A comparative study on long and short carbon nanotubes-incorporated Polydimethylsiloxane nanocomposites

Lei Hua [1, a *]

[1]Environmental Engineering, Tongji Zhejiang College, Jia Xing, Zhejiang, 314051, China;
Department of Civil Engineering, Tongji Zhejiang College, Jia Xing, Zhejiang, 314051, China

[*] hualei@tijz.edu.cn

Abstract. In order to analyze the different aspect ratio carbon nanotubes on the mechanical, electrical and thermal properties of the Polydimethylsiloxane (PDMS), long multiwalled carbon Nanotubes (LC), short multiwalled carbon nanotubes (SC) were incorporated into PDMS by solution blending method, respectively. Filling 2.0 wt.% of LC, the volume resistance (Rv) and surface resistance (Rs) were dereased 2, 3 orders of magnitude as compared with LC-PDMS-01. When the LC was increased to 3 wt.%, Rs and Rv dereased beyond the lower measurement range.The modulus of the SC/PDMS and LC/PDMS composites gradually increased with the filler content increased, while the elongation at break of the SC/PDMS and LC/PDMS composites decreased with the filler content increased. The LC-PDMS-02 also shows the excellent mechanical properties with the higher modulus of 2.84 MPa and elongation at break of 157.85% than those of SC-PDMS-02. Both LC and SC could enhance the thermal stability of PDMS. Furthermore, in the range of 530ºC to 600ºC, the thermal stability of PDMS with LC is more stable than that of PDMS with SC. In this case, LC is more advantageous than SC due to its greater aspect ratio. Thus, LC with high aspect ratio has the potential of being reinforcing filler than SC.

Keywords: Long, short multiwalled carbon Nanotubes ;PDMS; aspect ratio; conductive properties; mechanical properties；thermal properties.

1. Introduction

Nowadays, it is a major challenge for researchers to provide high-efficiently stretchable and flexible electrical devices. Stretchable and flexible electrical devices have gained a lot of interest in the fields of wearable devices[1,2]. Improving the electrical conductivity and mechanical properties of elastomer composites are crucial in a wide range of applications such as strain sensors for wearable devices and electronic skins[3].Considering the requirements of stretchability and flexibility of the electrical devices, poly(dimethylsiloxane) (PDMS) emerges as a prime elastomeric choice due to its excellent stretchability, superior flexibility, low modulus and good biocompatibility[4,5]. Recently, PDMS based composite sensors have attracted increasing scientific and technological interests[6]. To fabricate PDMS based flexible sensors with high conductivity and mechanical peoperties, nano fillers have been incorporated into PDMS, such as graphene[5], gold nanoparticles[7], silver nanowire [8]carbon nanotubes (CNTs)[9]and etc.

Among these fillers, CNTs has attracted significant research interest in the field of sensors owing to their nano-scale texture, large surface area, higher electrical conductivity (10^4~10^6 S/cm), chemical stability and low-cost[10,11]. CNTs is an important and proper filler for preparing PDMS based composite sensors with high prerformance[5],[12]. The enhanced electromechanical characteristics of CNTs allow researchers to produce high-quality electrical devices for various applications[13,14]. For example, CNTs/PDMS material was fabricated into a stretchable strain sensor for measuring blood pressure and wrist pulse[15,16]. The electrical devices were formed using CNTs and PDMS by optimizing the 4.0 wt.% of the CNTs[17,18]. At the filler content of 10.0 wt.%, the electrical conductivity of the CNTs/PDMS increased to 4.51×10^{-3}S/cm[5].

Up to now, no research focuses on the effect of aspect ratio of CNTs on the electrical conductivity, mechanical and thermal properties of PDMS composites. Here we will emphasize comparing the effect of long、 short CNTs (LC、SC） with different aspect ratio (diameter/length) on the electrical conductivity, mechanical and thermal properties of PDMS composites.

2. Experimental

2.1 Materials

PDMS (Poly Dimethyl Siloxane, $(C_2H_6OSi)n$), curing agent Sylgard 184 (silicone-based elastomer) was purchased from Shanghai Guiyou New Material Technology Co., Ltd. Long and short carboxylic multi-wall carbon nanotubes (LC and SC) containing 2.0 wt.% COOH were supplied by Jiang Su XFNANO Co., Ltd.with dimensions of 10~20 nm in outer diameter and 10~30μm and 0.5~2μm in length, respectively. Dichloromethane(CH_2Cl_2) and anhydrous ethanol (C_2H_6O≥98%) were purchased from Shanghai Aladdin Bio-chem Technology Co. Ltd.

