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Novel polyacrylonitrile nanocomposites containing Na-montmorillonite and nano SiO_2 particle

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Abstract

Polyacrylonitrile (PAN)/Na-montmorillonite (Na-MMT)/SiO_2 nanocomposites were prepared via in situ emulsion polymerization. X-ray diffraction (XRD) results suggest that the Na-MMT layers are exfoliated during the polymerization process. As evidenced by the transmission electron microscope (TEM), the Na-MMT and nano SiO_2 particles exhibit good dispersion in the polymer matrix. It was found that the PAN/Na-MMT/SiO_2 nanocomposites exhibit considerably enhanced mechanical properties compared with the PAN/Na-MMT and PAN/SiO_2 nanocomposites.

Keywords: Nanocomposites; Polyacrylonitrile; Inorganic nano material

1. Introduction

Nanocomposites are a class of hybrid materials composed of organic polymer matrix imbedded with inorganic materials which have at least one dimension in the nanometer size range [1–4]. Among various nanocomposites, much attention has been paid to polymer/Na-montmorillonite (Na-MMT) nanocomposites, because they have high stiffness [5,6], enhanced mechanical property [7–11], high thermal stability [10,11], flame-retarding [2,12], and better barrier properties [13–15] even with small amount of silicate. These excellent properties result from the silicate layers dispersed in continuous polymer matrix. Choi et al. reported synthesis of exfoliated polyacrylonitrile (PAN)/Na-MMT nanocomposites via emulsion polymerization [7]. It was demonstrated that the Na-MMT can be exfoliated during the polymerization. The obtained nanocomposites had enhanced storage modulus when compared with pure PAN.

Another importantly used nano material for the enhancement is nano SiO_2 particle [16–19]. For instance, the yield strength, yield strain, and tensile strength of the poly (vinylidene fluoride-tetrafluoroethylene)/nano SiO_2 composites are considerably increased with respect to the matrix polymer [18]. Dramatical improvement of the flame-retarding and thermal properties are also reported for poly(methyl methacrylate)/SiO_2 nanocomposites [19].

However, no studies on the nanocomposites containing both Na-MMT and nano SiO_2 particle have been reported so far. New reinforcement mechanism may emerge, when two kinds of nano materials with different forms, layered and particle are incorporated into the polymer matrix. In this work, the polymer/Na-MMT/SiO_2 nanocomposites were prepared via in situ emulsion polymerization. The polymer matrix used in the present studies is polyacrylonitrile (PAN). PAN is commonly used for fiber-spinning, raw material for fabrication of carbon fiber [20], precursor for high temperature superconductor [21], electrospinning of nano fiber [22,23] and matrix of nanocomposites [7,24]. The mechanical properties and morphologies of the obtained nanocomposites were examined. Incorporation of Na-MMT/SiO_2 into the PAN matrix results in a nanocomposite with highly enhanced mechanical properties compared with the PAN/Na-MMT and PAN/SiO_2 nanocomposites.

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2. Experimental

PAN/Na-MMT/SiO_2 nanocomposites were synthesized through an emulsion polymerization of acrylonitrile in presence of Na-MMT and SiO_2 dispersed in deionized water. 2-Acrylamido-2-methyl-1-propanesulfonic acid together with OP10 (polyoxyethylenealkylphenol ether) were used as surfactants. X-ray diffraction (XRD) patterns were obtained by using a Rigaku D/max-2550VB/PC diffractometer with a scanning rate of 2°/min in a 2θ range of 1.5–10° under room temperature. The storage modulus E' was obtained by a Rheogel-E4000 (UBM Co., Ltd) dynamic analyzer from 40 to 200 °C with a heating rate of 3 °C/min at 2 Hz of frequency. The film specimens for the DMA tests were obtained by redissolving the nanocomposites in DMF then cast from the solution. The cast films were further dried at 60 °C under vacuum for 48 h to remove the residual solvent. The morphology of the nanocomposite was observed after the redissolved nanocomposite solution dried on the copper grid by JEM-1200-EXII transmission electron microscope. The accelerating voltage is 120 kV.

3. Results and discussion

Fig. 1 shows the XRD diffraction patterns of Na-MMT and PAN nanocomposites containing Na-MMT and Na-MMT/SiO_2. Pristine Na-MMT exhibits a diffraction peak of the (001) plane at 5.7° in a 2θ value, and its basal spacing is 1.55 nm (curve a). Curve b is the result obtained for PAN/Na-MMT. No diffraction peak is shown, suggesting that the Na-MMT layers are exfoliated. Choi et al. reported similar results for PAN/Na-MMT nanocomposites [7]. According to their studies, the basal space of the Na-MMT are enlarged in the aqueous solution of AN with surfactant 2-acrylamido-2-methyl-1-propanesulfonic acid. When polymerization occurs, the Na-MMT layers can be fully exfoliated. Curve c gives typical XRD patterns of PAN/Na-MMT/SiO_2. The XRD results suggest that the Na-MMT layers are also exfoliated as indicated by the disappearance of the Na-MMT diffraction peak in curve c.

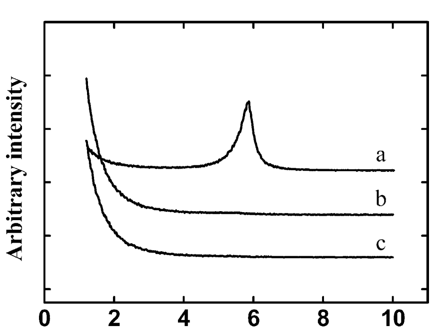

Fig. 1. X-ray diffraction patterns of pristine Na-MMT (a), PAN/Na-MMT with 4.0 wt% Na-MMT (b), and PAN/Na-MMT/SiO_2 with 2.0 wt% Na-MMT and 2.0 wt% SiO_2 (c).

