

# Novel interpenetrating polymer networks of polypropylene/poly(*n*-butyl acrylate)

Chun-tian Zhao\*, Mao Xu, Wei Zhu and Xiaolie Luo

Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080, China  
 (Received 4 November 1996)

Novel interpenetrating polymer networks of polypropylene/poly(*n*-butyl acrylate) have been prepared via *in-situ* polymerization within a biaxially stretched microporous polypropylene film. The volume fraction of poly(*n*-butyl acrylate) in composite films was higher than 40%. The fine-dispersed anisotropic dual-phase continuous interpenetrating network structure was confirmed by surface analysis and transmission electron microscope observation. The interfacial action between polypropylene and poly(*n*-butyl acrylate) was relatively clear. The elastic moduli of the composite films were lower than that of the matrix film. The swelling of poly(*n*-butyl acrylate) in organic solvent was strikingly limited by the polypropylene network. All these properties were in agreement with the anisotropic interpenetrating network structure. © 1997 Elsevier Science Ltd.

(Keywords: interpenetrating polymer networks; polypropylene; poly(*n*-butyl acrylate))

## INTRODUCTION

Interpenetrating polymer networks (IPNs)<sup>1</sup> are defined as the combination of two polymer networks: at least one of the polymers is synthesized or crosslinked (or both) in the presence of another polymer. Because of the poor compatibility between most polymers, the component polymers in IPNs are often phase separated and supermolecularly interpenetrated. IPNs are structurally optimum so that they often have excellent combinative properties and have been widely used in damping materials etc.

IPNs can be prepared via sequential<sup>2</sup> or simultaneous<sup>3</sup> synthesis (including emulsion polymerization<sup>4</sup>) of two polymer networks. Sequential synthesis is a frequently used method. It is practised by swelling polymer networks I in a controlled amount of monomer (containing dissolved initiator and crosslinker) and then polymerizing (and crosslinking) monomers *in situ*. The polymer network I can be chemically or physically crosslinked by crystallites or glass state points. It is easy to appreciate that the network polymer I is one of swellable polymers such as polyurethane, polyacrylate, polystyrene, etc. As a semi-crystalline polymer, isotactic polypropylene is difficult to be swelled by liquid monomers or organic solvents to a high enough degree. So few polypropylene-based IPNs have been prepared via the traditional sequential synthesis. However, we have successfully synthesized a novel polypropylene-based IPN, polypropylene/poly(*n*-butyl acrylate) (PP/PnBA), via a modified sequential method. A microporous polypropylene film prepared by biaxially stretching isotactic polypropylene was used as the polymer network I. The film possesses both excellent fluid transport ability and good mechanical properties. The pore space forms a continuous network in sub-micron and lower dimensions,

which is interpenetrated with polypropylene network. The matrix film was filled with liquid monomer such as *n*-butyl acrylate, and the monomer was then polymerized *in situ* within the pores of this porous film. The composite film had the typical properties of IPNs. This paper reports the preparation, structure and properties of the novel PP/PnBA IPN composite film.

## EXPERIMENTAL

### Materials

Microporous polypropylene film was prepared in our own laboratory<sup>5</sup> by biaxial stretching of isotactic polypropylene. The property of the film was controllable. The film thickness ranged from 15 to 50  $\mu\text{m}$ . The average pore diameter was 50 nm according to the pore water flux method, and the pore size distribution parameter ( $\Phi_{90}/\Phi_0$ ) was lower than 2. The porosity of the film varied between 30 and 50%. The monomer, A.R. *n*-butyl acrylate (nBA), was washed with aq. 5% NaOH solution, dried with anhydrous  $\text{CaCl}_2$  and then distilled under reduced pressure. The crosslinker, divinylbenzyl (DVB), was washed with aq. 5% NaOH solution and dried with anhydrous  $\text{CaCl}_2$ . The initiator was benzoyl peroxide (BPO).

### Preparation of PP/PnBA IPNs

The matrix polypropylene film was first dipped in the nBA monomer solution containing crosslinker and initiator. The previously white film became instantly translucent, which indicated that the monomer had penetrated into the pores. After 24 h the film was taken out of the monomer solution and clamped between two aluminium plates. The plates were sealed round with the oligomer of poly(*n*-butyl acrylate). In order to ensure that all the pores of the matrix film were filled with PnBA, a little more monomer solution was added between the aluminium plates, or the plates were

\* To whom correspondence should be addressed

previously covered with poly(*n*-butyl acrylate) oligomers. The DVB content in poly(*n*-butyl acrylate) oligomer was the same as in the monomer solution filling the matrix film. The sealed plates were pressed under a heavy load and heated at 70°C for 24 h to ensure the *in situ* polymerization was completed. Then the plates were opened, the film taken out, and afterwards the PnBA layers covering the film were removed. The resultant film was dried in a vacuum oven. A series of IPN composite films with different crosslinking degrees of PnBA (indicated by the content of divinyl benzyl in monomer solution) were prepared.

