Preparation and characterisation of PE films of carbon nanotube/polyaniline (PAN) composite mixture

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ABSTRACT
Polyaniline (PAN) composites filled with nanotube were prepared by twin-screw extruder in order to study the influence of PE reinforcing effect on the mechanical behaviour of the nanotube/polyaniline (PAN) composites. The mechanical property tests of the composites with and without PE were performed. The tensile and flexural strength of nanotube/polyaniline (PAN) composites with polyethylene (PE) was improved. In conclusion, the addition of PE favoured the improvement of the higher interface strength and so had good effect on improving the tensile and flexural properties of the composites. The dielectric strength was slightly increased with the PE content increasing and then decreased gradually. The hybrid film with 2 wt.% of PE shows the dielectric strength of 199 MV/m, which is about 6% higher than that of nanotube/polyaniline (PAN) film (188 MV/m).

1. Introduction
Carbon nanotubes are typically produced either by pyrolysing nanotubes spun from an organic precursor (e.g. polyaniline (PAN), or alternatively pitch) or by chemical vapour deposition (CVD) [1]. The spinning method can only produce microscale carbon nanotubes (diameter > 5 μm). CVD can synthesise carbon nanotube with diameters ranging from several microns down to 10 nm [2,3].

Recently, carbon nanotubes were produced by pyrolysing electrospun nanotubes from PAN [4-6] and from pitch [7] with typical diameters of few hundreds of nanometre and several microns, respectively. However, the structure and the mechanical properties of carbon nanotubes produced from an electropsun polymer precursor are largely unknown. The purpose of this paper is to characterise the structure and to explore the modulus and strength of electropsun PAN-derived carbon nanotubes. The survey of the literatures revealed that there is a very limited amount of information available on the mechanical properties of the modified PAN nanotubes and their metal complexes. Composite membranes have a low resistance in electrolyte solutions owing to the coating with conducting polymers inside the pores and can be used as package of stainless steel plate, aluminium and aluminium alloy profiles.
In this present study, our research has laid more stress on the mechanical properties and conductivity of the PE/nanotube/polyaniline (PAN) nanocomposite polymer electrolytes, in which PE particles were precipitated by \textit{in situ} synthesis after the fixed lithium ions had been initially installed in the solid polymer network which exhibited excellent properties and uniform distribution of PE in the polymer [8–10]. For the PE/nanotube/polyaniline (PAN) membranes, the morphology and mechanical properties were examined for comparison with those of the wetted poly(vinylidene fluoride) [PVdF]-based membranes with polar solvents, such as ethylene carbonate and propylene carbonate, in order to assess the possible structural factors contributing to ionic conduction and mechanical properties. The difference between the wet polymer electrolyte and the glycerol random polyether (GPE) is that the lithium ions have already been installed in the solid polymer network in the former, while in the latter they are introduced by the organic solvent. The purpose of this work is to study the tensile flexural and impact properties of the PE/nanotube/polyaniline (PAN) composites.

2. Experimental

2.1. Materials

The carbon nanotubes were polyaniline (PAN)-based, unsized and of length about 75 μm, diameter 7 μm, as obtained from Shanghai Xinxing Carbon Co. Ltd. Analytical grade pyrrole was purchased from Aldrich. Iron (III) chloride hexahydrate was received from Tianjin Chemical Reagent Institute without any further purification. Carbon nanotubes were received from Yizheng Chemical Nanotube Company, China.

2.2. Carbon nanotube treatment

Carbon nanotubes were soaked in an aqueous solution of 0.1% iron (III) chloride hexahydrate (catalyst) for 4 h at 30 °C, then these carbon nanotubes were treated by the coating machine (RT100) continuously, in which there were two or three reaction tanks filled with liquid phase pyrrole monomer. After pyrrole polymerisation (15 min, 30 °C) on the carbon nanotube, these polypyrrole (PPy)-coated carbon nanotubes turned black and were collected by a winder. At last, these PPy-coated carbon nanotubes were thoroughly washed with water in order to remove the monomer or loose PPy may excess. PPy-coated carbon nanotubes were immersed in distilled water and stirred with oscillator.