2.2 Preparation PDMS based composites

The CNTs/PDMS composites were prepared using the following procedure. First, 20 g of PDMS was added to 50 ml of CH_2Cl_2 followed by magnetic stirring for 30 min to obtain PDMS/CH_2Cl_2 Solution A. Next, CNTs (SC,or LC or SC blending with LC) were added to 50 ml of CH_2Cl_2. The CNTs dispersion was subjected to ultrasonication for 30 min to obtain a uniform CNTs/CH_2Cl_2 Solution B. After that, Solution A was blended with Solution B to obtain the mixture C and stirred for 30 min until complete dissolution. After 48 h for removing the solvent, the curing agent (2 g of Sylgard 184 , the mass ratio of base polymer to curing agent is 10:1) was then added into the mixture C. The resulting dispersion was transferred into a hydrothermal reactor. CNTs/PDMS composites were crosslinked at 120 ◦C for 1 h and cooled down to the room temperature for test. Sample No. and the weight fraction of LC and SC were shown in Table 1.

Table 1 sample No., weight fraction of LC and SC within PDMS Composites

Sample No.	PDMS /g	SC /g	SC /wt.%	LC /g	LC /wt.%
PDMS	20	/	/	/	/
LC-PDMS-01	20	/	/	0.1	0.5
LC-PDMS-02	20	/	/	0.2	1
LC-PDMS-03	20	/	/	0.3	1.5
LC-PDMS-04	20	/	/	0.4	2
SC-PDMS-01	20	0.1	0.5	/	/
SC-PDMS-02	20	0.2	1	/	/
SC-PDMS-03	20	0.3	1.5	/	/
SC-PDMS-04	20	0.4	2	/	/
S-1-L-1-PDMS	20	0.2	1	0.2	1
S-1.5-L-0.5-PDMS	20	0.3	1.5	0.1	0.5
S-0.5-L-1.5-PDMS	20	0.1	0.5	0.3	1.5

2.3 Characterization

Scanning electron microscopy (SEM, JSM-IT500LA) and Transmission Electron Microscope(TEM, FEI Talos F200X) were utilized to characterize the morphology of the SC and LC. Thermogravimetric analysis (TGA, TA Instrument TGA Q500) was conducted in the temperature range of 30~1000 ◦C at a heating rate of 10 ◦C min^{-1} under an N_2 atmosphere. All Electrical studies, measurements, and characterization were performed using high-resistance-meter (FT-304). The mechanical properties of CNTs/PDMS composites were measured by UTM6503 instrument. All the data obtained is plotted and analyzed using Origin Pro software.

3. Results and discussion

3.1 Morphology of LC and SC

The morphological structure of LC and SC were shown in Fig.1. It is clear that the CNTs were tubular in structure and uniformed in distribution. The aspect ratio of the LC was much higher than that of SC.

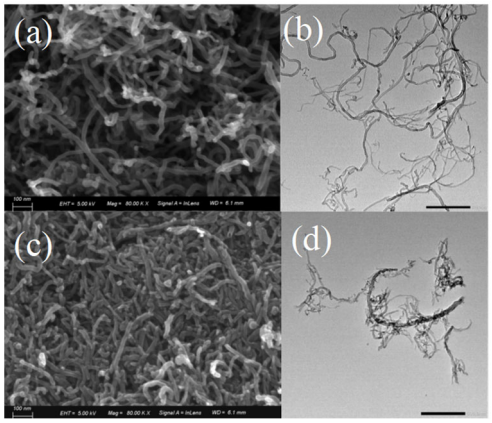

Fig.1 Morphology of LC (a in SEM , b in TEM)and SC(c in SEM, d in TEM)