In order to obtain IPN composite films with different interfacial properties, the matrix microporous polypropylene film may be pre-treated under various conditions. One was previously immersed in 1% aqueous Tween-80 solution for 30 min. Another was previously exposed in air plasma for 1 min.

For comparison, a mechanical blend of 85:15 polypropylene/poly(*n*-butyl acrylate) was also prepared by co-extruding at 190°C. The polypropylene used in this blend was PP-2401, a product of Yanshan Petrochemicals Corporation.

#### Analysis and characterization

The dimension and weight of composite and matrix films were measured and compared. The surface of the composite IPN film was observed under a Hitachi-530 scanning electron microscope, and the surface composition was analysed with an ES-300 X-ray photoelectron spectroscopy (X.p.s.).

In order to characterize the inner structure of the IPNs, the composite film was hydrolysed in 10% NaOH/ethanol solution at 70°C for 72 h so that a weakly acidic cation exchange membrane polypropylene/polyacrylic acid sodium salt was obtained. The dry ion exchange membrane was sectioned in two dimensions: the direction parallel to the surface of the membrane and the main machine direction I. The sections were stained with lead(II) nitrate, and observed under a Hitachi-700 transmission electron microscope (TEM).

The elastic moduli and dynamic mechanical curves of the matrix film, the IPN composite film and the mechanical blend of PP/PnBA were recorded in a Rheovibron DDV-II Viscoelastic Meter at a frequency of 3.5 Hz. The temperature was increased at a rate of 3°C min<sup>-1</sup> in the range of -120 to 160°C.

The swelling properties of IPN composite membrane in organic solvent were investigated. A square composite film was dipped in acetone at room temperature for 24 h. The dimensional change of the composite membrane in machine directions I and II and in the thickness direction was measured. The degree of volume swelling of PnBA in composite film was calculated according to the following equation:

$$D_s(\%) = (V_s - V_0)/V_0 \quad (1)$$

Here,  $D_s$ ,  $V_0$ ,  $V_s$ ,  $\epsilon$  respectively indicate the swelling degree, volume of composite film before and after swelling, and the volume fraction of PnBA in composite film. For comparison, pure PnBA of different degrees of crosslinking was measured and calculated according to the formula:

$$D_s(\%) = (V_s - V_0)/V_0 \quad (2)$$

Here  $D_s$ ,  $V_0$ ,  $V_s$  respectively indicate the swelling degree,

and volume before and after swelling of the PnBA sample.

## RESULTS AND DISCUSSION

### Dimension and morphology

The appearance of the composite film was obviously different from that of the matrix film. The composite film consisted of PnBA and PP with close refractive index (difference = 0.0365). The light-scattering ability of composite IPN films was very low, so that the composite films looked translucent or transparent.

Compared to the matrix films, the composite films shrank slightly. In machine direction I, the dimension contracted by about 0.9–3.0%. In machine direction II, the contraction degree was low. The dimension only slightly decreased or even did not change at all. The mass of all the films increased by above 100%. Accordingly, the thickness of the composite films increased by about 3–30%.

The volume of polypropylene,  $V_{pp}$ , can be calculated from the mass of the matrix film  $M$  and the density of the polypropylene phase  $\rho_{pp}$ , which was measured to be 0.89 g cm<sup>-3</sup>. The porosity  $\epsilon$  of matrix film was defined as the volume fraction of micropores

$$\epsilon = 1 - V_{pp}/V \quad (3)$$

where  $V$  was the total volume of the matrix film.

The volume fraction of PnBA phase in composite films,  $\epsilon^*$ , can be calculated as

$$\epsilon^* = V_{pba}/V^* \quad (4)$$

where  $V_{pba}$  is the volume of PnBA,  $V^*$  the total volume of the composite film.  $V_{pba}$  can be calculated from the mass increase and density of PnBA, which was measured to be 1.08 g cm<sup>-3</sup>.

