

Interpenetrating Polymer Networks: High Molecular Weight Natural Rubber and Poly(2,6-Dimethyl-1,4-Phenylene Oxide)

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SYNOPSIS

Simultaneous interpenetrating polymer networks (IPNs) of high molecular weight natural rubber (NR) from *Manihot glaziovii* and poly(2,6-dimethyl-1,4-phenylene oxide) were prepared and characterized. A number of pseudo IPNs and blends of these materials were also studied. A single phase morphology is found in full IPNs with either high or low weight percent of NR. The intermediate composition full IPNs, pseudo IPNs, and blends all exhibited microphase separation, as seen by both DSC and SEM studies with domains sizes in the range of 1000–4000 nm. In the discussion we briefly compare these IPNs with the other previously prepared IPNs of poly(2,6-dimethyl-1,4-phenylene oxide).

INTRODUCTION

A number of simultaneous, (SIN), binary interpenetrating polymer networks (IPNs) using poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), were previously prepared in our laboratory. Kinetic and thermodynamic factors control the compatibility of IPNs.¹ These factors are dependent on the properties of the polymer pair chosen, which, in turn, determines the morphology of those materials. IPNs prepared using PPO and a second polymer, such as poly(styrene) (PS), poly(methylmethacrylate) (PMMA), poly(butadiene) (PB), and poly(urethaneacrylate) (PUA), were homogeneous, showing no microphase domains.^{2–5} Phase separation is observed for pseudo IPNs or blends of PPO and PMMA, PUA, or PB.^{3–5} This behavior is in accord with theoretical predictions of Binder and Frisch¹ when they argued that weakly crosslinked immiscible linear polymer chains could become completely miscible as IPNs, over the entire composition range of the two simultaneous crosslinked polymers.^{1,6}

Recently, we described the use of a high molecular weight natural rubber to prepare simultaneous IPNs

using poly(carbonate-urethane) (PCU).⁷ The intimate mixture as IPNs of the two crosslinked polymers showed a morphology with phase domains varying from totally homogeneous materials to materials possessing microphase domains, depending on the average molecular weight between crosslinks of NR chain (\bar{M}_c) employed in the IPN. Here we report on the preparation and characterization of simultaneous IPNs of high molecular weight natural rubber and PPO. We are particularly interested in investigating the phase morphology of these new materials.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was supplied by General Electric Co. It was purified by following the same procedure previously described.¹ Natural rubber (NR) from *Manihot glaziovii* was a gift of Prof. Miguel Cunha Filho from the Federal University of Ceará. The natural rubber was purified and characterized as previously described.⁷ Divinylbenzene (DVB) was distilled prior to use and stored over molecular 4 A sieves. Ethylenediamine

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Table I Raw Materials

Abbreviation Used	Name and Characteristics	Supplier
PPO	Poly (2,6-dimethyl-1,4-phenylene oxide) $M_w = 43560$ $\delta = 9.1 \text{ (cal/cm}^3\text{)}^{1/2}$ $T_g = 210^\circ\text{C}^a$	General Electric Co.
NBS	N-Bromosuccinimide (99%) MW = 177.99	Aldrich Chemical Co.
EDA	Ethylenediamine (98%) MW = 60.1 $d = 0.899$	Aldrich Chemical Co.
DVB	Divinylbenzene MW = 130.19 $d = 0.912$	Aldrich Chemical Co.
BPO	Benzoyl Peroxide MW = 242.23	Aldrich Chemical Co.

^a from Ref. 10.

(EDA) was distilled at 55–60°C in a stream of nitrogen under vacuum. The other reagents used were of analytical grade. The abbreviations employed and characteristics of the raw materials are given in Table I.

