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Elastic Modulus Behavior of Multi-Walled Carbon Nano-Tubes/Polyurethane Composites using Nano-Indentation Techniques

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Abstract

Composites of uniformly dispersed Multi-Walled Carbon Nanotubes (MWCNTs)(1wt%, 3wt%, 7wt% and 10wt%) and Polyurethane(PU) were prepared by solution mixing method. Small disc shaped specimens were fabricated for static mechanical characterization using nano-indentation. Field Emission Scanning Electron Microscopy (FESEM) was done to validate the presence of MWCNTs in PU matrix. Mechanical characterization was performed on PU/MWCNTs nano-composites by using nano-indentation techniques. It was observed that the elastic modulus of PU/MWCNTs composites with 10wt% increased by 124.5% in comparison to pure PU.

Keywords: Elastic Modulus, Mechanical Properties, MWCNTs, Nano-Indentation, PU

1. Introduction

Polymers have been extensively used in the form of composites with various compositions of MWCNTs for a wide variety of applications[1], considering that polymers are easy to mould and acquire various shapes, their applications scopes get widened if their mechanical strength gets enhanced. Filler materials in the form of MWCNTs provide an efficient solution to be added to these polymers in minor quantities and hence successfully enhance mechanical properties without affecting the overall weight of the composite material[2]. MWCNTs possess exceptionally high mechanical strength[3] and thermal conductivity[4] due to which their application in fabrication pressure sensors, load resisting gears, impact absorbing equipment etc. is well established[5]. Two critical issues are associated with transferring the unique properties of MWCNTs to a polymer matrix. Firstly, homogeneous dispersion of MWCNTs into polymer matrix and secondly, there must be strong interfacial interaction between MWCNTs and polymer matrix[6]. There are essentially four ways to disperse MWCNTs in to polymer: (1) Melt mixing; (2) Solvent mixing (3) In-situ polymerization[7]. (4) Solution casting approach[8]

Among the polymers, PU is one such polymer which is extensively used in sports and clothing material. PU based shoes and gloves are commonly available and enhancing their impact absorption strength by addition of MWCNTs filler materials can propose an exciting proposition for their utility to the armed forces.

M. C Lopes et al.[9] used as-grown and modified MWCNTs and PU composites for static characterization with 0.5 wt% loading of MWCNTs. With as-grown MWCNTs they observed 27% and 20% improvement in hardness and elastic modulus respectively. The acid treated MWCNTs also improved mechanical properties but not as much as the non-functionalized MWCNTs.

T. K Gupta et al.[10] worked on nano indentation of PU and MWCNTs nano composites. Composite films with different MWCNTs loadings i.e. 1, 3, 5 and 10 wt% in PU were prepared by the solvent casting techniques and designated as PCNT1, PCNT3, PCNT5 and PCN10. It

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is observed that the value of hardness increase with the increase of MWCNTs content. The value for H for pure PCNT0 is 58.5 MPa and it increased to 217.5 MPa for PCNT10. Similarly, the elastic modulus increased from 385.7 MPa for PCNT0 to 1504.2 MPa for PCNT10. Thus, there is a noticeable improvement of 271% in the hardness and 290% in the elastic modulus of PU/MWCNTs is observed.

Jindal et al. used PC and MWCNTs nano-composites fabricated by solvent mixing for quasi-static testing. Result shows that for minor compositions like 0.5% to 0.75% the rise in hardness is nearly about 40%. They observed that increase in hardness is very consistent up to 5% of MWCNTs. A further increase in concentration of MWCNTs tends to saturate the hardness effect[11]

Guo et al.[12] used polyurethane and multi-walled nanotubes nano-composites prepared by in-situ polymerization and solution casting approach for dynamic thermal analysis. They observed that storage modulus of PU/MWCNT composites with 1% loading of MWCNT increased by 124% (at -75 °C). This significant rise in storage modulus is due to stiffening effect of MWCNT. They further noticed that the peak position of loss modulus of nanocomposites remains almost unchanged at about -30 °C. And this peak intensity decreases with increase in CNT content.