Another volume fraction,  $\epsilon^{**}$ , can also be defined, representing the fraction of volume apart from polypropylene in composite films:

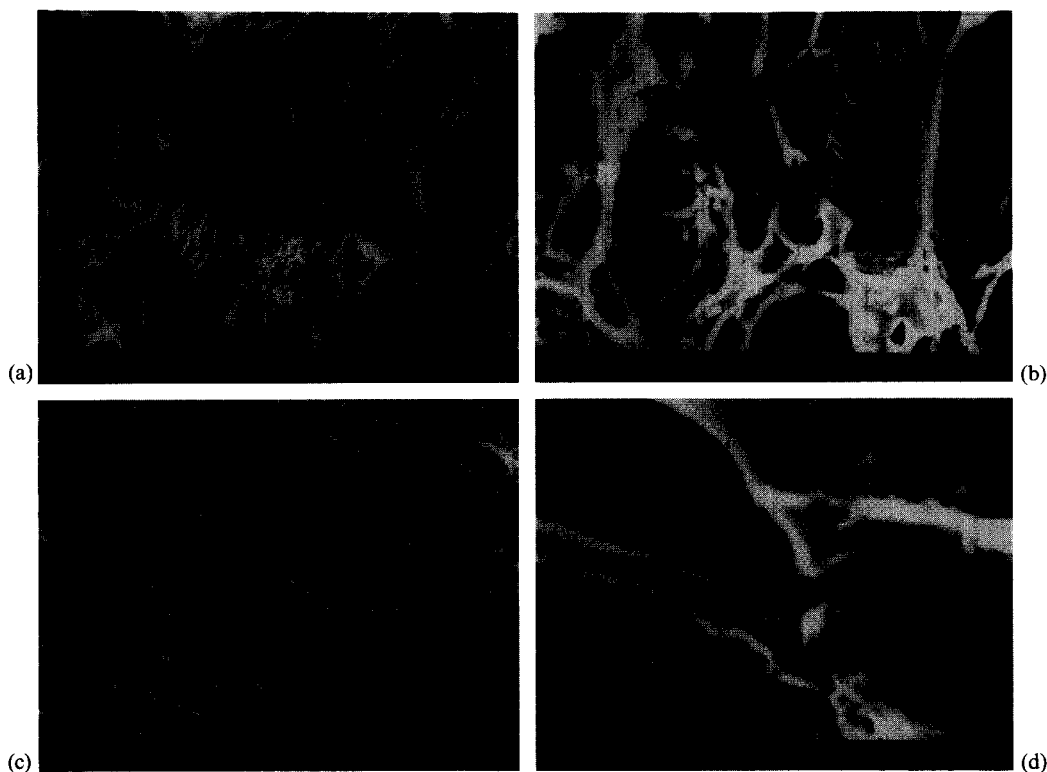
$$\epsilon^{**} = 1 - V_{pp}/V^* \quad (5)$$

The results for  $\epsilon$ ,  $\epsilon^*$  and  $\epsilon^{**}$  are listed in Table 1. The porosity of matrix microporous polypropylene films varied in the range of 30–50%, but the volume fraction of PnBA in all the composite films was higher than 40% and close to 46%. On the whole, there was a good agreement between  $\epsilon^*$  and  $\epsilon^{**}$ . This indicated that almost all the former pores were filled with PnBA. The composite films were pinhole free.

Figure 1 shows the scanning electron micrographs of the matrix microporous polypropylene film and the

Table 1 Physical properties of matrix and composite films

No.	Matrix films	Composite films		Mass increase $M_i$ (%)
	Porosity $\epsilon$ (%)	$\epsilon^{**}$ (%)	$\epsilon^*$ (%)	
1	34.0	45.1	46.8	100.1
2	39.5	46.5	45.9	100.6
3	44.1	51.0	50.4	120.7
4	46.2	47.3	46.3	103.1



**Figure 1** Scanning electron micrographs of matrix microporous polypropylene film (a, b) and the composite PP/PnBA film (c, d); the crosslinking degree of PnBA is 2%

composite PP/PnBA film. The degree of crosslinking of PnBA in the composite film was 2%. The surface of the microporous film was rather rough. Some areas were sunken caves measuring about  $4 \times 8 \mu\text{m}$ . Some sunken caves were round. Other areas were bulging fibrils measuring about  $0.5 \times 8 \mu\text{m}$ . Most of the fibrils tended to align along the same direction. Under high magnification, micropores could be observed. Most of the pores were round, ranging in size from  $0.02$  to  $0.2 \mu\text{m}$ . The surface of the IPN composite film was also rough. Partly oriented fibrils were still seen. The sunken caves were still present, though possibly not as deep. However, no micropores were observed. A little PnBA may have adhered to part of the sunken caves, but the surface of the IPN composite film as a whole was not covered by PnBA.

