

Preparation and Characterization of P(AN/VAC)/Clay Based Nanocomposites

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ABSTRACT: In this article, P(AN/VAC)/clay nanocomposites were prepared by an *in situ* polymerization and characterized by transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, nuclear magnetic resonance, and differential scanning calorimetry. The results show that the P(AN/VAC)/clay exhibit a multilayered structure. The montmorillonite layers are totally exfoliated and distributed uniformly in the P(AN/VAC)

matrix. The dimension stability and heat resistance property of P(AN/VAC)/clay are superior to those of P(AN/VAC) alone. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 703–706, 2006

Key words: P(AN/VAC)/clay; montmorillonite; nanocomposite

INTRODUCTION

Polyacrylonitrile (PAN) and its copolymers, because of their excellent light resistance and antimicrobial properties,¹ have been used widely in the fields of fibers and plastics. It is well known that it is easy for acrylonitrile to copolymerize with a variety of unsaturated olefins to generate polymers with various properties. And the materials based on PAN have attracted many researchers because of their differences, functionalities, and high-performances.²⁻⁴

In the past years, a great progress has been made in the development of various nanocomposites. As a new kind of materials, nanocomposites have lots of excellent physical and chemical properties and possess a good future. Layered silicate nano-filler can improve the mechanical properties of polymers remarkably. Such modified polymers show outstanding thermal stability, fire retardance, conductivity, and anisotropy. Layered silicate montmorillonites play a great role in modification of polymers and preparation of nanocomposites because of their outstanding structures, abundant resources, and low costs. Therefore, we used montmorillonite to modify P(AN/VAC) and attempted to prepare P(AN/VAC)/clay nanocomposites.

Polymer/montmorillonite nanocomposites have many other good properties in comparison with nor-

mal polymers, such as outstanding structures and shapes. They also show higher performances than other normal polymer-based composites. In recent years, there are many reports on the study of montmorillonite composites,⁵⁻⁷ but few on PAN based nanocomposites.

In this article, P(AN/VAC) and montmorillonite composites were studied on the basis of industrial acrylic fibers. Using layered silicate montmorillonite as the raw material, P(AN/VAC)/clay nanocomposites were attempted to be prepared by an *in situ* polymerization. P(AN/VAC)/clay can combine the dimensional stability of inorganic materials together with toughness and processability of polymer perfectly. The stability of dimension and heat resistance properties of P(AN/VAC)/clay are all superior to those of P(AN/VAC) alone, which are available for PAN to apply in a wider range. Additionally, low cost of montmorillonite leads to a lower consumption cost of acrylic fibers spinning, which is essential to extend the application fields of PAN.

EXPERIMENTAL

Materials

Organo-MMT (OMMT) was obtained from Huate Co. Cationic exchange value is 120 mmol/100 g. Acrylonitrile (AN) (polymeric grade) and vinyl acetate (VAC) (polymeric grade) were provided by the Daqing Acrylic Fiber Factory of China. All other reagents

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(potassium persulfate ($K_2S_2O_8$), dodecylbenzene sulfonic acid sodium salt (SDS), etc) were obtained from commercial sources and used without further purification unless otherwise indicated.

Intercalation of monomers

A certain amount of OMMT, AN, and VAC were mixed together and oscillated by ultrasound for 10 min.

Preparation of P(AN/VAC)/clay nanocomposite

Appropriate quantity of deionized water and SDS (0.2 g) were added into a three-necked flask equipped with a magnetic stirring bar, a reflux condenser, and a thermometer. Then the mixture of OMMT and monomers was charged into the flask under stirring. When the mixture was heated to the predetermined temperature, the solution of $K_2S_2O_8$ was added and the reaction mixture was allowed to polymerization for a certain time. Finally, the saturated solution of NaCl (13%) was used to destroy the formed emulsion and the products were filtered and washed. P(AN/VAC)/clay nanocomposites were obtained after dried at 70°C.

Characterization of P(AN/VAC)/clay nanocomposites

TEM analysis

P(AN/VAC)/clay nanocomposites was dissolved in ethanol, yielding 1.0 wt % solution. A drop of solution was subsequently cast onto a copper grid and left until dryness. Then the formed film was used to observe the morphology using JEM 2010 transmission electron microscope.

X-ray analysis

X-ray diffraction patterns of the samples were recorded on a D/MAX-B system diffractometer with $Cu K\alpha$ ($\lambda = 0.154$ nm). The tube voltage was 36 KV, electron current was 20 mA, scanning range was $2\theta = 1.5^\circ \sim 40^\circ$, and the speed was $8^\circ/\text{min}$.