Barick et al.[13] used acid treated MWCNT/thermoplastic polyurethane for dynamic thermal analysis. They noticed that the value of storage modulus decreases with increase in temperature due to the thermal expansion range of matrix. The storage modulus values PU/MWCNT nanocomposites between the temperature regions of -25 °C to +25 °C were reduced in comparison to the neat PU due to the presence of MWCNTs. They found that the peak of tan(δ) curve is maximum at around -48 °C due to soft segments of PU matrix. The introduction of MWCNT(2.5wt%) in to the PU matrix lead to shifting of glass transition temperature values to higher temperature of about -49.32 °C for pure PU to 42.80 °C.

Wu et al.[14] used carboxylic acid containing MWCNT and polycarbonate composites for dynamic thermal analysis with 2%, 5% and 7% loading of MWCNT. They observed that at temperatures below glass crystallization (T_g), there is 20.7%, 58.3% and 102% improvement in storage modulus of PC/MWCNT nanocomposites respectively as compared to pure PC. However these values start decreasing above Tg. The improvement of storage modulus for PC/MWCNT nanocomposites is more than one order in magnitude higher than those of pure PC. These results reveal that the presence of MWCNT in PC/MWCNT nanocomposites is possibly confined and retarded the segmental chain motion of PC.

Jindal et al.[15] evaluated dynamic mechanical properties of poly (methyl methylacrylate) (PMMA)/MWCNT composites. In between the frequency range of 50Hz to 210Hz they reported 10% improvement in storage modulus of 5% MWCNT/PMMA nanocomposites as compared to pure PMMA.

Xia et al.[16] used HNO_3 purified MWCNT and PU composites for dynamic mechanical thermal analysis for varying thermal conditions. They observed that modulus increased with increased of MWCNT content at room temperature and glass transition temperature decreased slightly.

2. Sample Fabrication

MWCNTs having diameter 50 nm were used to fabricate composites with PU beads. Solvent mixing approach[11] was adopted for fabrication of thin films of PU/MWCNTs which were transformed into small discs of 10 mm diameter and 5 mm thickness using compression moulding. PU beads were first ultrasonically dispersed with Dimethylformamide (DMF) solution. Various compositions (1%, 3%, 7% and 10%) were dispersed into same solvent by magnetic stirring to obtain a stable suspension. Both the solutions were added together and again dispersed ultrasonically for uniform dispersion of MWCNTs into PU matrix. Thin films of composites were casted from this solution by pouring the solution into glass petridish and allowing the solvent to evaporate. These films were then pressed into compression molding machine for fabricating disc shaped composites specimen having diameter of 10mm and thickness of 5mm. Field Emission Scanning Electron Microscopy (FESEM) was performed to validate the presence and dispersion of MWCNTs into PU matrix as shown in Figure 1.

3. Nano-Indentation

Nano-indentation tests were performed to evaluate static mechanical properties of PU/MWCNTs nano-composites with varying concentration of MWCNTs into PU matrix. Hysitron T1 950 TriboIndentor equipped with a Berkovich tip which is a three sided pyramidal tip with an included angle of 142.30 and tip radius of 150nm was used. Load of

500 μN was applied on pure and MWCNT/PU composite samples to obtain Load-displacement curves as shown in Figure 2. These Load-displacement curves were further used to find elastic modulus of the nano-composites as shown in Figure 3. Small indents were performed on the surface of sample and average values were taken as shown in Table1. From Figure 3 it is observed that the modulus of PU improves by addition of MWCNTs. The elastic modulus for pure PU is 25.7MPa while for 10wt% MWCNTs the value of modules is 57.7MPa, this correspond to improvement of 124.5% as shown in Table 1.

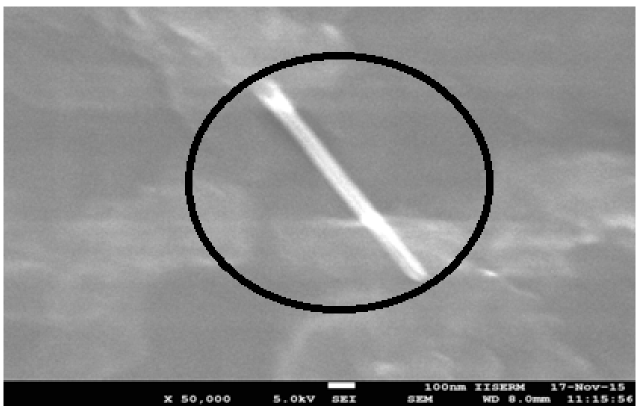

Figure 1. FESEM of 1wt% PU/MWCNTs composite.

