International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.3, pp 1873-1876, May-June 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Influence of Air Oxidized CNT Reinforcement on the Recovery Stress of Shape Memory Polyurethane

S.A.R Hashmi*, R. Abishera, Harish Chandra Prasad, H.N Bhargaw, Ajay Naik

Polymer Composite Group, Advanced Materials and Process Research Institute (CSIR),Bhopal, India.

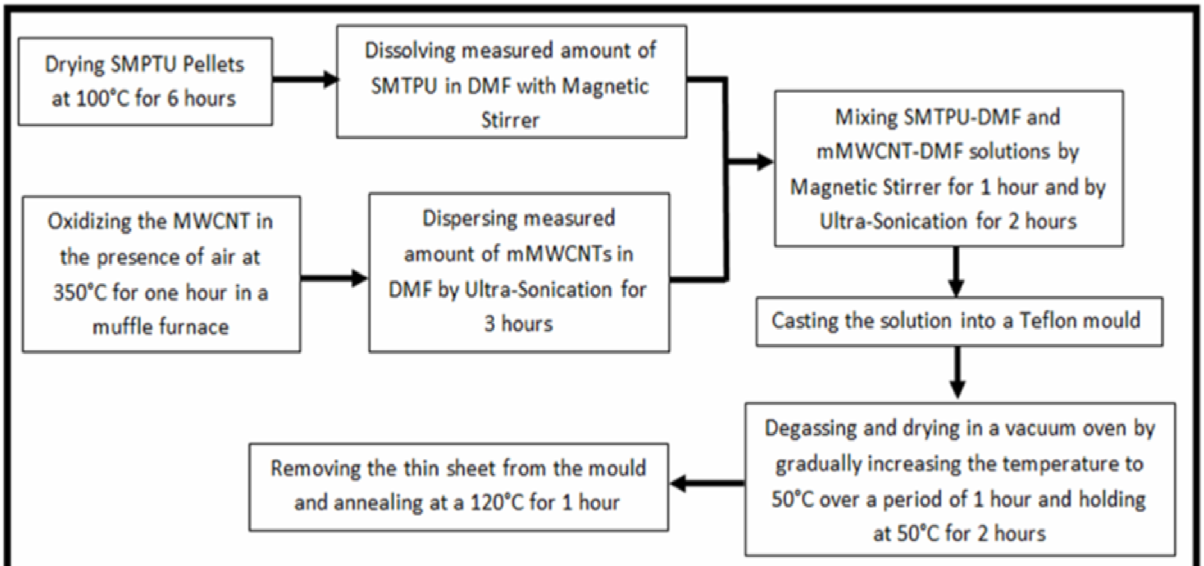
***Corres.author: sarhashmi@rediffmail.com**

Abstract: Shape Memory Thermoplastic Polyurethane (SMTPU) nano-composite samples reinforced with modified Multi Walled Carbon Nano-Tubes (mMWCNT) were prepared and their influence on the recovery stresses was analyzed. The MWCNTs were modified by oxidizing in the presence of air at 350°C to obtain mMWCNTs. The composite samples were prepared in the form of thin sheets using solvent casting method. A systematic process including sonication and stabilization was employed to disperse the MWCNT into the SMTPU matrix. The thermo-mechanical cycle test was carried out using a test set-up designed to characterize SMPs. The air oxidation helped in removing carbonaceous impurities from the MWCNT samples as observed in SEM micrographs. The modulus and recovery stress increased considerably with addition of MWCNTs. The mMWCNT also enabled in a better and stable dispersion compared to unmodified MWCNTs. The samples reinforced with mMWCNT showed an increase in modulus and recovery stress when compared with samples reinforced with unmodified MWCNT for the same filler content. The modification of MWCNTs enabled in better reinforcement efficiency with the SMTPU matrix thus increasing the recovery stress and modulus.
Keywords- Shape Memory Polyurethane; Carbon Nano-Tubes; Thermo-Mechanical Cycle; Recovery Stress.

