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CNT/POLYMER NANOCOMPOSITE AS AN ADVANCED LIGHT WEIGHT ENERGY STORAGE SYSTEM

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ABSTRACT

Interest in flexible, safe and light weight energy storage devices based on nanocomposites meet the various requirements of modern technology. The performance characteristics of energy devices are fundamentally determined by structural and electrochemical properties of electrode material. Electrolyte choice (aqueous or non-aqueous), limiting power capability and packaging designs is the other important factor in supercapacitor and batteries. In present study, multiwall carbon nanotube (MWNT)/polystyrene (PS) nanocomposites have been synthesized by solution cast method and characterized by X-ray diffraction (XRD), dynamical mechanical analysis (DMA), dielectric analysis and cyclic voltammetric measurements for their use in energy storage system. Enhancement in capacitance due to incorporation of MWNTs in polymer matrix reveals availability of more specific surface area as well as conductivity.

Key words: CNT, Nanocomposite, Energy storage, Light weight, Polystyrene.

INTRODUCTION

Interest in ultra thin, flexible and safe energy storage devices meet various design and power needs of modern gadgets. To build such fully flexible and robust electrochemical devices, multiple components with specific electrochemical and interfacial properties need to be integrated into single units[1,2]. Composite units are used to build various flexible super-capacitor, battery, hybrid and dual storage battery in supercapacitor devices. The thin free standing nanocomposite paper devices offer complete mechanical flexibility during operation. The supercapacitors operate with electrolytes including aqueous solvents, room temperature ionic liquids (RTIL) and bio electrolytes over record temperature ranges.

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These easy to assemble integrated nanocomposite energy storage systems could provide unprecedented design ingenuity for a variety of devices operating over a wide range of temperature and environmental conditions. CNT/polymer nanocomposites have been widely investigated due to unique properties of CNT such as large aspect ratio, good mechanical and thermal stability[3,4]. However, these properties of CNT/polymer nanocomposites strongly depend on the extent of CNT dispersion and strength of interfacial adhesion. The relationship between surface area, total pore volume, average pore size and pore size distribution of the material has a strong influence on the electrochemical characteristics of resulting capacitor[5,6]. Usually, electrolytes employed in electrochemical capacitors are acids, bases or salts dissolved in aqueous or organic solvents. Ionic liquids have been also investigated in super capacitors[7]. The use of corrosive liquid electrolytes may cause dangerous leakages, which decrease safety and lifetime of capacitors[8]. Good behaviour can be expected from multiwalled (MWNTs) and single walled (SWNTs) nanotubes due to their low mass density, morphology, mechanical properties and porous structure[9]. Electrochemical energy can be stored in two ways. In a battery, charge storage is achieved by electron transfer that produces a redox reaction in electroactive materials. In a supercapacitor, charge storage process is non-Faradaic, that is ideally no electron transfer takes place across the electrode interface, and the storage of electric charge and energy is electrostatic. Because the charging and discharging of supercapacitor involve no chemical phase and composition changes, such supercapacitors have a high degree of cyclability.

Here, we show that these basic components, the electrode, separator and electrolyte can all be integrated into single contiguous nanocomposites units that can serve as building blocks for a variety of thin mechanically flexible energy storage devices. Such a modification induces Faradaic pseudo capacitance effect apart from electrostatically charges accumulation. Several works[10] have demonstrated suitability of these methods to improve carbon nanotubes capacitance and consequently, their applicability as electrodes in supercapacitors. To reduce problems associated with the management of corrosive ionic conductors, as well as to allow preparation of thin film cells with high reliability, use of polymer has been proposed. In the present study, MWNT/PS nanocomposites have been tested as light weight energy storage system.

EXPERIMENTAL

Synthesis of MWNT/PS nanocomposites has been performed by taking MWNTs (d = 10-12 nm, length = 30 μm) in concentration range (0.01-0.05 wt. %) using solution cast method[11]. Solution casting is a method for fabricating nanocomposites with high uniformity but the quality may depend on the solvent removal and sonication time. In solution casting, polymer separately dissolved into solvent like dichloromethane and MWNTs separately

dissolved in benzene. The mixture of PS solution and MWNTs sonicated for two hours more after that it is casted into a petri dish floating on mercury for getting uniform thickness. Subsequently, it is subjected to solvent removal to get the final product. In present study, X'pert Pro diffractometer operated at 1.6 kW (i.e. 40 kV and 40 mA) with Cu-Kα (λ = 1.40526 Å) has been used for structure analysis. For dielectric analysis, Wayne Kerr (Model 6500B) has been used. For surface morphology, SEM (CARL ZEISS SUPRA-40) has been used.

