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Multi- walled carbon nanotubes reinforced polyurethane/polyvinyl chloride composite: structural and mechanical properties

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ABSTRACT

Nanocomposites based on (PU/PVC) polyurethane (PU) and poly (vinyl chloride) (PVC) loaded with low contents of multi walled carbon nanotubes (MWCNTs) were prepared using solution casting technique. The composition and structure of blend and nanocomposites were characterized by X-ray diffraction (XRD),Transmission electron microscope (TEM), and Differential scanning calorimetry (DSC). The X-ray study indicated that decrease crystallinity of polymer blend after addition of carbon nanotubes due to interaction between carbon nanotube (CNT) and the polymer matrix in the nanocomposites. Thermal stability was studied by Differential scanning calorimetry (DSC) analysis. The obtained data from these study described that the glass transition temperature (Tg), melting point (Tm) and degradation temperature (Td) of the samples were increased with an increase of different concentrations of MWCNTs. The behavior of thermal stability were enhanced. Mechanical properties were calculated by tensile universal testing machine. All results data showed well dispersed of MWCNTs in polymer matrix at all weight percentages.

Keywords: Nanocomposites; X-ray; Thermal stability; Mechanical properties.

INTRODUCTION

One useful techniques for developing materials with many different of properties is Polymer blending. The properties exhibit often in polymer blending which can be better in comparison to the properties of each one individual component polymer [1–3]. Blend systems have main advantages are simple preparation and simple of charge of physical properties by compositional change [4,5].There is considerable desire for the study regarding of polymer matrices due to their importance in technical aspects and academic. Particularly, much attention has become paid to phase behavior and miscibility in polymer matrix[6,7]. There are measurements utilized tostudy the phase behavior and miscibility of polymer matrix. To be able to examine phase behavior and miscibility of polymer matrix, DSC continues to be much utilized for the determination of T_g[8]. A miscible polymer blend would show a single transition between T_g of these two components. There's a broadening in the transition with increasing immiscibility, whereas an incompatible system could be marked by separate transitions of the polymer components in the blends [9] .

PU is known due to the has high toughness and wear resistance, however, poor heat resistance and low modulus[10,11]. Polyurethane are normally modified by introducing PVC to create flexible materials with improved hydrolytic, environmental stability, and chemical [12].PVC obtained generally by suspension and emulsion polymerization has become widely used in some industries. PVC has disadvantages for example poor thermal stability, low-notched impact strength, and huge melt viscosity. Blending of Polymer is a method for the enhancement of new polymeric matrix[13,14].The MWCNTs discovery by Iijima were produced at e high temperatures via use of an arc discharge between electrodes of graphite[15].Carbon nanotubes have won increasingly more and more intense interest since their discovery due to their unique structural, mechanical properties[16,17]. However, the processing of CNTs has become restricted to limited by their insolubility generally in most common solvents, because of the strong inter-tube vander Waals attraction[18].The addition MWNTs into the PVC increased its mechanical properties at low concentration MWNTs[19]. MWNTs with chlorinated polypropylene to reinforce polyvinyle chloride used by Blake et al.[20].This paper study influence of chemical structure of MWCNT on the structure and mechanical properties of PU/PVC to use in wind Turbines to produce energy.

MATERIALS AND METHODS

Polyurethane (PU) (average molecular weight of 330600)Cargill-Dow, South Korea.Tetra hydro furan (THF)was supplied by Duksan pure chemicals, Korea. High molecular weight polyvinyl chloride (PVC) supplied by (Fluka). THF wasutilized as solvent for the PU and PVC. Polymer blend was prepared byutilizing a casting technique. Different weight concentration, of PU/PVC 00/100, 75/25, 50/50, 25/75 and 100/00, and then the polymer blend solution was stirred continuously about 24 h at room temperature until a homogenous viscous liquid was formed. After complete dissolution onto on the glass plates until allow the solvent to evaporate. The resulting PU/PVC samples were then dried at room temperature in a vacuum oven for four days toensure all traces of solvent have already been removed. The films whose thickness ranges from100–270 μm.

