

Magnetic Carbon-Nanotube Thermoplastic Polyurethane Composites

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ABSTRACT

Carbon nanotubes (CNT) were functionalised with magnetite and compounded with polyurethane (PU). Two physical blending methods; melt-mixing and solvent dispersion, were used to prepare the compounds. Thermal stability, mechanical and thermal properties were characterised. Tensile properties, glass transition temperature (T_g) and magnetic properties increased with filler content. Filler concentration, processing technique and subsequent filler dispersion were factors that influenced material properties.

Keywords: polymer, carbon nanotubes, magnetite, polyurethane, viscoelasticity, magnetic

1 INTRODUCTION

Filler dispersion is a critical issue concerning property enhancement in polymer composites, particularly when nano-sized dispersion is desired. The surface chemistry of the fillers and the influence of particle interactions often lead to aggregate formation [1, 2]. Differences in polarity between the matrix and filler can provide further complications by limiting the interaction between the composite constituents [3]. This can result in polymer composites displaying inferior mechanical, thermal and optical properties. In addition, materials such as iron oxides require adequate interparticle space, critical particle-size and favourable matrix-filler interactions to maximise intrinsic properties, including superparamagnetism and electromagnetic wave absorption [4, 5].

The most common method to encourage filler dispersion is chemical modification of the filler surface [6, 7]. Other techniques available include ultrasonic disruption and shear during mixing, which are useful when preparing large volumes of material and when an unchanged filler surface is desired. In addition, physical blending provides a convenient option when functionalised-fillers have been prepared with the intention of being incorporated into a polymer matrix with the surface functionality intact.

The aim was to prepare composites of PU and magnetite-functionalised CNTs, using physical blending techniques to effectively disperse the filler. Objectives included functionalising the CNTs with magnetite (Fe_3O_4), preparing PU-CNT- Fe_3O_4 composites using solvent dispersion and melt mixing, and determining the influence of processing technique on the thermomechanical, thermal and magnetic properties of the composites.

2 EXPERIMENTAL

2.1 Materials

Polyether-polyurethane (Pellethane 2101-85A) was used as the polymer matrix. Multiwall carbon nanotubes (CNTs) with an average diameter of 9.5 nm, average length of 1.5 μm and purity of 90 % were provided by Nanocyl. Iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were obtained from BDH Chemicals. All chemicals were used as received.

2.2 Functionalisation of CNT with magnetite

CNTs were dispersed in a round-bottomed flask containing HNO_3 solution with the aid of an ultrasonic water bath for 1 h. The solution was refluxed at 80 °C with vigorous mixing for 24 h. The acid-modified CNTs were collected by centrifugation, then dried at 80 °C for 24 h. In a separate flask, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (molar ratio 1:2) was dissolved into deoxygenated water with constant stirring for 10 min. The acid-modified CNTs were added to the Fe^{2+} - Fe^{3+} solution and dispersed using ultrasonic disruption for 10 min under nitrogen. NaOH was added dropwise while stirring to precipitate magnetite-functionalised CNTs. The black precipitate was magnetically isolated and the solution decanted. The functionalised CNTs were washed with distilled water and dried in a vacuum oven at 35 °C for 24 h.

2.3 Synthesis of PU-CNT- Fe_3O_4 composites

A Haake Rheomix 600 Batch Intensive Mixer with Rheocord 90 Control System was used to prepare the composites via melt-mixing. Materials containing 1, 5 or 10 %-wt filler were blended using roller-blade type rotors at 50 rpm, at 190 °C for 5 min. Films for subsequent use were prepared using a heated press at 175 °C, 6 tonne of mass applied, held for 2 min and cooled to ambient. Pressed films were stored in sealed bags kept in a desiccator at 0 % RH.

Solvent dispersion was performed by adding PU to tetrahydrofuran (THF) and stirring for 1 h at 20 °C. Fe_3O_4 -functionalised CNTs were added to the solution at various concentrations (1, 5, 10 %-wt) and subjected to ultrasonic disruption (10 min, 25 °C, 20 kHz) to completely disperse the filler particles throughout the polymer matrix. The polymer solution was rapidly precipitated into a large volume of cold methanol, before being isolated by suction filtration and dried under vacuum at 75 °C for at least 8 h.

2.4 Characterisation of composites

A Perkin-Elmer TGA-7 thermogravimetric analyser with TAC-7/DX thermal analysis controller was used to analyse the thermal stability of the composites. Samples of ~10 mg were heated to 850 °C at 20 °C·min⁻¹ in an inert environment provided by a 20 mL·min⁻¹ nitrogen purge.