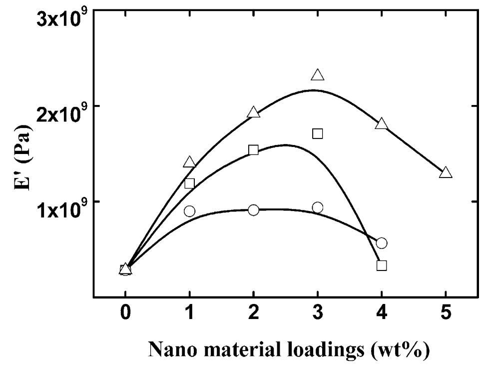

Fig. 2. Dependence of storage modulus E' (50 °C) on the content of nano materials for PAN/SiO_2 (○), PAN/Na-MMT (□) and PAN/Na-MMT/SiO_2 (△). For the PAN/Na-MMT/SiO_2, the Na-MMT/SiO_2 weight ratio is maintained at 1:1.

Shown in Fig. 2 is a plot where the storage moduli, E', at 50 °C of the PAN/SiO_2, PAN/Na-MMT, and PAN/Na-MMT/SiO_2 nanocomposites are plotted against the total nano material loadings (Na-MMT + SiO_2). For all the three systems examined, the storage modulus increases with increasing the nano material content to a maximum value, and then followed by a decrease. At a fixed nano material content, the PAN/Na-MMT/SiO_2 nanocomposites exhibit the highest elevated moduli among the three kinds of nanocomposites.

Further results regarding the reinforcement effect of incorporating Na-MMT/SiO_2 into the PAN matrix are demonstrated in Fig. 3 where the total nano material loadings are maintained at 4.0 wt%. For comparison, the results obtained for pure PAN, PAN/Na-MMT, and PAN/SiO_2 are also included. The E' values of the nanocomposites are higher than that of pure PAN over the entire range of temperature. The reinforcement effect of the Na-MMT/SiO_2 binary system is considerably better than that of either Na-MMT or SiO_2. With changing the Na-MMT/SiO_2 weight ratio from 4:6 to 7:3, the E' value increases first, and then decreases. The E' value at 50 °C of the nanocomposite

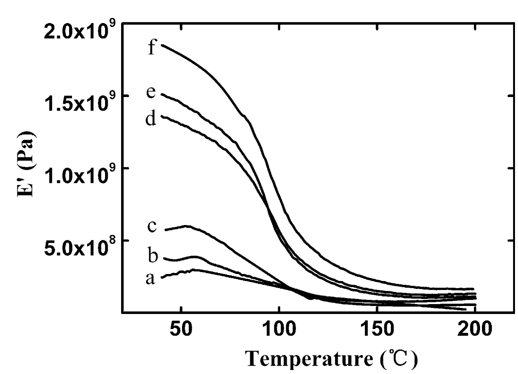

Fig. 3. Dependence of storage modulus E' on temperature for PAN matrix (a), PAN/Na-MMT with 4.0 wt% Na-MMT (b), PAN/SiO_2 with 4.0 wt% SiO_2 (c) and PAN/Na-MMT/SiO_2 with 2.8 wt% Na-MMT and 1.2 wt% SiO_2 (d), with 1.6 wt% Na-MMT and 2.4 wt% SiO_2 (e), with 2.0 wt% Na-MMT and 2.0 wt% SiO_2 (f).

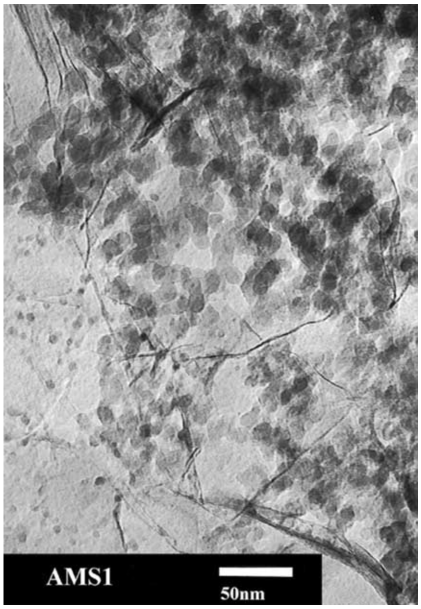

Fig. 4. TEM micrograph of PAN/Na-MMT/SiO_2 with 2.0 wt% Na-MMT and 2.0 wt% SiO_2.

containing 2.0 wt% Na-MMT and 2.0 wt% SiO_2 is 535.7% higher than that of the pure PAN, 381.1 and 196.7% higher than those of PAN/Na-MMT and PAN/SiO_2 nanocomposites, respectively.

Typical TEM photograph of PAN/Na-MMT/SiO_2 nanocomposite is given in Fig. 4. The dark slices stand for Na-MMT layers while the spherical dark particles are SiO_2. The PAN matrix appears as light region. The Na-MMT layers together with the SiO_2 particles show a good dispersion in the PAN matrix.

For the PAN/Na-MMT nanocomposites, the enhancement of the storage modulus results from the delamination of the silicates in the PAN matrix and the strong interactions between the polymer chains and the Na-MMT layers [7,8]. However, due to the strip shape of the Na-MMT layers, the reinforcement could be anisotropic. The crack along the direction of Na-MMT layers may not be resisted. Introduction of the SiO_2 particles dispersed in the nano scale could bridge the cracks which are not stopped by the Na-MMT layers. Coexistence of the Na-MMT layers and the nano SiO_2 particles could give rise to a considerably enhanced mechanical properties of PAN/Na-MMT/SiO_2 with respect to the PAN/Na-MMT and PAN/SiO_2 nanocomposites.

Acknowledgements

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