XRD scans were observed utilizing PANalytical X`Pert PRO XRD system utilizing CuKα radiation where, the tube operated at 30 kV, the Bragg's angle (2θ) in the range of 10-80°, λ = 1.540 Å). Transmission electron microscope (TEM), (JEOL-JEM-2100, Japan) was utilized to study the shape, size, and distribution of the nanoparticles within the polymeric matrix. DSC of prepared samples was carried out by utilizing (SETARAM labsys TG-DSC 16) which has heating rate of 10 ^{o}C min^{-1} from room temperature to 550 ^{o}C. For tensile testing, a computer controlled Lloyd LRX5K mechanical testing machine (Lloyd Instruments Ltd, UK) was used.

RESULTS AND DISCUSSION

3.1. X-ray diffraction (XRD)

XRD patterns of nanocomposite films are presented in Fig.1. Nanocomposites films shows that semicrystalline and characterized by two peaks at 2θ = 21.6º and 22.3º. Composite containing MWCNTs showed much lower diffraction intensity, compared to pure blend. Peaks become broadened with reduced intensity with addition of MWCNTs ascribed to a decrease of crystallinity in polymer blend with increasing of the MWCNTs concentration. Also can be ascribed to the changing in the crosslink density of blend with an increase CNTs concentrations [21]. Which inferred that the multi walled carbon nanotube considerably affect the well short-range microstructural phases of both hard and soft segments of the PU in polymer blend[22]. This can be ascribed to the presence of strong interfacial interactions between MWCNTs and polymer blend. furthermore, the bundled or individual nanotubes also influence the resulting steric hindrance effect of hard and soft phases of PU in polymer matrices [23]. No new sharp peaks pertaining to CNT appeared in complexes, indicating partial /complete dissolution of the CNT in polymer blend. [24]. The degree of crystallinity (K) of polymer nanocomposites is calculated as [25]:

$$K = \frac{A}{A^{-}} \times 100$$

Where A is the total area of peaks (area of crystalline and amorphous peak) and A^{-} is the total area under diffraction pattern. The peaks intensity decreased with content of MWCNTs in the composites. From this result, it could be logically assumed that the PU/PVC crystallinity became lower with increasing MWNTs concentrations in the polymer blend. This is a good agreement with the results in Table 1

3.2. Transmission electron microscope (TEM) analysis

Figure 2 a shows TEM of pure MWCNTs where it can be observed that no amorphous carbon stays in the MWCNTs. And also, are smooth, indicating no impurities on the surfaces and distinguishable from the others images. The CNT consist of long tubes with hollow cores as an observed insert image Fig.2a and many layers, indicating that they are multiwall with diameter is 6–15 nm. . From the TEM image of (PU/PVC) - MWCNT composite (Fig.2 b), it can be seen that MWCNTs homogeneously disperse in polymer solution matrix and form uniform entangled (PU/PVC) - MWCNT network. Images of TEM for specimen where some dark features can be observed. The presence of such some spots (Fig.2c) can be ascribed to covalent linkages between chains of polymer and MWCNTs. [26]. Fig.2 d show nanocomposites chains wrapped the nanotubes increasing their thickness in some regions as arrow indicates. The change of the diameters is more dramatic at the end of MWCNTs (Fig. 2d), which suggested that the more oxidation occur at the end of the nanotube. This leads to more polymers grafted to the oxidized site, namely, the end of the nanotube. Also after addition shows the micrograph of MWCNTs dispersion in polymer matrix. MWCNTs disperse well in polymer, which results in uniform dispersal. MWCNTs are implanted uniformly in the polymer and have close contact with these polymeric matrix Fig.5 d shows a TEM image of (PU/PVC) with MWCNTs where it can be chains wrapped of the nanotubes increasing their thickness in some locales; As a consequence, we believe such perfect wrapping would be the result of covalent grafting. The external diameter of the (PU/PVC) - MWNT is not uniform, which is probably dependent on the thickness of layer polymer. And providing strong evidence of well functionalized PU/PVC on the surface of MWCNTs[27].