RESULTS AND DISCUSSION

X-ray diffraction

Fig. 1 shows X-ray diffraction spectra for PS and MWNT/PS nanocomposites. Spectrum for pristine MWNTs is shown in inset of Fig. 1. A sharp (002) Bragg reflection at 25.80 is derived from ordered arrangement of concentric cylinders of graphitic carbon[12]. This peak is of small intensity for MWNT/PS nanocomposites.

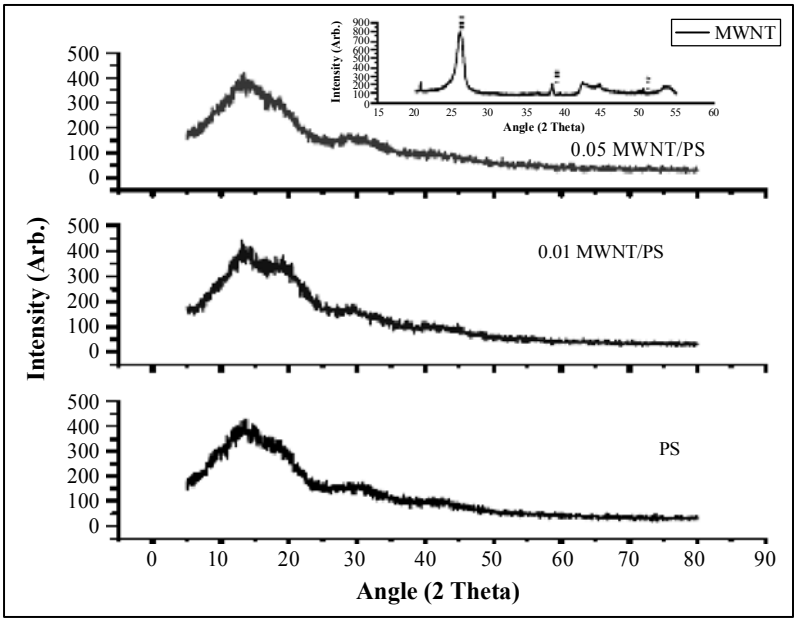


Fig. 1: X-ray diffraction spectra for MWNT/PS nanocomposites

Polystyrene polymer is amorphous in nature and peak obtained for this is at 13.60. The sharpness of peak at 13.60 increases on increasing MWNTs concentration in polystyrene matrix attributes generation of crystallinity in PS matrix[13].

Dynamic Mechanical Analysis (DMA)

DMA has been used to measure the mechanical properties of the MWNT/PS nanocomposites. DMA can be used to examine elastic and viscous properties of a polymeric material and its composites. The storage modulus (E) represents elastic properties of the polymer and demonstrates stiffness and loss modulus (tan ð) represents viscous properties of the polymer[15]. Figure 2 (a) and (b) show dynamic mechanical results for the MWNT/PS nanocomposites. Datas have been recorded at 1 Hz from 20 to 140^{o}C. A strong step change in the storage modulus (E') is evident beginning around 110^{o}C for all samples. This step change is an indication of the glass-rubber relaxation process, which also appears as a peak in the tan δ curve. As expected, the storage modulus of PS nanocomposites (2.0 GPa) increases by dispersing MWNTs in low concentration i.e (0.01-0.03 MWNT/PS) composites, it reaches to 3.1 GPa, which corresponds to 1.5 times the storage modulus of pristine PS matrix. The storage modulus for MWNTs was supposed to be about 1.28GPa reported in literature[16]. Experimental results obtained for MWNT/PS composites are consistent with the theoretical results produced by Halpin and Kardos[17].

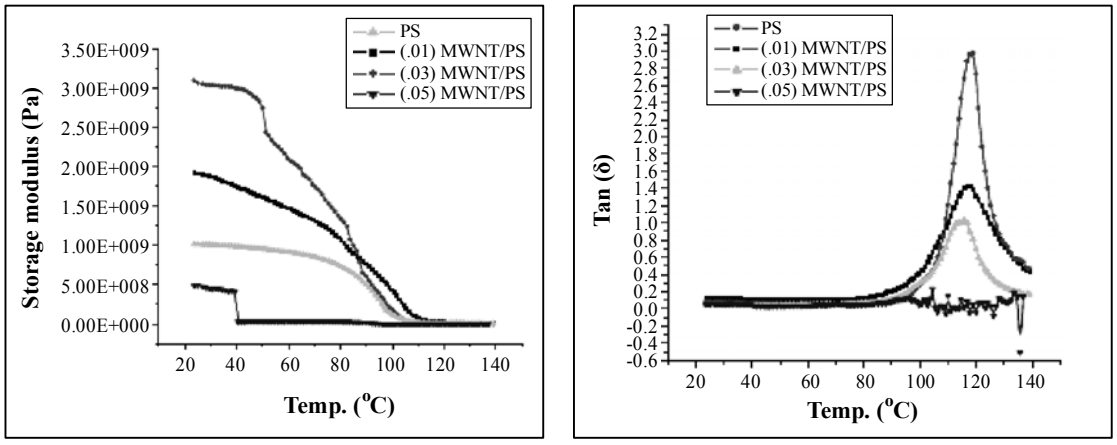


Fig. 2: (a) Storage modulus vs temperature and (b) Loss factor vs temperature for MWNT/PS Nanocomposites

