

Compatibility Studies with Blends Based on Poly(*n*-butyl methacrylate) and Polyacrylonitrile

Zhaogang Ge, Changfa Xiao

Tianjin Municipal Key Laboratory of Fiber Modification and Functional Fiber, Tianjin Polytechnic University, Tianjin 300160, China

Received 5 July 2008; accepted 6 April 2009

DOI 10.1002/app.30613

Published online 4 November 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, poly(*n*-butyl methacrylate) (PBMA) was prepared by a suspension polymerization process, and blending with polyacrylonitrile (PAN) in *N,N*-dimethyl acetamide to prepare PAN/PBMA blends in various proportions. Hansen's three dimensional solubility parameters of PAN and PBMA were calculated approximately through the contributions of the structural groups. The compatibility in these blend systems was studied with theoretical calculations as well as experimental measurements. Viscometric methods, Fourier transform infrared spectroscopy, dynamic mechanical analysis, scanning electron microscopy, and thermogravimetric analysis were

used for this investigation. All the results showed that a partial compatibility existed in PAN/PBMA blend system, which may be due to the intermolecular interactions between the two polymers. And, the adsorption experiment results showed that the addition of PBMA contributed to the enhancing adsorptive properties of blend fibers, which lays the foundation for further studying PAN/PBMA blend fibers with adsorptive function. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3357–3364, 2010

Key words: polyacrylonitrile; poly(*n*-butyl methacrylate); blends; compatibility

INTRODUCTION

Polyacrylonitrile (PAN) is one of the most important fiber-forming polymers, which was widely used in making acrylic fibers. Acrylic fibers have many advantages such as high-tensile strength, good abrasion resistance, good insect resistance, and easy-dyeing, which make the fibers popular in apparel as well as in out-door applications.¹

However, the acrylic fibers business overall went into decline during the late 1970s and early 1980s, and product developments of any significance were infrequent. As an outcome of restricting the business, those companies that have remained have been very active since 1995 and we have seen a resurgence in the development of innovative acrylic fibers. The desire to develop new functional fibers is driven by the added value. Polymer blending is an effective and an economically viable way for the preparation of new materials with desired properties.^{2,3} This method is usually cheaper and less time consuming for the creation of polymeric materials

with new properties than the development of new monomers and new polymerization routes. An additional advantage of polymer blends is that the properties of the materials can be tailored by combining component polymers. Several of the function fibers that have entered the market in the last few years are produced by adding stable dispersions of the functional chemical to the polymer solution before fiber formation, such as, moisture absorbent fibers, antistatic fibers, electroconductive fibers, insect and mite-repellent fibers, and deodorising fibers.^{4–8}

Polyacrylate copolymer was widely used in oil-adsorptive resin research.^{9–14} On this basis, we have performed much research work about methacrylate-hydroxyethyl methacrylate oil-adsorptive fiber.^{15,16} Methacrylate was used as a monomer and hydroethyl methacrylate as a potential crosslinker was put in polymerization. Resin synthesized by this method was dissolved in a solvent to prepare solution. After spinning, the fiber was heat treated at certain conditions to form adsorptive fiber. But, we found that the fiber was difficult to prepare and has poor mechanical properties.

The purpose of this research was to prepare PAN fibers with adsorptive function to low molecule organic matter. Blend modified in an effective way was used. The fibers will have desirable properties, such as adsorption, outstanding mechanical properties. And, it could be manufactured into various

Correspondence to: C. Xiao (cfxiao@tjpu.edu.cn).

Contract grant sponsors: National Science Foundation of China and Key Laboratory of Advanced Textile Materials and Manufacturing Technology (Zhejiang Sci-tech University), Ministry of Education.

forms of products, such as nonwoven fabrics, it is particularly convenient to use. So its use was effectively widened and has important significance in environmental protection in the fields of small amount of leak organic solvent treatment and wastewater purification.

In this study, we report progresses of preparing the polymer [poly(*n*-butyl methacrylate) (PBMA)] in a suspension polymerization process and blending the polymer with PAN through solution-blending process in various proportions. At present, studies on the compatibility of PBMA and PAN are very rare, but polymer–polymer compatibility has received much attention, it has a great influence on structure and properties of polymer blends.¹⁷ The objective of the present work was to study the compatibility between PBMA and PAN by theoretical calculations as well as experimental measurements. Viscometric methods, Fourier transform infrared (FTIR) spectroscopy, dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) were used for this investigation, which lays the theoretical foundation for further study of PAN/PBMA blend fibers with oil-adsorptive function.