The PE was acquired in powder form. The PE powder (type: CGM031) was supplied by Zhonghao Chenguang Research Institute of Chemical Industry with a particle size of approximately 200 mesh number. Powder mixtures with serpentine mass fractions of 0–30 vol.% were prepared and blended in a high-speed mixer traditionally used to make powders mix uniform and dispersive.

After mixing, the mixture was compressed and molded in a cylindrical cavity (Φ6 × 10). A laboratory pressure of 40 MPa was used to consolidate the mixture at room temperature in a cylindrical chamber made of Gr. D steel. This molding pressure was held for approximately 10–15 min. Then, the discoid samples were sintered in an electric heating furnace equipped with a temperature control system at 40 °C. Last, the sintered samples were machined into final specimens.
2.3. Measurement and characterisation

ILSS of PE/nanotube/polyaniline (PAN) composites was tested on a universal testing machine (AG-X10KNSTD, Shimadzu, Japan), using ASTM standard D2344 at room temperature. The movement of crosshead was 2 mm/min. Interlaninar shear strength (ILSS) for the short-beam test was calculated according to the following formula

\[ \text{ILSS} = \frac{3P_b}{4bh} \]

where \( P_b \) is the maximum compression load at fracture in Newton (N), \( b \) is the width of specimen in mm and \( h \) is the thickness of specimen in mm. Each reported ILSS value was the average of the results from six specimens. The relative error in ILSS values was estimated to be with 10% based on reproducibility of the data among different specimens. The membrane morphology was observed by using a scanning electron microscope (JEOL-JSM-6010LV). To get a sharp clear cross-section, membrane samples were fractured in liquid nitrogen. Surface chemistry of the membranes was investigated via attenuated total reflection Fourier-transform infrared (Bruker, Alpha) spectroscopy.

3. Result and discussion

ILSS of nanotube/polyaniline (PAN) composite reinforced by unidirectional PEs is shown in Table 1. It was seen that surface coated PE/nanotube/polyaniline (PAN) composite shows the highest ILSS, which is over 100 MPa. The result can be explained in the light of the inherent properties of PE surface bonded with reactive groups per molecule. The composites have high stiffness owing to the high crosslink density of nanotube/polyaniline (PAN). Although high viscosity of nanotube/polyaniline (PAN) resin can hinder resin impregnation into nanotubes, the large amount of groups can increase the crosslink density of nanotube/polyaniline (PAN), which results in better mechanical performance of PE/nanotube/polyaniline (PAN) composites.

Figure 1 shows the dielectric strength of the nanotube/polyaniline (PAN) hybrid films with different PE content. It can be seen that the dielectric strength was slightly increased with the PE content increasing and then decreased gradually. The hybrid film with 2 wt.% of PE shows the dielectric strength of 199 MV/m, which is about 6% higher than that of nanotube/polyaniline (PAN) film (188 MV/m). As the PE content increased to 20 wt.%, the dielectric strength of the hybrid film reduced to 159 MV/m, which is 20% lower than the hybrid film with 2 wt.% of PE. It is suspected that the PE aggregates, which found at the polyimide films with a relative high PE content, might act as an impurity that cause some defects to deteriorate the dielectric strength.

The variation of dielectric constant with PE mole fraction is shown in Figure 2. Very low dielectric constant of about 1.56–1.94 was obtained as a result of copolymerising PE with nanotube/polyaniline (PAN). The dielectric constant PE decreased with increasing

| Filler                  | ILSS (MPa)       |
|-------------------------|------------------|
| Surface coated PE       | 105.41 ± 5.09    |
| Raw PE                  | 60.02 ± 2.51     |
nanotube/polyaniline (PAN) concentration, indicating that the ionic insulating property is improved by the addition of nanotube/polyaniline (PAN). It is interesting to note that the relationship between the dielectric constant and mole fraction of PE is opposite to the relationship between glassy region storage modulus and the mole fraction of PE (Figure 2).

