

Soft Matter, Polymers, Composites

MS.1.P011

High performance carbon nanotube reinforced crosslinked high density polyethylene

E. Roumeli¹, E. Pavlidou¹, G. Vourlias¹, D. Bikiaris², K. Chrissafis¹

¹Aristotle University of Thessaloniki, Physics, Thessaloniki, Greece

²Aristotle University of Thessaloniki, Chemistry, Thessaloniki, Greece

hrisafis@physics.auth.gr

Keywords: carbon nanotubes, polyethylene, nanocomposite

Carbon nanotubes (CNTs) have exceptional mechanical, thermal and electric transport properties which make them ideal candidates as reinforcing and conducting fillers of composites for a wide range of applications [1, 2]. The outstanding strength and stiffness of CNTs are some of the most appealing properties that CNT-based nanocomposites are intending to achieve and an effective load transfer between the matrix and the filler may be the key to prepare composites with such superior properties [3, 4]. Crosslinked high density polyethylene (PEX) is a chemically or physically modified polyethylene that extends its use by raising its operating limit at much high temperatures and improving its mechanical properties due to the formation of a 3D structure [5, 6]. Since PEX is currently produced in large quantities for various types of applications, the further enhancement of its properties is of high interest. Therefore, the aim of the present work was to reinforce crosslinked high density polyethylene with small quantities of multi-walled carbon nanotubes (MWCNTs) in order to prepare nanocomposites of superior mechanical performance and examine the load transfer between the matrix and the fillers in tension.

PEX was prepared using the silane two-step process in which a high density polyethylene grafted with vinyl trimethoxysilane is mixed with a catalyst masterbatch containing the same polymer along with dibutyltin dilaurate (DBTDL), internal lubricants, stabilizers and various antioxidants and then the product is exposed to moisture in order for the final crosslinking to occur. Purified multi-walled carbon nanotubes were purchased from Chengdu Organic Chemicals Co. Ltd. The inner and outer diameters of MWCNTs were less than 2-5 nm and 8 nm respectively and they have 2.1 g/cm³ density. Mixtures of PEX and 0.5, 1, 3 and 5 wt% MWCNTs were solid-state mixed for 6 hours in a Retsch centrifugal ball mill (model S 100) and then, they were melt-mixed for 10 min at 200°C in a Haake-Buchler Rheomixer (model 600). Following that, the prepared materials were hot pressed and then rapidly cooled by immersion in water at 25°C. For the examination of mechanical properties an Instron 3344 dynamometer was used, in accordance with ASTM D638 using a cross-head speed of 50 mm/min. The dispersion of MWCNTs and the morphology of the failure surfaces of all nanocomposites after tensile testing were examined using scanning transmission electron microscopy (SEM, TEM). The SEM system was a JEOL JSM 840A-Oxford ISIS 300 SEM with accelerating voltage 20 kV, probe current 45 nA and counting time 60s and the TEM system was a JEOL 120 CX microscope operating at 120 kV.

The dispersion of MWCNTs in the polymer matrix was studied with TEM and two typical images of the nanocomposite with 1 and 5 wt% MWCNTs are presented in Figures 1-2. While a fine dispersion can be revealed in the case of low filler content, for the high filler loading the formation of some nanotube bundles with size up to 200 nm cannot be avoided. However, the aggregated tubes seem to be well dispersed in the polymer matrix. The results of the mechanical properties tests of PEX and its nanocomposites reveal an obvious enhancement of all the studied properties. The addition of 0.5 % MWCNTs leads to a 100 MPa enhancement of Young's modulus while a further increase of MWCNTs content leads to elastic modulus values higher than neat PEX but somewhat lower than the nanocomposite with 0.5 % MWCNTs. However, the nanocomposite with 5% MWCNTs had the highest elastic modulus (985 MPa) which is 310 MPa higher than the neat polymer's. The stress at yield values seem to follow the same trend; in the case of 0.5% MWCNTs the stress at yield is 3.4 MPa higher than that of neat PEX. For the nanocomposites with 1-3% MWCNTs, the stress at yield remains almost the same as for the nanocomposite with 0.5% MWCNTs, while for the nanocomposite with 5% MWCNTs the stress at yield is much higher (9.8 MPa higher than in neat PEX). It seems that the small amounts of MWCNTs (up to 1 wt %) lead to a notable increase of 6.9 MPa for the stress at break while a higher MWCNTs concentration causes a reduction of the ultimate stress, which reaches the same level as neat PEX. The elongation at break of the nanocomposites presents a similar trend to the ultimate stress values. Up to 1% MWCNTs the elongation at break values are higher than in neat PEX,

while for higher filler content they are drastically reduced. Therefore, it seems that two competitive mechanisms act upon the incorporation of MWCNTs in PEX: a tendency to enhance the mechanical properties of PEX by load transfer and a drive to form aggregates or bundles that reduces the positive effect on these properties.