Preparation of Crosslinked Poly (2,6-Dimethyl-1,4-Phenylene Oxide) (C-BrPPO)

After purification, PPO was brominated following the procedure described by Frisch and Hua.⁴ The identity of the material was checked by ¹H-NMR: δ 2.1 (—CH₃), 4.3 (—CH₂Br), 6.45, and 6.65 (aromatic).⁸ The degree of bromination was determined by comparing the area of the signal at 4.3 ppm (—CH₂Br) with the area of the signal at 2.1 ppm (—CH₃), which was approximately 0.01 bromomethyl groups per PPO structural unit.⁹ The cross-linked reaction¹¹ was carried out using 1 g of the methylbrominated PPO (Br-PPO) dissolved in toluene with subsequent addition of a stoichiometric amount of EDA to obtain the average molecular weight between crosslinks (\bar{M}_c) of 1.5×10^3 . The reaction mixture was stirred for 3 h at 60°C. The clear and homogeneous solution was poured into an aluminum dish, which was placed into an oven under N₂ atmosphere at 60°C for 24 h and then at 80°C for 24 h. The samples were light yellow, relatively stiff, transparent films.

Preparation of Crosslinked Natural Rubber (CNR)

Purified NR was dissolved in toluene (1% weight of polymer in unit volume of solvent, w/v). To 50 mL of solution was added a stoichiometric amount of DVB and 4% BPO (wt % BPO by unit weight of

NR). The average molecular weight between crosslinks, \bar{M}_c , from the stoichiometry used was 1.5×10^3 . The reaction conditions were essentially the same

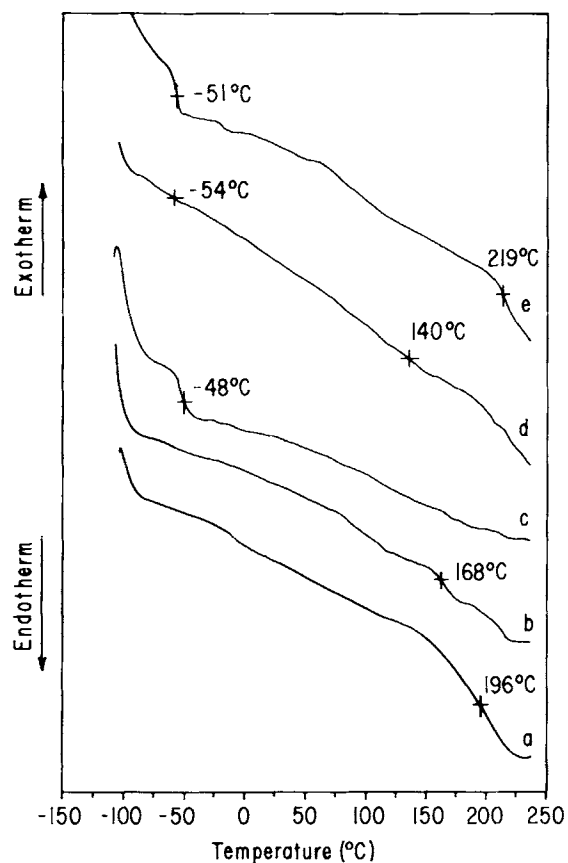


Figure 1 DSC thermograms of NR/Br-PPO system. (a) crosslinked Br-PPO, (b) Full IPN at 10/90 wt % composition, (c) Full IPN at 70/30 wt % composition, (d) Pseudo IPN of linear NR and C-BrPPO at 10/90 wt % composition, (e) Blend at 50/50 wt % composition.

Table II Thermal Measurements (DSC) of Full IPNs of NR/Br-PPO System

Sample	Composition NR/Br-PPO (wt. %)	T_g (°C)	Sample Remarks
Linear NR	—	-55 ^a	OP, W, rubbery
Linear Br-PPO	—	189	TP, PY
Crosslinked NR	100/0	-51	TP, PY, brittle
Crosslinked Br-PPO	0/100	196	TP, PY, stiff
FIPN 10	10/90	168	TP, PY, tough, stiff
FIPN 30	30/70	-53, . . . ^b	TU, PY, tough, stiff
FIPN 50	50/50	-51, . . . ^b	TU, PY, tough, flexible
FIPN 70	70/30	-48	TU, LB, tough flexible
FIPN 90	90/10	-47	TU, LB, flexible

TP, Transparent; TU, Translucent; LB, Light brown; PY, Pale yellow.