FT-IR analysis

IR spectra were measured on a NEXUS-670 spectrometer with the samples prepared as pellets with KBr.

NMR analysis

Solid-state ^{13}C and 1H NMR spectra were carried out on an Advance-400 spectrometer of Bruker co., Switzerland, and with DMSO- d_6 as solvent and tetramethylsilane (TMS) as internal standard in the 1H NMR measurement.

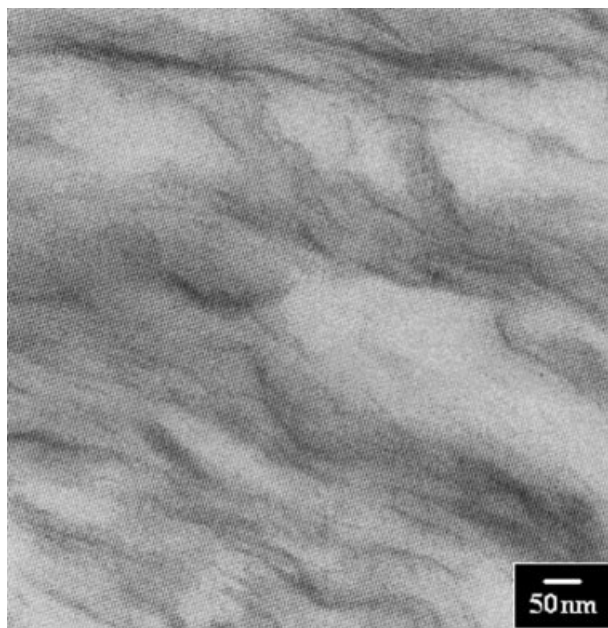


Figure 1 TEM photographs of P(AN/VAC)/clay.

DSC analysis

DSC spectra were obtained on a Perking-Elmer DSC-7 spectrometer. The measurement was carried out at a heating rate of $10^\circ\text{C}/\text{min}$ with the sample masses of about 5~6 mg and the nitrogen flow-rate of 20 mL/min. When the temperature was up to 400°C , the sample was cooled to the room temperature.

RESULTS AND DISCUSSION

Morphology and particle diameter of P(AN/VAC)/clay

The TEM micrographs of P(AN/VAC)/clay nanocomposite are shown in Figure 1. Figure 1 shows that the P(AN/VAC)/clay nanocomposite exhibits a multilayered platy structure. The morphology of alternating light and shade stripes is observed, and it is not an ordered intercalation structure but a basically ordered and exfoliated structure, which indicates that the molecular chains of the polymer have intercalated into the interlayers between the montmorillonite layers.

Distribution of clay in P(AN/VAC)

The X-ray powder diffraction curves of the three samples are shown in Figure 2. The X-ray curve of OMMT is displayed in Figure 2(4) The X-ray diffraction curves of the samples with 5 and 10%(weight fraction) OMMT are in Figure 2(2) and 2(3), respectively. The peak of (001) plane cannot be observed in the two curves, which indicates that the interlayer spaces of OMMT extend too large to find the peak. So it can be

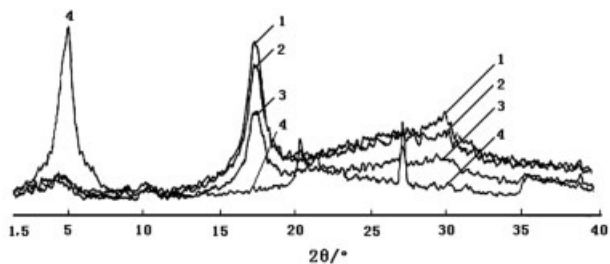


Figure 2 X-ray powder diffraction curves.

concluded that the multilayered platy structures have been totally destroyed and the montmorillonite layers were uniformly distributed in the P(AN/AC) matrix.

Crystal structure of P(AN/VAC)/clay

Figure 2 shows that the characteristic diffraction peak intensity($2\theta = 16.5^\circ$)of PAN decreases with the increase of the content of OMMT, which indicates the crystallinity of the composites decreases. Figure 3 is the diffraction photograph of the P(AN/VAC)/clay composites (15% OMMT). As it is shown, the crystallization cannot be observed clearly.