The characteristic fibrillar structure of PEX at failure was observed in all its nanocomposites. Upon failure, most of the MWCNTs were broken while a few were pulled out of the matrix as shown in Figures 3-4. Many of the tubes and bundles have fallen back onto the broken surfaces as a loosen network and they seem to be interconnecting the polymer lumps. The nanotubes and their bundles bridging across the cracks suggest that stress release and absorption of the fracture energy is possible and therefore the fillers may result in a toughness improvement. Also, some of the MWCNTs become loosened or curved, probably due to relaxation after fracture or uneven crack separation [4,7]. This interesting and typical breakage observation of the MWCNTs upon tensile stretching indicates a strong interfacial adhesion between MWCNTs and PEX matrix and a sufficient load transfer from the polymer to nanotubes [3, 4].

In conclusion, from the examination of the mechanical properties and observations of the failure surfaces of novel nanocomposites of crosslinked high density polyethylene reinforced with MWCNTs, a significant improvement of mechanical properties was found and it was suggested that two competitive mechanisms seem to govern the incorporation of MWCNTs in PEX: a tendency to enhance the mechanical properties of PEX by load transfer and a drive to form bundles that reduce the positive effect on these properties. Evidence of both these competitive mechanisms was found by SEM observations of the failure surfaces and TEM images of the dispersion of MWCNTs.

1. R.S. Ruoff, D.C. Lorents, Carbon, 33 (1995) 925-930.
2. J.N. Coleman, U. Khan, W.J. Blau, Y.K. Gun'ko, Carbon, 44 (2006) 1624-1652.
3. L.S. Schadler, S.C. Giannaris, P.M. Ajayan, Applied Physics Letters, 73 (1998) 3842-3844.
4. P.M. Ajayan, L.S. Schadler, C. Giannaris, A. Rubio, Advanced Materials, 12 (2000) 750-753.
5. S. Venkatraman, L. Kleiner, Advances in Polymer Technology, 9 (1989) 265-270.
6. J.E. Ritums, A. Mattozzi, U.W. Gedde, M.S. Hedenqvist, G. Bergman, M. Palmlöf, Journal of Polymer Science Part B: Polymer Physics, 44 (2006) 641-648.
7. V.G. Hadjiev, M.N. Iliev, S. Arepalli, P. Nikolaev, B.S. Files, Applied Physics Letters, 78 (2001) 3193-3195.

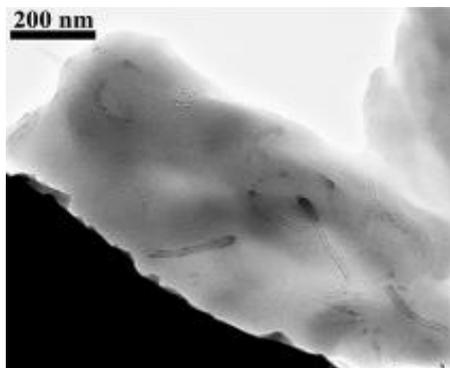


Figure 1. TEM image of PEX/1% MWCNTs

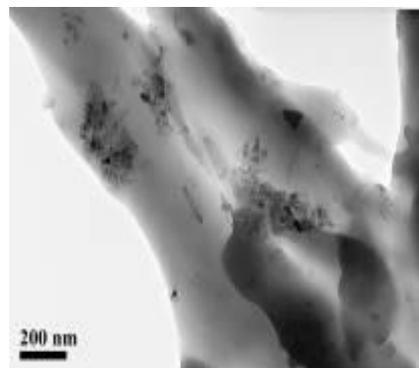


Figure 2. TEM image of PEX/5% MWCNTs

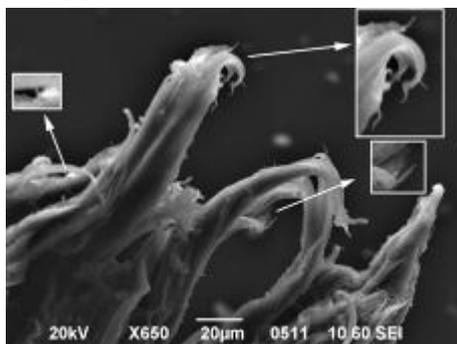


Figure 3. SEM image of the fracture surface after tensile testing of PEX nanocomposite containing 5% MWCNTs.



Figure 4. SEM image of the fracture surface after tensile testing of PEX nanocomposite containing 3% MWCNTs.