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Compatibility and interactions in polyacrylonitrile/soy protein isolate/polyurethane blends

Ru Xiao,[1] Duan Yin[1], Wei Fan[1], Gang Sun[1,2]*

[1*]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, P. R. China; e-mail: xiaoru@dhu.edu.cn
[2] Division of Textile and clothing, University of California, Davis, CA, 95616, USA

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Abstract: Polyacrylonitrile/Soy protein isolate/polyurethane (PAN/SPI/PU) blends were prepared in dimethylsulfoxide (DMSO). The compatibility and interactive properties of PAN/SPI, SPI/PU, and PAN/PU blend systems were studied using dilute solution viscometry and phase contrast microscopy. It was found that PAN/SPI and PAN/PU were immiscible systems, but that there was an attractive interaction between them. However, the SPI/PU was an almost miscible system. To improve compatibility, the main product of graft copolymerization of acrylonitrile and SPI (AN-g-SPI) and the alkaline hydrolysis polyacrylonitrile (HPAN) were used as compatibilizers. The results showed that the mechanical properties of both the PAN/SPI and PAN/SPI/PU systems were significantly improved.

Introduction

Soy protein isolate (SPI), a naturally renewable and relative inexpensive resource, has been considered a promising alternative to partially replace petroleum-based polymers for material applications. The utilization of these biodegradable proteins for materials development could be environmentally friendly and reduce dependence on petroleum-based polymer materials.

Blending is considered a practical polymer processing method since the blends can combine the advantages of each component, and have better properties than those of the individual components if a synergistic effect is achieved. Research on blends using SPI and other polymers has been reported elsewhere, such as with poly(ester amide) [1-2], biodegradable polyester [3], polyester [4], polylactide [5], polycaprolactone [6-7], chitin [8], lignin [9], cellulose [10], poly(vinyl alcohol) [11], and poly(ethylene-co-ethyl acrylate–co-maletic anhydride) [12].

In order to improve the moisture regain, antistatic properties, dyeing properties, elasticity, and possible biodegradation of the polyacrylonitrile (PAN) system, it was planned to use polyurethane (PU) and SPI as additives. In a previous study, dimethylsulfoxide (DMSO)/urea was chosen as a hybrid solvent system for SPI [13], so DMSO was therefore chosen as the common solvent for the PAN/SPI/PU blend system, in order to support the application of soy protein in a chemical fiber. However, the miscibility of PAN, SPI, and PU plays an important role in determining the processibility, and consequently the mechanical properties, of the blend. In this paper, the interactions and miscibility of the PAN/SPI/PU blend in the DMSO solvent were investigated using dilute solution viscometry and phase contrast microscopy. To improve the compatibility of PAN/SPI/PU in the solvent, two compatibilizers, partially hydrolyzed polyacrylonitrile (HPAN) and acrylonitrile grafted soybean protein isolate (AN-g-SPI), were prepared. The effects of AN-g-SPI and HPAN on compatibility and the properties of the PAN/SPI/PU blends were studied.

Results and discussion

Viscometry analysis

Viscometry was employed to study the miscibility of the solutions of the polymer blends[15-24]. As with a single polymer solution, the specific viscosity $\eta_{sp,m}$ of a mixed polymer solution is expressed as [16]

$$\eta_{sp,m}/c = [\eta]_m + k_{H,m}[\eta]_m^2 c \tag{1}$$

where, $k_{H,m}$ is the overall Huggins coefficient of the polymer mixture solution. For an ideal mixed system, $\langle k_{H,m}\rangle_{id}$, [24] it is assumed that

$$\langle k_{H,m}\rangle_{id} = \frac{k_{H,1}w_1^2[\eta]_1^2 + 2\sqrt{k_{H,1}k_{H,2}}\,w_1w_2[\eta]_1[\eta]_2 + k_{H,2}w_2^2[\eta]_2^2}{\left(w_1[\eta]_1 + w_2[\eta]_2\right)^2} \tag{2}$$

Tab. 1. Viscosity parameters of PAN/SPI, SPI/PU, and PAN/PU systems in DMSO at 30 ^{0}C.