Figure 2 shows the X-ray photoelectron spectra (X.p.s.) of the matrix microporous polypropylene film and the composite IPN film. There was a symmetric C1s peak only in the X.p.s. spectra of the matrix film. In the spectra of the composite film there were both an O1s peak and an asymmetric C1s peak, corresponding to the PnBA in the composite film. The ratio of elemental oxygen to carbon (O/C) was  $1/7.2$ , i.e. only about half of  $2/7$ , the O/C of the PnBA polymer. This fact indicated that there existed both polypropylene and PnBA in the surface of the composite film. This result agreed with the observation of the film surface under SEM. Polypropylene and PnBA were phase separated. The C/O value indicated that the area ratio of polypropylene to PnBA was about  $27/23$ .

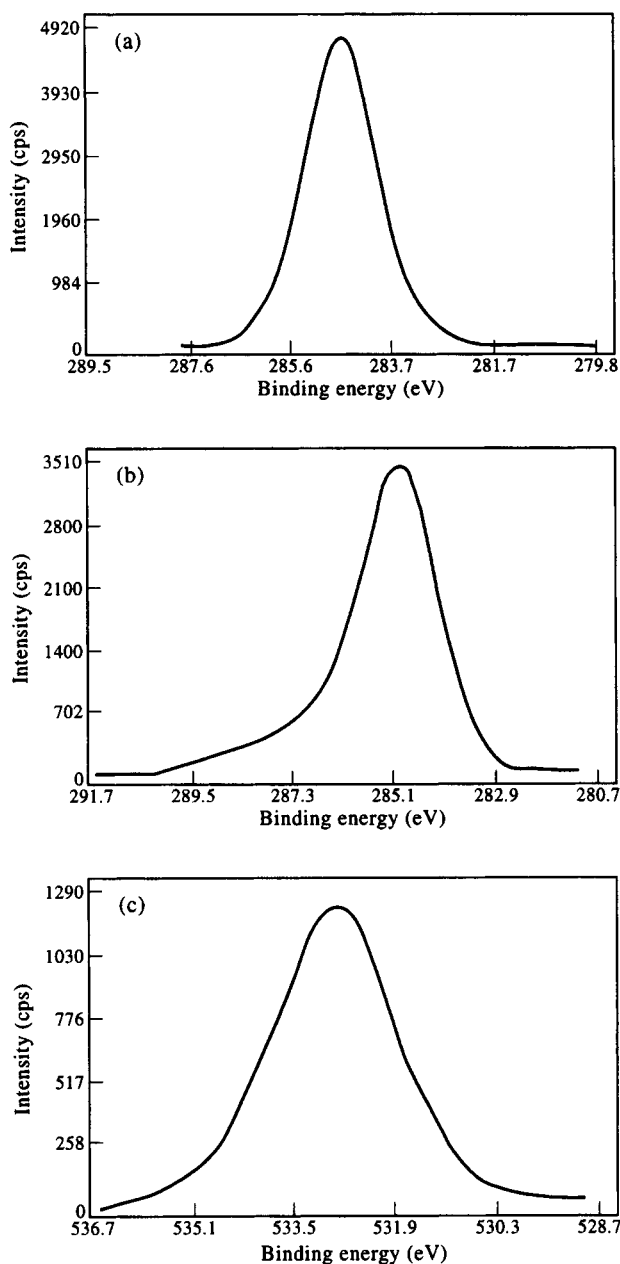
The above results indicated that the thickening of the composite films resulted from the expansion of the inner PnBA phase. The peculiar morphology of the composite film was assumed to result from the influence of the *in*

*situ* polymerization process<sup>6</sup>. (1) The matrix film was first soaked in monomer solution, then the monomers were polymerized *in situ* at  $70^\circ\text{C}$ . The permeation of *n*-butyl acrylate and long-term annealing would disorientate the polypropylene phase to some degree. (2) The preparation proceeded by way of 'permeation-polymerization (crosslinking)-swelling-polymerization (crosslinking)'<sup>6</sup>. Because of the expansion, the spaces occupied by the PnBA phase in the IPN composite films were larger than the micropores of the matrix films. The combined result was that the whole composite film expanded in the thickness direction and slightly contracted in the surface direction.

#### Bulk phase structure

The PP/PnBA composite film was successfully converted to an ion exchange membrane which could be stained with lead(II) nitrate. Such sections show good image contrast under the H-700 transmission electron microscope. Figure 3 shows representative transmission electron micrographs of the sections along the surface direction (a) and along the machine direction (b). Microphase separated two-component morphology was discernible. The bright and dark areas can be reasonably identified as the polypropylene region and poly-ion region respectively. The poly-ion region represented the original poly(*n*-butyl acrylate) phase in IPN PP/PnBA composite film.