3.2 Electrically conductive properties

Electrically conductive behaviors of CNTs/PDMS composites were studied for a better understanding of the filler dimensionality distinction on the electrical performance. Table 2 depicts the conductivity as a function of the filler concentration of CNTs/PDMS composites, respectively.The conductivity shows a drastic increase when the filler loading increases to a certain concentration range. For example, when incorporating 2 wt.% of LC into PDMS matrix, the Rs and Rv dereased dramatically to 4.31×10^{1}, 2.48×10^{2}MΩ·mm, respectively, 2,3 orders of magnitude as compared with LC-PDMS-01. When the LC was increased to 3 wt.%, Rs and Rv dereased beyond the lower measurement range. On the other hand, loading 2 wt.% of SC into PDMS matrix, the Rs and Rv dereased to 2.03×10^{3}, 3.24×10^{5}MΩ·mm, respectively. With increaing the weight content of SC in the PDMS, the Rs and Rv showed a linear downward trend. It was observed that a combination of 1.5wt.% LC and 0.5wt.% SC within the PDMS sample (S-0.5-L-1.5-PDMS) showed excellently electrical performance than those of S-1.5-L-0.5-PDMS and S-1-L-1-PDMS. The large increment of conductivity for LC/PDMS compared to the SC/PDMS composites might be due to the different filler dimension and aspect ratio[19].

The schematic drawing in Fig. 2 explains the electrical behavior of the nanocomposite in terms of the orientation of the conductive LC, SC used in the PDMS matrix. The LC has a high surface area that consists of the l/d (length to diameter) ratio.Thus, the lower weight fraction of LC was enough for the tube-tube interaction in the composites to create a conductive path, shown in Fig.2(a). However, the higher loading of SC particles are required to construct the conductive pathway. At the lower loading 2 wt.% SC, the SC particles did not result in electron tunneling due to the lower aspect ratio of the fillers, shown in Fig. 2 (b). The better electrical conductivity of S-0.5-L-1.5-PDMS （SC/LC=1:3）is that the LC could construct the conductive path way and the SC could fill the small gaps between LC to create more conductive pathway, shown in Fig.2(c). However, in the case of S-1.5-L-1-PDMS（SC/LC=3:1), SC clusters were not in contact with each other and the electron tunneling effect could not take place. Filling the higher aspect ratio LC could help to form the conductive an available path way, shown in Fig.2(d).

3.3 Mechanical properties

Tensile tests were conducted to find out the mechanical properties of CNTs/PDMS composites according to the aspect ratio and content of CNTs. Table 2 also shows the mechanical properties for

each composite. It was obtained Young's modulus (Elastic modulus) using Hooke's law[20].Young's modulus increased as the filler content and aspect ratio increased. The modulus of the SC/PDMS and LC/PDMS composites gradually increased with the filler content increased, while the elongation at break of the SC/PDMS and LC/PDMS composites decreased with the filler content increased. In this case, LC is more advantageous than SC due to its greater aspect ratio. The longer length of LC also makes it more advantageous for load transfer compared to SC[5].This finding means that composites are more mechanically reinforced at higher aspect ratio and CNTs tend to bridge the polymer cracks[21]. In the case of the composite with 3 wt.% of LC and 4 wt.% of SC, respectively, the reduction of elastic modulus could be observed obviously. The reason might be that the CNTs agglomeration phenomenon significantly reduced the elastic modulus of composites[21].

Table 2 Electrically conductive propertie and mechanical properties of PDMS based Composites

Sample No.	Surface Resistivity (Rs)/ MΩ·mm	Volume resistivity (Rv)/ MΩ·mm	Modulus/ MPa	Elongantion at Break /%
PDMS	+	+	2.15	208.06
LC-PDMS-01	9.5×103	8.27×105	2.58	170.67
LC-PDMS-02	4.31×101	2.48×102	2.84	157.85
LC-PDMS-03	1.51	-	2.36	145.74
LC-PDMS-04	-	-	1.81	116.52
SC-PDMS-01	1.65×104	1.36×106	2.33	185.97
SC-PDMS-02	2.03×103	3.24×105	2.46	162.91
SC-PDMS-03	7.33×102	1.67×104	2.67	140.34
SC-PDMS-04	3.15×102	2.88×103	2.25	121.58
S-1-L-1-PDMS	2.52×103	4.31×102	2.73	158.63
S-0.5-L-1.5-PDMS	1.17×101	1.04×101	2.80	161.23
S-1.5-L-0.5-PDMS	1.65×103	1.34×102	2.64	144.87

"+" Exceeding the upper range; "-" Beyond the lower range.