EXPERIMENTAL

Materials

PAN (vinyl acetate as the second monomer) was supplied by Acrylic Fiber Plant of Qilu Branch, Sinopec Co., Ltd. (Shandong, China). Poly(vinyl alcohol) used as suspension stabilizer was purified by washing with water. Benzoyl peroxide was purified by repeated crystallization (chloroform as solvent, methanol as the precipitation agent) and used as an initiator for *N*-butyl methacrylate (BMA) polymerization; BMA and *N,N*-dimethyl acetamide (DMAc) were purchased from Tianjin chemical reagent factory (Tianjin, China). BMA was purified by washing first with 2% aqueous sodium hydroxide (NaOH) solution, then by thorough and repeated washing with distilled water (to make alkali free as tested by litmus paper), and dried over fused CaCl₂. It was finally vacuum distilled. DMAc was used as a common solvent for PAN and PBMA.

Synthesis of PBMA and blends preparation

PBMA was prepared by suspension polymerization. A typical polymerization procedure is as follows. First, quantitative deionized water and poly(vinyl alcohol) (as suspension stabilizer, 0.5% by weight based on BMA) were dissolved in a four-neck round-bottom flask equipped with stirrer, condenser, and thermometer. Until fully dissolved, quantitative

BMA and benzoyl peroxide (as initiator, 0.3% by weight based on BMA) were added to the flask with a rubber pipe to introduce nitrogen gas into the flask to remove the air in the flask, the stirrer was driven to make the reaction proceeding for 6 h at 80–90°C under nitrogen atmosphere. After the reaction, the suspension was filtered and washed with deionized water to remove the unreacted monomer and dried under vacuum to obtain a white solid.

PAN/PBMA blends were prepared by solution mixing using DMAc as a common solvent. Component polymers, weighed to desired composition, were dissolved in the solvent and stirred until the solutions became clear. The total concentration of PAN and PBMA was kept as 26 wt %. The PAN/PBMA blend fibers were prepared by solution spinning. The coagulation bath was the solution of 50 wt % DMAc.

Measurements

Fourier transform infrared spectroscopy analysis

Fourier transform infrared (FTIR) spectroscopic measurements were carried out on a BRUKER TENSOR37 spectrophotometer (German). Scans were 32× signal averaged at a resolution of 4 cm⁻¹ from 4000 to 600 cm⁻¹.

Viscometric method

Viscosity measurements of all the blend solutions were carried out in a thermostatic transparent water bath at 25 ± 0.1°C using an Ubbelohde viscometer. Every value was measured three times and then averaged.

The intrinsic viscosities [η] of PAN and PBMA were 2.33 and 0.65 dL/g (25 ± 0.1°C, DMAc as solvent), respectively.

Dynamic mechanical analysis

Dynamic mechanical analyzer (DMA242C, NETZSCH, German) was used to measure the dynamic mechanical properties of PAN/PBMA blends. The experiments were carried out at a vibration frequency of 10 Hz and a heating rate of 10°C/min in a nitrogen atmosphere.

Scanning electron microscopy

Scanning electron microscopy (QUANTA200, FEI, Netherlands) was used to study and record the morphologies of fracture surfaces of the blends operating at 20 kV. The samples were cooled in liquid nitrogen and then were broken. The fracture surfaces were sputtered with gold in vacuum and surface characteristics were studied.

Thermogravimetric analysis

Samples studied by TGA were characterized after being dried in a vacuum oven at 50°C for 12 h. The samples were scanned with an NETZSCH STA409PC TGA at a scan rate of 10°C/min in a nitrogen atmosphere from room temperature to 800°C.

Adsorptive properties

Adsorptive properties of samples were measured by a weighing method. A weighed quantity of samples was immersed in solvent (such as toluene) at room temperature until equilibrium was reached, and the residual solvent was then removed by dropping for 10 min. The equilibrium was determined by measuring the solvent absorbency at each time until it reached a limiting value. The solvent absorbency Q was determined by weighing and calculated according to the following equation:

$$Q = (G_1 - G_0)/G_0$$

where, G_1 is the weight of fiber after immersed and G_0 is the weight of dried fiber. The solvents used in this research were toluene, chloroform, and kerosene.

RESULTS AND DISCUSSION

Compatibility based on theoretical calculations

The solubility parameter is one of the most common criterion to judge polyblend compatibility. The use of Hildebrand's solubility parameter δ is restricted to nonpolar substances. In Hansen's approach, the Hildebrand's solubility parameter of a compound is subdivided into three partial parameters. By separate consideration of the sum of the intermolecular forces, Hansen extended the application of the concept of solubility parameter to polar systems.