System	w_1	$[\eta]$ $(dl\cdot g^{-1})$	$k_{H,m}$	$\langle k_{H,m}\rangle_{id}$	α	Miscibility
SPI/PAN	1.0	1.41	2.22	2.22	-	-
	0.75	1.32	1.91	2.17	-0.26	immiscible
	0.5	1.27	1.88	2.12	-0.24	immiscible
	0.25	1.20	1.95	2.06	-0.11	immiscible
	0.0	1.18	2.0	2.0	-	-
PAN/PU	1.0	1.18	2.0	2.0	-	-
	0.75	1.11	1.45	1.95	-0.5	immiscible
	0.5	1.0	1.34	1.90	-0.56	immiscible
	0.25	0.94	1.24	1.83	-0.61	immiscible
	0.0	0.74	1.79	1.79	-	-
SPI/PU	1.0	1.41	2.22	2.22	-	-
	0.75	1.21	2.58	2.15	0.43	miscible
	0.5	1.06	2.53	2.07	0.46	miscible
	0.25	0.93	2.19	1.95	0.24	miscible
	0.0	0.73	1.79	1.79	-	-

Similarly, information about the interactions between different types of polymer can be obtained from comparing the experimental $k_{H,m}$ with the theoretical $\langle k_{H,m}\rangle_{id}$ values:

$$\alpha = k_{H,m} - \langle k_{H,m}\rangle_{id} \tag{3}$$

The dilute solution viscosity of the PAN, SPI, PU, PAN/SPI, SPI/PU, and PAN/PU blend systems were measured, and the viscosity parameters obtained are listed in Table 1. It was observed that $\alpha < 0$, therefore all of the PAN/SPI and PAN/PU blend systems are immiscible, although all of the SPI/PU blend systems are miscible in theory [23].

On the basis of cluster theory [25, 26], the apparent association constant, k_m, which characterizes the self-association tendency and ability of polymer chains in solution, can be related to the Huggins coefficient, $k_{H,m}$, as [26]

$$k_m = k_{H,m}[\eta]/6 \tag{6}$$

The k_m is actually an apparent measurement of the interactions that may exist between polymer chains in solution. The stronger the interaction between polymer chains, the greater the k_m. The apparent association constant of an ideal mixed polymer solution can be expressed as [26]

$$\langle k_m \rangle_{id} = \frac{\sum_i k_{m,i}[\eta]_i w_i^2}{\sum_i [\eta]_i w_i} \tag{7}$$

The comparisons of the experimental apparent association constant k_m with the theoretical values of the PAN/SPI, SPI/PU, and PAN/PU mixtures in a DMSO solution are shown in Fig. 1. The experimental k_m of PAN/SPI, PAN/PU, and SPI/PU has a positive deviation from the theoretical values of PAN/SPI, PAN/PU, and SPI/PU blend systems, respectively, indicating an attractive interaction between PAN/SPI, PAN/PU, and SPI/PU. Moreover, the experimental k_m shows a strong positive deviation in the SPI/PU blend system. It is more than the weight-average k_m of the SPI/PU blend system, and shows that the attractive interactions between PAN and SPI are very strong, due to their similar molecular structure. This indicates that the SPI/PU blend is a miscible system.