Composition of P(AN/VAC)/clay

Figure 4 presents the FT-IR spectra of P(AN/VAC)/clay nanocomposite. As we know, OMMT is a kind of montmorillonite that was modified by hexadecyltrimethyl aminobromide. In Figure 4(a), the peaks at 3632.89 cm^{-1} and 3432.46 cm^{-1} are corresponding to —OH and N—H absorption vibrant peaks, respectively. The absorption peaks at 2922.65 , 2851.26 , 1468.70 , 721.37 cm^{-1} are the evidence of the existence of —CH_2 , which is the characteristic peak of the hexadecyltrimethyl aminobromide modified montmoril-

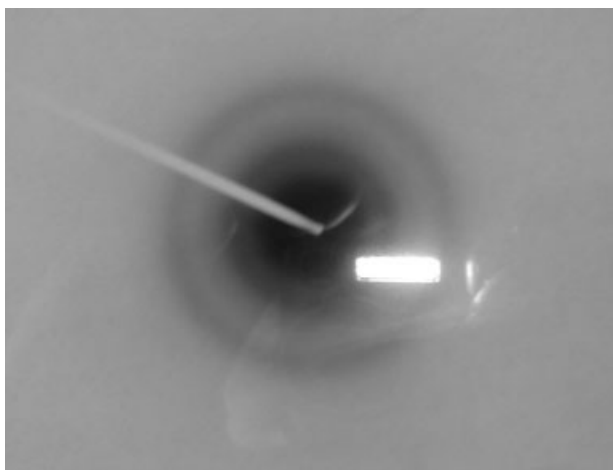


Figure 3 X-ray photograph of P(AN/VAC)/clay nanocomposites (15% OMMT).

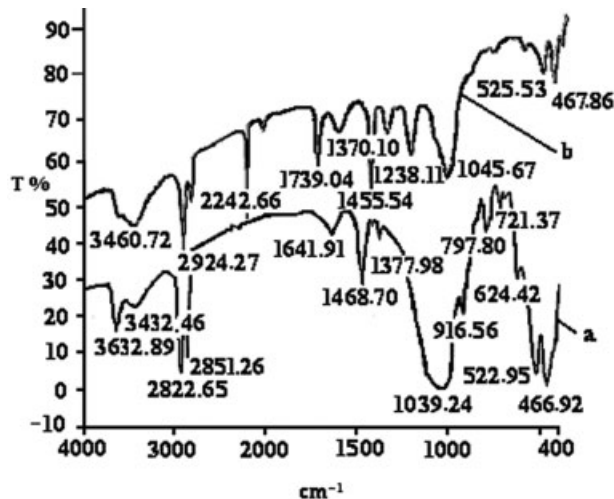


Figure 4 FT-IR spectra of OMMT and P(AN/VAC)/clay nanocomposites.

lonite. The absorption peaks at 1039.24 , 522.95 , 466.92 cm^{-1} , corresponding to the stretching vibration peaks of Si—O and Al—O , are also the characteristic absorption peaks of montmorillonite.⁸ Figure 4(b) is the IR spectra of P(AN/VAC)/clay nanocomposite (10% OMMT). It is observed that the peaks at 2243.71 , 2243.66 , 1738.96 , 1739.04 cm^{-1} are ascribed to —CN and —C=O absorption peaks, respectively. And the characteristic absorption peaks of montmorillonite also appear at 1046.27 , 524.26 , 468.13 , 1045.67 , 525.53 , and 467.86 cm^{-1} . All these indicate the formation of the P(AN/VAC)/clay nanocomposites.

Figures 5(a) and 5(b) present the ^1H NMR spectra of P(AN/VAC) and P(AN/VAC)/clay. In Figure 5(a), the chemical shift of —CH_3 is 1.02 , 373 ppm . In Figure 5(b), the chemical shift of —CH_3 is 1.2393 ppm . The difference is not large. However, the intensity increases from 0.0250 to 0.3453 , which indicates that methyl groups of VAC arranged more regularly under the confined environment of clay and the polymer also

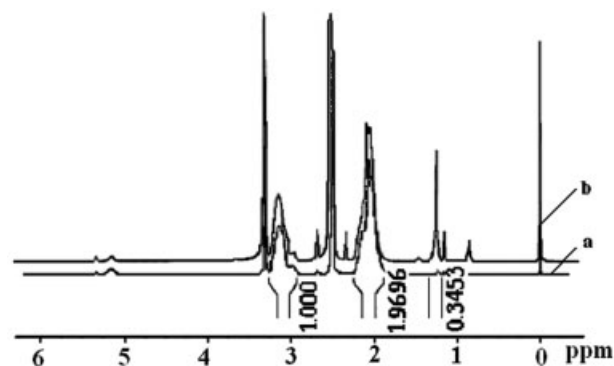


Figure 5 ^1H NMR spectra of P(AN/VAC) and P(AN/VAC)/Clay.

