nylon12-MWCNT nanocomposites

content, both the storage and loss moduli increase, particularly at lower frequencies. At 230°C and at lower frequencies, the polymer chains of Nylon12 are completely relaxed and show a regular thermal behaviour. However, by increasing the MWCNT content, this terminal behaviour is disappeared and the frequency dependence of both G' and G'' is weakened. Therefore, the MWCNTs impede the relaxation process. At low frequencies, when the MWCNTs content increases, G' is approximately independent of frequency, which is an affirmation of the viscoelastic transition from the solid like to the liquid like behaviour [35]. The flat region in the G' curve indicates that a 3D-network of MWCNT is formed in the whole of the sample. As shown in Fig. 4, by increasing the MWCNT percentage, this flat region shifts towards lower frequencies, indicating a stronger network structure. Fig. 8 shows the variation of storage and loss modulus for the synthesised MWCNT-containing nanocomposites at three frequencies. As is clear from this figure, the storage modulus sharply increases in the range of 0–0.1 wt% of MWCNT, indicating a sudden change in the material structure. This sudden change in G' and G'' means that the nanocomposite reaches its rheological percolation threshold, in which the MWCNT hinders the polymer chain mobility. Various equations were suggested for the relationship between G' and the MWCNT concentration which are listed in Table 2. As the square regression coefficients of suggested models show it can be concluded that the exponential equation is the best. In Table 2, φ and φ_c represent, respectively, the MWCNT concentration and the concentration of MWCNT at percolation threshold. Furthermore, a , b and c are the constants of the models.

Also, the power-law model for rheological percolation threshold of the synthesised Nylon12-MWCNT nanocomposites is shown in Fig. 9.

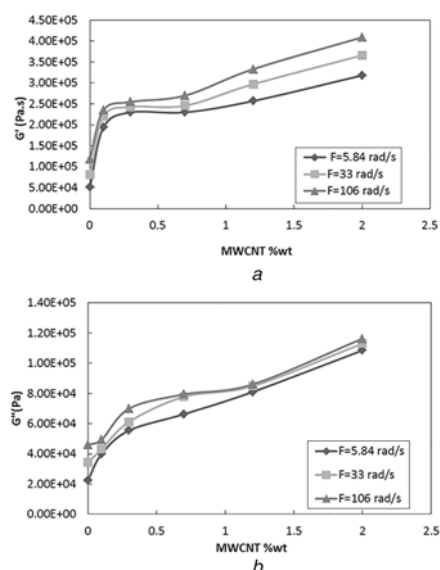


Fig. 8 Effect of MWCNT on storage and loss modulus changes at various frequencies

Table 2 Suggested models for the relationship between MWCNT wt% and G' in synthesised Nylon12-MWCNT nanocomposites

$G' = a \cdot \exp(b(\phi - \phi_c)) + c \cdot \exp(d(\phi - \phi_c))$		$G' = a \cdot \exp(b(\phi - \phi_c))$		$G' = a \cdot (\phi - \phi_c) + b$		$G' = a(\phi - \phi_c)^2 + b(\phi - \phi_c) + c$	
a	1.11×10^{-7}	a	8.81×10^{-6}	a	-7.50×10^{-4}	A	7.64×10^{-2}
b	-6.85×10^2	b	-9.31×10	b	9.93×10^{-6}	B	-1.23×10^{-3}
c	4.73×10^{-6}	R^2	8.66×10^{-1}	R^2	5.27×10^{-1}	C	6.58×10^{-6}
d	-3.19×10					R^2	9.70×10^{-1}
R^2	1.00						

3.6. Electrical percolation threshold of the synthesised Nylon12-MWCNT nanocomposites: The electrical volume resistivity versus the MWCNT content curve of the in-situ synthesised Nylon12 nanocomposites is illustrated in Fig. 10. By increasing the amount of MWCNT the resistivity decreased slightly until it reached its percolation ratio and a sudden decrease in the resistivity occurred. In this work, the percolation ratio is about 1.2 wt% MWCNT, which is less than the ratio of 1.7 wt% reported in the literature [36]. Electrical conductivity could be expressed as the following equation:

$$\sigma \sim (\varphi - \varphi_{ec})^{\beta_{ec}} \quad (1)$$

According to this equation, the power-law correlation for the electrical conductivity is shown in Fig. 11.

