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Electro-elastic Properties of MWCNT/PMMA Nanocomposite Thin Films

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Abstract—*Objective of this study is to investigate the electrical and mechanical properties of free standing thin films of poly (methyl methacrylate) (PMMA) embedded with multi walled carbon nanotubes (MWCNT), prepared by solvent casting method. MWCNTs are dispersed in PMMA by ultra-sonication using a bath type ultrasonicator. The film resistance is measured using a 2 probe method and plotted as a function of MWCNT weight fraction. The percolation threshold for electrical conductivity is found to be 3 % of MWCNT in PMMA matrix. Mechanical properties of thin films are evaluated via monotonic tensile test using INSTRON equipment. The load-extension behavior, tensile strength and tensile strain at failure is plotted and compared with the neat polymer. Results are expressed as a function of weight fraction of MWCNT. Experimental results shown improvement in all parameters with increase in MWCNT weight fraction.*

1. INTRODUCTION

Exceptional mechanical, electrical and thermal characteristics of carbon nanotubes (CNT) make them promising nano-structured elements for developing polymer matrix based nanocomposite materials for numerous applications such as strain sensors, gas sensing, electro mechanical actuators and power electronics [1-4]. Besides to their structural superiority, CNT shows piezoresisitive effect. i.e. change in its electrical resistance when it experiences a strain and deformation. This effect provides an easy and direct energy/signal transduction mechanism between the mechanical and the electrical domains of CNT. Based on this property, several smart materials and sensors are being developed using single walled (SW)/multi walled (MW) CNT embedded in various polymer matrix materials for structural health monitoring applications [5-9]. Polymers, such as thermoplastics, thermosets and elastomers have been used to make polymer nanocomposites [10].

CNTs are strongest materials till date and are super elastic about 1-1.4 TPa and can sustain large deformations. The maximum strain of SWCNT is 10%, which is greater than most structural materials. These strong mechanical properties are due to the C–C covalent bonding and the seamless hexagonal network. CNTs possess high flexibility, low mass density, and large aspect ratio [11-13].

Among CNTs, Multi-walled carbon nanotubes (MWCNTs) are widely used because of the cost advantage. MWCNT are reported to exhibit excellent mechanical strength of 1 TPa of Young's modulus and excellent electrical properties [14-16]. The tensile strength, tensile modulus have been reported to be in the range of 37–100 GPa, 640 GPa to 2 TPa respectively while Poisson ratio to be around 0.14–0.28 [17-21]. These properties make MWCNTs an ideal filler material for nanocomposites. Additionally, CNTs exhibit outstanding high specific surface area and tend to agglomerate strongly. These properties represent a potential for developing actuators with high stress, high strain and low operating voltage.

In the past decade, numerous experimental studies on the electrical and mechanical properties of nanocomposites made from insulating polymers filled by CNTs have been carried out [22-23]. Adding carbon nanotubes (CNT) to a polymer improved the strength, electrical and thermal conductivity of the composite [24-25]. Electrical resistance responses of MWCNT reinforced in polypropylene (PP) nanocomposites under mechanical tensile loading are studied and percolation threshold of electrical conductivity is around 3.8 wt% was observed [26]. Pham et al. [27] developed carbon nanotube polymer composite films that can be used as strain sensors with tailored sensitivity. The films were fabricated by either melt processing or solution casting of PMMA with MWCNT.

Mechanical properties of the nanocompopsites are studied by several researchers and reported improvement due to CNT. Coleman et al. fabricated composites based on poly(vinyl alcohol) demonstrating an increase of ×3.7 in Young's modulus and ×3.9 in strength by adding less than 1 wt% of CNTs [28]. Many authors have also reported the use of functionalized CNTs to improve the mechanical properties in polymer–CNT composites [29-31]. These treated nanotubes are blended with pure PMMA in solution before drop-casting to form composite films. Increases in Young's modulus, breaking strength, ultimate tensile strength, and toughness of ×1.9, ×4.7, ×4.6, and ×13.7, respectively, are observed on the addition of less than 0.5 wt% of nanotubes [32].

