HCREEP BEHAVIOUR OF PP/CNT NANOCOMPOSITES: AN EXPERIMENTAL STUDY VALIDATED WITH CREEP MODEL

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Abstract

The creep-recovery behaviour of isotactic polypropylene-multi wall carbon nanotubes (PP/CNT) nanocomposites has been studied with long-term tensile test at dynamic mechanical analysis. The state of dispersion-distribution of nanocompositesis determined by using scanning electron microscopy (SEM) and also crystallinity of nanocomposites which is obtained by using differential scanning calorimetry (DSC) to understand the carbon nanotube inclusion on the properties of nanocomposites. The specimen has been fabricated by injection molding with uniform sizes for tension film clamp of dynamic mechanical analysis (DMA). Furthermore, the purity of CNTs has been obtained from RAMAN spectroscopy and thermogravimetric analysis (TGA) as well. According to creep-recovery tests, the nanocomposites have shown an improvement in the properties of creep-recovery with increasing of CNT addition up to 1% weight fraction.

1. Introduction

Carbon nanotubes (CNTs) with their intrinsic properties due to low density, high aspect ratio, flexibility, high stiffness *etc.* have been used in applications either for smart materials in electronic devices, membranes, electron emitters as well as in structural components for aerospace, marine industries and sporting goods [1-6]. Most of the researchers have studied about investigation of effects of the CNTs addition into polymer matrix on the stiffness, toughness and viscoelastic properties of PNCs [7-10]. However, in most practical applications, strength not only depends on stress and strain but also on time [11, 12]. Therefore, Ganß et al. have studied about short-term creep compliance of PP/CNT composites at different temperature. It was found that creep compliance of PP/CNT composites has been improved with the addition of CNT into polymer matrix [12]. Furthermore, the model to explain creep-recovery of PP/CNT composites have also been proposed. Yang et al. studied about creep resistant of polymer nanocomposites using with MWCNTs having different aspect ratios as long and short. Long-MWCNT/PP nanocomposites behaved better creep resistance than short-MWCNT/PP nanocomposites because of good interfacial bonding between MWCNT and PP matrix [13]. However, the most of the studies reported in the literature has studied short-term creep behaviour of polymers as well as their composites. The motivation of this work is to investigate the effect of CNT addition on the creep behaviour of polypropylene (PP) and to find out 'long-term' creep behaviour of PP/CNT polymer nanocomposites. The results will also be verified by a proposed new model to understand the effect of CNT on the creep behaviour of polymer nanocomposite on long time duration and to correlate the crystallinity and mechanical property of the specimens within this model.

2. Experimental Studies

2.1 Fabrication of PP/CNT Polymer Nanocomposites

As a matrix, commercially available isotactic polypropylene (Sigma Aldrich-427888) was used and multi wall carbon nanotubes (MWCNTs) were supplied from Sigma Aldrich (773840), as fillers. According to supplier, MWCNTs have innermost diameter of 4.5±0.5 nm, outer diameter of 10±1 nm and length of 3-6μm. In this study, fabrication process of polymer nanocomposites consists of two main steps. First, isotactic PP and MWCNT was mixed at ethanol solution by using magnetic stirring approximately for 4 hours and the mixture has waited at vacuum oven for one day to remove the alcohol. Fig-1 shows that stereo microscopy images of these components. MWCNTs can adhere on the surface of the polymer easily within stirring and drying process.

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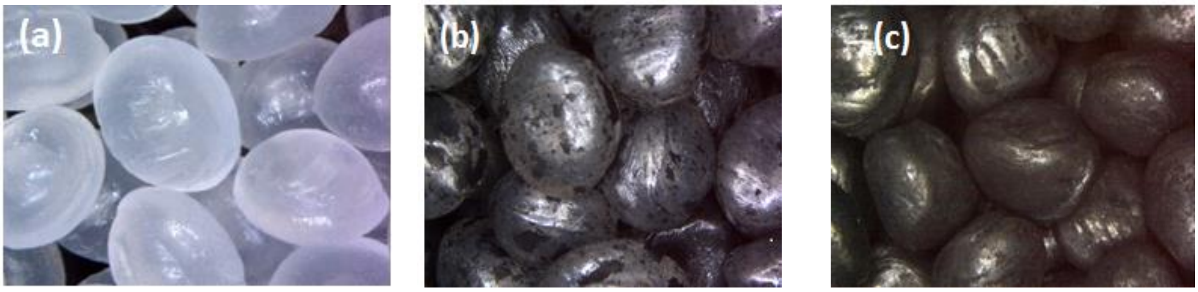

