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Development of polyurethane multiwall carbon nanotubes (MWCNTs) novel polymeric nanodielectric material



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ABSTRACT

Polyurethane/multi-walled carbon nanotube nanodielectric thin films of 25 µm thick were prepared by solution grown method. The microstructure of the nanodielectric was examined by scanning electron microscopy. The MWCNTs are observed to be dispersed in PU matrix well apart from a few of clusters. The MWCNTs/polymer nanodielectrics characterized with decrease in energy band gap and crystallinity. The analysis of dielectric properties of the composite samples of different weight ratio was studied by measuring the permittivity and tangential loss at room temperature. The frequency dependent permittivity obeys the percolation theory. Further, it has been observed that the dielectric properties of PU and PU nanodielectric are unaffected by UV-irradiation. XRD characteristics confirm the formation of PU/MWCNTs nanodielectrics.

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Introduction

Polymer nanodielectrics are polymer matrices reinforced with nano-scale fillers such as metal oxide nanoparticles, metal nanoparticles, nanofibres, carbon nanotubes etc. This new class of composite materials have shown enhanced mechanical and physical properties. The later include improved optical, electrical and dielectric properties [1]. The fascinating physical properties and unique structure of carbon nanotubes (CNTs) are receiving steadily considerable attention since their discovery in 1991 by lijima, because of their exceptional electrical and mechanical properties [2,3].

A polymer/MWCNTs nanodielectric is having multifunctional properties due to strong interactions of carbon nanotubes with polymer matrix and extremely large interfacial area. Thus, alignment of MWCNTs in the polymer matrix has a predominant role on the mechanical and electrical properties of polymer/MWCNTs nanodielectrics. The main challenges in nanodielectric materials are to improve the dispersion and alignment of MWCNTs in a polymer matrix. Recently, Thostenson et al. reviewed MWCNTs and their nanocomposites materials [4]. Carbon nanotubes can be dispersed uniformly in polymer matrix by aggressive chemical modification of the surface with acids or by the use of a surfactant prior to dispersion. The use of ultrasonic energy in solution of PU/MWCNTs allows the uniform dispersion of MWCNTs and to incorporate them into composites without chemical pre-treatment [5].

The addition of carbon nanotubes (CNTs) in polymer matrix is expected to improve the electrical properties due to the outstanding electrical properties of MWCNTs. MWCNTs are not only highly efficient conductors of heat and electricity [6,7], but also have a excellent tensile modulus and strength from 270 GPa to 1 TPa and 11–200 GPa respectively, this is 100 times that of steel with only one-sixth the weight (density is ~1.3 g/cm³). MWCNTs are thermally stable up to 2800 °C in vacuum, their thermal conductivity is twice that of diamond and their electrical conductivity is 1000 times higher than that of copper wires. Thus, the electrical conductivity of MWCNTs will greatly affect the energy band gap of insulating polymers [8].

Banda et al. [9] successfully used the electrospinning technique to align single wall carbon nanotubes in the polymer matrix, for improvement of electrical and the mechanical properties of the polymer. Recently, Rui Zhang et al. [10] has been reported the formation of conductive network in thermoplastic polyurethane with addition of carbon nanotubes by melt method. The conductivity of composite was enhances many times.

Permittivity is applied to explain the dielectric properties of polymer and polymer nanocomposites with respect to frequency and temperature. The behaviour of dielectric characteristics is



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different for lower and higher frequencies. The number of special features has been reported on polymer/MWCNTs nanocomposites in literature such as excitation of localized electronic states resulting in high intrinsic permittivity [11]. The microwave permittivity is found to be exhibited linear frequency dependent [12,13]. These results are demonstrated the scope for obtaining polymer/MWCNTs nanodielectrics with microwave properties which are more diverse than those obtainable with other types of carbon fillers, e.g., with various types of dispersive dielectrics, with high dielectric constant but having relative low tangential loss, and tunable dielectric under small bias voltage [14].

The morphology of MWCNTs nanodielectrics is responsible for dielectric properties. Dielectric spectroscopy is a high frequency technique to study the relaxation mechanism in polymeric material. It represents a method, which has been successfully applied to investigate the microscopic electronic structure of pristine and nanodielectric materials [15–22]. Therefore, we expect that this method can lead to new insights in MWCNTs filled PU systems too. In the present work, we will focus on improvement of dispersion by simple method and develop the polymeric nanodielectric material based on polyurethane and multiwall carbon nanotubes.

Experimental procedure

The Polyurethane was procured by Redox (India) and Multiwall carbon nanotubes of (i.e. outer diameter 20 nm and length 50 nm) were procured by Reinste India. The dimethylformamide (DMF) was used as received from Merck India Ltd. The pristine polyurethane and nanodielectric sample were prepared by solution grown method.