Hansen believed that there are three major types of interactions in common organic materials. These arise from intermolecular dispersion forces or Van der Waals' forces, intermolecular polar interactions, and intermolecular hydrogen bonding. These interactions cause three types of cohesion energy—the dispersion cohesion energy, E_d ; the polar cohesion energy, E_p ; and the hydrogen bonding cohesion energy, E_h . The total cohesion energy, E , must be the sum of the individual energies that make it up.

$$E = E_d + E_p + E_h \quad (1)$$

Dividing this by the molar volume gives the square of the total (or Hilderand) solubility parameter as

the sum of the squares of the Hansen d , p , and h components.

$$E/V = E_d/V + E_p/V + E_h/V \quad (2)$$

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

$$\delta_d = \sum F_{di}/\bar{V} \quad (4)$$

$$\delta_p = \sqrt{\sum F_{pi}^2/\bar{V}} \quad (5)$$

$$\delta_h = \sqrt{\sum E_{hi}/\bar{V}} \quad (6)$$

The Hansen three dimensional solubility parameters (δ_d , δ_p , and δ_h) were calculated theoretically through the contributions of the structure groups in the polymers using eqs. (4)–(6).¹⁸ Equations (4)–(6) were used to calculate δ_d , δ_p , and δ_h . Equation (3) was used to calculate δ , where δ_d is defined as the dispersion component, δ_p as the polarization component, and δ_h as the hydrogen-bonding component, respectively. F_{di} , F_{pi} , and E_{hi} are defined as the molar attraction constant of additive atoms or groups in the repeated structure. Subscript di represents the dispersion component, pi represents the polarization component, and hi represents the hydrogen-bonding component. \bar{V} is the molar volume constant.

An ideal chemical structure of PBMA with an average of one $-\text{COO}-$, one $>\text{C}<$, two $-\text{CH}_3$, and four $-\text{CH}_2-$ was referenced to calculate the three Hansen solubility parameters (HSP). The three HSPs of PBMA were $\delta_d = 16.79$ (J/cm³)^{0.5}, $\delta_p = 3.68$ (J/cm³)^{0.5}, $\delta_h = 7.25$ (J/cm³)^{0.5}, and $\delta = 18.65$ (J/cm³)^{0.5}, which was calculated based on eq. (4). The three HSPs of PAN were $\delta_d = 16.47$ (J/cm³)^{0.5}, $\delta_p = 23.25$ (J/cm³)^{0.5}, and $\delta_h = 7.27$ (J/cm³)^{0.5}. It is well known that the compatibility of polymers requires a closed as well as having similar values for the three HSPs.¹⁹ Clearly, the three HSPs of PBMA did not match those of PAN. Because PAN contains the nitrile groups, there is a greater contribution to the polarization component of HSP, and therefore, the δ_p value of PAN was greater than that of PBMA. The differences in the three HSP values of these two molecules indicated impossible compatibility when they were blend. But, hydrogen bonding or dipole interactions may exist between PBMA and PAN (vinyl acetate as the second monomer) polyblend systems. In addition, the calculation of PAN solubility parameter did not consider the impact of the second monomer, vinyl acetate, and adding second monomer tends to reduce the polarity of PAN macromolecules, the actual δ_p value of PAN was

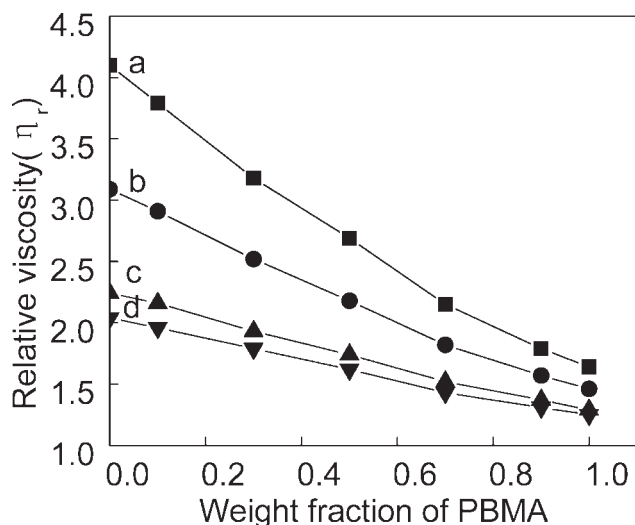


Figure 1 Dependence of the relative viscosity on the composition plots for PAN/PBMA blends (solvent: DMAc, temperature: $25 \pm 0.1^\circ\text{C}$). Curves from a to d represent various solution concentrations, which are as follows: (a) 0.82 g/100 mL; (b) 0.62 g/100 mL; (c) 0.41 g/100 mL; (d) 0.35 g/100 mL.

smaller than that calculated using eq. (5). Therefore, we further investigate the compatibility of PBMA and PAN through the following experiments: viscosimetry, FTIR, DMA, SEM, and TGA.