The PnBA region was composed of many domains ranging in size from about  $0.01$  to  $0.3 \mu\text{m}$ . The polypropylene region was also separated into domains (Figures 3a and 3b) and microfibrils (easily found in Figure 3a). The PnBA domains were distributed fairly regularly. A kind of multilayer structure was observed in Figure 3b. The layers of PnBA or polypropylene domains



**Figure 2** X-ray photoelectron spectra: (a) C1s of matrix microporous polypropylene film; (b, c) C1s and O1s of the composite PP/PnBA film; the crosslinking degree of PnBA is 2%

were approximately parallel to the surface direction of the composite membrane.

It is clear that the PnBA domains were not isolated. The domains in the same layer were frequently connected via relatively narrow paths, with the domains in adjacent layers also probably connected via similar narrow paths. The PnBA domains were therefore joined together into a continuous PnBA network. Because these domains were linked statistically, the PnBA network was very sinusoidal. The polypropylene region correspondingly existed in the form of a network. The two networks interpenetrated across the whole composite film. Of course, the polypropylene was really composed of two phases: crystalline and amorphous. Without misunderstanding, the structure of the IPN can still be illustrated as interpenetrated two-phase.

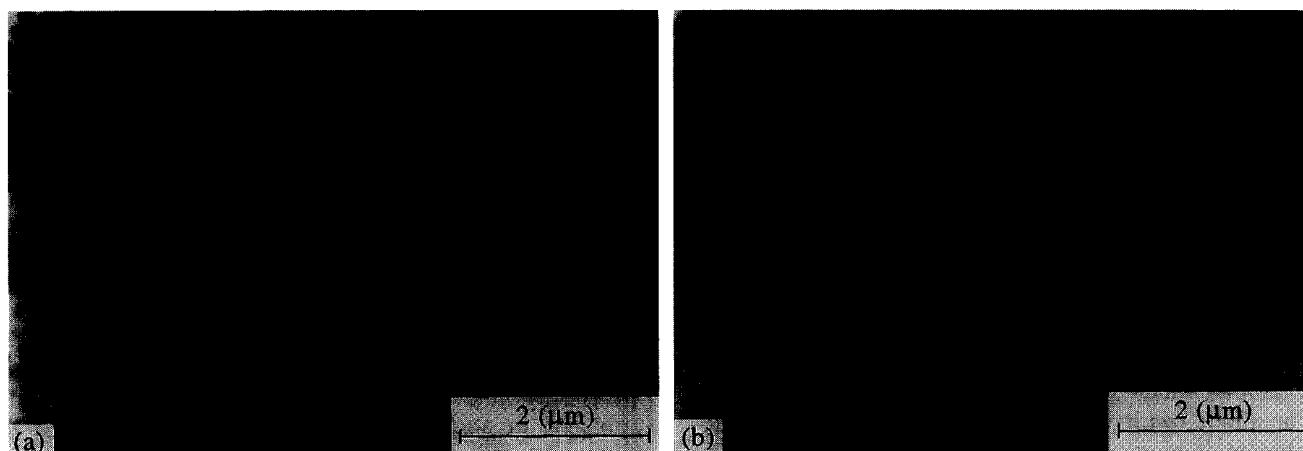
The layer structure indicated that the present IPN is structurally anisotropic to some degree. As observed, the structure parallel to the surface direction varied from that perpendicular to the surface direction. And the structure parallel to the machine direction II was also slightly different because of the probable different degree of stretching degree<sup>5</sup>. The polypropylene and PnBA networks were thus both three-dimensionally anisotropic. In addition, the polypropylene phase was actually molecularly oriented because of stretching and insufficient annealing in the preparation process of the matrix film. The anisotropic property of the present composite films was a characteristic different from traditional IPNs.

It must be pointed out that the matrix film can also be regarded as an IPN, the two interpenetrated phases being polypropylene and air. Although the polypropylene network structure was almost the same as that of the IPN, as indicated above, the structure and morphology of the composite films was somewhat different from that of the matrix film. The final structure and morphology of the IPN composite films was influenced by the preparation process.

*Dynamic mechanical properties and interfacial properties*

Figure 4 shows the dynamic mechanical analysis curves of the PP/PnBA mechanical blend, microporous PP film and PP/PnBA IPN composite films with different degrees of crosslinking of PnBA.