^a Ref. 7

^b T_g value unable to be determined.

as described in the previous section. The prepared sample was a transparent, light yellow, brittle solid.

Preparation of Full IPNs

The full IPNs were prepared by dissolving proportional amounts of linear Br-PPO in 50 mL of a 1% NR toluene solution to give the desired composition by weight of NR and Br-PPO. The crosslinking agents, DVB and EDA, were added to the stirred reaction mixtures at stoichiometric amounts to give an \bar{M}_c value of 1.5×10^3 for both simultaneously crosslinked polymers, NR and Br-PPO. The initiator for the crosslinking of the NR, BPO, was added at 4 wt % (per unit weight of NR). The reaction

Table III Thermal Measurements (DSC) of Pseudo IPNs of NR/Br-PPO System

Sample	Composition NR/Br-PPO (wt. %)	T_g (°C)	Sample Remarks
LNR/C- BrPPO	10/90	-54, 140	TU, PY, tough, stiff
LNR/C- BrPPO	30/70	-51, . . . ^a	TU, PY, tough, stiff
LNR/C- BrPPO	50/50	-55, . . . ^a	TU, PY, tough, stiff

TU, Translucent; PY, Pale yellow.

^a T_g value unable to be determined.

procedure was the same as described in the previous sections.

Preparation of Pseudo IPNs and Blends

Pseudo IPNs were prepared using the same conditions as employed for the synthesis of IPNs, except for the deletion of the crosslinking agent of NR (DVB) and the initiator of the crosslinked NR re-

Table IV Thermal Measurements (DSC) of NR/Br-PPO Blends

Sample	Composition NR/BR-PPO (wt. %)	T_g (°C)	Sample Remarks
Linear NR	—	-55	OP, W, rubbery
Linear Br- PPO	—	189	
A	10/90	-52, 143	TU, LB, stiff
B	30/70	-51, 209	TU, PY, flexible
C	50/50	-51, 219	OP, LB
D	70/30	-50, 223	OP, B, rubbery, sticky

OP, Opaque; W, White; TU, Translucent; PY, Pale yellow; LB, Light brown; B, Brown.

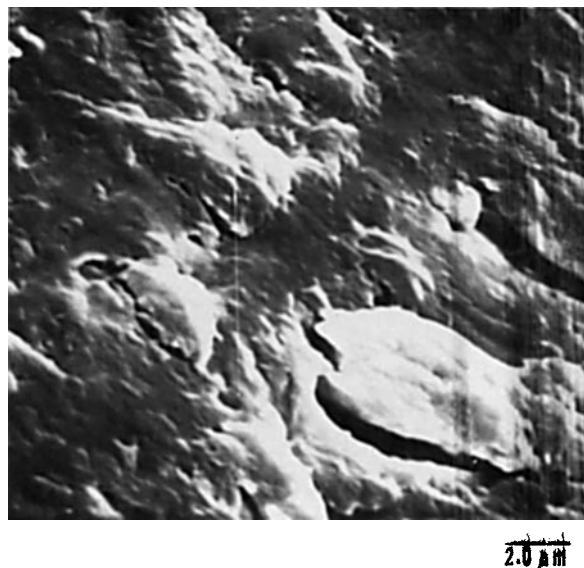


Figure 2 SEM of crosslinked Br-PPO.

action, BPO. For the preparation of the blends, no crosslinking agent or initiator for either polymer network was added to the reaction mixture prepared under the same conditions described above.