Stress-strain and creep-recovery analysis was performed using a TA Instruments Q800 Dynamic Mechanical Analyser while tensile modulated force-thermomechanometry (mf-TM) was performed using a Perkin-Elmer Diamond DMA.

Stress-strain was performed using an initial force of 10 mN followed by an applied force increasing at a rate of 1 N·min⁻¹, reaching a maximum of 18 N. Films with average dimensions of 12.80 x 5.50 x 0.80 mm³ were tested at 30 °C. Results presented are the average of triplicate measurements. Creep-recovery analysis was performed by subjecting films (average dimensions: 12.80 x 5.50 x 0.80 mm³) to an applied stress of 1 MPa for 20 min, followed by a recovery period of 80 min with 0.01 MPa applied stress. Tests were conducted at 30 °C and all results presented are the average of triplicate measurements. mf-TM analysis was conducted using a static force of 500 mN, modulated force of 100 mN and frequency of 1 Hz. The storage modulus (E'), loss modulus (E''), loss tangent ($\tan \delta$) and glass transition (T_g) temperatures of the films (average dimensions: 10.00 x 5.50 x 0.80 mm³) were measured from -80 to 110 °C at a heating rate of 2 K·min⁻¹.

Magnetometric analysis was performed using a Lakeshore Model 7404 vibrating sample magnetometer at 25 °C. A maximum field of 12 kG was applied parallel to the samples. Test specimens were made into disc shapes of ~5 mm in diameter, with results presented being the average of three repeats.

2.5 Material nomenclature

In the interest of clarity, the composites will be presented as “mix x” or “sol x”, where ‘mix’ and ‘sol’ refer to the melt mixing or solvent dispersion technique and ‘x’ corresponds to the weight percentage of CNT-Fe₃O₄ within the composites (1, 5 or 10 %·wt).

3 RESULTS AND DISCUSSION

3.1 Thermal stability

Composites prepared via melt-mixing exhibited an increase in degradation temperature (T_d) with increasing filler concentration, as shown in Figure 1. A number of mechanisms have been proposed to describe the influence of CNTs on thermal stability. Nanotubes may hinder the flux of degradation of the polymer, delaying the onset of degradation [8]. Polymer segments near the nanotubes may degrade more slowly due to the CNTs providing the ‘most torturous path’ for degradation. Another proposed

explanation is that the polymer-CNT composites exhibit superior thermal conductivity properties, facilitating better heat dissipation [9]. All composites displayed final mass values corresponding to the amount of filler present, confirming the correct amount of functionalised-CNTs were incorporated during material preparation.

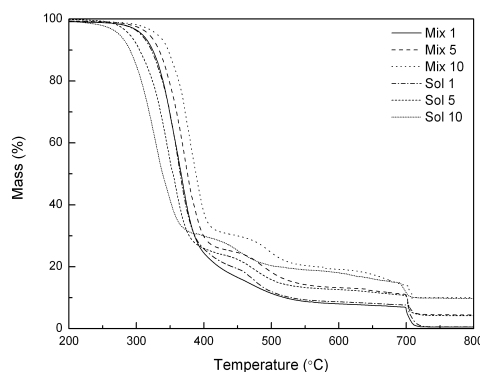


Figure 1 Mass loss curves of PU-CNT-Fe₃O₄ composites

In contrast, the thermal stability of films prepared using solvent dispersion decreased with the addition of filler, with the 10 %·wt composite displaying degradation onset at the lowest temperature. The thermal stability of composites containing CNTs is influenced by the effectiveness of filler dispersion [8]. One probable explanation is that filler agglomeration occurred during solvent evaporation, leading to inhomogeneous particulate distribution [8]. Kashiwagi et al [10] reported that poorly dispersed CNTs are likely to agglomerate into ‘islands’ of filler, compromising the composite thermal stability. In addition, well dispersed CNTs possess a larger surface area, increasing heat dissipation and thermal properties of the films.

3.2 Stress-strain

The stress-strain data of the composites is summarised in Table 1. PU filled with 1 %·wt CNTs prepared by melt mixing and solvent dispersion exhibited tensile modulus (E) values of 24.02 and 10.96 MPa, respectively. Addition of functionalised-CNTs had a positive effect on E , which increased with filler concentration, reaching a maximum at loadings of 10 %·wt. CNTs allow for the transfer of stress during load application, enhancing the strength and durability of the film. Elongation at yield decreased with filler concentration, due to the reduced elasticity which accompanies the incorporation of rigid filler.