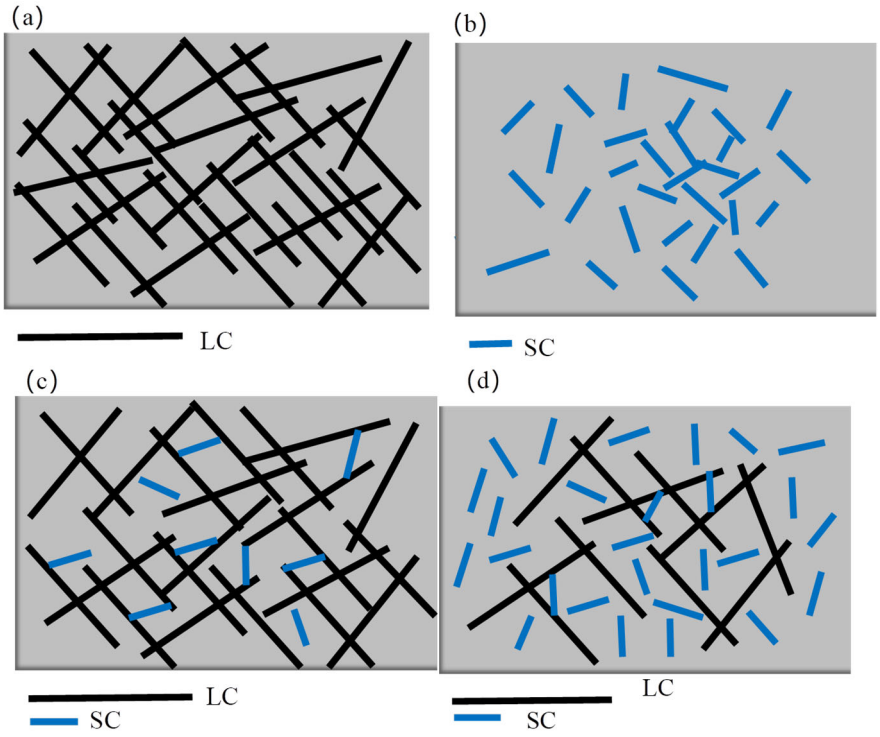

Fig 2. Schematic conductive path of the carbon nanofiller composites with filler loadings 2 wt.% : (a) LC-PDMS-02, (b) SC-PDMS-02, (c) S-0.5-L-1.5-PDMS,(d)S-1.5-L-0.5-PDMS

3.4 Thermal properties

The thermal stability of CNTs/PDMS composites were analysed by TGA. PDMS was also tested for comparison. Results of TGA data are illustrated in Fig. 3.TGA measurements carried under the nitrogen atmosphere in these samples show similar results in weight loss of PDMS. The weight loss during the initial stage of burning was attributed to the presence of moisture on the sample surface and to the volatile substances contained in the resin[22]. As expected, filling the PDMS with LC and SC increased the initial burning temperature, the first apparent weight loss for PDMS occurred between 300ºC and 400ºC and a rapid weight loss was found around 455ºC, then 41% of residual PDMS appeared to be stable up to 600ºC. However, for the samples with 2 wt.% of LC, SC filler, the obvious weight loss peaks were only observed in the range of 450ºC to 600ºC . The composites showed the dramatically enhanced thermal stability than PDMS in the range of 450ºC to 600ºC. According to Table 3, the temperatures at 5% weight loss for PDMS, SC-PDMS-02 and LC-PDMS-02 were 405℃, 419 ℃ and 429℃, respectively, while the temperatures at 20% weight loss for the PDMS, SC-PDMS-02 and LC-PDMS-02 were 502 ℃, 561 ℃ and 582℃, respectively. The LC and SC aggregated function as a barrier, preventing the diffusion of the degradation products from the bulky polymer into the gas phase[23].In addition, the entrapment of the polymer between the tubes delayed the thermal degradation process, reducing the mobility of the silicone rubber around the nanotubes and improving the thermal stability of the CNTs/PDMS composite[19],[24]. On the other hand, SC-PDMS-02 showed a lower thermally stable than that of LC-PDMS-02 in the range of 530^{o} C to 600^{o} C. The reason is that aspect ratio plays an important role in determining the thermal stability and conductivity of the nanocomposites. A filler with a high aspect ratio can form bridges among the neighboring fillers and form a conductive network.Thus, the conductive network facilitates the electron and phonon transfer, which leads to high thermal stability and conductivity of the nanocomposites[19].

