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Role of carbon nanotubes in polycarbonate composites for modification in hardness

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Abstract

Nano-indentation technique has been used for mechanical characterization of multi-walled carbon nanotubes-polycarbonate (MWCNT-PC) composites. The composites was prepared by solution blending followed by compression molding. The amount of MWCNT was varied by weight from 0.5 to 10% in PC. Hardness increased by 68% for minor compositions (0.5%) of MWCNTs and increased to nearly 400% for compositions of MWCNT approaching 10% as compared to pure PC, indicating clearly the effective role of MWCNTs in better load transfer property. These results are in agreement with studies conducted for smaller compositions of carbon based nano-materials and also in other polymers.

Keywords: Nano indentation; composites; hardness.
PACS:62.25.-g, 68.35.Gy, 81.07.-b, 81.05.Ni, 81.05.Qk, 62.20.Qp.

1. Introduction

With the discovery of new Carbon based nanomaterials like fullerenes and carbon nanotubes (CNTs) [1-4], which have been found to have remarkable electronic, mechanical and structural properties, engineering applications have motivated the use of these materials in various areas, be it electronic or mechanical response. Further supplemented by ever increasing emphasis on nanotechnology, which has resulted in extremely unique characterization techniques at nano dimension, serious attempts have been made in recent years to make composites of these nanomaterials as reinforcements in matrix of various polymers and polycarbonates.

Polycarbonate (PC) is a light weight polymer which is available in bulk form and is widely used for several engineering applications due to its easy moldability. However, its drawbacks like low mechanical strength, limit its role in several applications. Therefore a material to make composites with CNTs, need to be explored in enhancement of the deficient properties. Apart from PC, many other polymers are extensively used with multi-

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wall carbon nanotubes (MWCNTs) which are also variants of CNTs but much cheaper compared to single walled CNTs. From mechanical engineering view point, some of the properties [5] which need to be investigated for any material before applying it into practical use are hardness, elastic modulus, stress-strain response to external load, elasticity, resilience, toughness etc. Among these properties, hardness resistance of the specimen to any external abrasion, scratch or indent becomes very important for static load applications. It is a complicated function of the grain size and composites tend to modify the size in comparison to host matrix grain size. A measure of hardness is usually obtained by using a nano indentation equipment [6, 7] and characteristics of an indent formed by a nano tip under a preset fixed load value for a given loading time are evaluated [8, 9] to determine the hardness. During this process, the maximum penetration depth (h_{max}) is calculated. After reaching the fixed load the indenter starts unloading and moves away from the sample towards its initial position. The indent in the sample starts recovering elastically and finally reaches a depth (h_f). Fig. 1 represents the general process of indentation on any specimen.

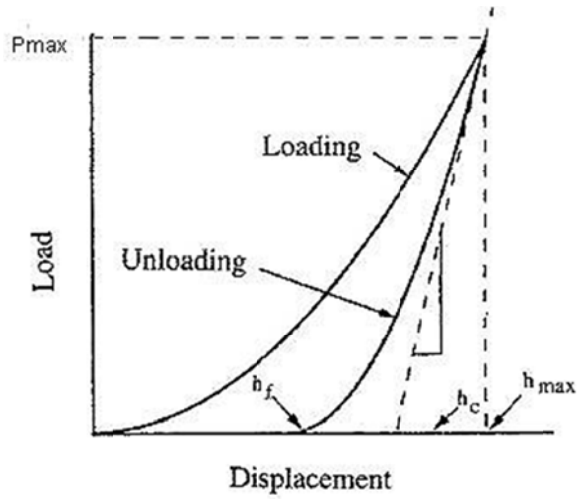

Fig. 1: General loading and unloading flow during Nano-indentation process.

The most commonly used tip is a three sided pyramid shaped diamond indenter tip, commonly known as Berkovich tip [9]. Based upon the labeling as indicated in Fig. 1, the hardness is calculated by $H = \frac{P_{max}}{A(h_c)}$, where $A(h_c)$ is the contact area as calculable from the measured indent under maximum load P_{max}.

Recently, results have also been reported pertaining to static load tests on composites comprising of MWCNTs other than PC as host matrix. When the host consists of neat nylon-6 (PA6) hardness (61MPa) increased consistently by 85% when composed of only 1% MWCNTs by weight [10]. Lower compositions of MWCNTs also showed improved results and these static properties also improved when other type static load tests were performed on them, however the values were very much different due to different loading directions. Few-layer grapheme (FG) reinforcement with polyvinyl alcohol (PVA) and poly (methyl methacrylate) (PMMA) was also tested for hardness using nano-indenter by Das et al [11]. For compositions of 0.6% FG in PVA, the hardness was found to be increased by almost 1.5 times than pure PVA. Similarly, FG reinforcement in PMMA improved the hardness by same factor. Effective load transfer and larger surface area of FG has been the suggested reason for this improvement. Another experiment conducted by Olek et al [12] observed that the presence of MWCNTs in the polymer poly (methyl methacrylate) (PMMA) did not improve any static mechanical property. The reason suggested for this was that the indenter

displaces the slippery MWCNTs due to which the actual measure was of PMMA matrix only. When the MWCNT composition was increased from 1 to 5%, the hardness still remained unaffected. Further, they coated MWCNTs with silica, this resulted in enhanced hardness for the composite. 4% MWCNT-silica in PMMA measured twice the hardness in comparison to pure PMMA.