Compatibility based on experimental estimation

Viscosity method

Viscosimetry is one of the simplest methods for studying the interactions and properties of polymer-polymer systems in solutions. Blend solutions of PBMA and PAN were prepared in DMAc with different weight fractions of PAN—0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0. It has been reported that the plots for compatible blend solutions are linear and otherwise the plots are s-type. But for partially compatible blend solutions the plots are between linearity and s-type.²⁰ For PAN/PBMA blend solutions, the plots of relative viscosity versus composition were neither linear nor s-type as shown in Figure 1. This suggested that PAN was partially compatible with PBMA. And, the viscosities of the systems reduced with increasing PBMA content are depicted in Figure 1. This can be quite well explained from the fact that the entry of PBMA molecules within the PAN throws apart the regularly arranged chains of PAN and breaks up the molecular alignment to a certain extent. This increases the intermolecular spaces and occupies more volume and the addition of PBMA may decrease the number of interacted sites between nitrile groups. This is further increased with the rise

in PBMA content. The viscosities of the systems under consideration are thus reduced.

Fourier transform infrared spectroscopy

The useful information regarding the structural changes was collected by a BRUKER TENSOR37 spectrophotometer. FTIR analysis was based on the identification of absorption bands associated with the vibrations of functional groups presented in PAN and PBMA. Figure 2 shows the FTIR transmittance spectra for PAN, PBMA, and PAN/PBMA blends.

The FTIR spectrum of pure PBMA is characterized by a very strong absorption peak at 1724 cm^{-1} , which is attributed by C=O stretching vibration of the ester group [Fig. 2(a)], and the less intense peak at 1240 and 1020 cm^{-1} was designated to the

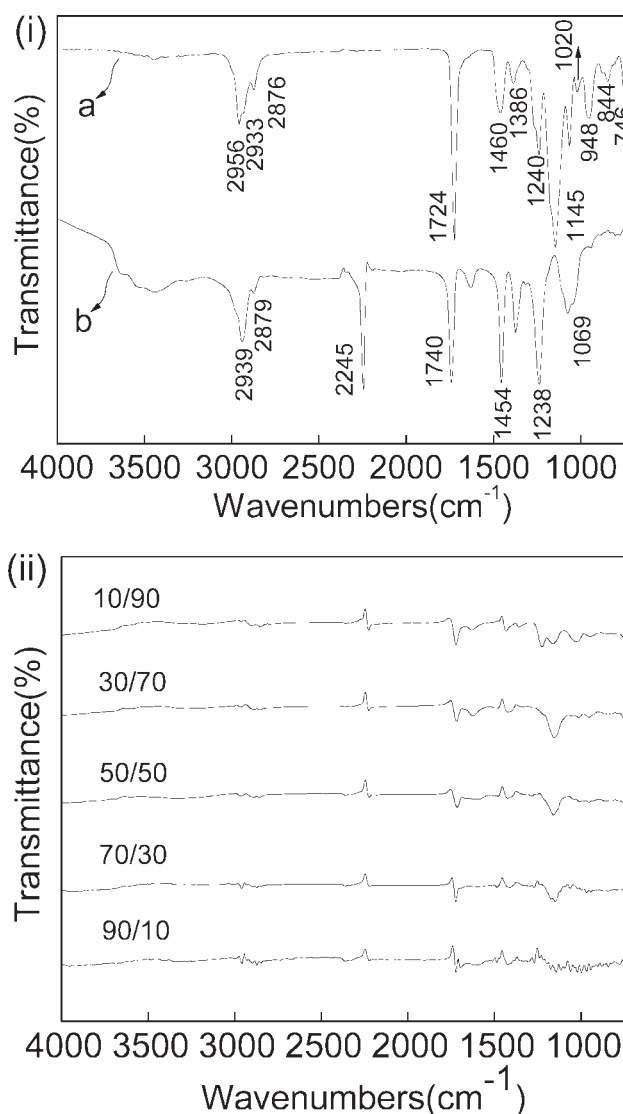


Figure 2 FTIR spectra of the PAN/PBMA blend system. (i) PBMA and PAN; (ii) "reciprocity spectrum" (c-a-b, c, spectra of PAN/PBMA blends; a, spectra of PBMA; b, spectra of PAN).