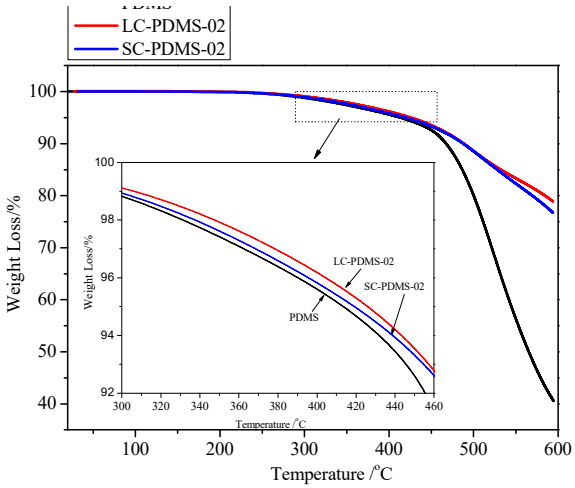

Fig3.Thermogravimetry analysis on CNTs/PDMS composites:PDMS , LC-PDMS-02, SC-PDMS-02

Table 3. Thermogravimetry analysis on CNTs/PDMScomposites

Sample No.	Loading/ Wt.%	T5%/ oC	T20%/ oC	Res /wt.%
PDMS	0	405	502	41
LC-PDMS-02	2	419	561	76
SC-PDMS-02	2	429	582	78

4. Conclusion

When the LC and SC filling in the PDMS, the conductivity of CNTs/PDMS shows a drastic increase when the filler loading increases to a certain concentration range. Incorporating 2 wt.% of LC into PDMS matrix, Rs and Rv dereased dramatically to 4.31×10^{1}, 2.48×10^{2}MΩ·mm, respectively. When the LC was increased to 3 wt.%, Rs and Rv dereased beyond the lower measurement range. On the other hand, loading 2 wt.% of SC into PDMS matrix, Rs and Rv dereased to 2.03×10^{3}, 3.24×10^{5}MΩ·mm, respectively. The modulus of the SC/PDMS and LC/PDMS composites gradually increased with the filler content increased, while the elongation at break of the SC/PDMS and LC/PDMS composites decreased with the filler content increased. The LC-PDMS-02 show the excellent mechanical properties with the higher modulus of 2.84 MPa and elongation at break of 157.85% than those of SC-PDMS-02. Filling the PDMS with LC and SC increased the thermal stability for CNTs/PDMS as well. The thermal stability for LC/PDMS composites was higher than SC/PDMS composites. In summary, LC has the potential of being reinforcing filler than SC, due to its high aspect ratio of CNTs.

Acknowledgements

This research was funded by the Zhejiang Provincial Natural Science Foundation of China, grant number LGF21E030001, and the Jia Xing Public Welfare Project, grant number 2021AY10076.

References

[1] T. Yan, Y. Wu , W.Yi , Z.Pan, Recent progress on fabrication of carbon nanotube-based flexible conductive networks for resistive-type strain sensors, Sensor. Actuat. A-Phys. 327(2021)112755.

[2] P. Vinay Deep, R. Sravendra, Y. Hye Jin abs and et.al, Functionalization of carbon nanomaterials for advanced polymer nanocomposites: A comparison study between CNT and graphene, Prog. Polym. Sci. 67(2017) 1-47.

[3] A. Nag, S. C. Mukhopadhyay, Fabrication and implementation of carbon nanotubes for piezoresistive sensing applications, Mater. Technol.7 (2022) 100416.

[4] J. Chen, J. Zheng, Q. Gao, J. Zhang, J. Zhang, O.M. Omisore, L. Wang, H. Li, Polydimethylsiloxane (PDMS)-based flexible resistive strain sensors for wearable applications, Appl. Sci. 8 (2018) 345.

[5] J. Meng , J. Song , X. Zhang , J. Wang , S. Li, A highly stretchable carbon nanotube/reduced graphene oxide/ poly (dimethylsiloxane) composite with high thermal conductivity as a flexible strain sensor, Compos. Commun.42 (2023) 101693.

[6] Y. He, X. Lu, D. Wu, and et. al, CNT/PDMS conductive foam-based piezoresistive sensors with low detection limits, excellent durability, and multifunctional sensing capability,Sensor. Actuat. A-Phys. 358(2023) 114408.

[7] W.Y. Wua, Z.P.Bianb, W. Wang and et.al, PDMS gold nanoparticle composite film-based silver enhanced colorimetric detection of cardiac troponin I, Sens.Actuators B. 147 (2010) 298-303.

[8] P. Pandey, S. Vongphachanh, J. Yoon, B. Kim, C.J. Choi, J.I. Sohn, and et. al, Silver nanowire-network-film-coated soft substrates with wrinkled surfaces for use as stretchable surface enhanced Raman scattering sensors, J. Alloy. Compd. 859(2021)157862.