The glass transition temperatures ( $T_g$ ) of polypropylene in the microporous matrix film and in the mechanical



**Figure 3** Transmission electron micrographs of the composite PP/PnBA film; the crosslinking degree of PnBA is 2%: (a) section parallel to film surface; (b) section along machine direction I

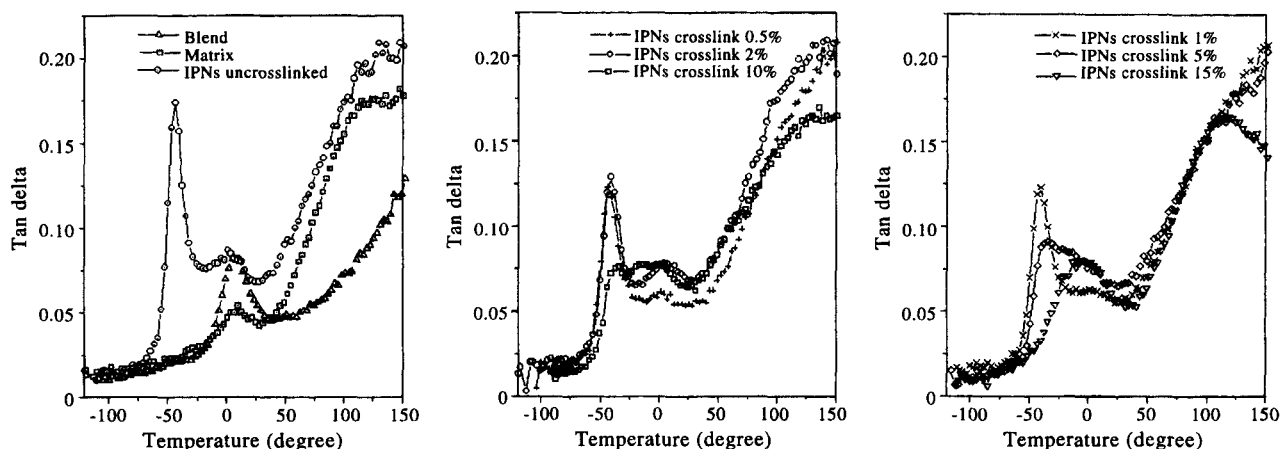


Figure 4 Dynamic mechanical analysis curves of PP/PnBA blend, matrix microporous polypropylene film and the IPN composite PP/PnBA films

blend were 10.1°C and 8.2°C respectively. The polypropylene resin in the matrix microporous film was not PP 2401, and the amorphous polypropylene phase in the matrix film is oriented to some degree. The  $T_g$ s are therefore incompatible.

The  $T_g$ s of crosslinked PnBA in the mechanical blend and in the so-called semi-IPN composite film were respectively -45.5°C and -43.8°C. The  $T_g$  of PnBA in the IPN composite films increased with the degree of crosslinking. The  $T_g$  of polypropylene in the composite films was lower than that of the matrix film, and it seems that there was an obscure trend for the polypropylene  $T_g$  to decrease with the degree of crosslinking of PnBA. When the crosslinking degree of PnBA was 2.0%, the  $T_g$  of polypropylene was lower by 5.2°C. When the crosslinking degree of PnBA was greater than 5.0%, the  $T_g$ s of PnBA and polypropylene were so close that they combined into one wide damping range.

The composite films were prepared by immersion in monomer and *in situ* polymerization. The monomer treatment<sup>7</sup> and prolonged heating in the preparation process would relieve the orientation of polypropylene to some degree, which would lead to a decrease in the polypropylene  $T_g$ .

In addition, we suppose that there existed some weak interfacial interaction between polypropylene and PnBA. Such interaction was not obvious in the traditional mechanical blend, since their dispersed state was coarse. However, in the present IPN composite films, the dispersed state was much finer, in the submicron and even lower dimensions. The interfacial interaction behaved strikingly, and was somewhat enhanced by the increase of crosslinking degree of the PnBA. The interaction also partly responded to the decrease in polypropylene  $T_g$ .

The interfacial interaction may be further confirmed by the dynamic mechanical analysis results for IPN composite films with different interfacial properties. The surface polarity of the microporous polypropylene film was increased by being exposed in air plasma<sup>8</sup>. After treatment in 1% aqueous Tween-80 solution, a small amount of nonionic surfactant was absorbed onto the surface of the microporous polypropylene film<sup>9</sup>. IPN composite films made from the untreated plasma and surfactant-treated matrix films (respectively abbreviated IPNCFU, IPNCFP and IPNCFCS) had different interfacial properties. Figure 5 shows the dynamic mechanical