C—O—C stretching vibrations in esters. The peaks at 2956, 2933, and 2876 cm^{-1} were due to stretching vibrations of CH_3 , CH_2 , and CH bond; the peaks at 1460 and 1386 cm^{-1} were due to scissoring and bending of C—H; The bands at 1145 and 800 cm^{-1} could be assigned to the in-plane and out of plane CH bending modes, respectively. The spectrum of PAN is characterized by a BRUKER TENSOR37 spectrophotometer, having very strong absorption peak at 2247 cm^{-1} , which is due to $-\text{C}\equiv\text{N}$ stretching vibration [Fig. 2(b)], and the peaks at 1740, 1238, and 1069 cm^{-1} were attributed by the second monomer—vinyl acetate.

From the literature, “reciprocity spectrum” can be used to clearly evaluate whether the interactions involved between the components in the blends.²¹ When the interaction between the components to be determined, the spectral additivity is violated. According to the definition, reciprocity spectrum (c-a-b, c, spectra of PAN/PBMA blends; a, spectra of PBMA; b, spectra of PAN) can be obtained by using subtractive infrared spectroscopic software. Figure 2 presented the reciprocity spectrums of PAN/PBMA in various proportions. From the analysis of the FTIR spectra, similar behaviors are observed in different PAN/PBMA blends.

The reciprocity spectrum plots of PAN/PBMA blends showed that the spectral additivity is violated, which showed that there is interaction between PAN and PBMA in blends, causing the positions or vibration strength of the adsorption peaks of groups of PAN and PBMA to change after mixing, especially the adsorption peaks nearby 2247, 1740, 1460, and 1240 cm^{-1} . This may possibly be attributed to the interaction generated among the carbonyl group, carbonitrile, and the hydrogen of PAN and PBMA in blends. Thus, the observed changes in the cited region of the FTIR spectra from reciprocity spectrum show the existence of interaction between PAN and PBMA in the blends.

Dynamic mechanical analysis

DMA was used to determine the compatibility of the blends by investigating the variation of the glass transition temperature (T_g) of the blend components. The T_g of polyblend depends largely on the compatibility of the two components. If two components are incompatible, the blends presented two T_g corresponding to that of pure components. If two components are partly compatible, there is a certain interaction between two components molecules. As a result, the T_g of the two components approached each other. If the two components were fully compatible, there is only one T_g , and as random copolymer case, the T_g basically matches the Fox formula:

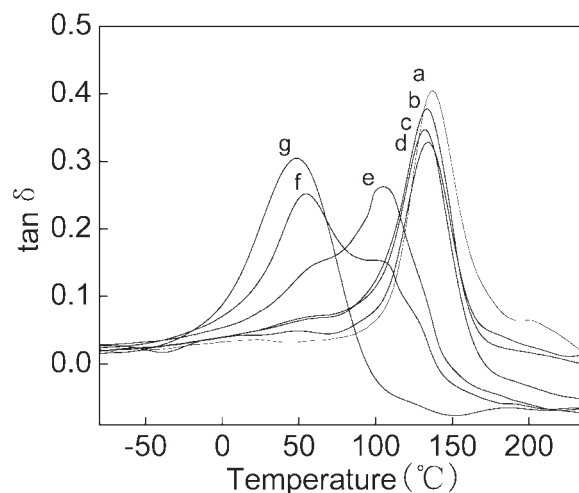


Figure 3 Plots of $\tan \delta$ vs. temperature for the PAN/PBMA blend system. The curves from a to g represent the various weight fractions of PBMA, which are as follows: (a) 0; (b) 0.1; (c) 0.3; (d) 0.5; (e) 0.7; (f) 0.9; and (g) 1.0.

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

where T_g is the glass transition temperature of blends; T_{g1} , T_{g2} , W_1 , and W_2 are the glass transition temperature and weight fraction of the two pure components and the blends, respectively.

The $\tan \delta$ curves as a function of temperature for two pure components and their blends are presented in Figure 3, and the T_g values obtained are presented in Table I. For the PAN/PBMA blends, two distinct $\tan \delta$ peaks are discernible. The peak corresponding to higher temperature is due to the T_g of PAN (PAN- T_g), whereas the peak corresponding to low temperature is due to the T_g of PBMA (PBMA- T_g). In contrast to the pure components, it could be observed that blending causes the PBMA- T_g to shift toward the PAN- T_g . Meanwhile, the PAN- T_g also shifts inward. And the $\tan \delta$ peaks corresponding to PBMA were very weak and almost disappeared when the PBMA content was below 50 wt %. These indicate the existence of interactions between the polymers in a short extension. These interactions occur in molecular level and indicate the existence of partial compatibility between PBMA and PAN. And for the DMA observation, it is worth noting that the location of peaks in $\tan \delta$ against temperature curves, which provides the T_g of the PAN/PBMA blends, changes with increasing PBMA content.