3.3. Differential scanning calorimetry (DSC)

Thermal techniques are the appropriate tool to determine the chemical and physical changes like phase transitions, glass transition temperatures (T_g), melting point T_m, and decomposition temperature T_d. A temperature from 30–450 ^oC at a heating rate of 10 ^oC/min was used under nitrogen atmosphere. The properties of thermal for (PU/PVC) and their nanocomposites were examined by Differential scanning calorimetry to evaluation, how the thermal transitions of the prepared samples were influenced by the various amount of MWCNT.

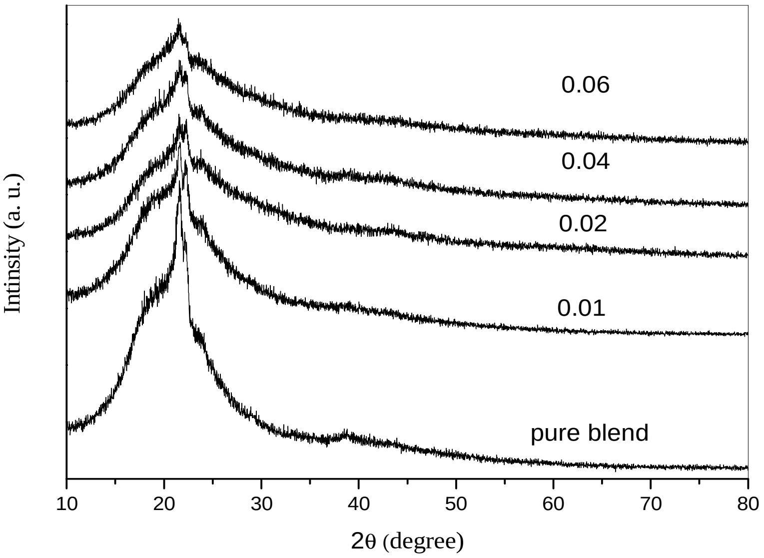

Fig. 1: X-ray diffraction of (PU/PVC) with different concentrations of MWCNT

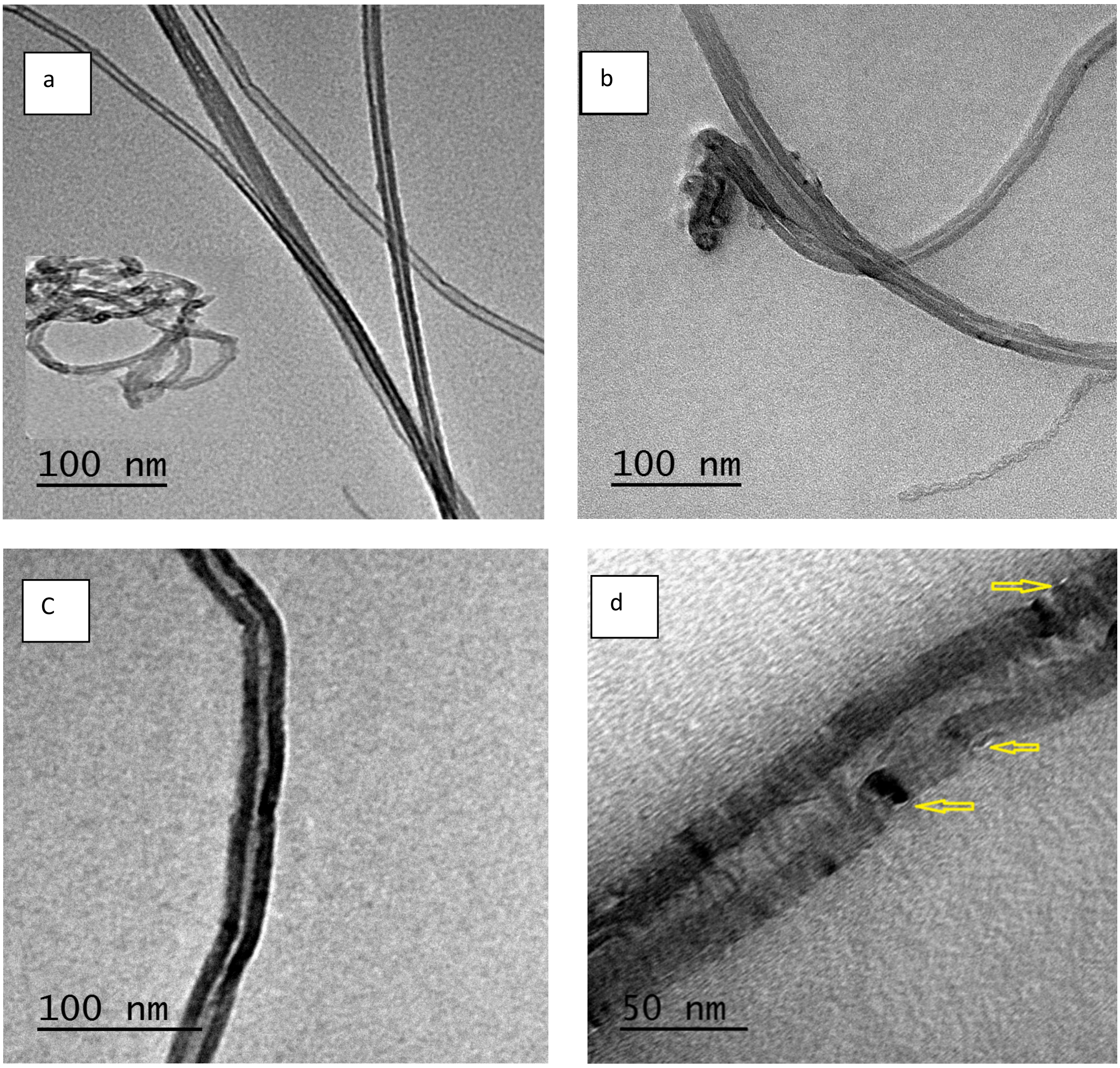

Fig.2: TEM micrographs for: (a) pure MWCNTs; (b), (c) and (d) (PU/PVC)-MWCNTs at 0.01, 0.02, 0.06 Wt. % concentrations respectively