becomes more regularly. This is due to the polymerization effect caused by the polymerization of PAN and P(AN/VAC) in the one-dimensional limited space of the nanocomposite interlayers.⁹

Figures 6(a) and 6(b) show the ^{13}C NMR spectra of P(AN/VAC) and P(AN/VAC)/clay nanocomposite, respectively. In Figure 6(a), the chemical shifts of characteristic peaks at 220.040, 170.886, 120.966, 70.327, 29.774, and 22.351 ppm are corresponding to the functional groups of $-\text{C}=\text{O}$, $-\text{OOCCH}_3$, $-\text{CN}$, $-\text{C}-\text{O}-$, $-\text{CH}_2-\text{C}-$ and $-\text{C}-\text{CH}_3$, respectively. As it is shown, the ^{13}C NMR spectra of P(AN/VAC)/clay in Figure 6(b) is similar to those of P(AN/VAC) in Figure 6(a), which indicates that there are not chemical reactions but only physical transformation between the interlayer. The clay between the interlayers exfoliates and then expands the layers. However, the peaks of P(AN/VAC)/clay are narrow than those of P(AN/VAC). This is because the amount of PAN and P(AN/VAC) penetrated into the interlayers between the montmorillonite layers decreases due to the improved regularity of the polymer under the confined environment of clay.¹⁰

Thermal properties of P(AN/VAC)/clay nanocomposites

Figure 7(a) is the DSC spectra of P(AN/VAC). It is shown the onset and endset temperature for the thermal decomposition are 296.1°C and 323°C, respectively. The peak temperature of the highest peak is 308.9°C. Figure 7(b) is the DSC spectra of P(AN/VAC)/clay. The onset and endset temperature for the thermal decomposition are 300°C and 334.2°C, respectively. The peak temperature of the highest peak is 317.0°C. Compared with P(AN/VAC), the tempera-

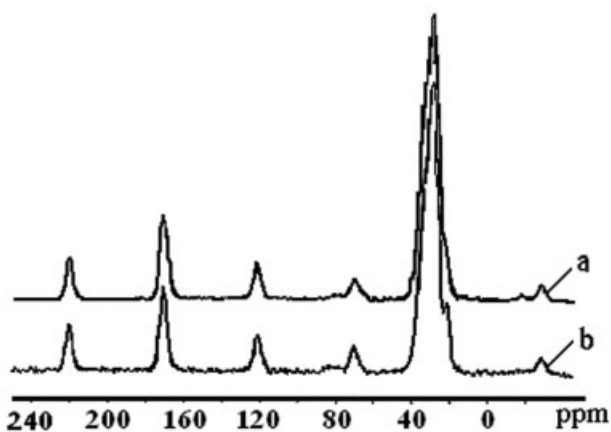


Figure 6 ^{13}C NMR spectra of P(AN/VAC) and P(AN/VAC)/clay.

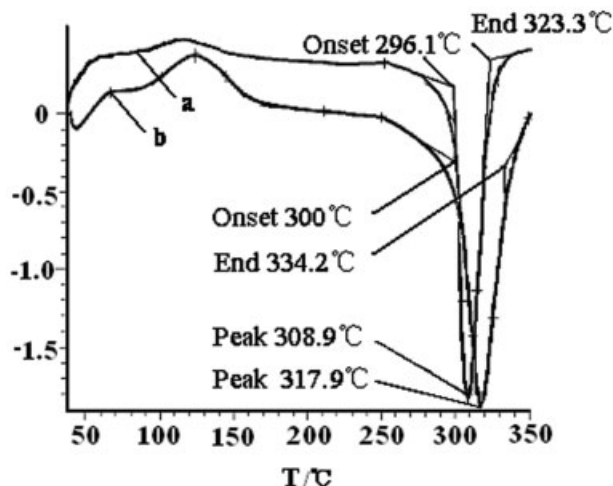


Figure 7 DSC thermograms of P(AN/VAC) and P(AN/VAC)/clay.

ture of thermal decomposition of P(AN/VAC)/clay increases to 8.1°C, which indicates the thermal property of P(AN/VAC)/clay is improved compared with that of P(AN/VAC).

CONCLUSIONS

P(AN/VAC)/clay nanocomposites were prepared by an *in situ* polymerization based on OMMT. The nanocomposites exhibit a multilayered structure. The montmorillonite layers are totally exfoliated and distributed uniformly in the P(AN/VAC) matrix and so the exfoliated nanocomposites are formed. The temperature of thermal decomposition of P(AN/VAC)/clay nanocomposite is 8.1°C higher than that of P(AN/VAC), which means that the thermal property of the nanocomposite is improved.

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