Thermogravimetric analysis

TGA provided quantitative information on the process of weight loss. All of the samples were

TABLE I
The T_g Values of Pure PAN, Pure PBMA and PAN/
PBMA Blends

Samples	Glass Transition Temperature (T_g /°C)	
	PBMA	PAN
PAN	–	136.7
PAN/PBMA (90/10)	60.7	133.6
PAN/PBMA (70/30)	62.4	132.7
PAN/PBMA (50/50)	49.6	134.7
PAN/PBMA (30/70)	62.8	105.0
PAN/PBMA (10/90)	54.7	101.1
PBMA	45.7	–

pyrolyzed at the heating rate of 10°C/min in the temperature range of room temperature to 800°C in an N₂ atmosphere. Figure 4 presents the TGA curves for pure PBMA, pure PAN, and different mixtures of the blend samples.

For pure PBMA, it is observed that a loss of mass in the range from 180 to 320°C could be assigned to side-chain decomposition. Moreover, another loss of mass occurs in the range from 320 to 450 due to rupture of the chains. And, it can be completely degradable in the range of measure temperature. The recorded TGA plots for pure PAN showed better thermal stability than that of PBMA. Below 200°C, there was no obvious loss of quality of PAN and with increasing temperature, PAN occurs at the inner molecular ring and intermolecular crosslinking reaction, release of HCN, NH₃, H₂, CO, CO₂, and other small molecules to form heat-resistant structure, meantime part of nonring or non-crosslinking of the macromolecules pyrolyzed, and in the form of small molecules to escape. This was characterized by a weight loss of about 50% for PAN at 800°C. In contrast to TGA curves of pure PBMA, the PBMA scattered in the PAN-based body, the joined PAN significantly improved the thermal stability of the PBMA. The degradative step in blend samples demonstrated an intermediate between those of the two pure components. And this suggested that the intermolecular interactions exist in the blends.²²

Scanning electron microscopy

The samples used for SEM measurements were the same as those used in DMA analysis. SEM micrographs at 10,000× magnification of fragile-fractured surface of PAN, PAN/PBMA (70/30), and PBMA were shown in Figure 5. The morphologies of pure PAN and pure PBMA samples were homogeneous. Besides, many bright stripes were observed in the

image of pure PAN. With the addition of PBMA to PAN, the morphologies of the PAN/PBMA (70/30) blends changed dramatically. The bright stripes presented in the pure PAN reduced or disappeared, but no obvious phase-separation boundary was visible. Interestingly, interfacial adhesion can be seen from SEM micrograph of blend samples that the dispersed PBMA are adhered to the PAN matrix by the formation of the bridges, and breakage can be clearly seen in micrographs, not been pulled-out during samples preparation. These could indicate the existence of interactions between the two components, which indicated that the two polymers were partially compatible but not incompatible.

Adsorptive properties

The adsorption of organic solvents on PAN and PAN/PBMA blend fibers were measured by a weighing method in this study, and the results are recorded in Figure 6. From the figure, the adsorption of PAN fiber was obviously lower than PAN/PBMA blend fibers, and with the increasing of PBMA content, the adsorption of the PAN/PBMA blend fibers increased accordingly, which was due to the combination of PBMA and PAN as confirmed by the SEM, PBMA uniformly dispersed in PAN matrix. PBMA is a hydrophobic polymer consisting mainly of hydrophobic ester groups and long side chains on molecular chain. It has been discovered that organic solvent molecules have high affinity interaction toward PBMA. Furthermore, the existence of long side chain could raise the interdistance of adjacent chain segments and reduce the degree of orientation, so the void fraction in the fiber got increased. That is