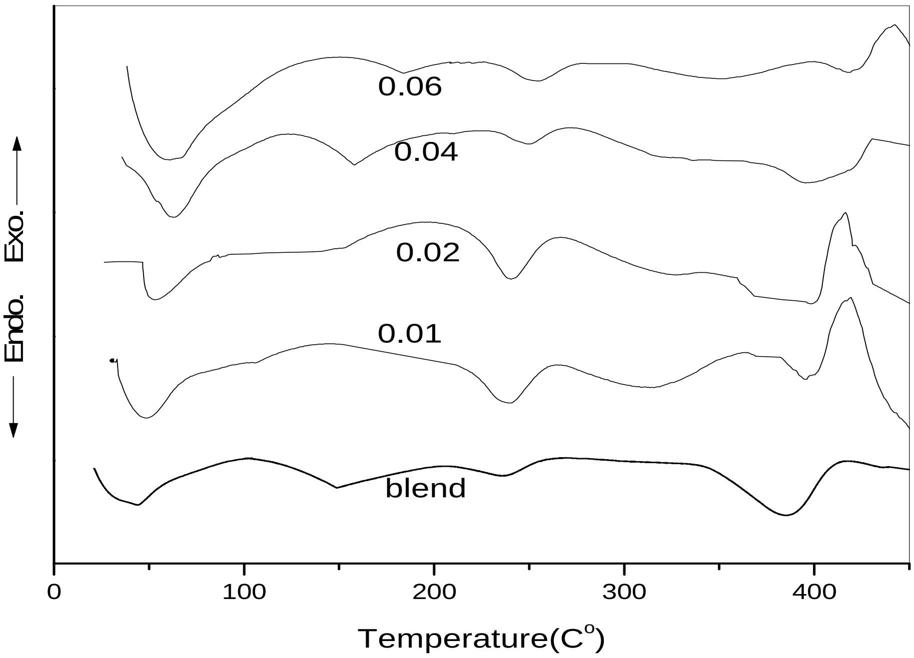

Fig.3: DSC thermograms of (PU/PVC) with different concentrations of MWCNT

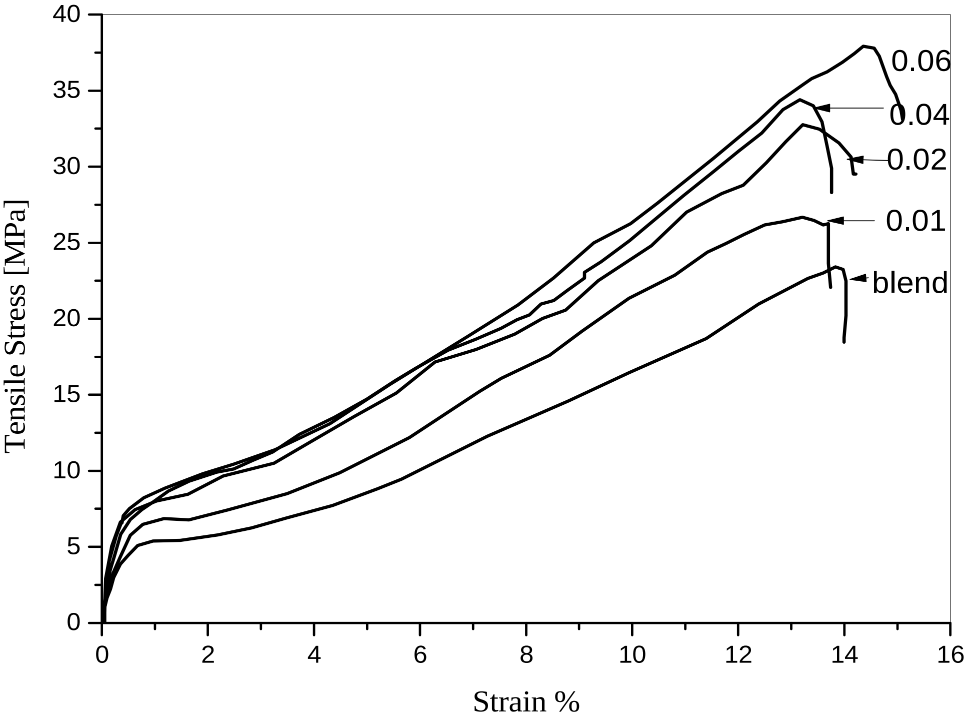

Fig.4: Stress -Strain curves of (PU/PVC) with different concentrations of MWCNT

Table (1) DSC parameters for (PU/PVC) with different concentrations of MWCNT

(PU/PVC) MWCNT (Wt.%)	Glass transition temperature T_g (°C)	Melting temperature T_m (°C)	decomposition temperature T_d (°C)	Crystallinity (%)
0.00	45	233	383	55
0.01	50	238	397	45
0.02	54	242	400	30
0.04	63	250	405	25
0.06	65	256	420	20

Table (2) Mechanical properties of (PU/PVC) with different concentrations of MWCNT

Sample (PU/PVC) MWCNT (Wt. %)	Tensile strength (MPa)	Elastic modulus (GPa)	Toughness (MJ/m3)	Elongation at break (%)
0.00	23.3	1.1	1.65	1340
0.01	27.1	1.6	2.10	1330
0.02	32.7	1.7	2.65	1317
0.04	34.4	1.78	2.66	1322
0.06	39.4	3.8	3.43	1475