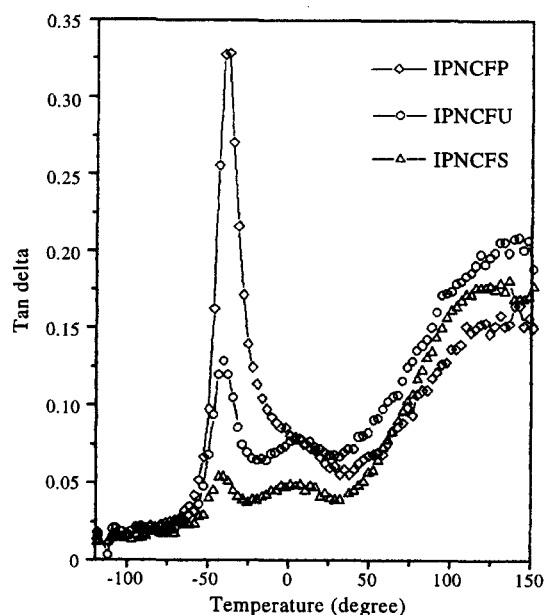


Figure 5 Dynamic mechanical analysis curves of IPN composite PP/PnBA films with different interfacial properties

curves of these IPN films. The  $T_g$  of PnBA in different composite films obviously follows the order of IPNCFP (37.8°C) > IPNCFU (-40.5°C) > IPNCFCS (-42.2°C).

These results suggest that the variation of interfacial properties could strikingly influence the interfacial interactions. Because of the polarity increase of the polypropylene surface after plasma treatment, the adhesion between polypropylene and PnBA in IPNCFP was better than that of IPNCFU. In other words, the two phases were more miscible at their interfaces. The stronger interfacial interactions made the glass transition of fine-dispersed PnBA shift to a higher temperature.

The nonionic surfactant may have had two influences on the dynamic mechanical properties of IPNCFCS. The first was the 'lubricant' effect. It can be assumed that most of the surfactants were aggregated at the interface of polypropylene and PnBA, so that the interfacial interaction between polypropylene and PnBA was buffered to some degree. The second was the 'plasticizer' effect. A little surfactant may have dissolved in and plasticized the PnBA phase, so that the PnBA was more

mobile and its glass transition moved to a lower temperature.

#### Elastic moduli

The tensile elastic moduli of the matrix and composite films were obtained from dynamic mechanical analysis. In this experiment, the porosity of all the corresponding matrix films was controlled to about 36%. The results are listed in *Table 2*. Although the data were somewhat divergent, the elastic moduli of all the IPN composite films ranged from  $1.33$  to  $1.57 \times 10^{10}$  dyn cm<sup>-2</sup> in machine direction I, and from  $4.2$  to  $6.2 \times 10^9$  dyn cm<sup>-2</sup> in machine direction II. The elastic moduli of the matrix film in the two directions were respectively  $1.80 \times 10^{10}$  and  $8.00 \times 10^9$  dyn cm<sup>-2</sup>. In general, the elastic moduli of the composite films were lower than that of the matrix film.

The moduli of both matrix and composite films can be explained in terms of the two-phase interpenetrated structure. The modulus of air can be neglected, so the modulus of the matrix film was actually the modulus of the polypropylene network. This modulus was related to both the modulus of the matrix phase and the shape of the two-phase structure. The network was structurally three-dimensionally anisotropic. Because of the original stretching, the matrix polypropylene phase was molecularly oriented. The modulus of the matrix polypropylene phase in the surface direction was bigger than that in the thickness direction. Moreover, the modulus in machine direction I was somewhat bigger than that in machine direction II. Furthermore, it can be assumed that the shape anisotropy of the polypropylene network gave rise to a difference in modulus, similarly to the matrix phase orientation.

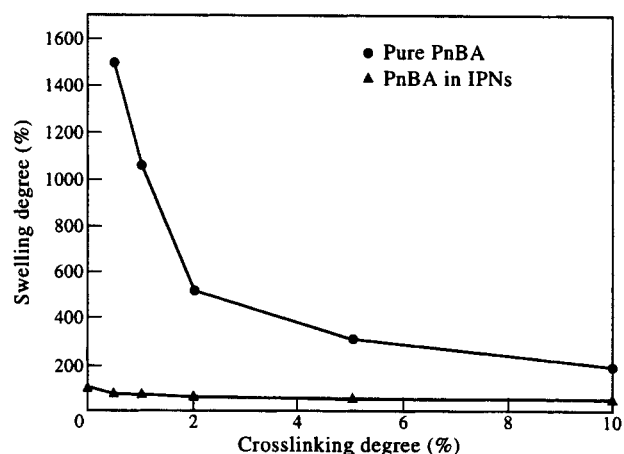
The moduli of IPN composite films were determined by the final structure, which was influenced by the preparation process. Because the orientation of polypropylene was relaxed to some degree, the modulus of the matrix polypropylene phase was decreased accordingly. Moreover, the volume fraction of PnBA was obviously higher than the porosity of the matrix films. At room temperature the modulus of the PnBA phase was lower by  $1 \times 10^7$  dyn cm<sup>2</sup>. So the increase of volume fraction of PnBA would lead to a decrease of the modulus. These two factors both responded to the modulus decrease of the IPN composite films.