Figure 1: Stereo microscopy images of (a) neat polypropylene (PP), 0.3%wt.CNT/PP and (c)0.5%wt.CNT/PP.

As a second step, injection molding process was used to fabricate polymer nanocomposites with required tension film dimensions of dynamic mechanical analysis (21x10x0.29). The CNT content was added into the matrix from 0.3% weight fraction up to 3%weight fraction to improve creep-recovery behaviour .Table-1 illustrates injection molding parameters for fabrication of PP/CNT nanocomposites. All parameters optimized with previous studies about polypropylene.

Table 1: Injection molding parameters for the fabrication PP/CNT nanocomposites.

	1.zone	2.zone	3.zone	4.zone	5.zone
Screw zone temperature	200°C	205°C	210°C	215°C	220°C
Molding temperature	25°C				
Rate of injection	15-25ccm/sec.				
Calendering pressure	1200-1400 bar				
Injection pressure	5m.min^{-1}				

2.2 Creep-recovery Measurements by DMA

Creep is a time dependent plastic deformation under constant stress. Since polymers show non-linear viscoleastic behaviour, it is difficult to estimate creep behaviour of polymers under the constant stress. Since amount of deformation recovery after eliminated load [13, 14]. Creep-recovery tests were conducted on tensile mode at room temperature using DMA. The specimens of creep-recovery test were the same size by means of injection molding. Fig-2(a) shows schematically a creep-recovery test setup and Fig-2(b) shows that fabricated specimens of pure PP, 0.3%wt.CNT/PP, 0.5%wt.CNT/PP, 1%wt.CNT/PP and 3%wt.CNT/PP from left to right respectively. Tensile tests were carried out with tensile mode of DMA to obtain elastic region of nanocomposites before creep-recovery tests and stress level was fixed at 4MPa to ensure the creep measurement remained in linear viscoelastic regime. All tests were conducted on tensile mode in the elastic region of polymers under room temperature. For each creep-recovery test, a new specimen was used. The creep and recovery strain are defined as a function of time (t_{creep}=1440 min. and $t_{recovery}$=1440 min.). Fig-2(c) illustrate that a typical strain-time curve in creep-recovery test. It changes with applied force, temperature, types of polymer and also addition of nano reinforced materials. The specimen was equilibrated for 5 min. at room temperature before the measurement.

