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Preparation and Properties of Multiwalled Carbon Nanotubes/Poly (Vinyl Chloride) Nanocomposites

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Abstract

The functionalized multiwalled carbon nanotubes/Poly (vinyl chloride) (F-MWNTs /PVC) films were prepared by solution casting technique. The F-MWNTs were functionalized by Friedal-Craft acylation reaction, which introduced p-amino benzoic acid on the surface of nanotubes. The scanning electron microscopic (SEM) studied presented that the F-MWNTs were dispersed well within the PVC matrix. The morphological studied also presented that the F-MWNTs embedded well within the polymer matrix. The mechanical properties (tensile strength, modulus and elongation at break) of the F-MWNTs/PVC nanocomposites were increased up to an optimum level (F-MWNTs 2 wt %) and then decreased gradually when the quantity of nanotubes increased in PVC. The decrease in mechanical properties might be due to the agglomeration of F-MWNTs at high concentration. The thermo gravometric analysis (TGA) thermograms showed that the thermal stability of the F-MWNTs/PVC nanocomposite, which was improved as compared to neat PVC. The DSC and rheological studies were also performed for neat PVC and MWNTs/PVC nanocomposites.

Introduction

Carbon nanotubes (CNTs) are graphene sheets which rolled into a tubes and attained considerable interest because they display a wide range of unique chemical, electrical, mechanical, and optical properties [1-3]. The CNTs are either metallic or semiconducting properties, which depend on their charility and diameter and that make them an ideal reinforcing filler in composite materials [4].

The CNTs have high elastic modulus (1 TPa) Khalid Applid Polym Sci, thermal conductivity (3000 $WM^{-1}K^{-1}$), Specific surface area (10-20 m^2/g), [K Saeed Review on CNTs], and aspect ratios of CNTs vary from 500 to 100 000]. Due to these exceptional properties, researchers have paid great attention to utilize these remarkable characteristics of CNTs for various engineering applications like polymeric composites [5], hydrogen storage [6], actuators [7], chemical sensors [8], and nanoelectronic devices [9]. However, the CNTs have unique properties and wide range of applications in various fields but dispersion of pristine CNTs are great problem because they are present in the form of bundles and ropes due to a vander Waals attraction among the tubes. This problem can be overcome by chemical functionalization of CNT, which disperses CNTs in an organic solvent [10], water [11,12], or polymer matrix [13]. Non-covalent functionalization is another technique that can be used to modify carbon nanotubes, and which does not destroy the conjugation system in the carbon nanotubes. A number of routes to the non-covalent modification of carbon nanotubes have been reported such as polymer wrapping [14], the adsorption of amine [15], and radiofrequency glow-discharge plasma modification [16].

The various properties like electrical conductivity, mechanical properties, optical and thermal conductivity of majority of polymeric materials are low, which can be improve by the incorporation of even a minute quantity of CNTs. For example, Park et al studied the effect of carbon nanotube pre-treatment on dispersion and electrical properties of melt mixed multi-walled carbon nanotubes / Poly(methyl methacrylate) Composites [17]. Liu et al studied the effect of spinning conditions on the mechanical properties of MWNTs/polyamide-6 nanofiber filaments and they were found that the mechanical properties increases when the concentration of MWNTs were below 0.8 wt % [18]. Ni et al studied the shape memory effect and mechanical properties of CNTs/shape memory polymer nanocomposites and they were investigated that the CNT/ shape memory polymer nanocomposites showed a good shape memory effect [19]

PVC is an important commercial thermoplastic, which is widely used in construction and industrial fields due to its durable, low cost and good properties. However, its brittleness, low thermal stability and poor processability limit its application. The properties like thermal and mechanical properties of PVC can be enhanced by the incorporation of CNTs into PVC polymer matrix. In our present study we functionalized MWNTs by Friedel Craft acylation and used as reinforcing filler in PVC. The F-MWNTs/PVC nanocomposites films were prepared solution casting techniques. The various properties like morphology, solvent uptake, thermal, and mechanical properties of F-MWNTs/PVC nanocomposites were studied in detail.

Experimental

Materials

PVC was kindly provided by Kawsar PVC Company Peshawar, Pakistan, having average molecular weight 90,000. The N, N-dimethyl formamide (DMF) was purchased from Aldrich Company and was used as received. The MWNTs were provided by Iljin Nanotech and prepared by thermal chemical vapour deposition (CVD). Diameter and length of MWNT were 10-20 nm and 10-50 μm respectively, and its purity was higher than 97 wt %. The functionalization of MWNTs were performed by the same method as discussed somewhere else [20].

Preparation of F-MWNTs/PVC

The PVC and F-MWNTs/ PVC nanocomposite films were prepared by solution casting technique. The known amount of F-MWNTs was first dispersed in 10 mL DMF via stirring (15 min) and then sonicated for 40 min. The homogenous dispersed F-MWNTs were introduced in known amount of PVC solution. The F-MWNTs/PVC solution was stirred for 5 min and then sonicated for 1 h. The 1wt % F-MWNTs/PVC nanocomposite films were obtained by by casting technique. The same procedure was used to prepared **3 and 6 wt %** F-MWNTs/PVC composite films.