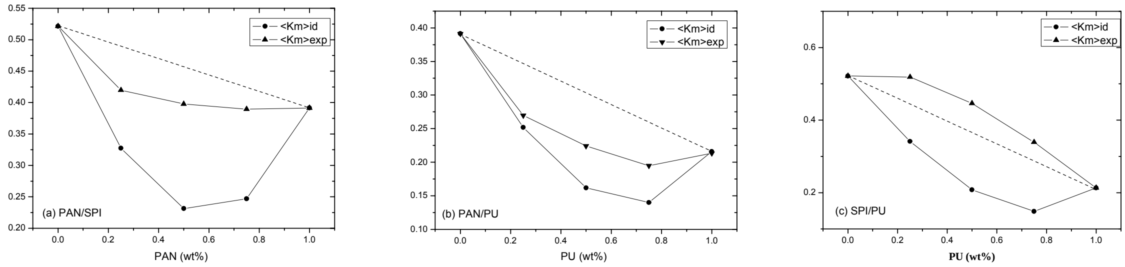


Fig. 1. Variation of overall apparent association of contents of the (a) PAN/SPI (b) PAN/PU (c) SPI/PU mixture in a DMSO solution.

Optical microscopy

The optical micrograph is a very convenient tool for observing phase behaviors. Optical micrographs of PAN/SPI and SPI/PU blend systems of different proportions are shown in Fig. 2. The obvious phase separation behavior is observed in the PAN/SPI blend system even when the SPI proportion is 5 wt%, and the size and number of SPI dispersed phase domains increases with the increasing SPI content. However, the morphology of the SPI/PU shows good properties, even when the SPI content is more than 30 wt%. The macrostructure is tolerably uniform for all systems.

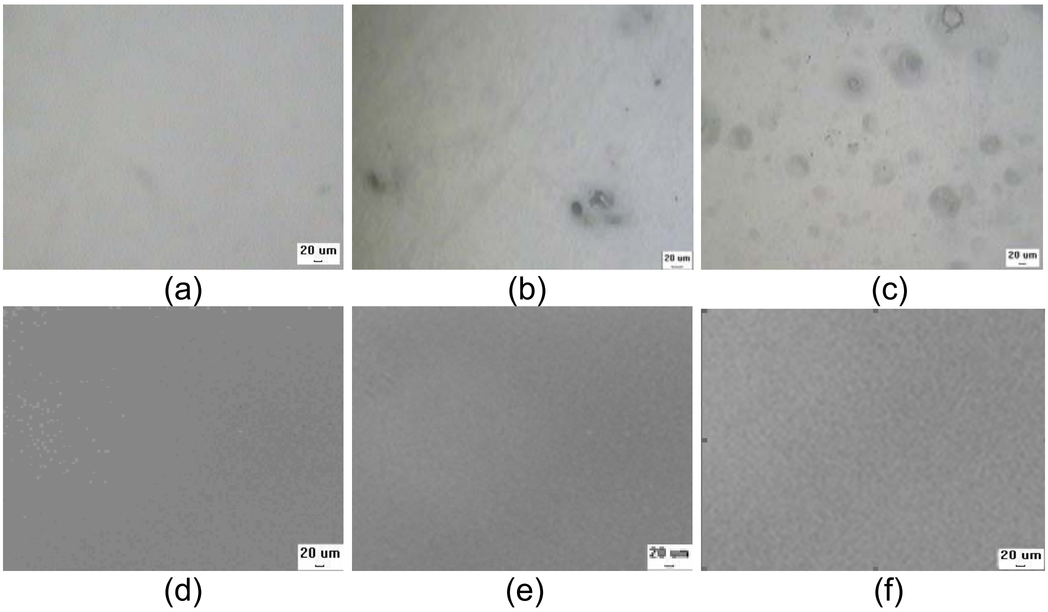
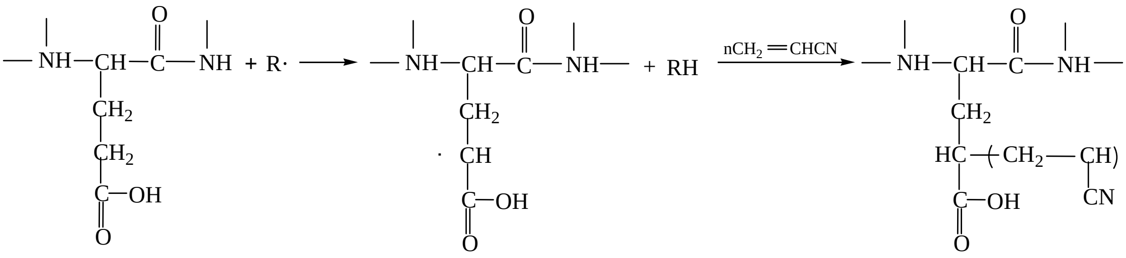