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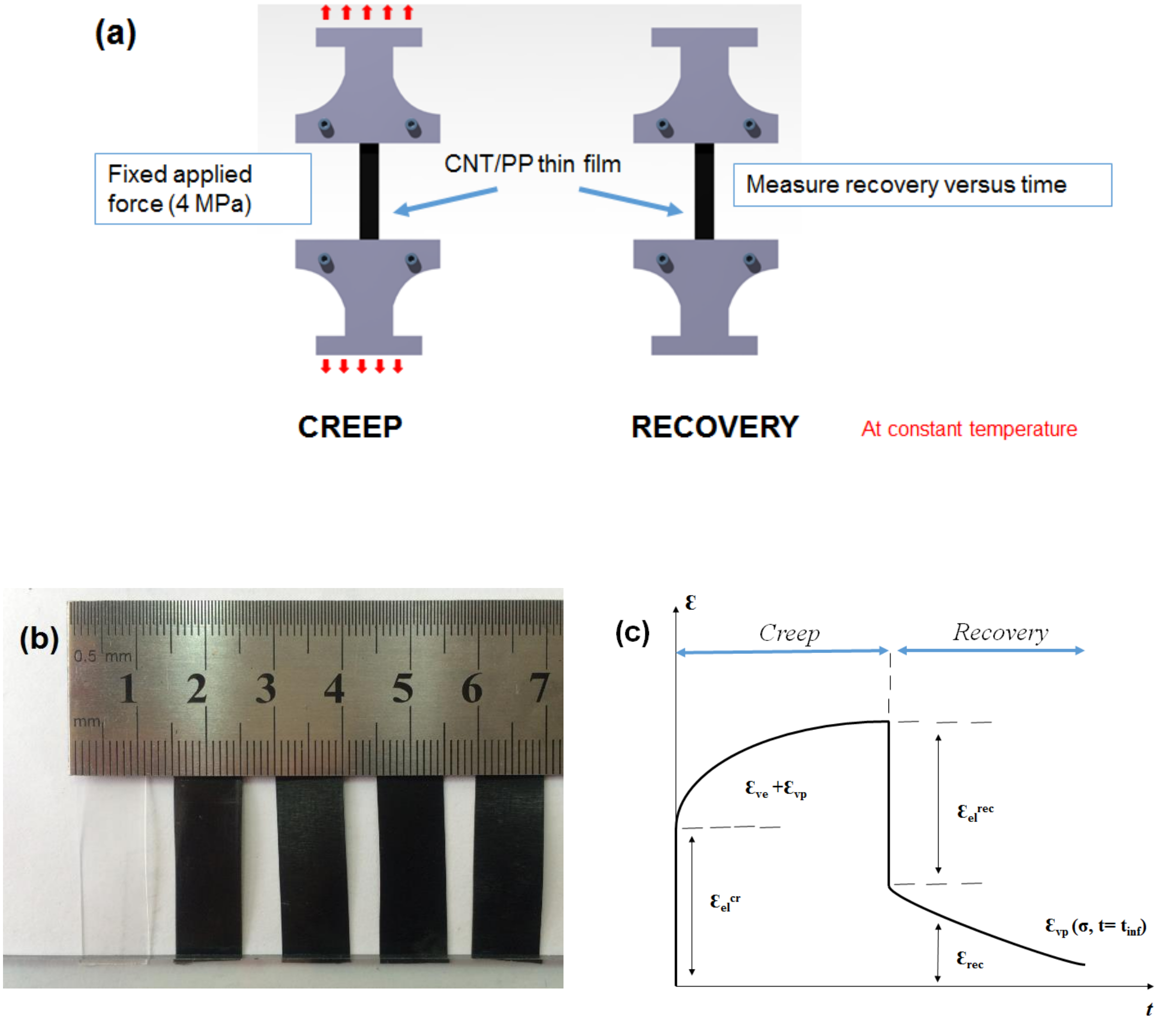


Figure 2: (a) The schematics illustrating the details of creep-recovery test, (b) the specimen of pure PP, 0.3%wt.CNT/PP, 0.5%wt.CNT/PP, 1%wt.CNT/PP and 3%wt.CNT/PP from left to right respectively ,(c) a typical strain-time curve in a creep-recovery test.

3. Results and Discussion

3.1 Characterization of MWCNTs

Different carbon forms such as single wall carbon nanotube (SWCNT), multi wall carbon nanotubes (MWCNT), graphite and graphene are distinguished one another by using RAMAN spectroscopy. Furthermore, RAMAN spectroscopy result yields information about purity, defects and innermost diameter of CNTs especially SWCNT and also chirality of CNTs [15-19]. While the graphite G-peak located at 1590cm^{-1} indicates that degrees of graphitization, D-peak located in 1346cm^{-1} are attributed the presence of the amorphous carbon at 2.52 eV. G/D ratio is the ratio of intensity at G (graphite) band and at D (defect) band. Fig-3(a) shows the RAMAN spectroscopy of MWCNT from Sigma Aldrich (773840) using Renishaw inVia reflex microscopy and spectroscopy with an excitation energy 2.32 eV and acquisition range from 100-3000cm^{-1}. The ratio of bands is calculated as 0.74 which shows similar results within commercial CNTs purchased from several companies. On the other hand, some researcher believed that G*peak located at 2695cm^{-1} may indicates more definite measurement of MWCNT purity [20]. Furthermore, thermogravimetric analysis (TGA) is a technique for measuring the oxidation resistivity of CNTs. Thermal analyses are carried out in TA instruments SDTQ 600 model TGA.