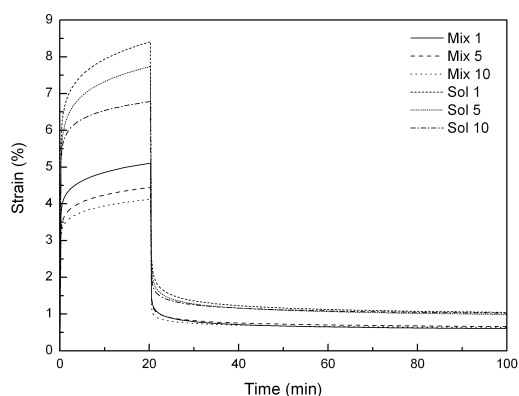
Composites prepared via melt mixing exhibited higher modulus and strength values than composites prepared using solvent dispersion, suggesting the melt-mixed films are more rigid and less elastic in nature. This can be attributed to the influence of processing; during melt mixing, flexible polyester segments within the PU matrix may partially degrade, reducing the elasticity of the polymer and increasing stiffness and strength. In contrast, the PU matrix remains relatively unchanged during solvent dispersion, maintaining its initial degree of elasticity.

Table 1 Stress-strain data of PU-CNT-Fe₃O₄ composites

Material	Tensile modulus (MPa)	Yield strength (MPa)	Elongation at yield (%)
Mix 1	24.02	4.13	74
Mix 5	26.27	4.31	56
Mix 10	29.08	4.64	51
Sol 1	10.96	3.04	96
Sol 5	12.33	3.60	84
Sol 10	20.06	3.82	71

3.3 Creep-recovery

Creep deformation decreased with increasing functionalised-CNT content, as displayed in Figure 2. Due to its intrinsic rigidity and strength, the incorporation of CNTs imparts stiffness into the matrix and restricts molecular motions of the PU chains as expected. As the filler concentration increased, composites exhibited flatter creep curves with a lower gradient, indicating a decrease of deformation of the viscous component. Composites prepared using melt mixing displayed less creep deformation than their solvent dispersed counterparts, attributed to the influence of processing technique. Permanent deformation increased with CNT concentration, due to the restrictions imposed on PU chain relaxation, resulting in irreversible chain slippage and unraveling.

Figure 2 Creep-recovery of PU-CNT-Fe₃O₄ composites

3.4 Modulated force-thermomechanometry

The storage moduli (E') of the composites are presented in Figure 3a. E' values increased with filler concentration, reaching maximum values at 10 %·wt. Melt-mixed composites exhibited considerably larger E' values than their solvent dispersed counterparts. This can be attributed to the degree of filler dispersion within the composite films. Increasing the dispersion of CNTs increases the filler-rubber interface [11], providing the material with enhanced stiffness and reinforcement. An increase in dispersion also leads to an increase in bound rubber. These trapped polymer chains are shielded from deformation by the CNTs and act as part of the filler rather than the matrix.

Figure 3b displays the loss moduli (E'') of the composites. The melt-mixed and solvent dispersed PU composites containing 1 %·wt filler exhibited T_g values of -47 °C. Increasing filler content raised the T_g , reaching a maximum value of -38 °C in both 10 %·wt composites. The increase in T_g attributed to the ability of CNTs to restrict molecular motions of the polymer chains. Composites exhibited glass transitions over a larger temperature range, as indicated by broader E'' peaks. This was attributed to an increase in the segmental relaxation times of the matrix.

The loss tangent ($\tan(\delta)$) of the composites is shown in Figure 3c. The T_g obtained from the loss tangent maximum displayed similar trends to those obtained from the loss moduli curves. Composites exhibited a decrease in $\tan \delta$ peak height with filler concentration, indicating diminished dampening ability. As with the E'' curves, peak broadening of the $\tan(\delta)$ curves was observed at higher filler loadings. Melt-mixed films exhibited taller peaks than their solvent dispersed counterparts, while composites prepared using solvent dispersion yielded broader peaks. This suggests that the dampen properties of the materials are determined by two mechanisms; increased relaxation times in solvent dispersed films and greater internal friction between the filler and matrix and between the filler particles across the glass transition region in the melt-mixed films [12].

3.5 Magnetic properties

The hysteresis of the composites are represented by Figure 4 and the corresponding results are listed in Table 2. The M_s and M_R for the composites prepared by both processing techniques increase with increasing filler content due to the effect of inter-particles interaction in magnetic properties. When the concentration of CNT-Fe₃O₄ is high, the level of interaction between Fe₃O₄ nanoparticles themselves increases and this restricts free rotation of the magnetic particles in the polymer matrix. However, both composite sets exhibited different values of M_s . The values of M_s for composites prepared using melt mixing are much higher than those prepared by solvent dispersion technique. This can be attributed to the different processing technique which leads to the different degree of dispersion of CNT-Fe₃O₄ in PU matrix as discussed earlier.