From Fig. 3 we observed a single glass transition temperature (T_g) in the range of about 40-67°C, evidencing the blend's miscibility, However, it should be borne in mind that the utilization of temperature glass in evaluation of polymer/ polymer miscibility is based on the premise that a single T_g shows that the domain size is down domains diameter(dd), where (2< dd< 15) nm [28].Melting point (T_m) and decomposition temperature (T_d) and glass transition temperature (T_g) are reported in Table 2. The transitions presented in Fig. 6 and summarized in Table 2. It is observed that the position of glass transition temperature (T_g) resulting from the micro-Brownian motion of the main chain backbone, shifted to higher temperature with addition CNTs may be due to increase of branching and steric effects in the polymer matrix molecules. A broad transition at about 144 °C can be attributed to the a relaxation process $T\alpha$ associated with crystalline regions, endothermic crystalline (T_m) and endothermic (T_d) peaks also slightly shifted toward higher temperature than pure blend these lead to improvement of thermal stability for samples after addition CNTs [29]. These change results is attributed to the molecular interactions between polymer blend and MWCNTs and good dispersion of MWCNT in polymer matrices.

3.4. Mechanical properties

Tensile test was performed to study the effect of MWCNTs on the properties of mechanical for PU/PVC composite. The properties of mechanical for the composites should be better than those of the polymer matrix if MWNTs could be well distributed in the polymer matrix. The tensile strength and modulus of the pure polymer blend and composites containing the MWNTs can be calculated from stress- strain curve in Fig.4. It is clear that the addition of MWCNTs in polymer matrices increased the modulus and tensile strength, which suggests that the pure blend became more resistant to deformation[23]. Finally, the modulus and tensile strength of the nanocomposites enhanced from 1.1 GPa in pure blend to 3.8GPa and 23.3 MPa from to 39.4 MPa, respectively, when the CNTs concentration reached 0.06 Wt.% in nanocomposites as shown in Table 3. These results indicate that the mechanical properties of nanocomposites are substantially superior to pure blend, probably due to the reinforcement of dispersed high performance MWNTs with the polymer matrices and strong interaction between MWNTs and polymer matrix. Carboxylic groups located onto the MWNT surface will react under formation of covalent bonds with the polymer blend, thus resulting in significantly enhanced interfacial adhesion this is confirmed by X-ray and TEM. Following the similar trend of the increases of strength, strain and toughness of the nanocomposites is substantially enhanced, with increase toughness of (PU/PVC)-MWCNT from 1.65 MJ/m^3 to 3.43 MJ/m^3 indicating that composite become much more energy absorbing before rupture, attributed to the reinforcement of the carbon nanotubes.

CONCLUSION

X-ray data of the nanocomposites revealed a peaks for the blend, indicate that MWCNTs influence the short range structure of hard and soft segments phases in polymer matrices, resulting in strong interfacial interactions between nanocomposites. DSC results showed that the glass temperature T_g, melting temperature T_m, and degradation temperature T_d somewhat increased with inclusion of MWNT, which suggested the functionalized MWNT substantially affected both amorphous and crystalline structure in the polymer matrices and show single glass transition temperature for pure blend this finding shows that this blend system is only miscible. TEM images indicated that MWNTs were dispersed well in polymeric matrix. The broken ends of MWCNTs revealed that the nanotubes broke aside instead of being pulled out of the fracture surface. Mechanical tests indicated that incorporating of MWNT drastically enhanced the tensile properties, toughness and elastic modulus of the nanocomposites without having to sacrifice the elongation at break by the addition of MWNTs. The homogeneous dispersion of MWNTs through the polymer matrix at reduced MWNT loading and existence of strong interfacial adhesion between MWNTs and polymer matrices lead to the significant enhancement of overall material properties of the (PU/PVC)-MWNT nanocomposites. From these results, the PU/PVC-MWCNT nanocomposites can be used to produce wind turbines to power generation.

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