Introduction and Experimental:

Shape Memory Materials are known to hold a temporary shape and recover the original shape at the application of right stimulus[1]. Among these materials Shape Memory Polymers (SMP) have advantages like low density, can hold strains up to 800%, low cost, easy processing and respond to various stimuli like heat, light, pH, moisture, etc[2], however their low modulus, low recovery stress and low thermal conductivity are drawbacks for engineering applications[3]. Many types of fillers have been employed by researchers to improve the desired properties. Among them CNTs are being investigated extensively due to their exceptional mechanical, thermal and electrical properties[4]. This study aims to develop SMTPU reinforced with MWCNT and mMWCNT and to study reinforcement effect on the Recovery Stress, Shape Fixity and Shape Recovery. Materials used in this study; MWCNTs were obtained from M/s Nanoshel Ltd. India. SMTPU (ether type) MM6520 was obtained from SMP Technologies Inc. Japan. Laboratory reagent Dimethylformamide (DMF) was obtained from Central Drug House (P) Ltd, India. To remove the carbonaceous impurities from the commercial grade MWCNTs, they were oxidised in air at a temperature of 350°C in a muffle furnace for a period of 1 hour [5], and mMWCNT is obtained. A process chart showing all the details in the development of MWCNT- SMTPU nanocomposites and the sample nomenclature is shown in figure 1. Field Emission

Scanning Electron Microscopy (FESEM) was used to study the morphology of the modified and unmodified MWCNT. The Thermo-Mechanical experimental setup included a tensile stress measuring set-up placed inside a hot water bath. The thermo-mechanical analysis involved stretching the sample at 70°C in steps of 2mm, up-to a strain of 250% and measuring the corresponding stresses with the help of a calibrated load cell. Cooling the sample to room temperature while holding the strain and fixing the temporary shape. Re-heating the sample to 70°C and decreasing the strain in steps of 2mm and measuring the corresponding recovery stresses.



DESIGNATION	COMPOSITION		DESIGNATION	COMPOSITION	
	SMTPU (Parts by wt.)	MWCNT (Parts by wt.)		SMTPU (Parts by wt.)	mMWCNT (Parts by wt.)
PU1CNT	100	1	PU1mCNT	100	1
PU3CNT	100	3	PU3mCNT	100	3
PU5CNT	100	5	PU5mCNT	100	5

Figure 1: Process details in development of mMWCNT-SMTPU thin sheets and sample nomenclature

Results and Discussion:

From the SEM micrographs in figure 2 it can be clearly seen that air oxidation is an effective method for the removal of carbonaceous impurities like amorphous carbon and carbon nanoparticles. Figure 3 clearly shows that the developed nanocomposites showed a considerable increase in stresses both during stretch and recovery. The increase in the stresses of reinforced SMTPU can be attributed to the effective transfer of stress to the MWCNTs through interfacial shear stress between the MWCNTs and the matrix[6]. The increase in recovery stress shows the reinforcement efficiency of MWCNTs by storing the elastic strain energy during stretching and by reheating, the stored elastic strain energy was released and the nanocomposites exhibited larger recovery stress[7]. It was observed that SMTPU reinforced with modified MWCNT exhibits larger stresses as compared to SMTPU reinforced with unmodified MWCNT, which shows that by removing the impurities, more MWCNTs are made available in the stress transfer between the matrix.

The shape fixity (R_f) is the ability of the material to retain the temporary shape. It is quantitatively expressed as, $\mathbf{R_f = \frac{\varepsilon_f}{\varepsilon_d} * 100\%}$, where ε_f and ε_d are fixed and deformed strains respectively. It was observed that all samples exhibited excellent R_f (above 95%). Figure 4 shows the effect of the filler content on the shape recovery. Shape recovery (R_r) quantifies the ability of the material to memorize and recover its original shape. It is generally expressed as, $\mathbf{R_r = \frac{(\varepsilon_d - \varepsilon_r)}{\varepsilon_d} * 100\%}$, where ε_r is the residual strain after recovery. An increase in R_r was observed with small amount of MWCNT (1phr). However there was a decrease in R_r as the filler content increased. This is might be due to inclusion interaction of aggregated MWCNTs in SMTPU, which restricts the movement of the polymer chains[7]. Compared to MWCNT-SMTPU, mMWCNT-SMTPU showed a slight increase in R_r.

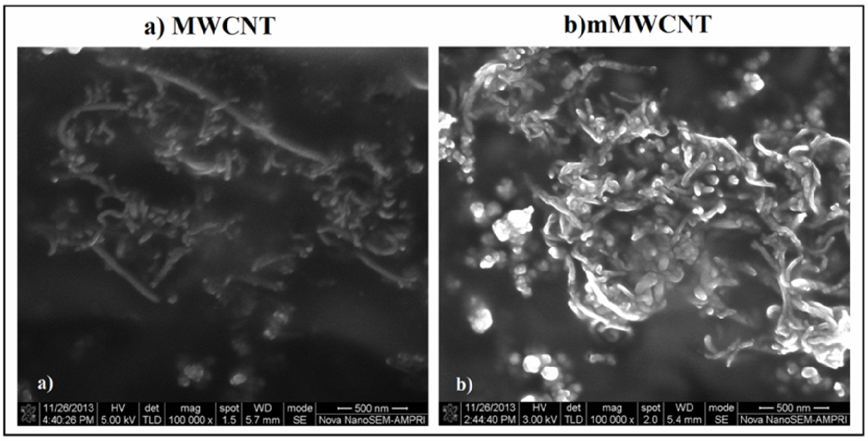


Figure 2: SEM micrographs of a) MWCNT and b) mMWCNT.