PHYSICAL MEASUREMENTS

Electron Micrographs

The phase morphology of the samples were studied by scanning electron microscopy (SEM). The samples were fractured after being frozen in liquid nitrogen. The specimens were prepared for SEM by mounting them on a stub using silver paint and then coating them with gold ($\sim 90 \text{ \AA}$ thick) in a Hummer V Sputter coater. A ISI super-mini II scanning electron microscope, operating at middle voltage, was used.

Differential Scanning Calorimetry (DSC)

Glass transition temperatures, T_g , were obtained by means of a DSC V2.2A DuPont 9900 differential scanning calorimeter, operating at a scanning rate of $20^\circ\text{C}/\text{min}$. The sample measurements were done in the range of temperature of -150°C to 250°C .

RESULTS

Thermal Measurements (DSC) of the Full and Pseudo IPNs and Blends of NR/Br-PPO System

The simultaneously crosslinking reaction between NR and Br-PPO was performed for several wt %

composition ratios of NR to Br-PPO. A weight loss of up to 20 wt % was observed for most of the samples after Soxhlet extraction using toluene. These solubility studies showed that the crosslinking reaction was approximately 80% complete.

The DSC thermograms obtained for crosslinked Br-PPO, full IPN, pseudo IPN and blends in specified compositions are shown in Figure 1. Their relative shape exhibited no significant change. However, a broadening of the glass transition is observed

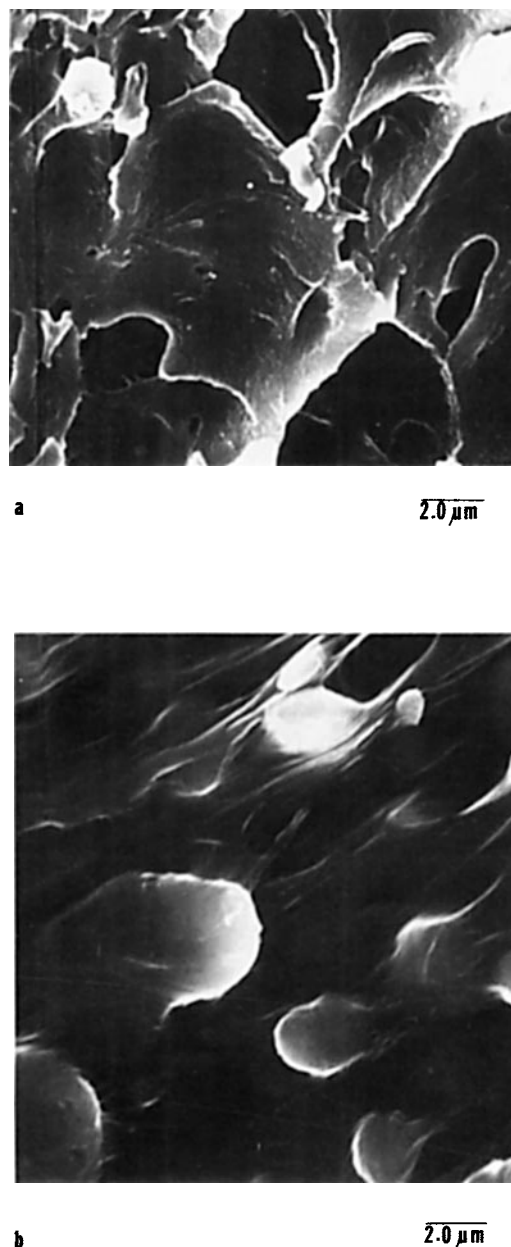
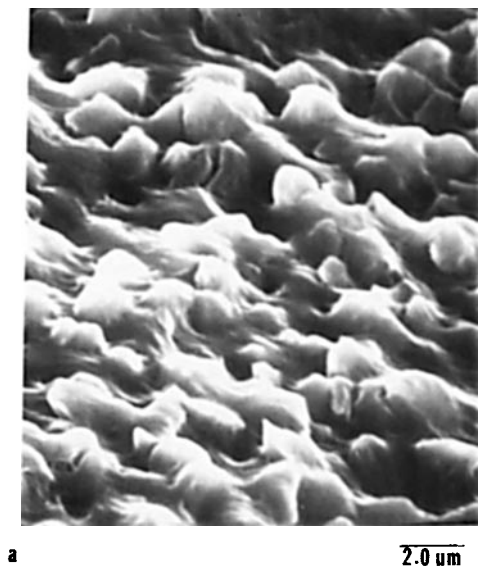
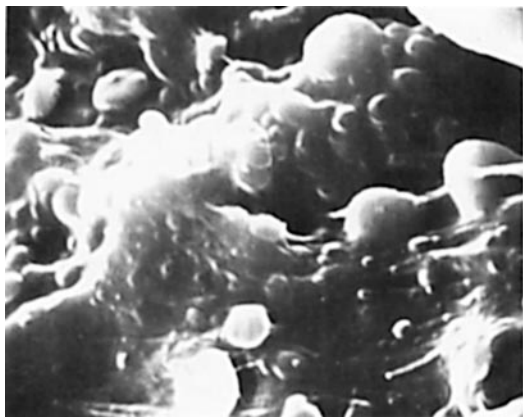


