

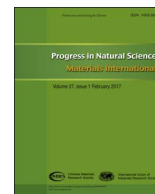
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Original Research

Enhancement of the thermal and mechanical properties of polyurethane/polyvinyl chloride blend by loading single walled carbon nanotubes[☆]A.M. Hezma^a, I.S. Elashmawi^{a,b}, E.M. Abdelrazek^{b,c}, A. Rajeh^{c,d,*}, Mustafa Kamal^c^a Spectroscopy department, Physics Research division, National Research Centre, Cairo, Egypt^b Physics department, Faculty of Science, Taibah University, Al-Ula, Kingdom of Saudia Arabia^c Physics department, Faculty of science, Mansoura University, Mansoura, Egypt^d Physics department, Faculty of Science and education, Amran University, Yemen

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ABSTRACT

Structural, thermal, and mechanical properties of pure blend and nanocomposites based on polyurethane (PU) and polyvinyl chloride (PVC) doped with low different content of single walled-carbon nanotubes (SWCNTs) were studied. The nanocomposites at different concentration were prepared via casting technique. The interaction between PU/PVC and CNTs were examined via FT-IR studies. The changes in the structures of the nanocomposites were examined using X-Ray Diffraction (XRD), and the results indicated that the amorphous domains of nanocomposites increased with increasing SWCNTs content. Transmission electron microscope (TEM) observation indicated that SWCNTs surface was wrapped with the polymer with the thermal properties of nanocomposites improved. The mechanical behavior of the nanocomposites was evaluated as a function of SWCNTs content. The main enhancement in tensile properties was observed, e.g., the tensile strength and elastic modulus increased compared with the pure blend, which may be attributed to the interaction and adhesion between CNTs and the polymer matrices due to the hydrogen bonding between carbonyl groups (C=O) of polymer blend chains and carboxylic acid (COOH) groups of CNTs.

1. Introduction

Carbon nanotubes (CNTs) have exceptional chemical, structural and physical properties, and have been utilized generally as good fillers to strengthen authentic polymer matrices and enhance its thermal, electrical and mechanical properties [1]. Nanocomposites (CNTs/polymer) have attracted an extensive consideration in the scholarly community due to their excellent characteristics including, thermal properties, strength and conductivity even at low dopant contents [2] which make them suitable for diverse applications such as electronic devices, polymeric composites, hydrogen storage and field emission display. Furthermore, CNTs aggregate easily and form bundles due to their interactions arising from the strong Vander Waals force and large smooth surface areas. These properties made them uniformly dispersed in polymer blends, as well as in either different organic liquids or in aqueous solutions. Various techniques are applied to enhance the dispersion quality of CNTs in polymer matrices. These CNTs functionalization can be accomplished by covalent/non-covalent methods [3], surfactant, in-situ polymerization [3], melt mixing [4,5], and organic solvent dispersion [6,7].

Moreover, the modification of the polymer and/or polymer blend by the nanofillers can improve their properties and reduce the cost of their nanocomposites [8]. In traditional polymer nanocomposites, inorganic nanofillers have been used to improve the pure blend properties. Also, the nanofillers used in the nanocomposites are prepared in different parameters, such as different shapes, volumes and sizes [9,10]. The new class of polymer nanocomposites is a type of material that is considered to be an alternative to the classical filled polymers. The good dispersion of inorganic nanofillers in the polymer matrices improves the performance properties of the pure polymer. SWCNTs as a nanofiller improves the thermal, electronic and mechanical properties of the nanocomposites [11,12]. One of the most popular polymers used in industrial applications is polyurethane because of its high performance properties. Generally, polyurethane is composed of a high molecular weight polyether macrodiol, and a hard segment which is composed of diisocyanate and low molecular weight diamine or diol. The addition of inorganic nanofillers into the PU matrix is the most effective method to improve its thermal and mechanical properties. PU/CNTs nanocomposites have the advantages of PU and CNTs and have some special functions that pristine polyurethane does not

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possess. PU/ MWCNTs nanocomposites were prepared via direct solution mixing as described by Koerner *et al.* [12] One of the most important polymers with many application fields is Poly vinyl chloride (PVC), which is widely used in construction industry, for floor coverings, window profiles, pipes, and wallpapers. Recently in our group, we have enhanced the electrical, mechanical, and thermal properties of poly vinyl chloride using MWCNTs [13–15]. In another extensive study of the better PU/PVC blend ratio, Hezma *et al.* have also found that for the PU/PVC blend, the ratio (75/25 wt%) PU/PVC was the best to get better compatibility and physical properties [16]. This paper studies the influence of SWCNTs doping on the structural, thermal and mechanical properties of PU/PVC with its potential to stand strongly to work in the field of wind turbines blades for electrical power generation.

2. Experimental section

2.1. Materials

PU (MW 330,600) was supplied by (Cargill-Dow, South Korea). PVC with high molecular weight was supplied by (Fluka, Romania). Tetra Hydro Furan (THF) was supplied by (Duksan, South Korea). Functionalized Single Walled Carbon Nanotubes (SWCNTs- HCOO) (NTX10) were supplied by (Nanotech, Greece) with average length $\approx 22 \mu\text{m}$, diameter between 5 and 15 nm and purity 95%.