Overall, a gradual increase in mechanical properties with increase in MWCNT composition in various types of polymers has been reported over the years.

In this paper, we investigate the effect of varying compositions of MWCNTs in PC on the hardness property which supplements the results of dynamic loading on similar samples reported by us already [13].

2. Sample Fabrication

We procured MWCNTs having diameter about 10-30nm and length 1-10 microns from Nanoshel Intelligent Materials Pvt. Ltd, USA. These were characterized using Fourier Transform Infrared Spectroscopy (FTIR) as shown in Fig. 2. The spectrum shows peaks at 1567cm^{-1} and 1176cm^{-1} which are indicative of the MWCNTs.

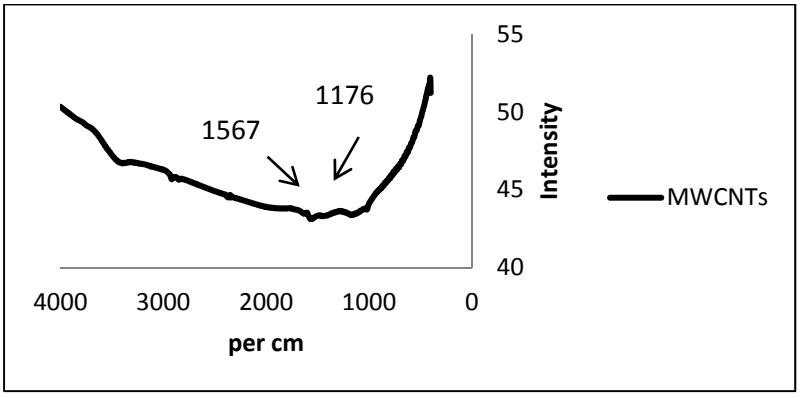

Fig. 2: FTIR spectra for MWCNTs with peaks at 1567cm^{-1} and 1176cm^{-1}

We adopted the solution blending method for fabricating composite films of MWCNT-PC [14] and then molded them into desired shape. Pure PC beads of about 1gram were dissolved in a solvent 10ml of Chloroform. The mixture was suspended and stirred to form a clear solution. Then MWCNTs of different weight % of PC were taken and ultrasonically dispersed in Chloroform to obtain stable suspensions. The PC solution and MWCNTs suspensions were then mixed together forming a series of different weight % (0.5, 0.75, 2, 5.0 and 10 wt %) compositions of MWCNT-PC mixtures. These compositions were then again ultra-sonicated to obtain a uniform dispersion of MWCNTs in PC. Thin films of thickness nearly 0.3mm were cast from this solution by pouring the solutions into glass petri dish and allowing the solvent to evaporate for more than 24 hours. These films were then characterized using FTIR. Fig. 3 shows the spectra for pure PC film whole Fig. 4 is the spectra for MWCNT-PC film. In Fig. 4 the peak at 1584cm^{-1} is visible while there is no such peak in Fig. 3. This peak is indicative of the MWCNTs presence. Scanning Electron Microscopy (SEM) image is shown in Fig. 5 which indicates the presence of randomly oriented MWCNTs in PC base matrix. These films were then separated from the petri dish and one by one broken into small pieces. For each composition, the small pieces were inserted in a small die of the compression moulding machine. After filling the die completely with these small pieces, a plunger was used to manually press a steel plate which

covered the die. The die was kept at high temperatures to facilitate melting of the films. After nearly 15 mins of pressing, the arrangement was allowed to slowly cool. Finally, the finished specimen in the form of a cylindrical disc of diameter 10mm and thickness 5mm was extracted from the die. Minor finishing operations like buffing were performed on the surface of the disc. After these operations, the discs were ready to be used for indentation testing.