A slightly enhanced glass transition temperature for the MWNT/PS nanocomposite vs pristine PS corresponds to peak of the loss tangent. It has been suggested that enhancement of storage modulus and glass transition temperature results from strong interfacial interaction between polymer and MWNTs. At higher concentration, decrease in storage modulus and glass transition temperature may be due to agglomeration of MWNTs in PS matrix or plasticizer leading may be there.

Cyclic voltammetry

Fig. 3 shows cyclic voltametric characteristics for MWNT/PS nanocomposites. Cyclic voltammetry is most widely used technique for acquiring qualitative information about electrochemical reactions.

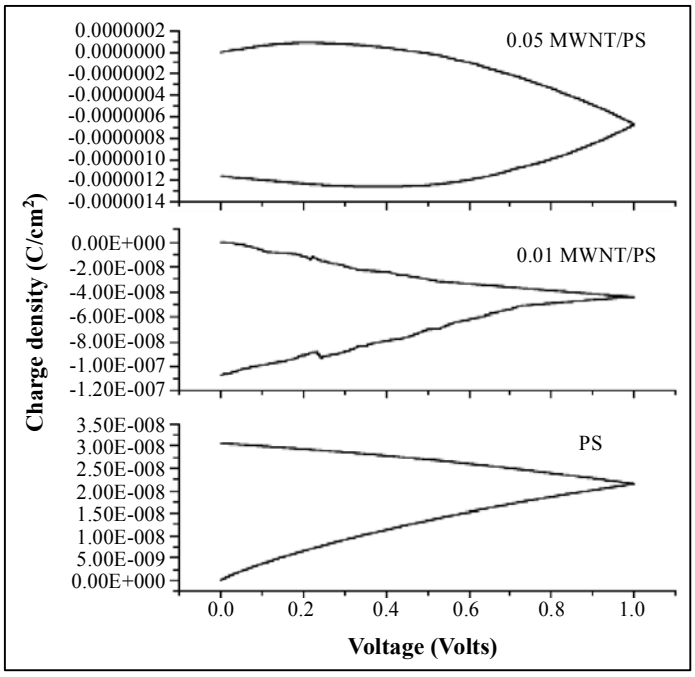


Fig. 3: Cyclic Voltammetric response for MWNT/PS nanocomposites

It offers a rapid location of redox potentials of the electroactive species. In the present study, C-V characteristics have been measured at scan rate of 50 mV/s in the potential range 0-1 V by using electrolyte of 1M KOH. The composites present various shapes due to varying concentration of MWNTs in PS matrix. It is observed that on increasing the MWNTs concentration in PS matrix, the stability in specific capacitance of composites is high, decay of this value with cycling is much lower than for the pristine PS matrix. Surface that is accessible to electrolyte ions can contribute to charge storage; therefore, role of pore size, pore structure, surface properties and conductivity of electrode materials is important. This storage mechanism allows for very fast energy uptake, delivery and high stability of electrochemical double layer (EDLCs) capacitors during millions of charge/discharge cycles. In contrast to EDLCs, pseudo capacitors involve Faradaic (i.e. redox) reactions between the solid electrode materials and electrolyte[18].

Dielectric analysis

Fig. 4 shows frequency vs dielectric constant for MWNT/PS nanocomposites. Frequency dependent dielectric measurement have been used in order to characterize capacitive and conductive nature of MWNT/PS nanocomposites at room temperature in frequency range (100 Hz-10 KHz) by using Wayne Kerr 6500 LCR meter. The dielectric constant has been measured across thickness of the nanocomposite by using the formula –

$$\in' = Cd/\in_0 A \quad \ldots(1)$$

Where C, is capacitance of nanocomposite, d is sample thickness and A, is surface area of composite, ε_0 is dielectric constant in vacuum (8.854×10^{-12} F/m) and A (effective area) = πr^2

The effect of MWNT concentration on dielectric constant of MWNT/PS nanocomposites at 100Hz is shown in Fig. 4. It can be seen from Fig. 4 that dielectric constant increases on increasing concentration of MWNTs. This interesting difference of dielectric constant of different nanocomposites can be understood by interfacial polarization. Interfacial polarization arises for electrically heterogeneous materials, where two phases differ from each other. The interface polarization takes place, when electron oriented under electric field. Finally, interfacial polarization results in an increase in dielectric constant due to random mobility of charge carriers, which gets trapped at interface of a multiphase material with different conductivity. The interface across PS and MWNTs may be a source of the large dielectric constant, So higher concentration of MWNTs will increase number of interfaces, which will result in increase of dielectric constant.