Table 1. Improvement in elastic modulus

MWCNTs composition	0%	1%	3%	7%	10%
Elastic modulus (MPa)	25.7	30.9	37.9	52.2	57.7
percentage Improvement		20.2%	47.7%	103.1%	124.5%

4. Results and Discussions

Static mechanical properties were experimentally investigated for various compositions of MWCNTs in the PU matrix. Figure 2 demonstrates the load-displacement curves for various compositions (0wt%, 3wt% and 10wt %). These curves show loading and unloading for various compositions during indentation process with maximum load of 500μN. The final depth for pure PU was about 631 nm while 10wt% PU/MWCNTs composition showed final depth of 478 nm indicating enhancement of strength to indentation for 10wt% specimen. The elastic modulus of PU/MWCNTs composites also improved significantly, as shown in Figure 3. A noticeable improvement of 124.5% observed for PU/MWCNTs composite with 10wt% in comparison to pure PU.

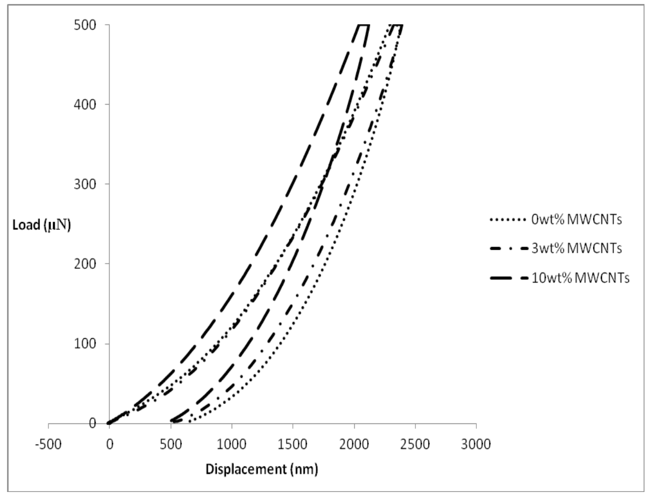

Figure 2. Load-displacement curves for pure PU and PU/MWCNTs composites.

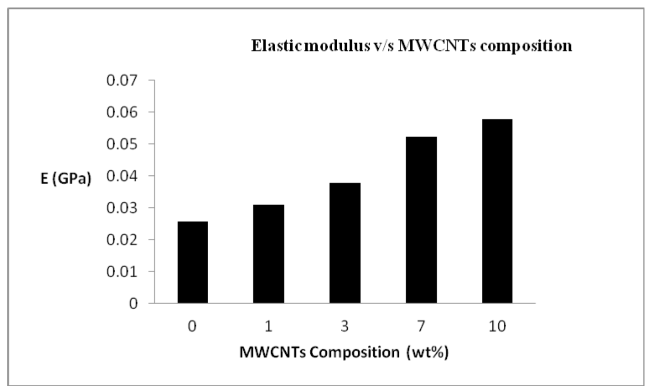

Figure 3. Variation in elastic modulus of PU/MWCNTs composites with varying MWCNTs compositions.

Presence of MWCNTs into PU matrix enhanced the static mechanical properties of PU/MWCNTs composites which makes it useful for fabrication of shoes, gloves and clothing material especially for armed forced personnel. Proper dispersion of MWCNTs in PU matrix enhances its adhesion[17] with PU and as MWCNTs posses better load transfer[18] properties therefore, it has been suggested that presence of MWCNTs enhanced modulus significantly.

5. Conclusion

This work presents the results of static mechanical characterization for elastic modulus obtained by nano-indentation performed on a MWCNTs based PU composites. These results show that addition of MWCNTs into PU matrix improves its static mechanical strength. Minor composition of 3% enhanced modulus by nearly about 50%. Further investigations on these composites can be done by using Dynamic Mechanical Analysis (DMA) and tensile testing to evaluate the mechanical behavior under variable tensile loading conditions.

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