3.7. Comparison of the electrical and rheological percolation thresholds of the synthesised Nylon12-MWCNT nanocomposites: The rheological percolation threshold is usually lower than the electrical percolation threshold. The difference between the percolation thresholds is attributed to the different filler-filler distances required to achieve the electrical or rheological percolation. Actually, the rheological response of nanocomposites will be limited through the organised network by the polymer chains and the polymer-nanoparticle interactions. However, for the electrical percolation threshold, enough closeness of nanotubes is needed to form the conductive networks. Different electrical and rheological percolation thresholds of the polymer-MWCNT systems indicates the different nature of enhanced properties through MWCNTs [37, 38]. If the Newtonian region is disappeared, a transition from the liquid-like to solid-like behaviour is occurred, which is considered as the rheological threshold [39, 40]. The percolation threshold could be distinguished through the G' versus frequency diagram. In this Letter, the in-situ polymerisation technique was applied in order to synthesise the Nylon12-MWCNT nanocomposites, and the MWCNTs were dispersed inside the monomer, through the mechanical mixing for 24 h, before the polymerisation. This process leads to a relatively better dispersion of MWCNT in the polymer matrix, comparing to other methods.

Table 3 shows a comparison between the electrical and rheological percolation thresholds, reported in the literature and in this Letter. According to Table 3, test results show that by using in-situ polymerisation method, electrical and rheological percolation thresholds happened at a lower percent of MWCNT than the previous studies for nylons [14, 41–44]. This difference could be due to the polymer crosslinking which may be occurred during the previous works. In this mode, MWCNT addition up to high concentrations cannot lead to the significant increase in electrical conductivity. Therefore, there is a fewer charge carrier, and the probability of charge trapping enhances due to cross linking. According to this phenomenon, the connection of nanotubes together and tunnelling the electrons is difficult to achieve.

3.8. SEM and TEM results of the synthesised Nylon12-MWCNT nanocomposites: According to the fact that 0.1 and 1.2 wt% are rheological and electrical percolation thresholds, respectively, the samples containing 0.1 and 1.2 wt% MWCNT were chosen as

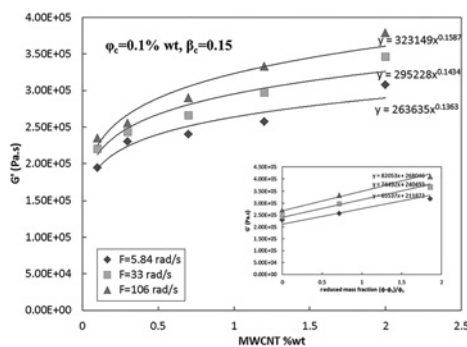


Fig. 9 Power-law correlation for rheological percolation threshold of the synthesised Nylon12-MWCNT nanocomposites

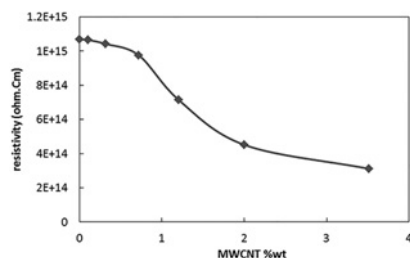


Fig. 10 Electrical volume resistivity versus MWCNT content for the Nylon12-nanocomposites synthesised through in-situ polymerisation

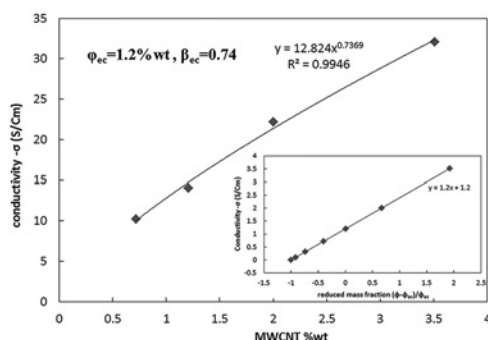


Fig. 11 Power-law correlation for electrical percolation threshold of the synthesised Nylon12-MWCNT nanocomposites