Fig. 2. Optical micrographs of PAN/SPI/PU blend systems with different compositions (wt%): (a) PAN/SPI (95/5), (b) PAN/SPI (90/10), (c) PAN/SPI (85/15), (d) SPI/PU (95/5), (e) SPI/PU (85/15), and (f) SPI/PU (70/30).

Improving compatibility of PAN/SPI/PU

As we know, the presence of a compatibilizer can improve the miscibility of multi-component systems. Therefore, HPAN and AN-g-SPI were used as compatibilizers in the PAN/SPI and PAN/SPI/PU blend systems. The following is a schematic representation of possible interactions between PAN and polypeptide chains, using glutamic acid as an example [27].



The FTIR spectra of PAN (A), PAN-go-SPI (B), and SPI (C), are shown in Fig. 3. PAN (A) shows bands at 2243, 1452, 1261, and 1732 cm^{-1}, which are attributed to the vibrations of nitrile (CN), methylene (CH_2), and methyl (CH) from the monomer acrylonitrile (AN), and carbonyl (C=O) from the monomer methyl acrylate (MA), respectively, in agreement with the literature [28]. SPI (C) shows bands at 1654, 1535, and 1240 cm^{-1} in this region, which are attributed to the vibrations of amideI, amideII and amide III. The FTIR spectra of PAN-g-SPI show the bands of both PAN and SPI, respectively, in this region. This indicates that the grafting of the copolymer PAN-g-SPI was successfully achieved.

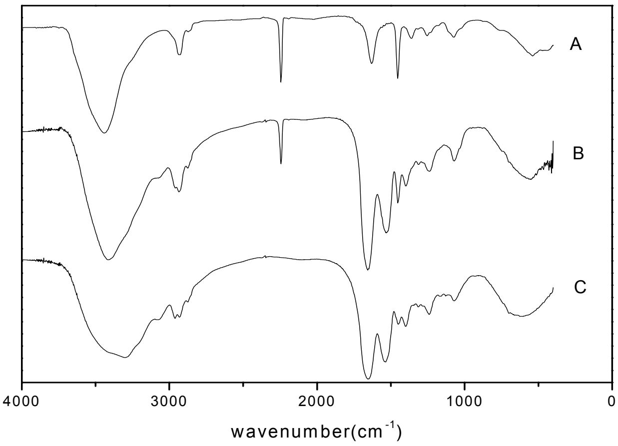


Fig. 3. FTIR transmittance spectra of PAN (A), AN-g-SPI (B), and SPI (C).

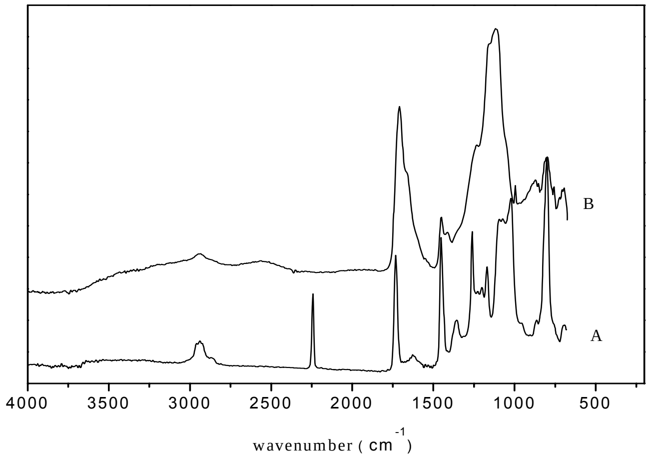
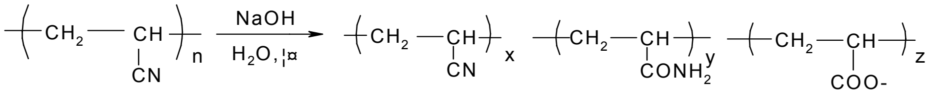


Fig. 4. FTIR absorbance spectra of PAN (A) and HPAN (B).