[9] T. Li, J. Li, A. Zhong, F. Han, R. Sun, C.P. Wong, F. Niu, G. Zhang, Y. Jin, A flexible strain sensor based on CNTs/PDMS microspheres for human motion detection, Sensor. Actuat. A-Phys. 306 (2020) 111959.

[10] B. Shin, S. Mondal, M. Lee, S. Kim, Y.-I. Huh, C. Nah, Flexible thermoplastic polyurethane carbon nanotube composites for electromagnetic interference shielding and thermal management, Chem. Eng. J. 418 (2021) 129282.

[11] J. Chen, Y. Zhu, W. Jiang, A stretchable and transparent strain sensor based on sandwich like PDMS/CNTs/PDMS composite containing an ultrathin conductive CNT layer, Compos. Sci. Technol.186 (2020)107938.

[12] I. Akhtar, S.H. Chang, Stretchable sensor made of MWCNT/ZnO nanohybrid particles in PDMS, Adv. Mater. Technol. 5 (2020) 2000229.

[13] M.N. Barshutina, S.O. Kirichenko, V.A. Wodolajsky and et.al, PDMS-CNT composite for soft bioelectronic neuronal implants,Compos. Part B-eng.247(2022) 110286.

[14] Y. Xia, T. Su, Z. Mi and et.al,Wearable electrochemical sensor based on bimetallic MOF coated CNT/PDMS film electrode via a dual-stamping method for real-time sweat glucose analysis, Analytica Chimica Acta.1278(2023)341754.

[15] J. Shi, L. Wang, Z. Dai, L. Zhao, M. Du, H. Li, Y. Fang, Multiscale hierarchical design of a flexible piezoresistive pressure sensor with high sensitivity and wide linearity range, Small. 14 (2018) 1-7.

[16] S.M. Lee, H.J. Byeon, B.H. Kim, J. Lee, J.Y. Jeong, J.H. Lee, J.H. Moon, C. Park, H. Choi, S.H. Lee, K.H. Lee, Flexible and implantable capacitive microelectrode for bio-potential acquisition, Biochip J. 11 (2017) 153-163.

[17] L. Wang, H. Peng, X. Wang, X. Chen, C. Yang, B. Yang, et al., PDMS/MWCNTbased tactile sensor array with coplanar electrodes for crosstalk suppression, Microsyst. Nanoeng.2 (2016) 1-8.

[18] L.Wang, W. Dou, J. Chena,and et.al.A CNT-PDMS wearable device for simultaneous measurement of wrist pulse pressure and cardiac electrical activity, Mat. Sci. Eng. C.117 (2020) 111345.

[19] M. Norkhairunnisa, A. Azizan, M. Mariatti, H. Ismail, L.C. Sim, Thermal stability and electrical behavior of polydimethylsiloxane nanocomposites with carbon nanotubes and carbon black fillers, J. Compos. Mater. 46 (2012) 903-910.

[20] O.N. Hur, J.H. Ha,S.H. Park,Strain-Sensing Properties of Multi-Walled Carbon Nanotube/ Polydimethylsiloxane Composites with Different Aspect Ratio and Filler Contents, Materials. 13（2020) 2431.

[21] Y. Zheng, Y. Li, and et.al.The effect of filler dimensionality on the electromechanical performance of polydimethylsiloxane based conductive nanocomposites for flexible strain sensors, Compos. Sci. Technol. 139 (2017) 64-73.

[22] P.L.Teh, M. Mariatti, A.N.R.Wagiman, K.S.Beh,Effect of curing agent on the properties of mineral silica filled epoxy composites, Polym. Compos. 29 (2008)27-36.

[23] D.Bikiaris, A.Vassiliou, K. Chrissafis, K.M. Paraskevopoulos, A. Jannakoudakis, A. Docoslis, Effect of cidtreated multi wall carbon nanotubes on the mechanical permeability, thermal properties and thermo-oxidative stability of isotactic polypropylene, Poly. Degrad. Stab.93 (2008) 952-967.

[24] H.Ismail, P. Prabakash, M.N. Ahmad Fauzi and A.Abu Bakar, Morphological, thermal and tensile properties of halloysite nanotubes filled ethylene propylene diene monomer (EPDM) nanocomposites, Polym. Test. 27(2008) 841-850.