In this paper, electrical and mechanical properties of MWCNT/PMMA nanocomposite films fabricated by solvent casting method are determined. Simultaneous drying and ultra-sonication technique is adopted to avoid the re-agglomeration of MWCNT within the matrix to give away MWCNT/PMMA free standing film. A range of composite dispersions with various nanotube mass fractions were formed. Load-elongation measurements were then taken for a range of films fabricated from these dispersions. Mechanical parameters such as the load and elongation of the composite at break, ultimate tensile strength and failure strain displayed significant improvement in the presence of MWCNT. The data is compared with that of the neat polymer film.

2. EXPERIMENTAL

2.1 Materials

MWCNT of diameter 3-10 nm and length 40-50 µm produced via vapour deposition technique was purchased from Sigma Aldrich, New Delhi (India) and used them without any further treatment. Poly (methyl methacrylate) (PMMA) (m.w.,4,95,000) purchased from SD Fine Chemicals. Tetra hydrofuran (THF) (HPLC-grade) is used as a solvent and purchased from Ranbaxy Fine Chemicals. Transsonic Ti-H-5 Bath Sonicator (Elma make), 135 kHz is used for ultra-sonication. Fluke, 17B, digital multi meter is used for resistance measurements. Instron equipment is used for tensile testing of the nanocomposite films.

2.2 Methods

A certain quantity of MWCNT weighed and dispersed in THF using a bath sonicator for 3 hrs. Definite amount of previously dissolved PMMA-THF solution is added in to this and ultra-sonicated further for 1 hr. The viscous solution was poured in to a Petri dish. To prepare a range of composite mass fractions, definite quantity of PMMA first dissolved in THF using magnetic stirrer. To achieve a good dispersion, the solution was degasified for 30 min. using bath sonicator. Fig. 1 shows the steps followed in the preparation of MWCNT/PMMA film. The solvent is evaporated slowly by slow ultra-sonication (130 kHz, 30 %) to avoid re-agglomeration during drying. After initial solidification, the Petri dish is removed from the ultra-sonicator and further drying carried at room temperature. After 24 hrs, the films were carefully peeled off from the Petri dish and subsequently cured in a vacuum oven for 24 hrs at 60°C. Likewise three sets of films are prepared. The thickness of these free standing thin films are measured to be 100 µm approximately.

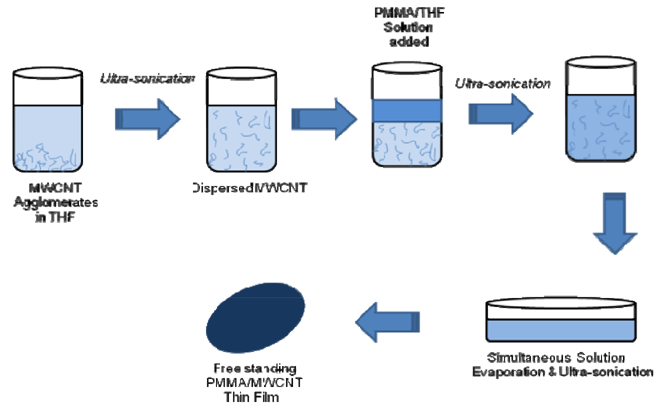

Fig. 1: Schematic illustration of fabrication of MWCNT/PMMA nanocomposite film via solvent evaporation technique.

3. RESULTS & DISCUSSION

SEM micrograph of MWCNT/PMMA thin film sample at 20 % weight fraction of MWCNT is shown in Fig. 2. It can be observed from the bundles of CNT that at this high weight fraction loading of CNT only a moderate dispersion could be achieved. Electrical resistance of the MWCNT/PMMA films are measured via a two probe method and shown as a function of MWCNT weight fraction in Fig. 3. When the CNT loading is 1 %, the film resistance is in the order of kilo ohms and reduced drastically to ohms with mere 3 % CNT loading. After this critical weight fraction there is no further significant improvement in the conductivity of the films. Hence, the electrical percolation threshold for

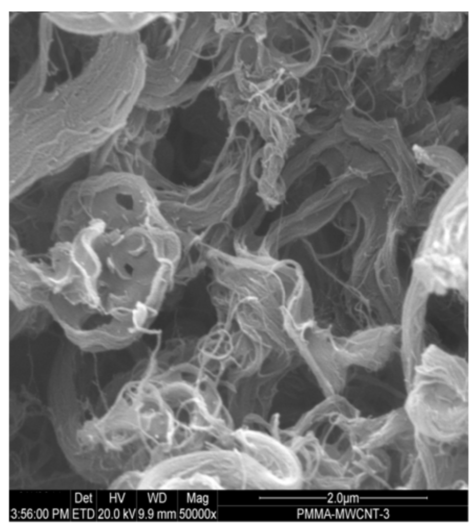

Fig. 2: SEM micrograph of MWCNT/PMMA thin film at 20 % of CNT weight fraction loading.