**Figure 1.** The dielectric strength of the nanotube/polyaniline (PAN) hybrid films with different PE content.

**Figure 2.** Effect of PE mole fraction on dielectric constant storage modulus of composites copolymers.
All the samples were thermally molded at 220 °C for 30 min under 17.5 MPa. Two curves in Figure 3 distinctly show that the electrical conductivity decreases almost linearly with the increase of PE content while the change of the flexural strength is just the opposite. Please note that the neat PAN plate affords an electrical conductivity as high as 335.80 S cm$^{-1}$ but with 3.35 MPa of the flexural strength. In contrast, the neat polyimide (PI) plate bears an intrinsic insulation around 10$^{-15}$ S cm$^{-1}$ and a powerful flexural strength of 122.05 MPa. In view of these facts, for the nanotube/polyaniline (PAN) composite plates, both the electrical conductivity and the flexural strength can be considered to be the individual balance of each property of nanotube/polyaniline (PAN) in proportion. This means that the properties of the composite plates are really dependent on the physical nature of the two components in the composite.

Flexural strength of the treated surface-coated PE/nanotube/polyaniline (PAN) composites is found to be higher than that of the raw nanotube/polyaniline (PAN) composites. Since PE is high strength material, higher polymer content demands higher stress for the same deformation and increased filler adhesion provides for increased stress transfer from the matrix to the filler. This result can be attributed to the addition of the filler, resulting in an increase in the strength because of the incorporation of rigid PE into the soft nanotube/polyaniline (PAN) matrix. The morphology of the fracture surface shows the phase information reflecting the reasons why the mechanical properties of the composites fabricated under different conditions are different.

Figure 4 shows a direct relationship between the plate density and the PE content. The decrease in the plate density with increasing PE content is due to the low density of neat PE plate (0.809 g cm$^{-3}$) as compared with that of the neat PAN plate (1.610 g cm$^{-3}$). The change of plate shore hardness with the PE content is correspondingly related with the inherent hardness of two composing materials. Cured PE is known to be a compact material possessing molecular crosslink network. By contrast, PAN particle is characteristic of layer structure accompanying with a large number of cavities circled by graphitic layers.
Therefore, PAN plate is softer than the neat PE plate but could become harder if intruding PE into the cavities opened in PAN.

The stress–strain curves of the two kinds of composites, i.e. PE and nanotube-reinforced polyaniline (PAN), shown in Figures 5 and 6, become steeper as the PE content increases. The initial modulus and the modulus at low strains are higher than that of the nanotube/polyaniline (PAN) matrix. The reinforcing effect of PE is slightly less than that of nanotubes. When the PE content is up to 5 phr, the stress–strain curves of the composites in the main direction (MD) are similar to that of nanotube/polyaniline (PAN). The

**Figure 4.** Changes in density and hardness of PE/nanotube/polyaniline (PAN) composites with PE content.

**Figure 5.** Stress–strain curves of PE short nanotube/polyaniline (PAN) composites along MD.
The relationship between stress and strain does not obey Hooke’s law, and yielding does not occur. For a PE content of 10 phr, the composites would break after yielding. When the PE content increases from 15 to 25 phr, the stress–strain curves become linear, the composites yield and break at the same time, and the yield strength coincides with the tensile strength.

4. Conclusion

The tensile fracture surface morphology of the nanotube/polyaniline (PAN) composites with PE-treated fibre exhibited better adhesive properties between the fibres and PAN matrices, while the untreated fibres had poorer adhesive properties to the PAN matrices. The fibre surface treatment favoured the improvement of the interface adhesive strength and so had good effect on improving the mechanical properties of the composites.

In conclusion, the mechanical properties of the nanotube/polyaniline (PAN) composites with PE treatment were higher than that with untreated fibres, although their overall behaviour was broadly similar.

Disclosure statement

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