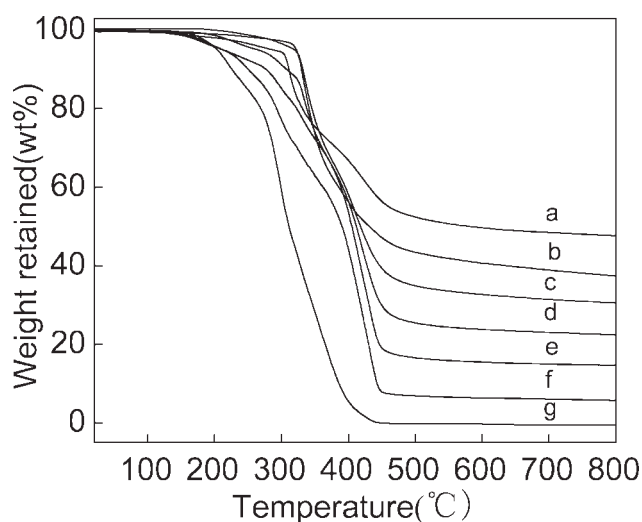


Figure 4 The dependence of mass loss on temperature for TGA. The curves from a to g represent the different weight fractions of PBMA, which are as follows (a) 0; (b) 0.1; (c) 0.3; (d) 0.5; (e) 0.7; (f) 0.9; and (g) 1.0.

also helpful for increasing adsorptive capacity, this adsorption mechanism can be described by the theory of volume filling of micropores. And, hence, the presence of PBMA contributed to the enhancing adsorptive properties of blend fiber. In Figure 6, the adsorption of organic solvents on PAN/PBMA (70/

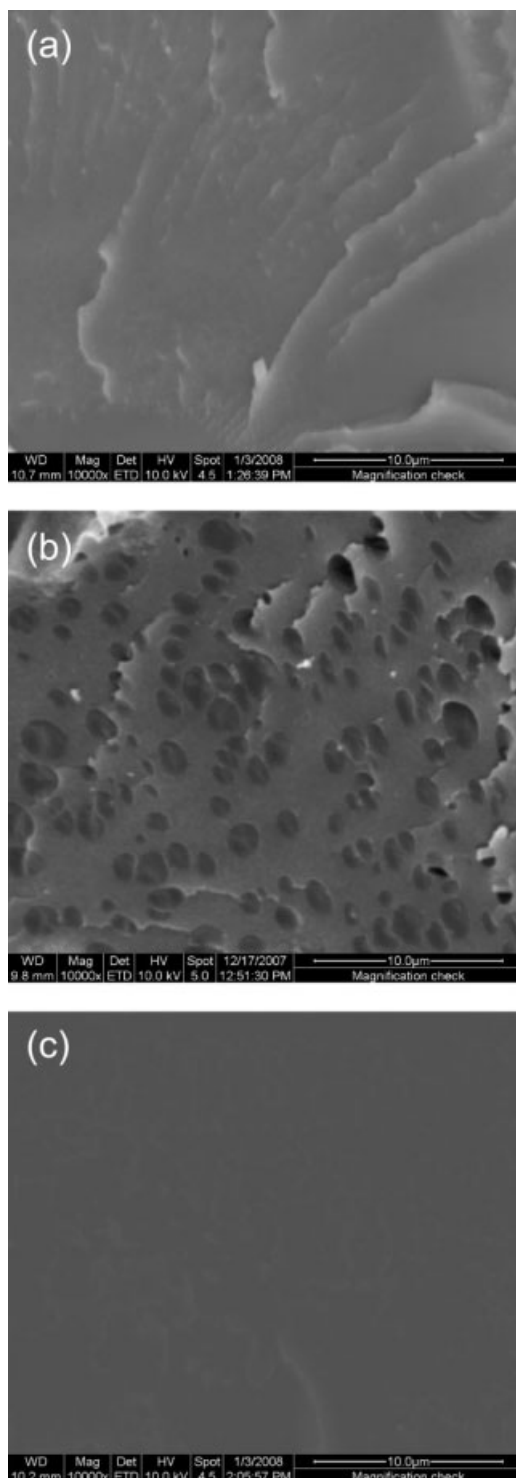


Figure 5 SEM micrographs of (a) pure PAN; (b) PAN/PBMA (70/30); and (c) pure PBMA.

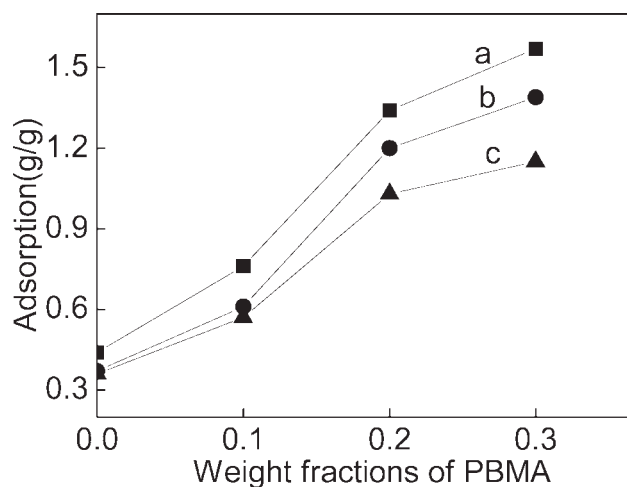


Figure 6 The adsorption of PAN and PAN/PBMA blend fibers on organic solvents. (a) Toluene; (b) chloroform; and (c) kerosene.