MWCNT in PMMA can be evaluated as 3 % of weight fraction. The inset in Fig. 3 shows change in electrical resistance up to 20 % of MWCNT loading. It can be observed that after 10 % of MWCNT loading the curve becoming flat.

Important parameters that affects electrical conductivity of the polymer nanocomposites are type of CNTs, the aspect ratio, their dispersion, type of matrix material and most significantly method of film preparation. For MWCNT/PMMA with the present solvent casting method an electrical percolation of 3 % weight fraction MWCNT is observed.

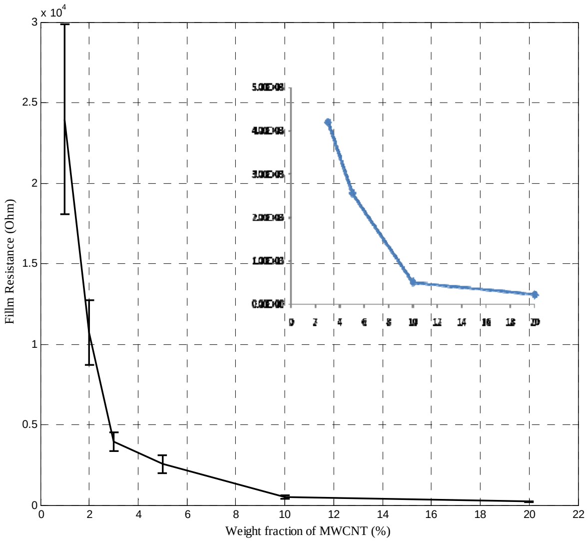

Fig. 3: Change in MWCNT/PMMA film resistance as a function of MWCNT loading.

Fig. 4: Tensile test setup

Mechanical properties of the thin films are evaluated via monotonic uniaxial tensile load-extension test using Instron equipment. Fig. 4 shows the tensile test setup. The MWCNT/PMMA film is carefully cut in to 45 mm X 5 mm pieces, free of any sharp edges to avoid shear failure during loading. Care is taken to minimize the Poisson's effects by selecting high aspect ratio specimen. The rate of loading is 1mm/min. Applied load and crosshead displacement are sampled at 10 Hz.

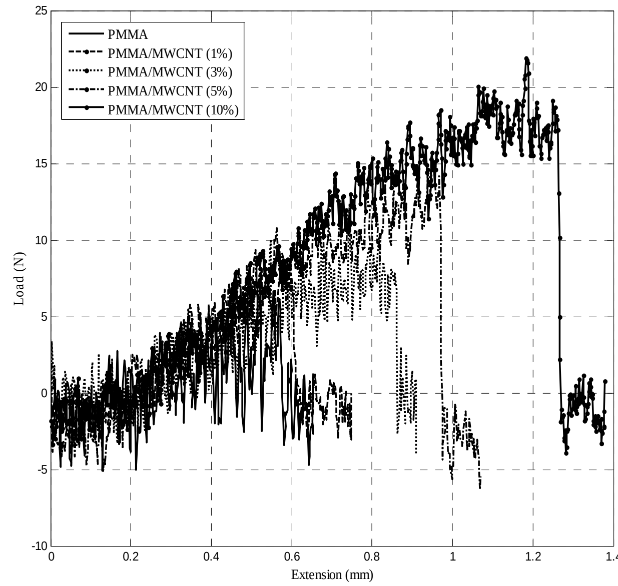

Fig. 5: Load and extension behavior of the MWCNT/PMMA composite films.

The load and elongation behavior, tensile strength and tensile strain at failure is plotted and compared with the neat polymer. Fig. 5 shows the load and film extension behavior of MWCNT/PMMA nanocomposite films. It can be observed that as the weight fraction of MWCNT increased, the strength at film fails and the elongation of the film are increased. The data is compared with that of the neat PMMA film of the same thickness.