Instrumentation

The SEM analyses of gold-coated fractured surfaces of F-MWNTs/PVC nanocomposites were analyzed using JEOL, JSM-5910 Scanning Electron Microscope. The TG thermograms of pure PVC and F-MWNTs/PVC nanocomposites were obtained in nitrogen atmosphere at heating rate of 20 ºC/min from room temperature to 800 ºC using TGA (TG/DTA, Perkin Elmer). The mechanical properties of pure PVC and F-MWNTs/PVC nanocomposites were analyzed using UTM (Model 100-500 KN, Iestomeric Inc. UK).

Result and Discussion

The dispersion of pristine CNTs are difficult within the polymer matrix, in order to overcome this problem p-amino benzoic acid groups were introduced on the surface of MWNTs. The morphology of fractured films (which were broken in liquid nitrogen) of pure PVC and F-MWNTs/PVC nanocomposites are shown in figure 1. The SEM image showed that the F-MWNTs were well embedded within the PVC. The SEM image also presented that the F-MWNTs were not in agglomerate but dispersed well within the PVC marix.

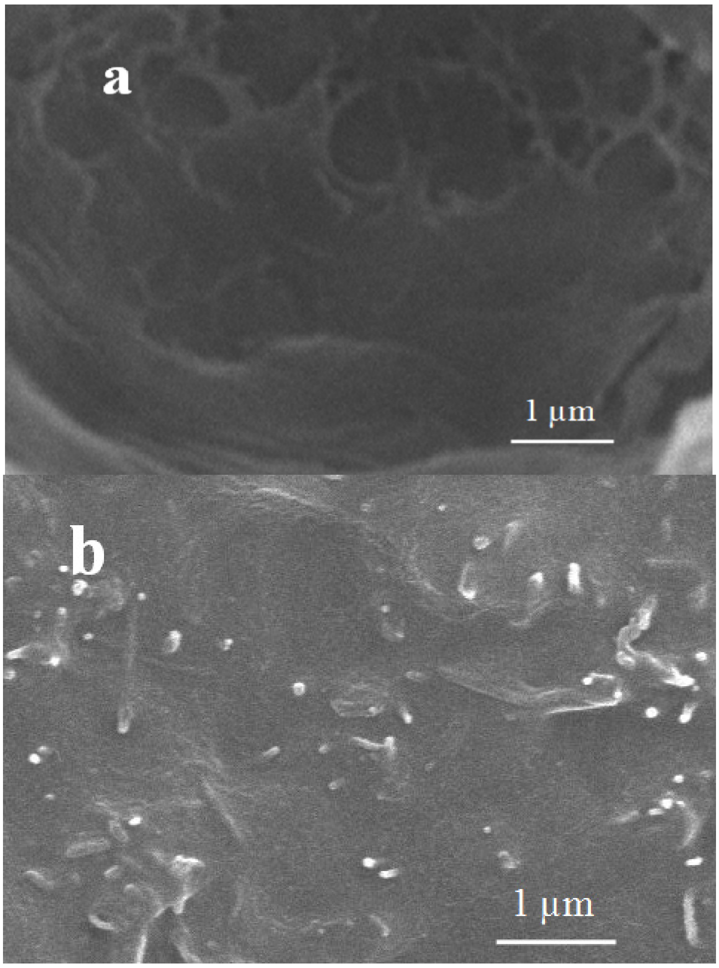

Figure 1. SEM images of the fractured surface (a) Pure PVC (b) F-MWNTS (6 wt%)/PVC.

The TG thermograms of pure PVC and F-MWNTs/PVC nanocomposites are shown in figure 2. The TGA curve of pure PVC presented two stages thermal degradation. The first thermal degradation of PVC was observed at about 260-360 °C, while the second degradation was found between 440-530 °C. The two stage degradation was also reported by Chakrabarti et al in the case of PMMA/PVC blend. They were reported that the first stage degradation is due to dehydrochlorination during the thermal degradation of PVC [21]. The F-MWNTs/PVC nanocomposites also showed similar thermograms (two stages thermal degradation) with that of pure PVC. The TGA thermograms also presented that the thermal stabilities of F-MWNTs/ PVC nanocomposites was slightly shafted towards higher temperature as compared to the neat PVC polymer matrix. The residual quantities, which show the presence of F-MWNTs in the nanocomposites, remained at higher temperature.