Magnetic nanoparticles tend to agglomerate due to strong magnetic dipole-dipole attractions between particles [13]. The agglomerations made from magnetic nanoparticles show demagnetizing effect due to random dipole-dipole interaction between particles resulting in antiferromagnetically coupling [14]. Thus, the enhancement of magnetic properties implies that composites with a better dispersion and less agglomeration of nanoparticles in polymer matrix were obtained by melt mixing technique. This is in agreement with the increment of storage moduli of the composites which is also attributed to the higher degree of filler dispersion. The H_C for both composites sets are in the range of 20-26 G, indicating that the composites prepared are magnetically soft at room temperature.

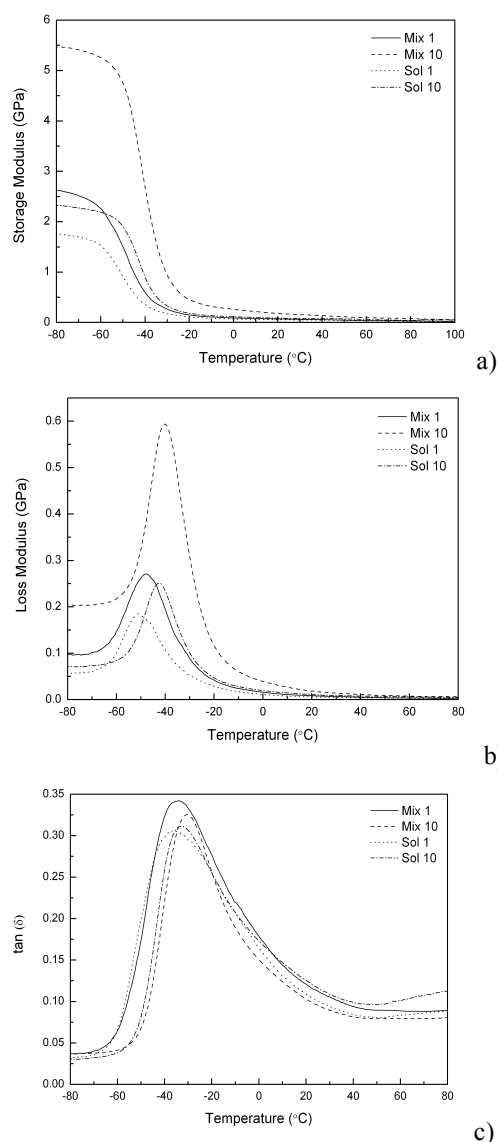


Figure 3 mf-TM curves of PU-CNT-Fe₃O₄ composites; a) storage, b) loss, c) tan (δ)

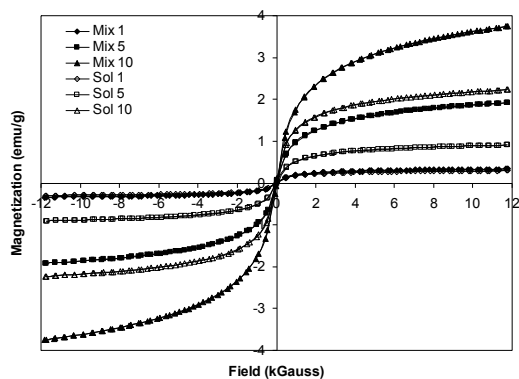


Figure 4 Magnetic hysteresis loops of PU-CNT-Fe₃O₄ composites

Table 2 Magnetic properties of PU-CNT-Fe₃O₄ composites

Material	M _S (emu/g)	M _R (emu/g)	H _C (Gauss)
Mix 1	0.34	0.008	26.93
Mix 5	1.92	0.036	24.24
Mix 10	3.74	0.066	24.68
Sol 1	0.30	0.007	25.70
Sol 5	0.91	0.017	21.53
Sol 10	2.23	0.052	25.56

4 CONCLUSION

PU composites containing Fe₃O₄-functionalised CNTs were prepared using solvent dispersion and melt mixing. Melt-mixed composites displayed superior thermal properties to their solvent-dispersed counterparts, which became less stable. Tensile properties and T_g increased with filler concentration, while creep deformation decreased. Melt-mixed films were stronger and less-elastic in behaviour than those prepared using solvent dispersion. Melt-mixed composites exhibited better magnetic behavior and the difference between two techniques became obvious at higher filler concentration. Material properties were influenced by filler concentration and processing technique.

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