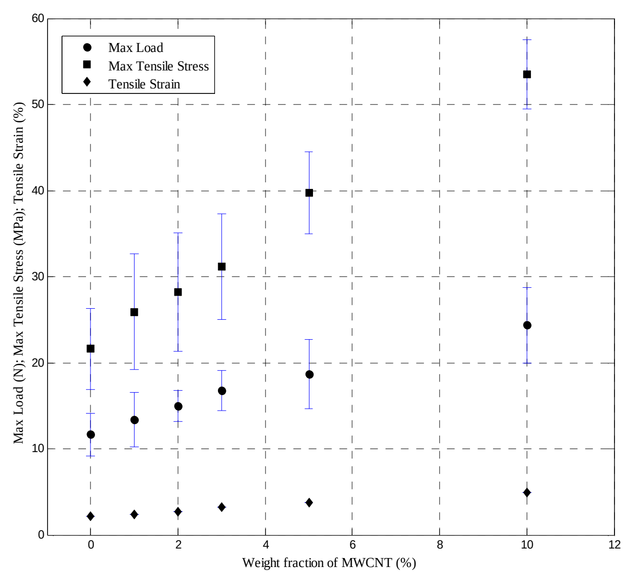

Fig. 6: Variation of maximum load carrying capacity before failure, maximum tensile stress and tensile strain at failure as a function of weight fraction of MWCNT.

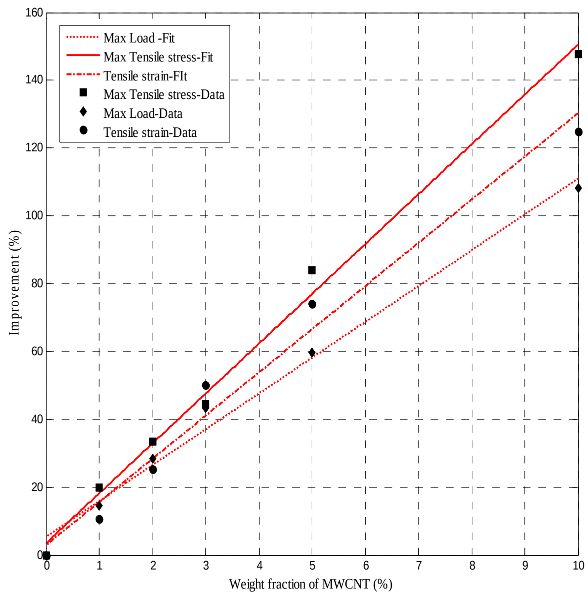

Fig. 7: Improvement in mechanical properties of the MWCNT/PMMA nanocomposite films as a function of weight fraction of MWCNT.

Maximum tensile stress and failure strain of the nanocomposite films are calculated from experimental load-elongation response and shown in Fig. 6. The maximum film strength of neat PMMA is observed to be 11.68 N and as the MWCNT weight fraction is increased, the strength of the films increased and at 10 % MWCNT film strength of 24.34 N is observed. Similarly for 10 % MWCNT loading 53.48 MPa of Tensile stress is observed as compared to the 21.59 MPa of the neat polymer film. Same trend is also observed in the failure strain of the films. Tensile strain for 10 % MWCNT loading is improved to 4.91% from 2.18 % for neat PMMA film. Fig. 7 shows, improvement in mechanical properties of the nanocomposite film as a function of MWCNT weight fraction. Data shows a liner fit in the improvement of mechanical properties. It is evident that as the loading of MWCNT in increased, the mechanical properties of the films are improved. For mere 1 % of MWCNT there is 20 % improvement in tensile strength, and 10 % improvement in failure strain is observed. For 10 % weight fraction of MWCNT film strength and failure strain are improved by 148 % and 125 % respectively.

4. CONCLUSION

In summary, MWCNT/PMMA nanocomposite thin films are prepared via solvent casting method and a novel technique of simultaneous sonication and slow evaporation is adopted to avoid the re-agglomeration of MWCNT during final stage of film forming. Three sets of nano-composite thin films are prepared to have statistical data. Experimental results shows that addition of MWCNT in to PMMA matrix, improved the electrical conductivity and mechanical properties. For a MWCNT/PMMA nanocomposite film prepared by solvent casting method, electrical percolation of 3 % weight fraction of MWCNT is observed. Mechanical properties are also improved due to MWCNT loading. With 10 % MWCNT loading, 148 % improvement in tensile strength, 125 % improvement in the failure strain under tensile loading is observed.

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