Samples were heated in a platinum pan at 10°C/min. in air. Fig.3(b) shows that ten percentage of thermal degradation ($T_{d\ 10\%}$) is found ~528°C) also similar to commercially available products of MWNTs.

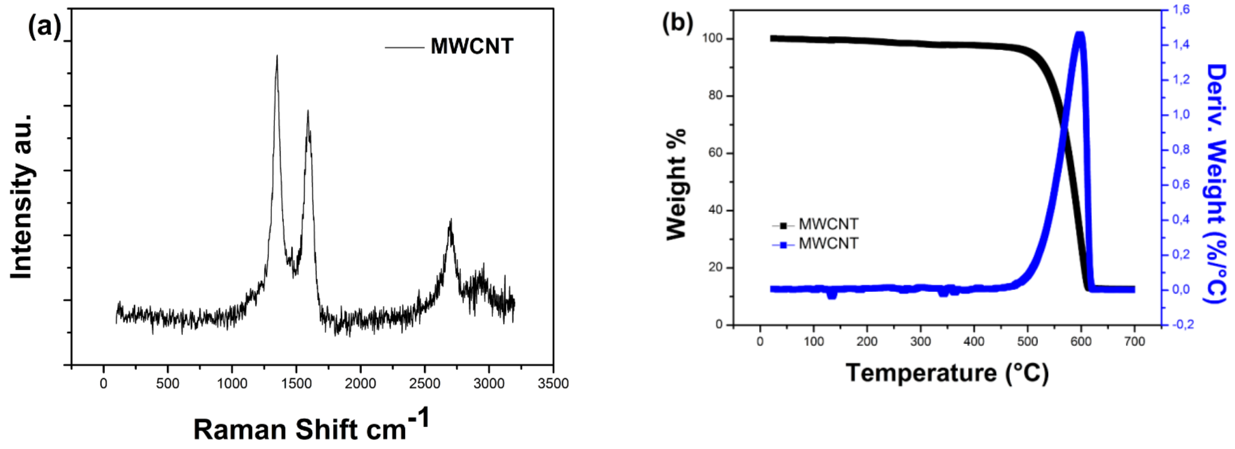
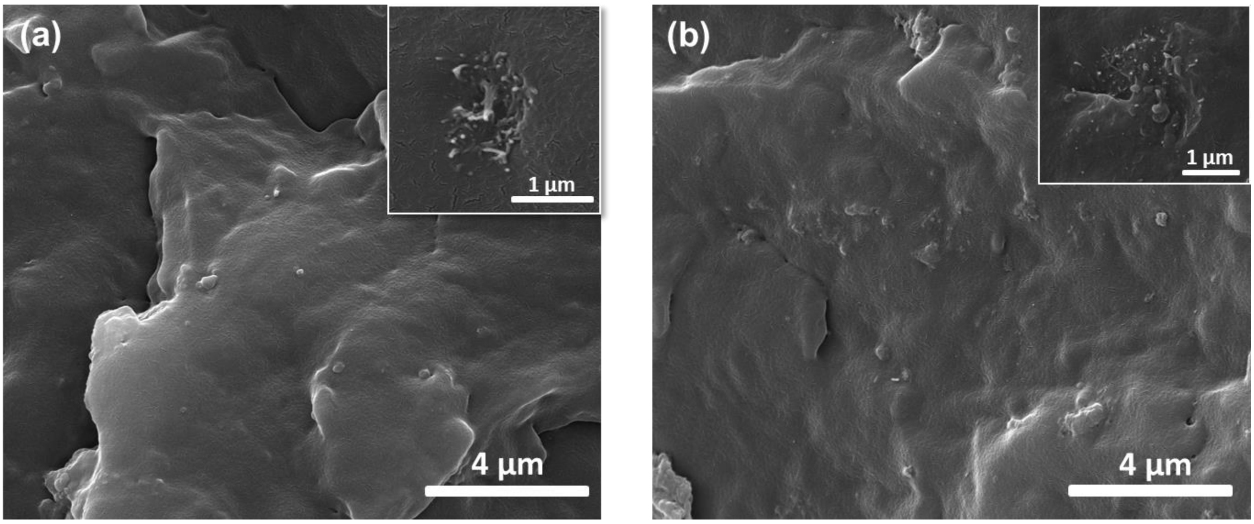


