



# Ternary blend with both molecularly and supermolecularly interpenetrating networks

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## Abstract

Ternary blends were prepared via in situ polymerisation of n-butyl acrylate within microphase separated interpenetrating polymer networks, polypropylene/poly(n-butyl-co-styrene). Dynamic mechanical thermal analysis indicated that the resulting blends were polymer networks structurally interpenetrated in both molecular and supermolecular level. © 1998 Elsevier Science Ltd. All rights reserved.

**Keywords:** Interpenetrating polymer networks; Molecular; Supermolecular

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## 1. Introduction

Interpenetrating polymer networks (IPNs) is one special kind of polymer blend with optimum structure and favourable cooperative properties [1,2]. In IPNs, two or more polymers are combined together in network forms, in which at least one of them is synthesised or cross-linked in the immediate presence of the other. Because of the poor miscibility between most polymers, most IPNs are actually microphase separated, i.e. supermolecularly interpenetrated polymer networks.

As a semi-crystalline polymer, isotactic polypropylene (iPP) cannot be swelled by liquid monomers to a degree suitable for in situ polymerisation. So few polypropylene based IPNs have been prepared via the traditional sequential synthesis method [3]. We have successfully synthesised novel polypropylene based IPNs via a modified sequential method [4,5]. A microporous polypropylene film [6] prepared by biaxial stretching of iPP was used as the polymer network I. The micropore space formed a continuous network in sub-micron and lower dimensions [7] interpenetrated with iPP. Liquid monomer was filled in the matrix film, and then polymerised in situ to form polymer network II. The resulting composite film, such as polypropylene/poly(n-butyl acrylate) (PP/PnBA), had the typical properties of microphase separated IPNs.

We have also prepared polypropylene/poly(n-butyl acrylate-co-styrene) (PP/P(nBA-St)) IPNs composite films. These IPNs films could be swelled by the monomer of n-butyl acrylate (nBA). The absorbed monomers were polymerised in situ, so that ternary blend films were prepared. The latterly formed PnBA could be molecularly interpenetrated with the random copolymer P(nBA-St). So the resulting films might be in fact ternary blends with structure of both molecularly and supermolecularly interpenetrating networks. This peculiar novel IPNs is of academic and application interest.

## 2. Experimental part

### 2.1. Materials

Microporous polypropylene film was prepared in our own laboratory by biaxial stretching of iPP [6], which was purchased from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The film thickness was controlled in the range of 15–50  $\mu\text{m}$ . According to pore water flux method [7] the average pore diameter was 50 nm and pore size distribution parameter ( $\Phi_{90}/\Phi_{10}$ ) was lower than 2. The iPP in microporous film was crystallised in  $\alpha$ -form. its degree of crystallinity was  $\sim 50\%$  and the melting point was 165°C–168°C (DSC, 20°C  $\text{min}^{-1}$ ). The monomers, A.R. n-butyl acrylate (nBA) and A.R. styrene (St) were washed with 5% aq. NaOH solution, dried with anhydrous  $\text{CaCl}_2$  and then distilled at reduced pressure. The

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cross-linker, divinylbenzyl (DVB) was washed with 5% aq. NaOH solution and dried with anhydrous CaCl<sub>2</sub>. The initiator was benzoyl peroxide (BPO).

## 2.2. Preparation of PP/P(nBA-St) IPNs

The matrix polypropylene films were dipped in the mixed (nBA-St) monomer solution containing initiator and cross-linker (2% by mass fraction, designated as the cross-linking degree of copolymers) for 24 h to soak enough monomers. Then the films were clamped between two aluminium plates. The sealed plates were pressed under a heavy load and heated at 70°C for 24 h to in situ polymerise the monomers. In order that all the pores of matrix film were fully filled, a little more monomer solution was added between the aluminium plates to enclose the 'swollen' sheet before polymerisation. At last the films were taken out and the covered layers of P(nBA-St) in two sides of the sheet were cleared away afterwards. The resultant films were dried in a vacuum oven. By changing the mass ratio of nBA and St, a series of IPNs PP/P(nBA-St) composite films (designated as intermediate films) were prepared.