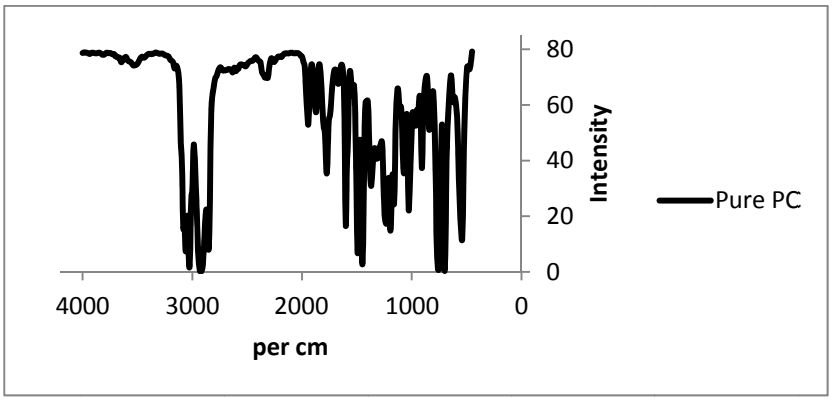

Fig. 3: FTIR spectra for pure PC.

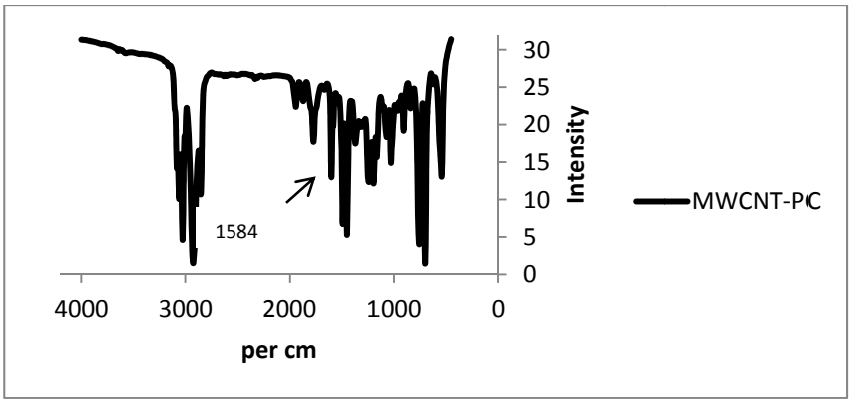

Fig. 4: FTIR spectra for 10% MWCNT-PC composite with a peak at 1584cm^{-1}.

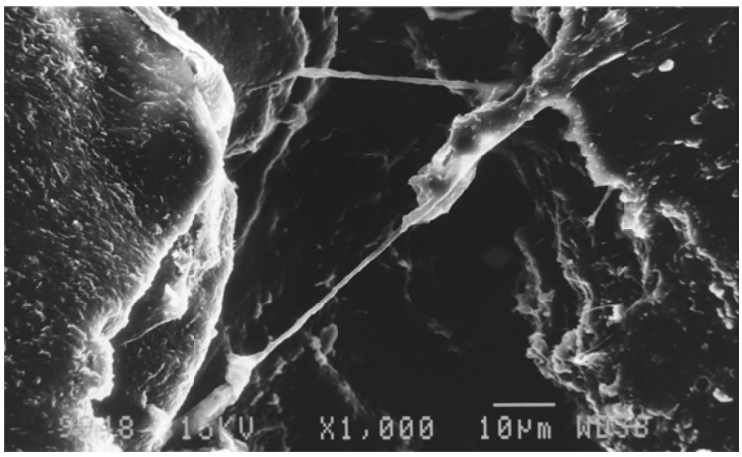

Fig. 5: SEM image for 10% MWCNT-PC composite.

3. Nano Indentation

Nano-indentation tests were performed on the above samples using Hysitron T1 950 TriboIndentor. Different compositions of MWCNT-PC composites were used as specimen for indentation and the results were then compared to the indentation results of pure PC samples.

Fig. 6 depicts the complete loading and unloading process for various samples which were subjected to a peak load of 1000μN. The figure indicates that both h_f, h_{max} (as discussed in Fig. 1) for samples comprising higher amounts (5% and 10%) of MWCNTs are much lower than that of pure PCs. Based on the equations given by Oliver and Pharr [8, 9] hardness is calculated. Fig. 7 depicts how penetration depth and hardness varies as MWCNT composition increases in PC.