Figure 3: (a) RAMAN spectrum of MWCNT, (b) TGA results of MWCNT.

3.2 Morphological Chacterization of PP/CNT Nanocomposites

SEM images of 0.3%wt.CNT/PP, 5%wt.CNT/PP, 1%wt.CNT/PP and 3%wt.CNT/PP composites are shown in Fig-4 respectively with different magnitude at cryofracture surfaces. In order to observe distribution and dispersion state of CNTs low magnification (x20000) was selected. On the other hand, high magnification (x80000) was used to good dispersion by using QUANTA FEG at high vacuum. The images of composites reveals that adhesion at interface between CNTs and polymer is quite good.



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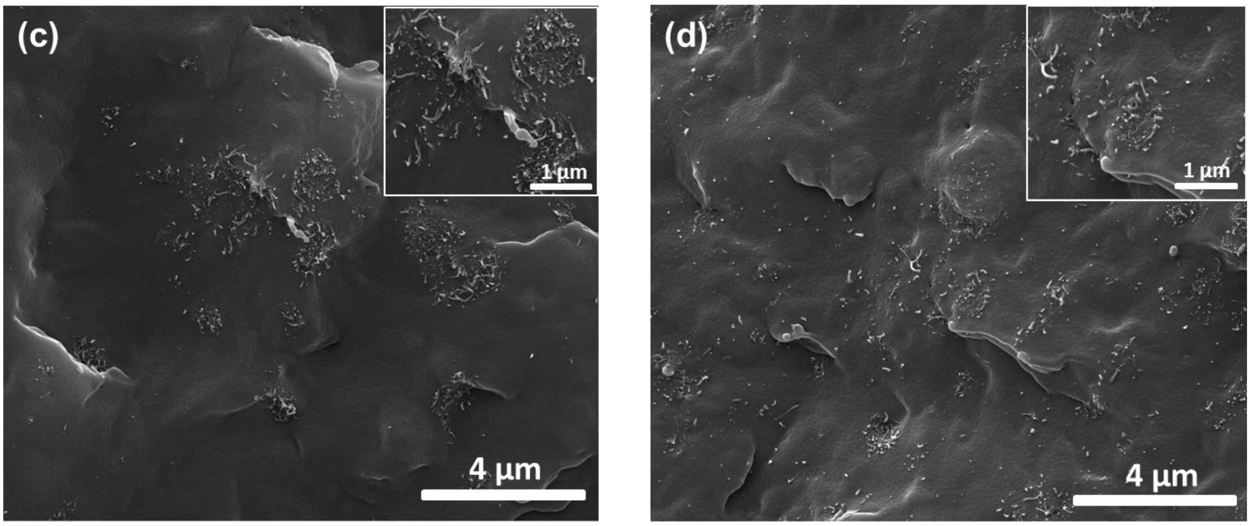

Figure 4: SEM images of (a) 0.3%wt.CNT/PP, (b)0.5%wt.CNT/PP, (c) 1%wt.CNT/PP, (d) 3%wt.CNT/PP.

3.3 Determination of crystallinity of PP/CNT nanocomposites

Differential scanning calorimetry (DSC) measurement, to obtain information about effects of the CNTs on the crystallization behaviour of nanocomposites, were conducted on DSC Q200 (TA Instrument) at scan rate 10°C/min over a temperature range from 80 to 200°C. The crystallinity of PP/CNT nanocomposites are shown in Table-2. All crystallinity is increasing by incorporation of CNTs into polymer matrix with 0.3%, 0.5%, 1% and 3% weight fraction of MWCNTs.