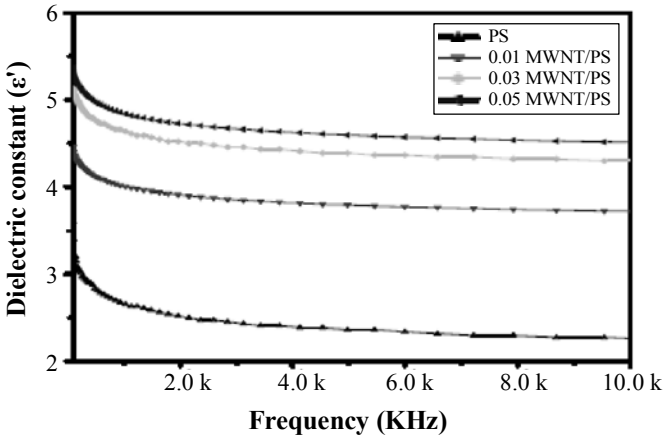
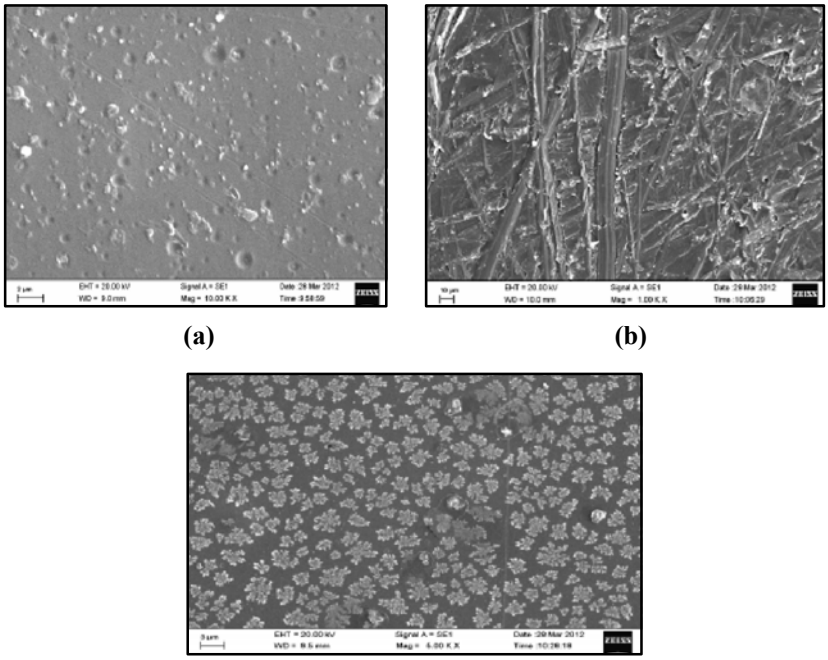


Fig. 4: Frequency vs dielectric constant for MWNT/PS nanocomposites

Scanning electron microscopy (SEM)

To investigate dispersion of MWNTs in polystyrene (PS) matrix at microscopic scale, SEM observations have been performed for MWNT/PS nanocomposites by varying MWNTs concentration in polystyrene matrix.



(a) **(b)**

(c)

Fig. 5: SEM images for (a) PS, (b) 0.01 MWNT/PS and (c) 0.05 MWNT/PS nanocomposites

As expected, dispersion of MWNTs at higher concentration is obtained agglomerated in nanocomposites. A large aggregate of MWNTs is shown in Fig. 5(c). According to images observed by SEM, it can be concluded that at higher concentration, nanotubes take curved type shape instead of being straight. Based on these observations, Fischer et al.[19] illustrated that the reduction of storage modulus at higher concentration may be due to curvature of CNTs.

CONCLUSION

XRD results show amorphous nature of polystyrene (PS) and generation of crystallinity on increasing MWNTs concentration in PS matrix. DMA results show enhanced

storage modulus at low loadings. C-V characteristics show stability in specific capacitance for MWNT/PS composites. Dielectric constant has been found to increase on increasing MWNTs concentration in PS matrix. It can be concluded that if a capacitor with long durability is needed, composites are preferable. SEM images show well dispersion of MWNTs in PS matrix and surface morphology. The well dispersability of MWNTs in PS matrix obtained at low concentration while at higher concentration, it gets agglomerated. Finally, it can be concluded that well dispersed MWNT/PS nanocomposites can be introduced and can be utilized as an advanced electrode for storage of energy.

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