#### Swelling in organic solvent

The swelling properties of the PP/PnBA IPN composite film in acetone were investigated. The uncrosslinked pure PnBA can readily dissolve in acetone or ethyl acetate. The uncrosslinked PnBA confined semi-IPN

**Table 2** Elastic tensile modulus ( $E$ ) of PnBA, matrix and IPN composite films at 25°C, in machine directions I and II (MDI, MDII)

Film	Crosslink (%)	$E$ in MD I ( $10^9$ dyn cm <sup>-2</sup> )	$E$ in MDII ( $10^9$ dyn cm <sup>-2</sup> )
PnBA matrix	4	< 0.01	< 0.01
IPN	0	18.0	8.00
IPN	0.5	15.7	4.26
IPN	1.0	13.4	4.86
IPN	2.0	13.3	4.85
IPN	5.0	15.5	5.13
IPN	10.0	14.2	5.10
IPN	15.0	14.3	4.76
IPN	15.0	6.13	6.13



**Figure 6** Dependence of swelling degree of PnBA on crosslinking degree

composite film, on the contrary, was found not to have dissolved in the two solvents even after a 10-day immersion. The degree of swelling of PnBA decreased with the increase of degree of crosslinking. *Figure 6* displays the relationship between swelling degree and crosslinking degree of pure PnBA or PnBA in composite films. The swelling degree of PnBA in composite films was obviously lower than that of pure PnBA with the same crosslinking degree. The swellability of the PnBA phase filling the IPN was strikingly limited.

The swelling degrees of the present IPN composite films were characteristically different in the surface and thickness directions. *Table 3* lists the equilibrium dimensional degree of increase of IPN films dipped in acetone in machine directions I, II and the thickness direction. After swelling in acetone for enough time, the composite films hardly expanded in machine direction I, expanded a little in machine direction II and mainly expanded in the thickness direction. The swellability of the present IPNs is therefore anisotropic.

The swelling properties of the composite films were attributed to the anisotropic IPN structure. In composite films, the PnBA phase would absorb organic solvent (acetone) and expand. Polypropylene is well known not to be swelled by acetone. So, in addition to the shrinkage stress due to crosslinking, the swelling of PnBA in IPNs is limited by the polypropylene phase, being restricted by the modulus of the polypropylene network. Because of the anisotropic interpenetrating two-phase structure, the modulus of the polypropylene network in the present IPN followed the order: machine direction I > machine direction II  $\gg$  thickness direction, while the swelling degree followed the opposite order.

**Table 3** Dimension increase (DIN) of acetone swelled IPN composite films PP/PnBA in machine directions I, II (MD I, MD II) and thickness direction (TD)

Film No.	Crosslink (%)	DIN in MD I (%)	DIN in MD II (%)	DIN in TD (%)
1	0	0.5	2.6	54.41
2	0.5	1.6	4.0	40.32
3	1.0	0	5.0	38.65
4	2.0	0.5	2.0	36.07
5	5.0	0	5.0	31.20
6	10.0	0	5.0	24.07

#### ACKNOWLEDGEMENT

We are grateful to the National Natural Science Foundation of China and the Science Foundation of Polymer Physics Laboratory, Academia Sinica, for support of this work.

#### REFERENCES

1. Sperling, L. H., *Interpenetrating Polymer Networks and Related Materials*. Plenum Press, New York, 1981.
2. Sperling, L. H. and Friedman, D. W., *J. Polym. Sci., A-2*, 1969, **7**, 425.
3. Sperling, L. H. and Arnts, R. R., *J. Appl. Polym. Sci.*, 1971, **15**, 2731.
4. Sperling, L. H., Chiu, T. W. and Thomas, T. A., *J. Appl. Polym. Sci.*, 1973, **17**, 2443.
5. Xu, M., Hu, S., Guan, J. *et al.*, US Patent 5 134 173.
6. Zhao, C., Xu, M. *et al.*, submitted to *Polym. Bull.*
7. Zhao, C., Zhang, X., Hou, J. and Xu, M., *Chin. J. Polym. Sci.*, 1996, **14**(4), 376.
8. Zhao, C., Zhu, W., Xu, M. *et al.*, *Gongneng Gaofenzi Xuebao*, 1996, **9**(3), 337.
9. Zhao, C., Ph.D. dissertation, Chinese Academy of Sciences, 1994.