Table 2: Degrees of crystallinity of nanocomposites by using DSC

Degrees of crystallinity	**Pure PP**	**0.3%wt.CNT/PP**	**0.5%wt.CNT/PP**	**1%wt.CNT/PP**	**3%wt.CNT/PP**
DSC (%)	49.04	49.30	52.92	53.50	53.87

DSC results are shown in Fig-5 according to melting and crystallization from 80°C to 200°C. Overall tests were conducted with 3 cycles to eliminate residual stress from fabrication. According to test results, crystallization temperature increases with incorporation of CNTs since crystallites are folded polymer chain at restricted domain [12].On the other hand, 1%CNT/PP shows better crystallization behaviour than others. It is thought to be cause from the state of dispersion-distribution of nanocomposites.

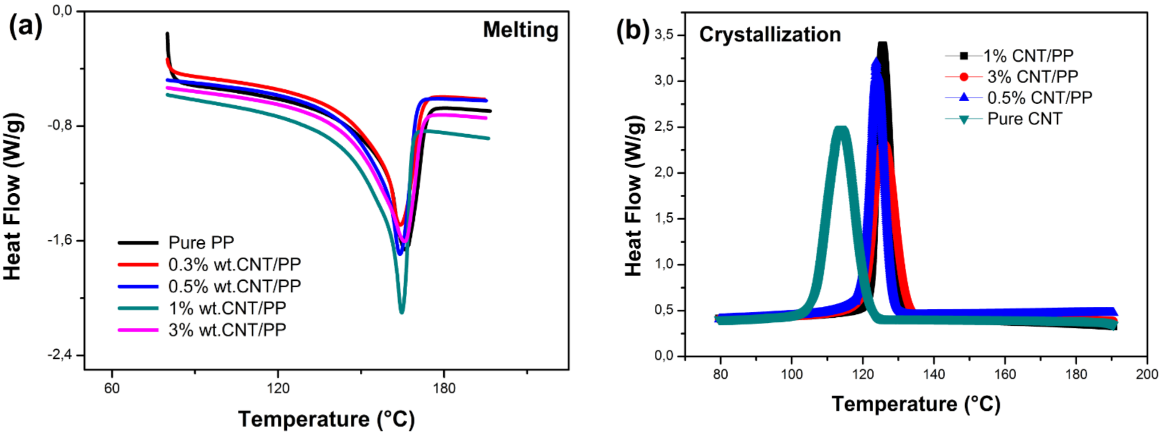

Figure 5: DSC thermograms showing (a) heating, (b) cooling curves of PP/CNT nanocomposites.

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3.4 Tensile and thermomechanical analysis of PP/CNT nanocomposites

Dynamic mechanical analysis (DMA) was made in tensile mode at 1Hz using DMA Q800 (TA Instrument). The specimens for DMA tension clamp were 21x10x0.29. Table-3 shows that mechanical properties of nanocomposites.

Table 3: Mechanical characteristics of nanocomposites.

MWCNTs %wt.	Young’s modulus (GPa)
PP	1.15
0.3%wt. CNT/PP	1.01
0.5%wt.CNT/PP	1.03
1%wt.CNT/PP	1.11
3%wt.CNT/PP	1.08

3.5 Creep-recovery test

Fig-7 displays the trends of creep-recovered strains as a function of time for pure PP, 0.3%wt.CNT/PP, 5%wt.CNT/PP, 1%wt.CNT/PP and 3%wt.CNT/PP composites at room temperature. Stress level was selected carefully to remain elastic regime for each nanocomposites. While primary and secondary creep can be clearly observed in Fig-7(a), creep rupture (tertiary creep) has not been observed since 2 days at 5MPa stress. As seen in Fig-7(a), creep strain of nanocomposites are lower than neat polymer. It is the evidence that incorporation of CNTs with different weight fractions improves the creep behaviour of polymers. Moreover, incorporation of CNTs into polymer matrix improves the elastic recovery. Although 3%CNT/PP nanocomposites contains higher weight fraction of CNTs, 1%CNT/PP shows better behaviour of creep-recovery. It is consistent with DSC results.