PAN was hydrolyzed in NaOH aqueous solutions as follows:



$$\left(CH_2 - \underset{CN}{CH} \right)_n \xrightarrow[H_2O,\text{¦¤}]{NaOH} \left(CH_2 - \underset{CN}{CH} \right)_x \left(CH_2 - \underset{CONH_2}{CH} \right)_y \left(CH_2 - \underset{COO-}{CH} \right)_z$$

The FTIR spectra of PAN (A) and HPAN (B) are shown in Fig. 4. The absorption bands at 1708 cm^{-1}, which are attributed to the vibration of the -COOH group in HPAN, indicate that PAN was successfully hydrolyzed.

The tensile strength or Young's modulus of the PAN/SPI (80/20 wt%) and PAN/SPI/PU (60/20/20 wt%) systems with different contents of AN-g-SPI or HPAN are shown in Fig. 5 and Fig. 6, respectively.

It was found that all tensile strengths and Young's modulus increased with increasing amounts of AN-g-SPI and HPAN. This implies that the compatibility of the PAN/SPI or PAN/SPI/PU systems was significantly improved after adding the compatibilizer. SPI is a kind of globulin with a large surface energy, so these molecules easily aggregate in order to decrease the surface energy. AN-g-SPI acts like a bridge to link PAN and SPI, and HPAN is a mixture containing an amine and a carboxyl group. Therefore, they are able to emulsify the SPI molecules and reduce the surface energy, possibly due to strong hydrogen bonds and Van der Waals forces between PAN/SPI and AN-g-SPI or HPAN.

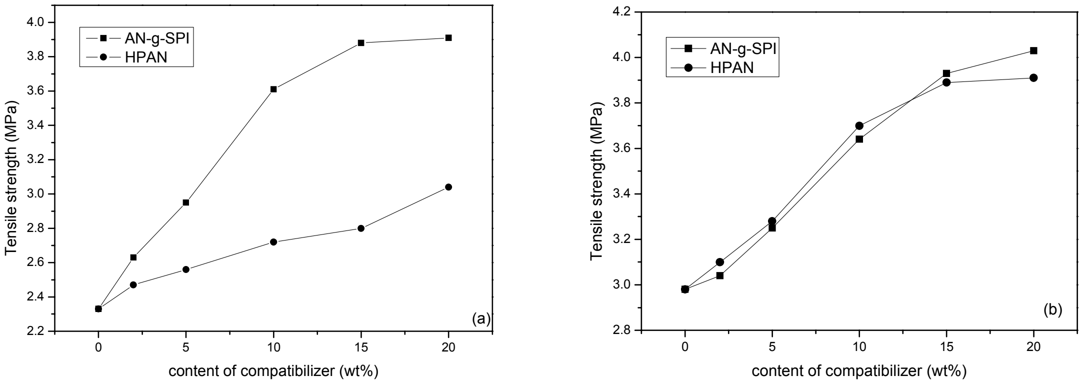


Fig. 5. Influence of AN-g-SPI (■) and HPAN (●) content on tensile strength of (a) PAN/SPI and (b) PAN/SPI/PU blends with 80/20 wt% or 60/20/20 wt%.