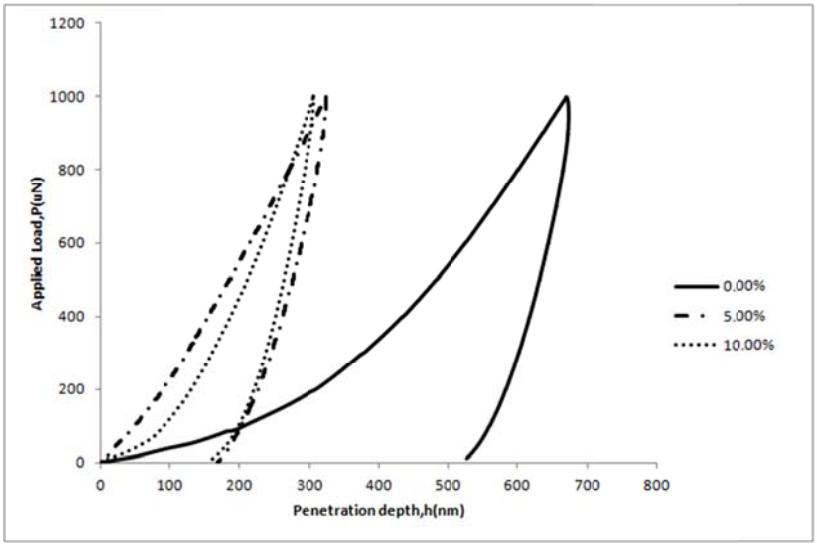

Fig. 6: Loading and unloading curves for various compositions under a static applied load of 1000μN.

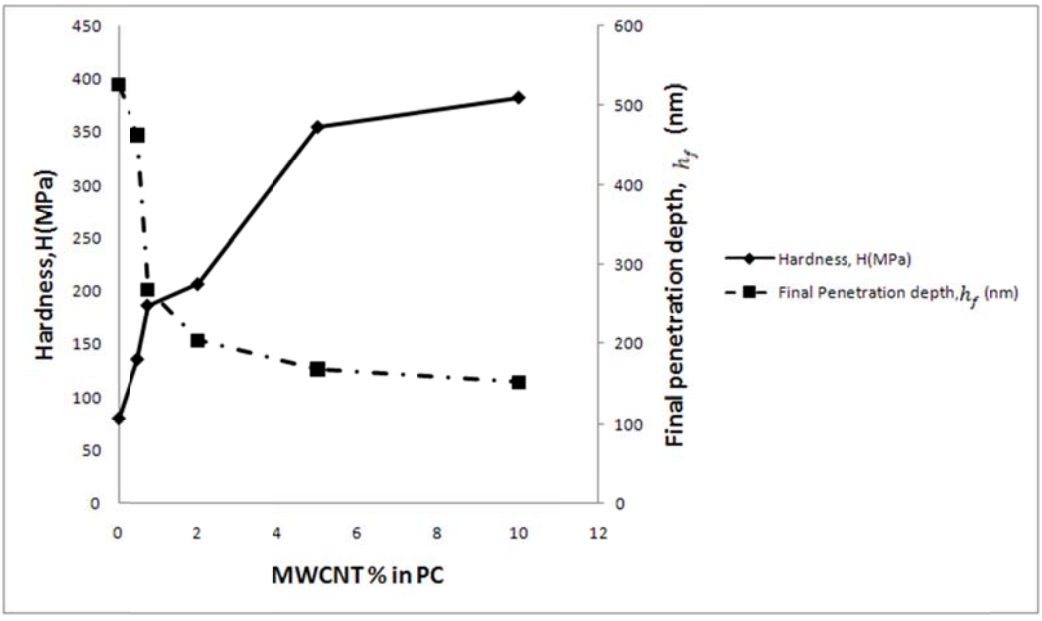

Fig. 7: Variation of hardness and penetraion depth with MWCNT composition in PC.

4. Results and Discussion

It is clear from Fig. 7 that hardness increases consistently as MWCNT composition increases in PC. As we can observe hardness for 10% composition in comparison to 5% composition is only about 10% higher, but for minor compositions like 0.5% to 0.75% this rise is nearly 40%. This means that increase in composition of MWCNTs in PC tends to saturate the hardness effects. Vivekchand et al [15] have shown that MWCNTs enhance the load transfer capability in polymers which results in the enhancement of their mechanical properties. Apart from this, stronger π-π interactions between MWCNTs and the base material and high surface to volume ratio [11] of MWCNTs in base material enhance the overall strength of the composite. So, in this case also MWCNTs play a similar role with PC.

We had earlier investigated [13] the dynamic loading response on similar samples using Split Hopkinson Pressure Bar (SHPB). We had found that for low concentrations of 0.5% MWCNTs, the increase in dynamic strength was most significant while for higher concentrations of 5% MWCNTs, this increase was negligible. At low compositions, proper dispersion of MWCNTs ensured binding the PC with MWCNTs due to which the absorption capacity of the composite surface enhanced. From the results of this paper, hardness number which gives is a measure of local performance was found to be high because short range interactions get enhanced for higher concentrations of MWCNTs. However, apart from hardness other static properties also need to be evaluated to categorically find out the most suitable composition of MWCNTs in PC.

5. Concluding Remarks

This paper presents results of hardness obtained by a nano-indenter on MWCNT based PC composites with varying compositions of MWCNTs. The results indicate categorically that about 5% MWCNTs is sufficient to enhance the hardness of PC by a factor of nearly 4.5 using a simple solution blending fabrication technique. This increase in hardness enables usability of PC for several new applications related to severe loading conditions like stress protective shields, load resisting jackets and covers.

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