Some of techniques are applied for functionalization of MWCNTs surface such as use of surfactants, oxidation or chemical functionalization of surfaces. Chemical methods may be more effective, particularly for polymer and ceramic matrices. Physical blending and in situ polymerization are used for improving dispersion in case of MWCNTs reinforced polymer composites. The 5g Polyurethane was dissolved in 50 ml of dimethylformamide (DMF) at 60 °C with continuous stirring of 4h. However, MWCNTs are functionalized in dilute H₂SO₄. The solution was kept for 2h in magnetic stirrer at 60 °C. After that MWCNTs were mixed slowly in Polyurethane solution. Further, the solution was sonicated with the frequency of 33 kHz (sonicator model D-250, Aicil India Ltd.) for the period of 30 min. The optically plane glass plates are slowly drawn from solution and put in the oven at 60 °C for 2h and then oven is switched off. The films are allowed to dry for 24 h at room temperature with outgassing of 10^{-5} torr to remove the moisture and other volatile contents. The circular thin films were easily removed from glass plates of diameter 3.5 cm. Thickness of the film was observed to be 25 µm. Permittivity and tangential loss was measured by using LCR meter (Hioki 3532-50). UV-Vis was recorded by using Hitachi double beam spectrophotometer (Hitachi U-2800). SEM and XRD were recorded by Scanning Electron Microscope (EVO-40, ZEISS) and the powder X-ray diffraction (XRD) patterns respectively. The XRD characteristics were performed by PANalytical X'pert PRO X-ray diffractometer using CuK_α radiation at 45 kV and 35 mA diffraction angles between 5 and 65° with a graphite secondary monochromator. SEM-EDX and XRD was recorded from Jawaharlal Nehru University, New Delhi (India).

Results and discussion

Scanning electron microscopy (SEM)

Fig. 1 (a) and (b) are showing the SEM images of pristine polyurethane and PU/MWCNTs nanodielectrics. It has been observed that nanodielectric image is quite different than pristine PU. The microscopic distribution of MWCNTs in PU matrix is observed to be almost uniform. However, it is observed from Fig. 1 (b) that MWCNTs are agglomerated in some places of polymer matrix because of less or more interaction. The agglomeration of MWCNTs in PU matrix is also reported by Joanna Ryszkowska [23]. The MWCNTs interacted with PU and changes the bulk structure of PU. Overall MWCNTs appeared to be showed good dispersion in the PU matrix. The most possible reason of dispersion in polyurethane is the molecular backbone contained large amounts of polar groups, such as -CONH-, $-CH_2-O$ - had more compatibility with MWCNTs that possessed high surface energy.

X-ray diffraction studies (XRD)

XRD spectra of pristine polyurethane and PU/MWCNTs nanodielectric films are shown in Fig. 2. Pristine polyurethane and PU/ MWCNTs nanodielectric films shows that semicrystalline and characterized by two peaks. The position of pristine PU and MWCNTs peak is very close to each other. The position of MWCNTs peak observed at $2\theta = 25$ as has been reported in literature [24]. PU/ MWCNTs nanodielectric shows two peaks, first peak observed at 19.96, 19.67 and 22.32, second peak observed at 25.99 and 26.05 with respect to different wt%. These two peaks depict the characteristics peak of PU and MWCNTs respectively. The appearance of second peak in nanodielectric thin film is an evidence for the presence of MWCNTs in PU matrix. This spectra shows that the peak intensity and full-width at half maximum (FWHM) increases with increasing wt% of MWCNTs. The average crystallite size L, have been calculated by Scherer formula:

$$\mathcal{L} = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where β is the FWHM of the peak and k is the shape factor whose value is equal to 0.9. The lattice spacing and percentage crystallinity have been also calculated. The more details of calculation for XRD parameters are reported in our earlier publication [25].

The percentage crystallinity, FWHM and lattice spacing are listed in Table 1. The PU is a polar polymer of semicrystalline nature. Indeed, nanodielectric shows the decrease in % crystallinity with increase in MWCNTs contents in PU. The pristine PU show diffraction peaks at $2\theta = 23.7^{\circ}$ due to the presence of soft segments crystals. The X-ray pattern of the nanodielectric showed mixing of the peaks appearing for the MWCNTs and the pristine PU. The peaks assigned to nanodielectrics are anomalous in behaviour. PU containing MWCNTs showed much lower diffraction intensity as compared to pristine PU. This is a good agreement with the result reported in literature [26].

The peak intensity anomously decreased with content of MWCNTs in the nanodielectrics. From these result, it could be logically assumed that the PU crystallinity became lower with increasing MWCNTs concentration.

UV-Vis absorption spectra (UV-Vis)

UV–Vis absorption spectra of pristine PU and PU/MWCNTs nanodielectric are shown in Fig. 3. It shows that the absorption band is shifted towards lower wavelength side with increasing wt% of MWCNTs of PU matrix. In order to calculate the direct band gap of pristine PU and PU/MWCNTs nanodielectric thin film, the absorption coefficient (α) and photon energy ($h\nu$) were calculated by the relation using UV–Vis absorption spectra. The values of ($\alpha h\nu$)² were plotted as a function of photon energy ($h\nu$). From the intercept of the best-fit lines in the plots of ($\alpha h\nu$)² versus $h\nu$, the values of

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