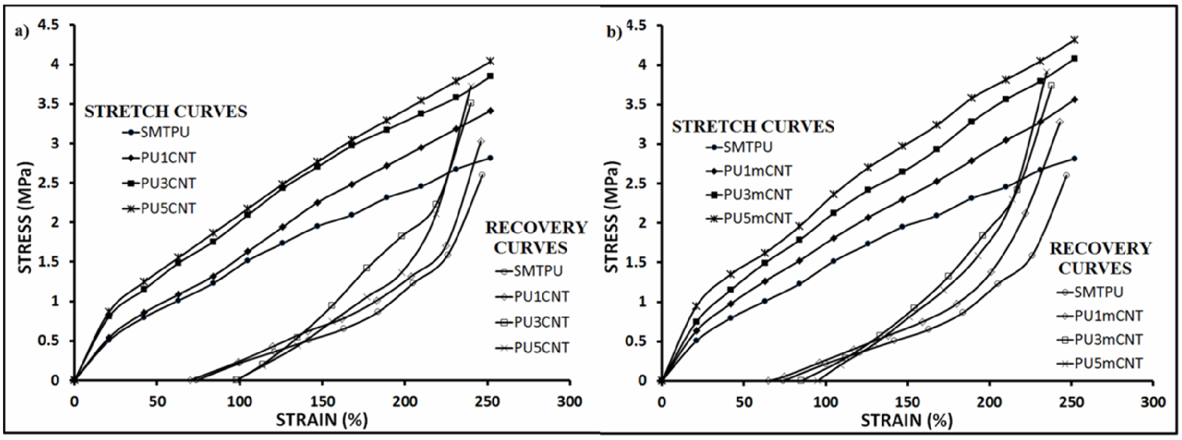


Figure 3: Stretch-Recovery curves of a) MWCNT reinforced SMTPU and b) mMWCNT reinforces SMTPU in comparison with bulk SMTPU

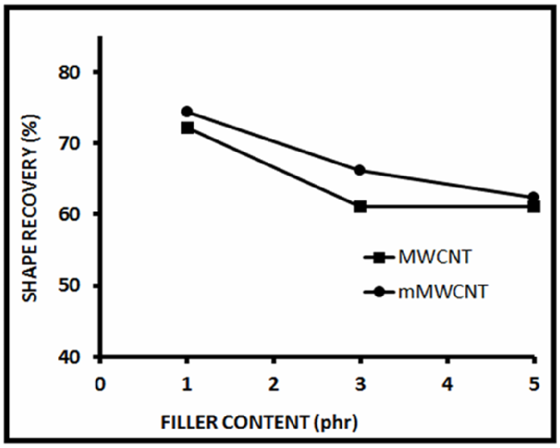


Figure 4: Effect of MWCNT and mMWCNT reinforcement on the Shape Recovery

References:

1. Lendlein A., Kelch S. Shape-Memory Polymers. Angew. Chem. Int. Ed. 2002, 41, 2034.
2. Sun L., Huang W.M., Ding Z., Zhao Y., Wang C.C., Purnawali H., Tang C. Stimulus-responsive shape memory materials: A review. Mater. Design. 2012, 33, 577.
3. Hu J., Zhu Y., Huang H., Lu J. Recent advances in shape–memory polymers: Structure, mechanism, functionality, modelling and applications. Prog. Polym. Sci. 2012, 37, 1720.
4. Thostenson E.T., Renb Z., Chou T.W. Advances in the science and technology of carbon nanotubes and their composites: a review. Composites Sci. and Tech. 2001, 61, 1899.

5. Hou P., Liu C., Cheng H. Purification of carbon nanotubes. CARBON, 2008, 46, 2003.
6. Coleman J.N., Khan U., Gun'ko Y.K. Mechanical Reinforcement of Polymers Using Carbon Nanotubes. Adv. Mater. 2006, 18, 689.
7. Ni Q.Q., Zhang C.S., Fu Y., Dai G., Kimura T. Shape memory effect and mechanical properties of CNT/SMP nanocomposites. Composite Structures. 2007, 81, 176.

*****