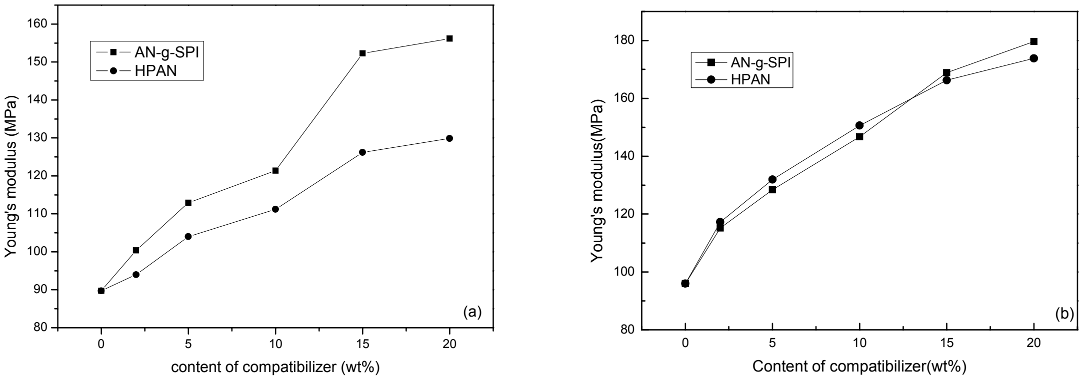


Fig. 6. Influence of AN-g-SPI (■) and HPAN (●) content on Young's modulus of (a) PAN/SPI and (b) PAN/SPI/PU blends with 80/20 wt% or 60/20/20 wt%.

As a result, these interactions increase with the increasing content of AN-g-SPI and HPAN. Moreover, the tensile strength and Young's modulus of the PAN/AN-g-SPI/SPI system is greater than that of the PAN/HPAN/SPI system, which indicates that the compatibility effect of AN-g-SPI in the PAN/SPI system is better than that of HPAN. However, the effects of AN-g-SPI and HPAN on PAN/SPI/PU were almost equal, due to their strong attractive interactions with SPI/PU and PU/HPAN.

Conclusions

The results of dilute solution viscometry and phase contrast microscopy indicate that PAN/SPI and PAN/PU are immiscible, while SPI/PU is a miscible system in a dimethysulfoxide (DMSO) solvent. However, the results also showed that interactions exist between PAN/SPI and PAN/PU systems. Partially hydrolyzed polyacrylonitrile (HPAN) and acrylonitrile-grafted soybean protein isolate (AN-g-SPI) were used as compatibilizers to improve the compatibility of the PAN/SPI/PU blend system. The tensile strength and Young's modulus of the blends increased significantly. Moreover, the compatibility effect of AN-g-SPI was better than that of HPAN in the PAN/SPI blend.

Experimental part

Materials

PAN, with a viscosity-average molecular weight of 52,000 and a composition of 91.2% acrylonitrile (AN), 7.8% methylacrylate, and 1.0% methylallyl sulfonate, was kindly supplied by the Department of Polyacrylonitrile Fibers of SINOPEC, the Shanghai Petrochemical Co. Ltd. SPI was supplied by the Shanghai Shenyuan Food Company. PU was synthesized from polyether glycol, diphenyl-methane-diisocyanate (MDI), and 1,4-butanediol [14]. The monomer acrylonitrile (AN), purchased from the Zhangxing Chemical Reagent Co. Ltd., was purged to remove the hydroquinone and monomethyl ether hydroquinone inhibitors before use. Azobisisobutyronitrile (AIBN) as an initiator was recrystallized twice at 50 °C. DMSO and dimethylformamide (DMF) were supplied by the Shanghai Wulian Chemical Plant. Urea, sodium thiocyanate (NaSCN), polyether glycol, 1,4-butanediol, methanol, sodium hydroxide (NaOH), hydrochloric acid (HCL), and tris-(hydroxymethyl) amino methane were supplied by the China Medicine (Group) Shanghai Chemical Reagent Corporation. MDI was supplied by Yantai Wanhua Polyurethane Co. Ltd. All reagents and chemicals were of analytical grade.