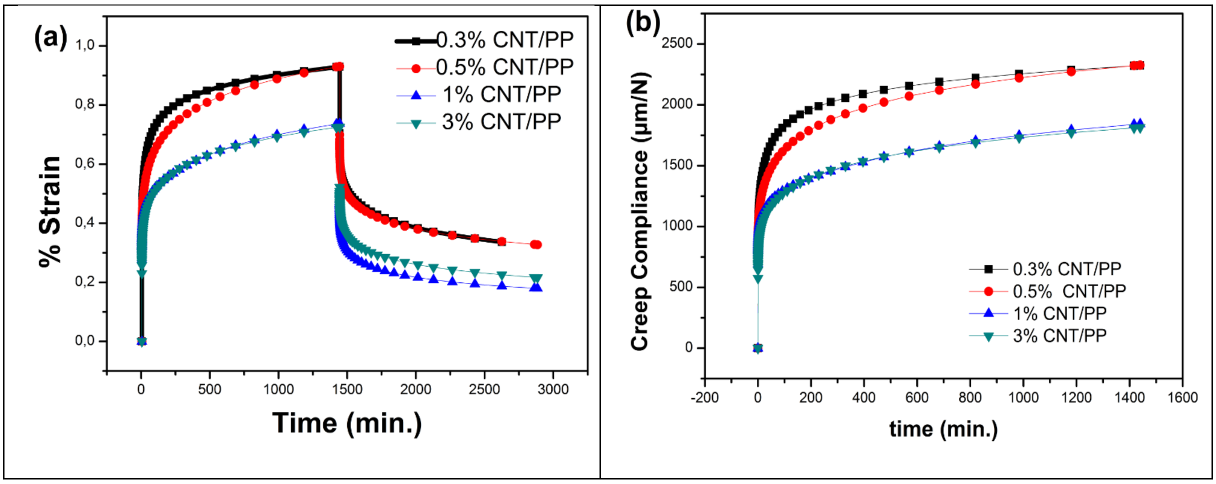

Figure 6: (a) Temperature dependent creep strain of PP/CNT nanocomposites, (b) creep compliance of nanocomposites as a function of time.

3.6 Model of creep-recovery

Experimental work will be simulated with the model algorithm and calculations will be performed for longer periods for all nanocomposites. Model parameters will also be found by comparing with the test results by dynamic mechanical analysis method (DMA) the aim is to estimate the parameter correlations with the mechanical properties of the constituents.

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4. Conclusion

This paper has been studied about creep-recovery behaviour of CNT/PP nanocomposites at room temperature. The creep strain decreases with the content of CNTs. While recoverable strain of 0.3%CNT/PP nanocomposite is 0.34%, the strain of 1%CNT/PP nanocomposite is 0.17%. It is the evidence that incorporation of MWCNTs improved the twofold. However, creep-recovery behaviour of 3% CNT/PP nanocomposite is lower than 1%CNT/PP nanocomposite under room temperature. It is the evidence that our fabrication methods are suitable for up to 1%CNT dispersion into polymer matrix. On the other hand, DSC measurement of nanocomposites is consistent with creep-recovery test results.

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References

[1] Zdenko Spitalsky, Dimitrios Tasis, Konstantinos Papagelis, Galiotis C. Carbon nanotube–polymer composites: Chemistry, processing, mechanical and electrical properties. Progress in Polymer Science. 2010;35:357–401.

[2] Yu Jia , Ke Peng , Xing-long Gong, Zhang Z. Creep and recovery of polypropylene/carbon nanotube composites. International Journal of Plasticity. 2011;27:1239–1251.

[3] Tianxi Liu, In Yee Phang, Lu Shen, Shue Yin Chow, Zhang W-D. Morphology and Mechanical Properties of Multiwalled Carbon Nanotubes Reinforced Nylon-6 Composites. Macromolecules. 2004;37:7214-7222.