## 2.3. Preparation of PP/P(nBA-St)/PnBA films

The base PP/P(nBA-St) films soaked enough nBA monomer solution containing cross-linker (2% by mass fraction) and initiator, and then the monomers in situ polymerised. Followed procedures were similar to the preparation of intermediate films. These PP/P(nBA-St)/PnBA composite films were designated as resulting films.

## 2.4. Analysis and characterisation

The dimensions and weights of matrix, intermediate and resulting composite films were recorded with 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°C to 160°C.

## 3. Results and discussion

The intermediate and resulting composite films were transparent/translucent. Table 1 gives the basic physical properties of the films. Compared to the matrix microporous film, the mass of all the intermediate films increased by above 100%. The thickness of the intermediate films increased and the dimensions in the machine directions slightly decreased. It could be proved that all the micropores of original matrix films were filled. The intermediate films were pinhole free. The detailed interpretation can be referred to our other paper [5].

Compared to the intermediate films, the mass of all the resulting IPNs films increased by above 80%. The thickness increase was noticeable. The resulting IPNs composite films were ternary blends composed of iPP, poly(n-butyl acrylate-co-styrene) (P(nBA-St)) and poly(n-butyl acrylate) (PnBA). In this blend, the mass fraction of iPP was below 25%, the mass fraction of P(nBA-St) copolymer, PnBA was 35–45%, 45–55% respectively.

Fig. 1 gives SEM photographs of the three kind of films. The surface of the matrix film was rough and micropores in the dimension of 0.02–0.2 μm were seen under high magnifications. No such micropores were observed in the surface of the intermediate and resulting films. However, the surface of the composite films was still rough with outlines similar to that of matrix film.

The structure of the composite films was determined by the structure of original microporous film and influenced by the two in situ polymerisation processes. The micropore structure of the present film [7] was more complex than that of Celgard film [8]. Separated by micro-fibrils, the microporous region in the film was made up of space units or pores in sub-micro and lower dimensions. The micropores were connected so that a continuous pore network formed and interpenetrated with iPP. In PP/P(nBA-St), iPP and chemically cross-linked P(nBA-St) were microphase separated. P(nBA-St) occupied mainly the original pore region and still interpenetrated with iPP.

Table 1  
Basic physical properties of the intermediate and resulting films

No.	Composition of copolymers (%)		Variation of intermediate films (%) <sup>a</sup>				Variation of resulting films (%) <sup>a</sup>	
	Mass fraction		Dimension			Mass		
	nBA	St	L1i	L2i	Thi	Mi	Thi	Mi
1	88.2	9.8	-1.0	-1.7	30.4	113.8	57.9	81.0
2	78.4	19.6	-1.1	-2.5	6.57	128.9	83.2	105.3
3	68.6	29.4	-0.5	-1.3	13.7	128.4	63.6	88.3
4	58.8	39.2	-0.5	-1.3	13.9	110.8	58.4	87.5
5	49.0	49.0	-1.0	-1.6	11.6	151.9	92.4	92.4
6	39.2	58.8	-1.3	-1.7	32.0	121.5	93.9	92.9
7	29.4	68.6	-2.8	-3.2	50.6	154.3		
8	19.6	78.4	-1.3	-1.9	14.1	177.4		

<sup>a</sup>L1i, L2i and Thi are respectively the increase degree of length of the films in machine direction 1 and 2, and thickness direction. Mi indicates the increase of mass of the films.