specific cases in order to be investigated morphologically. The nano-dispersion of MWCNTs observed by TEM (Fig. 12) shows a good dispersion for both samples. It is clear that the distribution within the matrix is very homogeneous. At 1.2 wt% MWCNT the carbon nanotubes formed a conductive network, while for 0.1 wt% MWCNT the formation of MWCNT network is not noticeable. The polymer chains coated the MWCNT network and this fact is clear from the TEM results. Fig. 13 shows the SEM micrographs of the fractured surfaces of the MWCNT and Nylon12/(0.1 and 1.2 wt%) MWCNT nanocomposites, respectively. The morphology of pure Nylon12 and its nanocomposites are shown in Figs. 13b–d. The SEM micrograph of pure Nylon12 was smooth and contained some common fracture patterns on the surfaces. It is apparent from Figs. 13c and d that the MWCNTs conversely showed the fantastic and homogeneous dispersion throughout the matrix as can be seen from the white parts. This dispersion of MWCNTs in the MWNT/Nylon12 nanocomposite is due to the in-situ polymerisation of the lauro lactam in the presence of MWCNT. It should be mentioned that the length of carbon nanotubes was remained constant after polymerisation and although an acceptable dispersion was achieved. It can be clearly seen that all the nanotubes are tightly embedded into the matrix. This proves the existence of strong interfacial bonding between the Nylon12-MWCNTs in the composites, resulting in high load transfer capacity and no slipping of the nanotubes

Table 3 Electrical and rheological thresholds for different MWCNT/polymer nanocomposites

Nanocomposite	$P_{c,rheo}$	$P_{c,elec}$	Ref
MWCNT/PC	0.38–0.5	0.5–0.75	[41]
MWCNT/ABS	2–4	2–4	[43]
MWCNT/PCL	0.5–0.7	0.7	[44]
MWCNT/PE	7.5	7.5	[42]
MWCNT/Nylon6/ABS	2–4	2–4	[43]
CNT/Nylon12	1.4	1.4	[14]
MWCNT/Nylon12	0.1	1.2	present work

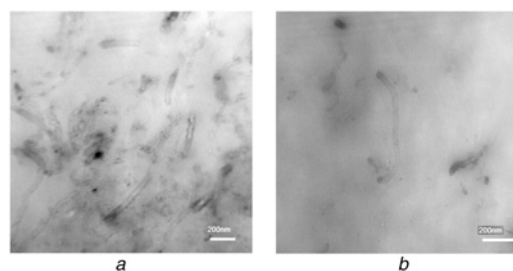


Fig. 12 TEM image of synthesised Nylon12-nanocomposite containing
a 1.2 wt% MWCNT
b 0.1 wt% MWCNT

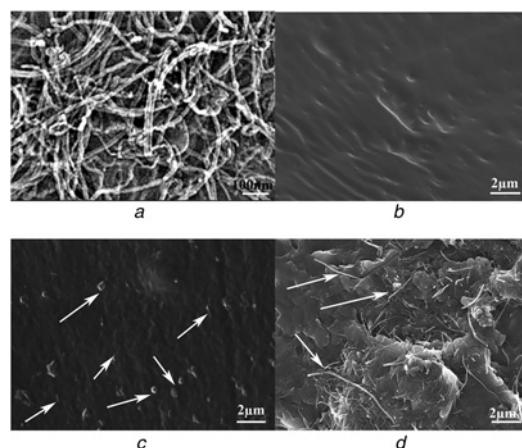


Fig. 13 SEM image of
a Pure MWCNT
b Pure Nylon12
c Nanocomposites containing 0.1 wt% and
d 1 wt% MWCNT

from the matrix during tension. It is also apparent that MWCNTs formed outstanding and strong networks within the matrix.

4. Conclusion: Generally, electrical and rheological measurements allow to determine and compare different types of percolation thresholds and them. This work has investigated the percolation thresholds of MWCNT/Nylon12 nanocomposites prepared by an in-situ polymerisation process by keeping constant the L/D ratio of nanotubes. The values of rheological and electrical percolation thresholds were obtained equal to 0.1 and 1.2 wt%, respectively. From these results, it was concluded that the rheological percolation threshold was less than the electrical percolation threshold and also they were both lower than the values reported by the literature.

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