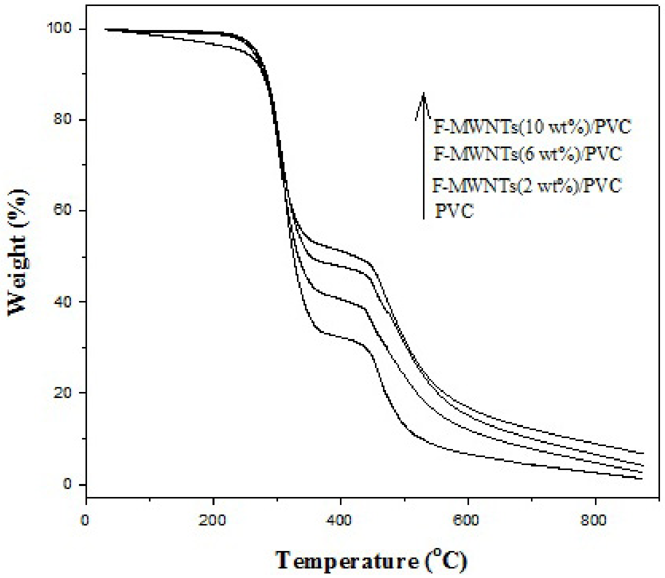

Figure 2. TGA thermograms of Pure PVC and F-MWNTs/PVC composite.

The mechanical properties of pure PVC and F-MWNTs/PVC nanocomposites are listed in table 1. The tensile strength of the pure PVC and the F-MWNTs/PVC (2, 6 and 10 wt% F-MWNTs) nanocomposites were 29.503, 59.137, 28.195 and 25.731N/mm^2, respectively. While the Young's modulus of the pure PVC and the F-MWNTs/PVC (2, 6 and 10 wt% F-MWNTs) nanocomposites were 5.6411, 5.9449, 5.4583 and 5.3892 N/mm^2, respectively. The tensile strength and Young's modulus of the nanocomposite was improved greatly by the incorporation of 2 wt% F-MWNTs, which might be due to the good dispersion of F-MWNTs in the PVC matrix as well as the improved interfacial adhesion between the PVC and F-MWNTs. Similarly, the elongation at the break was increased by the incorporation of 2 wt% of F-MWNTs into PVC. However, by the incorporation of high quantity of F-MWNT into the polymer matrix, the mechanical properties of F-MWNTs/PVC nanocomposites were decreased, which might be due to the agglomeration of the CNTs at high concentrations. The results showed that the addition of F-MWNTs into polymer matrix up to an optimum level resulted in a considerable reinforcing effect. The enhancement in the mechanical properties by the addition of clay in PEO, followed by a decrease at high concentrations, was also observed by Ratna et al. [22]

Table 1. Mechanical properties of PVC and F-MWNT/PVC.

Sample	Tensile-Strength (N/mm^2)	Modulus (N/mm^2)	Elongation at Break (%)
PVC	29.503	5.6411	136.07
PVC-2% MWNT	59.137	5.9449	196.11
PVC-6% MWNT	28.195	5.4583	78.370
PVC-10% MWNT	25.731	5.3892	58.52

Solvent uptake study of Pure PVC and F-MWNTs/PVC

The swelling behavior of pure PVC and F-MWNTs/PVC nanocomposites were studied in various solvents like distilled water, kerosene and chloroform. The percent swelling of neat PVC and F-MWNTs/PVC are shown in tables 2, which presented a rapid increase in the solvents uptake initially for pure PVC and F-MWNTs/PVC and then almost constant after reaching a specific time. Similar, trend of swelling behavior was also observed by Shahzad in the case of hemp fiber composites in water [23]. Tables 2 also presented the solvents uptake by F-MWNT/PVC nanocomposite, which showed similar trend with that of pure PVC. The results also presented that the solvent uptake of nanocomposite was lower than neat PVC. The lower absorption of solvents F-MWNTs/PVC than pure PVC might be due to the irregular distribution of F-MWNTs in PVC polymer matrix and they formed three-dimensional network within the polymer matrix, which result to prevent solvent diffusion into PVC matrix [24].

Table 2. Solvent uptake study of Pure PVC and F-MWNTs/PVC.

Time (h)	Pure PVC			F-MWNTs (2 wt %)/PVC			F-MWNTs (6 wt %)/PVC		
	Water	Kerosene	Chloroform	Water	Kerosene	Chloroform	Water	Kerosene	Chloroform
0.5	125	175	325	40	150	500	66.667	133.33	212.5
1	130	225	875	60	225	1133.3	150	233.33	650
2	125	200	850	60	225	1133.3	166.67	250	650
3	150	200	875	80	225	1066.7	200	233.33	650
6	125	200	925	100	200	1033.3	183.33	233.33	662.5
24	125	250	950	100	225	1133.3	166.67	250	712.5
48	125	230	1050	80	225	900	183.33	233.33	700
120	150	250	1025	80	225	866.67	183.33	250	650
168	150	225	925	80	200	733.33	183.33	233.33	562.5

Conclusion

It is concluded that the F-MWNTs were well dispersed within the PVC matrix. The F-MWNTs/PVC nanocomposites showed higher mechanical properties than pure PMMA, which was decreased as increased the quantity of F-MWNTs in the PVC. The neat PVC and nanocomposite showed rapid solvents uptake initially and then almost constant after reaching a specific time. It was also found that the solvents uptake of F-MWNTs was lower than pure PVC. The thermal stability of was also enhanced by the incorporation of F-MWNTs in PVC.

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