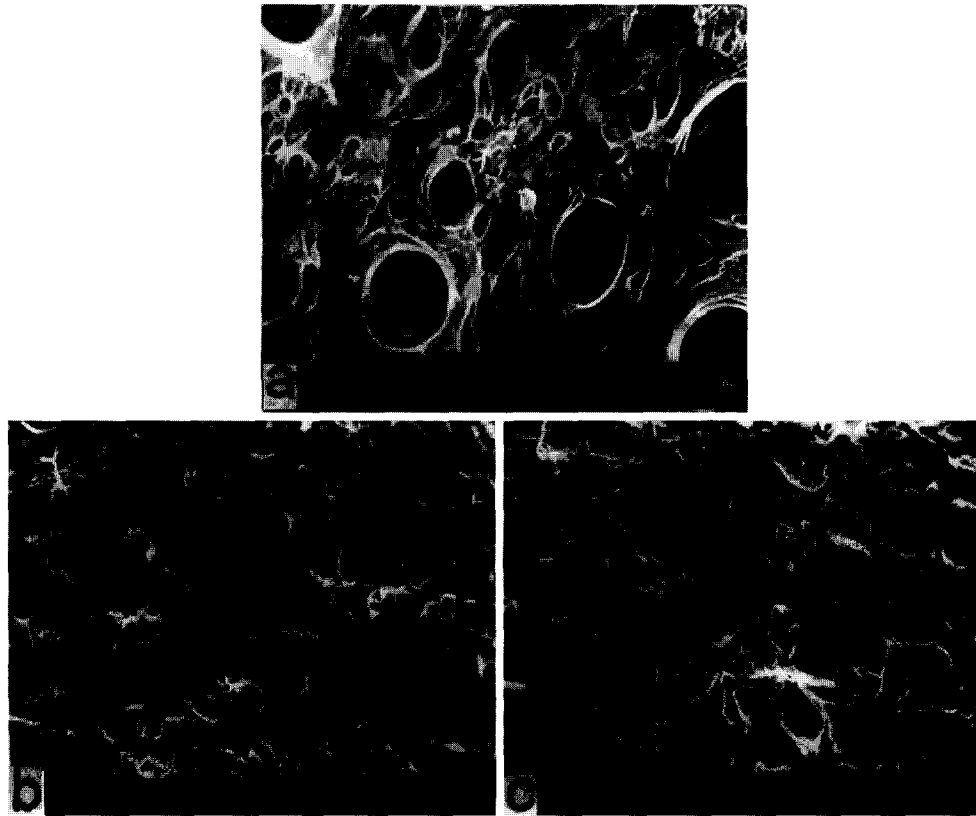


Fig. 1. Scanning electron micrographs of the matrix microporous polypropylene film (a), the intermediate IPNs composite film PP/P(60%nBA-40%St) (b) and the corresponding resulting film PP/P(nBA-St)/PnBA (c).

Because of the swelling effect in the process of in situ polymerisation, the domain of P(nBA-St) might be a bit larger than that of the original pore units in the thickness direction [3]. The intermediate films were really supermolecularly interpenetrating polymer networks. Fig. 2 gives dynamic mechanical thermal analysis curves of the intermediate IPNs. The slightly sharp loss peaks corresponded to the glass transitions of copolymers. The glass transition temperature ( $T_g$ ) increased with the content of St in copolymers. The loss peak in relation to the glass transition of iPP, was covered.

PnBA was not miscible with iPP. In the resulting films, PnBA and P(nBA-St) together occupied the space units corresponding to the domains of P(nBA-St) in intermediate films. The volume of iPP did not change, but the thickness of resulting films increased noticeably. That indicated the 'domain' of blend PnBA, and P(nBA-St) became considerably larger. In other words, although limited by iPP network, the space of original micropores or the P(nBA-St) domains expanded strikingly in the thickness direction because of the incorporation of PnBA.