[4] Mahmood M. Shokrieh, Rafie R. On the tensile behavior of an embedded carbon nanotube in polymer matrix with non-bonded interphase region. Composite Structures. 2010;92:647–652.

[5] Jonathan N. Coleman, Umar Khan, Werner J. Blau, Gun'ko YK. Small but strong: A review of the mechanical properties of carbon nanotube–polymer composites. Carbon. 2006;44:1624–1652.

[6] Erik T. Thostenson, Zhifeng Ren, Chou T-W. Advances in the science and technology of carbon nanotubes and their composites: a review. Composite Science and Technology. 2001;61:1899–1912.

[7] L.Ci, J.Suhr, V. Pushparaj, X. Zhang, P.M.Ajayan. Continuous Carbon Nanotube Reinforced Composites. Nano Letters. 2008;8:2762-2766.

[8] Chung-Lin Wu , Hsueh-Chu Lin , Jiong-Shiun Hsu , Ming-Chuen Yip , Fang W. Static and dynamic mechanical properties of polydimethylsiloxane/carbon nanotube nanocomposites. Thin Solid Films. 2009;519:4895-4901.

[9] Arash Montazeri , Montazeri N. Viscoelastic and mechanical properties of multi walled carbon nanotube/epoxy composites with different nanotube content. Materials and Design. 2011;32:2301–2307.

[10] A. T. Sep´ulveda, R. Guzman de Villoria, J. C. Viana, A. J. Pontes, B. L. Wardle, Rocha LA. Full elastic constitutive relation of non-isotropic aligned-CNT/PDMS flexible nanocomposites. Nanoscale. 2013;5:4847-4854.

[11] W.Zhang, A.Joshi, ZWang, R. S. Kane, Koratkar N. Creep mitigation in composites using carbon nanotube additives. Nanotechnology. 2007;18:1-5.

[12] Martin Ganß, Bhabani K. Satapathy, Mahendra Thunga, Roland Weidisch, Petra Potschke, Janke A. Temperature Dependence of Creep Behavior of PP–MWNT Nanocomposites. Rapid Communications. 2007;28:1624-1633.

Excerpt from ISBN 978-3-00-053387-7

[13] Jinglei Yang, Zhong Zhang, Klaus Friedrich, Schlarb AK. Creep Resistant Polymer Nanocomposites Reinforced with Multiwalled Carbon Nanotubes. Macromolecular Rapid Communications. 2007;28:955–961.

[14] Ming Xu, Don N.Futaba, Motoo Yumura, Hata K. Carbon Nanotubes with Temperature-Invariant Creep and Creep-Recovery from − 190 to 970 ° C. advanced materials. 2011;23: 3686-3691.

[15] S. Santangelo, G. Messina, M. G. Donato, M. Lanza, C. Milone, Pistone A. Low-frequency Raman study of hollow multiwalled nanotubes grown by Fe-catalyzed chemical vapor deposition. Journal of Applied Physics. 2006;100.

[16] John H. Lehman, Mauricio Terrones, Elisabeth Mansfiel, Katherine E. Hurst, Meunier V. Evaluating the characteristics of multiwall carbon nanotubes. Carbon. 2011;49:2581-2602.

[17] J. Maultzsch, H. Telg, S. Reich, Thomsen C. Radial breathing mode of single-walled carbon nanotubes: Optical transition energies and chiral-index assignment. Physical Review B. 2005;72:1-16.

[18] Ajayan PM. Nanotubes from Carbon. ChemRev. 1999;99:1787-1799.

[19] M.S. Dresselhaus, G. Dresselhaus, R. Saito, Jorio A. Raman spectroscopy of carbon nanotubes. Physical Reports. 2005;409:47-99.

[20] Roberta A. DiLeo, Brian J. Landi, Raffaelle RP. Purity assessment of multiwalled carbon nanotubes by Raman spectroscopy. Journal of Applied Physics. 2007;101:1-5.