Preparation of PAN/SPI, PAN/PU, and SPI/PU dilute solutions

SPI was added to a DMSO/urea hybrid solvent containing 3 M of urea in DMSO at ambient temperature. The solution was heated to 90 °C at a rate of 1 °C/min, and held at 90 °C for 1 hr. A known amount of PAN or PU was soaked in DMSO at 40 °C. After swelling for 2 hrs, the solution was heated to 75 °C and stirred for 5 hrs at this temperature. Then the PAN, PU, and SPI solutions were blended in controlled proportions, and continually mixed and stirred at 75 °C for 1 hr. The blend solutions had a total polymer content of 0.5 g/100 mL.

Preparation of PAN/SPI and SPI/PU blend membranes

The above SPI solutions were heated to 90 °C at a rate of 1 °C/min, and held at 90 °C for 30 min. Then the temperature was lowered to 50 °C and PAN or PU added. The blend solutions had a total polymer content of 8% by weight. After swelling for 2 hrs, the blends were heated to 75 °C and mixed well at this temperature for about 4 hrs. After sufficient mixing, the blend membranes were cast on glass plates. The membranes were washed with distilled water for 12 hrs to remove the DMSO and urea, and then dried in a vacuum oven at 50 °C for 24 hrs. All samples were stored under vacuum conditions in a desiccator to minimize water absorption.

Preparation of AN-g-SPI

Soy protein isolate was soaked in distilled water for 1 hr at pH 8. The swollen SPI was mixed with NaSCN to reach a concentration of 45 wt% at 45 °C for a sufficient duration to obtain an SPI solution. Then the SPI solution, acrylonitrile (AN), and AIBN were added to a 250 ml three-necked flask in known proportions. After 3 h of grafting reaction at 75 °C, the products were repeatedly washed with distilled water to remove the NaSCN and monomer, then dried in a vacuum to obtain a crude product. The crude product was extracted with Tris-Hcl for 6 h to remove the ungrafted SPI. The extracted product was then washed and filtered in water and dried in a vacuum to obtain a mixture of PAN homopolymer and AN-g-SPI. Then the mixture was extracted with dimethylformamide for 6 h to remove the PAN, washed and filtered in water, and dried in a vacuum to get the mass of graft copolymer.

Preparation of HPAN

2 g PAN was added to a three-necked flask equipped with a stirrer, a thermometer, and a direct condenser. Then NaOH and H_2O were added, and the weight proportion of PAN, NaOH, and H_2O was 1:0.5:8. After reacting at 60 °C for about 30 minutes, the product was cooled to ambient temperature. The pH of the resulting solution was adjusted to between 6 and 7, and the product was precipitated in a large excess of methanol. The resulting precipitate was filtered in a vacuum and then washed twice with water and methanol. Finally, it was dried in a vacuum oven at 60 °C for 24 hrs. The resulting HPAN was stored in a desiccator.

Preparation of PAN/SPI/AN-g-SPI/PU and PAN/SPI/HPAN/PU blend membranes

Preparation of the PAN/SPI/AN-g-SPI and PAN/SPI/HPAN blend membranes was similar to that of the PAN/SPI and SPI/PU blend membranes. The AN-g-SPI or HPAN was first dissolved completely, and then PAN or PU was added to produce the blend system.

Characterization

The intrinsic viscosities of the soy proteins were measured using an Ubbelohde type capillary viscometer at 30 ± 0.02 °C. The phase morphology of the blend membranes with either AN-g-PAN or HPAN was observed using a BX-51 polar optical microscope (Olympus, Japan) at ambient temperature. FTIR spectra were recorded on a NEXUS-670 spectrometer (Thermo Nicolet Corp., USA) by the transmission method. The mechanical properties of the blend membranes were measured using an XQ-1 tensile tester (Donghua University, China). The sample length was 20 mm, and the extension rate was set at 10 mm/min. The statistical results were derived from more than 10 measurements for each specimen. All measurements were performed at 20 °C and 65% relative humidity.

Acknowledgements

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