The random copolymers were composed of units of nBA and St. Depending on their composition, the copolymers had different miscibility with PnBA homopolymer. Fig. 3 gives the dynamic mechanical thermal analysis curves of the resulting films. When the mass content of St in copolymers

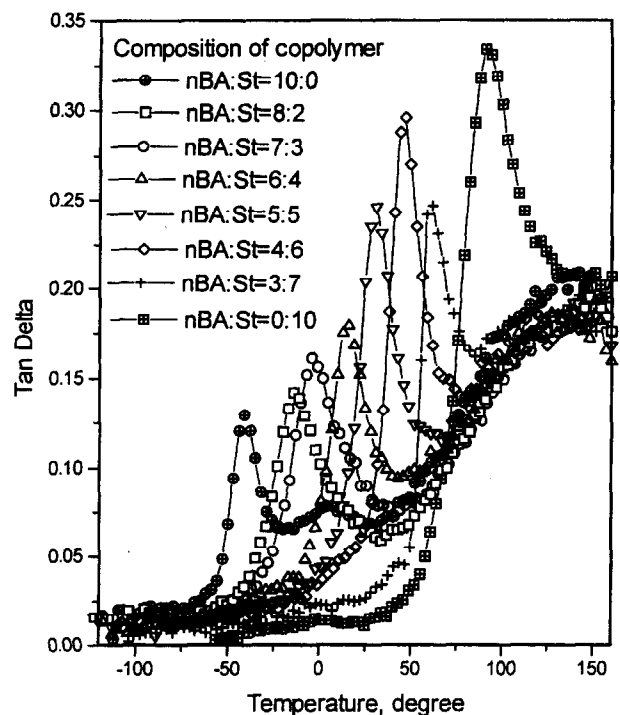


Fig. 2. Dynamic mechanical analysis curves of the composite IPNs film: PP/P(nBA-St), the composition of the copolymers were different.

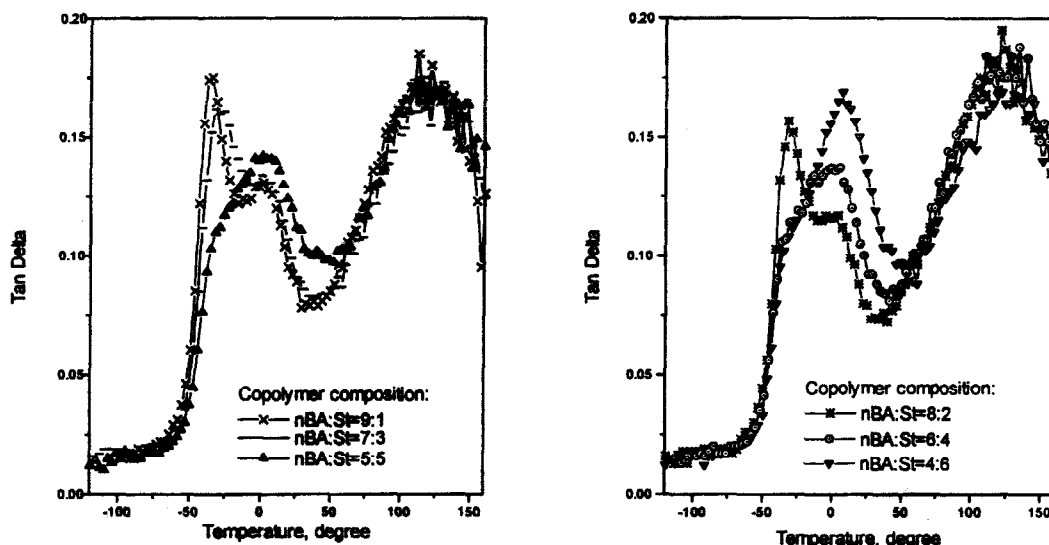


Fig. 3. Dynamic mechanical analysis curves of the resulting composite IPNs films PP/P(nBA-St)/PnBA, the composition of the original copolymers were different.