2.2. Nanocomposites preparation

The Polyurethane and polyvinyl chloride(75/25) wt% were dissolved in THF as a solvent at room temperature with continuous stirring for one 24 h to get a homogeneous solution. Also the SWCNTs concentrations were 0.01, 0.02, 0.04, and 0.06 wt% of the total PU/PVC weight dissolved in THF with sonication for 1 h. The CNTs solution was added drop wise separately to polymer solutions with continuous stirring and occasional shaking in an ultrasonic until to give us a well dispersion of carbon nanotubes achieved.

Solution was poured into clean Petri dishes and left to dry at room temperature for 3 days to ensure the removal of solvent traces. After drying, films were peeled of the Petri dishes and kept in vacuum desiccators until use. The thickness of the samples was in rang of \approx (0.1–0.3) mm.

2.3. Structural and morphological analysis

FT-IR spectra of the samples prepared were studied by using single beam light, spectrometer (Nicolet iS10, USA). The spectra of the films were obtained in the spectral range of 4000–400 cm^{-1} . XRD examination was performed using PANalytical X'Pert PROXRD system (Holland) in reflection or transmission region, using Cu-K α target radiation (where $\lambda=1.540 \text{ \AA}$, and tube operating at 45 kV-40 mA) where, the Bragg's angle (2θ) in range of 10–80°.

High-resolution transmission electron microscopy from (JEOL-JEM-2100) attached to a CCD camera at an accelerating voltage of 200 kV was used to investigate the morphology of the SWCNT in polymer solution. The thermal degradation has been studied over a temperature range from 35 to 650 °C by using Shimadzu Thermogravimetric-45H under air environment at heating rates of 10 °C/min.

2.4. Mechanical properties

The properties of mechanical of pure blend and filled nanocomposites were scanned utilizing the tensile strength method on a universal testing machine (Lloyd Instruments Ltd, UK). Each sample was scanned at a crosshead speed of two mm / min at 25 °C.

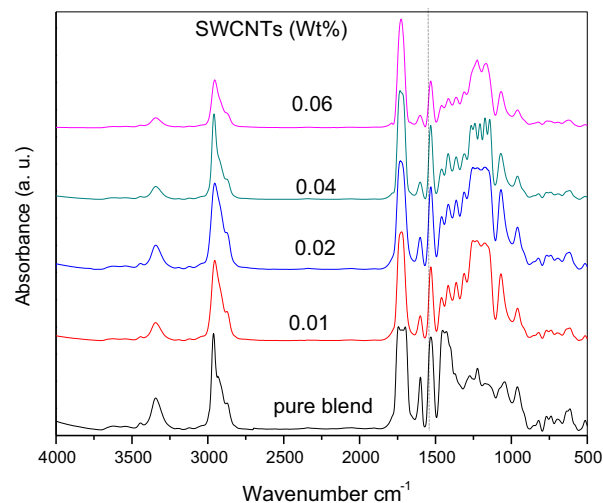


Fig. 1. FTIR spectra of pure PU/PVC and nanocomposites with different concentrations of SWCNT.

3. Results and discussion

3.1. Fourier transform infrared (FT-IR)

The FT-IR spectroscopy examines the structure and reactions between different chemicals. For polymeric material, the results of FT-IR spectra are utilized to investigate the types of chemical bonds and functional groups in polymeric structures.

The FT-IR spectra of pure blend and blend doped with low concentrations of SWCNTs in the range of 4000–500 cm^{-1} at room temperature is shown in Fig. 1. The FTIR spectrum of pure PU/PVC reveal the presence of the stretching mode of N–H group at 3342 cm^{-1} in PU. The two peaks at 2955 cm^{-1} and 2860 cm^{-1} are attributed to asymmetric and symmetric stretching of the –CH band, respectively [13,17]. The absorption band at 1730 cm^{-1} for free carbonyl group and at 1703 cm^{-1} are assigned for hydrogen bonded carbonyl group. The split of C=O peak observed in Fig. 1 is due to the existence of inter-hydrogen bonding in polymer matrices [16]. The peaks at 1620 cm^{-1} and at 1540 cm^{-1} are attributed to –NH bending vibration and C–C stretching respectively. The absorption bands at 1460 cm^{-1} , 1425 cm^{-1} and 1225 cm^{-1} ascribed to the alkane C–H bending, CH₃ stretching and C–N stretching vibration modes in the PU/PVC blend. The IR bands at 837 cm^{-1} is due to C–Cl stretching mode while at 1166 cm^{-1} is due to C–O stretching modes of urethane groups [18]. The FT-IR spectra for the nanocomposites (Fig. 1) show that intensities of the peaks 3341 cm^{-1} , 1621 cm^{-1} and 821 cm^{-1} decrease with increasing the ratio of CNTs. The peak at 1540 cm^{-1} shifts towards lower wavenumber which is attributed to chemical interaction between SWCNTs and PU/PVC in nanocomposites. These changes in the spectra confirmed interaction and complexation between SWCNTs and PU/PVC due to excellent dispersion of SWCNTs in polymeric matrix. Fig. 2 indicates the possible mechanism of interaction between PU/PVC and SWCNTs.

3.2. X-Ray Diffraction Analysis (XRD)

Fig. 3 shows XRD for PU/PVC and PU/PVC doped with different concentrations of SWCNTs. It is observed that XRD pattern of PU/PVC blend indicate a sharp peak at 21.7° and a small peak at 22.4° due to semicrystalline nature of pure blend [19].

The XRD data show a decrease in the intensity and increase in the broadening of the nanocomposites diffraction peaks with increasing the SWCNTs content. This could be due to the disruption of the PU/PVC crystallinity and the changing in the crosslink density of PU/PVC with increasing of SWCNTs content which decrease the crystallinity of

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