30) blend fiber was two or three times higher than PAN fiber.

CONCLUSIONS

The following conclusions could be drawn from this study:

1. PBMA has been prepared by a suspension polymerization process, and blend with PAN in DMAc to prepare PAN/PBMA blends in various proportions via solution blending.
2. The Hansen's three dimensional solubility parameters of PAN and PBMA were calculated approximately through the contributions of the structural groups. The polarization component (δ_p) of three HSPs were remarkably different between PBMA and PAN, not considering the impact of the second monomer, VAc. We concluded based on our theoretical calculations that this blend system was incompatible. But the PAN/PBMA blends were found to be partially compatible in our experimental results. Viscometry, FTIR, DMA, TGA, and SEM were valuable tools for the characterization of the compatibility of polymeric blends. The same compatibility results were deduced from experiment analysis in this investigation, especially the FTIR and DMA analysis. Reciprocity spectrum of PAN/PBMA blends obtained by using subtractive infrared spectroscopic software and show the existence of interaction between PAN and PBMA. This may possibly be attributed to the interaction generated among the carbonyl group, carbonitrile, and the hydrogen of PAN and PBMA in the blends. The PAN/PBMA blends were partially compatible, and the

compatibility of the two polymers was partly produced by the intermolecular interactions between the PBMA and PAN molecules during blending.

3. The adsorption experiment results showed that the addition of PBMA contributed to the enhancing adsorptive capacity of blend fibers, and the adsorption of the PAN/PBMA blend fibers increases with increasing the PBMA content. The adsorption of organic solvents on PAN/PBMA (70/30) blend fiber is two or three times higher than that of PAN fiber. This research increases our knowledge of the compatibility in these systems and provides the promising possibilities of spinning PAN/PBMA adsorptive fiber.

References

1. Sun, Y. Y.; Sun, G. *J Appl Polym Sci* 2001, 81, 1517.
2. Jiang, W.; Han, S. *J Chem Ind Eng* 2002, 53, 285.
3. Cunha, V. S.; Paredes, M. L. L.; Borges, C. P.; Habert, A. C.; Nobrega, R. *J Membr Sci* 2002, 206, 277.
4. McIntyre, J. E. *Synthetic Fibres*; Woodhead Publishing Ltd: USA, 2005.
5. Hongu, T.; Philips, G. O. *New Fibers*; Woodhead Publishing Ltd: UK, 1997.
6. Barani, H.; Bahrami, S. H. *J Appl Polym Sci* 2006, 103, 2000.
7. Jiang, J. M.; Pan, W.; Yang, S. L.; Li, G. *Synth Met* 2005, 149, 181.
8. Wang, L. Y.; Xie, J.; Gu, L. X.; Sun, G. *Polym Bull* 2006, 56, 247.
9. Hozurni, Y.; Toru, U. Production of swellable oil absorbing agent JP 05, 32708, 1993.
10. Hiroyoshi, T.; Kiichi, I. Production of self-swelling oil-absorbent polymer, agent for recovering oily substance JP 05, 209017, 1993.
11. Hiroshi, N.; Kunihiro, K. Water and oil absorptive sheet JP 05, 105729, 1994.
12. Hozumi. Oil-absorbent polymer and use therefore US Pat. 5374600, 1994.
13. Hozumi. Oil-absorbent polymer and use therefore US Pat. 5641847, 1997.
14. Blaney. Oil-asorbing article and methods for making and using same US Pat. 5834385, 1998.
15. Feng, Y.; Xiao, C. F. *Int Polym Process* 2004, 3, 1.
16. Feng, Y.; Xiao, C. F. *J Appl Polym Sci* 2006, 101, 1248.
17. Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*. Academic Press: New York, 1979.
18. Liang, B. R. *Macromolecule Physics*. China Textile Press: Shanghai, 2000; p 143–150.
19. Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press: Boca Raton, FL, 2000.
20. Mamaza, P. A. A. P.; Folarsnmi, F. M. *Eur Polym J* 1996, 32, 909.
21. Xue, Q. *Means of Spectrum in the Research on the Structure of Polymer*; Higher Education Press: Beijing, 1995; 144–147.
22. Li, H.; Shen, X. Y.; Gong, G. L.; Wang, D. *Carbohydr Polym* 2008, 73, 191.