was 10%, 20% or 30%, two loss peaks were discernible in the  $\text{Tan}\delta$  curves. The low-wide peaks located at 2°C, 3°C and 1°C were considered to be related to the glass transition of iPP. The slightly high peaks at -34°C, -32°C and -32°C were determined to be related to the glass transition of blends of PnBA and P(nBA-St). These  $T_g$  were between the  $T_g$  of pure PnBA and P(nBA-St). So on these occasions, the blends of cross-linked PnBA and P(nBA-St) were reasonably regarded as completely homogeneous polymer networks interpenetrating at molecular level. When the St content in copolymers was 40%, 50% and 60%, very broad single transition stages were observed in loss-temperature curves. The stages were really the combination of the losses of glass transitions of both iPP and blend of PnBA and P(nBA-St). All the stages began at about -33°C and respectively ended at about 10°C, 17°C and 23°C. The initial temperatures of the stages were higher than the  $T_g$  of pure cross-linked PnBA and the end temperatures were lower than the  $T_g$  of corresponding cross-linked P(nBA-St). It appeared that the blends of PnBA with P(nBA-St) were also molecularly interpenetrated networks. However, the blends were not homogeneous; there was a composition distribution of PnBA and P(nBA-St) in the blends so that

the loss stages were diffusive. As a whole, if the content of nBA in P(nBA-St) copolymer was higher than 40%, the resulting composite films were blends with both molecularly and supermolecularly interpenetrating structure.

Table 2 lists the tensile elastic moduli of the composite films in machine direction I at room temperature. For the intermediate films, when the St content in copolymers was lower than 30%, the modulus was almost constant; when the St content was higher than 40%, the modulus increased rapidly. Compared to the intermediate films, the moduli of the resulting films decreased and changed very little with St content. The moduli were relatively low, but far higher than that of PnBA and big enough for stable dimension of the films.

These facts can be interpreted with the structure shown above. Both the intermediate and resulting IPNs films can be regarded as the combination of iPP network and a filling constituent in network from either. The moduli were determined by the two networks. The iPP network was prepared via biaxial stretching so that its tensile modulus was relatively high. On the other hand, in the thickness direction the iPP network would expand slightly because of the dynamic

Table 2  
Tensile moduli (E) of the IPNs composite films in machine direction I at 25°C

Comp. Copolm. (mass frac., %)		E, intermediate films	E, resulting films
nBA	St	(MPa)	(MPa)
98.0		513	
88.2	9.8		163
78.4	19.6	550	160
68.6	29.4	500	168
58.8	39.2	650	220
49.0	49.0	1040	245
39.2	58.8	1600	217
	98.0	2480	

swelling in the first in situ polymerisation process, and expanded to a considerable degree because of the incorporation of PnBA in the preparation process of resulting films. The expanding led to decrease of volume fraction of iPP in the whole of the composite films. Consequently the modulus of iPP network decreased, although in general it was higher than  $10^8$  Pa. The modulus of the filling constituent varied with its composition. If the filling constituent was in rubber state at room temperature, its modulus would be quite low so that the modulus of the whole IPNs films was determined mainly by iPP network. This was true for the intermediate films when the St content in copolymers was below 30%. In these cases, the moduli of the intermediate films were almost constant and slightly lower than that of matrix film. When the St content was above 40%, the copolymers became glassy at 25°C with high moduli. Their moduli, and therefore the moduli of resulting films was clearly increased with St content. In the case of resulting film, the evident expanding of iPP network led to a striking decrease of the modulus of the network, and consequent decrease of the modulus of the whole resulting film. When the St content in copolymers was lower than 30%, indicated by the loss peak temperatures, the blends were in rubber state even well below 25°C. The moduli of these resulting films were rather low. When the St content copolymers was 40%, 50% or 60%, the end temperatures of the loss stages were close to room temperature. Their moduli might be in or close to the order of  $10^8$  Pa. Accordingly, the moduli of these resulting

films were affected by the blends, and the moduli were relatively high and close to 250 MPa.

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