Figure 3 SEM of full IPNs. (a) CNR/C-BrPPO at 10/90 wt % composition, (b) CNR/C-BrPPO at 50/50 wt % composition.



a

2.0 μm



b

2.0 μm

Figure 4 SEM of pseudo IPN and blend. (a) Linear NR/C-BrPPO at 50/50 wt % composition, (b) Blend NR/C-BrPPO at 50/50 wt % composition.

near crosslinked Br-PPO transition for the full IPNs at middle compositions and for all compositions of the pseudo IPNs that were prepared. This leads in some cases to difficulties in obtaining a best T_g value. The broadening of the transitions region may reflect a microheterogeneity of phase domains¹² in the full IPNs at certain compositions, and is found in all pseudo IPNs.

The characteristics and the glass transition temperature, T_g , obtained by the thermal measurements (DSC), of full IPNs, pseudo IPNs, and blends are listed in Tables II, III, and IV. The full IPNs showing intermediate wt % compositions (50/50 and 30/70

wt %) of CNR/C-BrPPO exhibited two distinct T_g values, indicating microphase separation (Table II). However, full IPNs became essentially miscible for the high percentages (70 and 90 wt %) of NR and higher percentage (90 wt %) of Br-PPO. In these cases only one T_g value (a sharp transition) was observed around the boundaries of the T_g value of one of the pure crosslinked components (NR or Br-PPO). The glass transition temperatures have intermediate values between those of the pure constituents. The samples appear to be pale yellow, translucent to transparent (90 wt % Br-PPO) solids. For high wt % composition of NR (70 and 90) they are light brown and translucent.

Table III shows the T_g values for pseudo IPNs of linear NR and crosslinked Br-PPO. These materials are, in general, translucent solids showing a pale yellow color. They exhibit two T_g values, intermediate to the values corresponding to the pure polymers. These results indicate microphase separation over all the compositions of the pseudo IPNs.

The blends of the linear polymers exhibit two T_g s, which are intermediate and near the boundaries of those of the pure linear polymers (Table IV).

Scanning Electron Microscopy (SEM) Studies of the Full and Pseudo IPNs and Blends of NR/Br-PPO System

Scanning electron micrographs for pure crosslinked Br-PPO, full IPNs, pseudo IPN and blends are shown in Figures 2, 3, and 4. Crosslinked Br-PPO presents a morphology with some delamination cavities in the structure, probably due to solvent evaporation during the crosslinking reaction,⁷ but the material itself seems to be homogeneous (Fig. 2). The micrographs for full IPNs (10 and 50 wt % NR) showed two different morphologies (Figs. 3a and 3b). The full IPN at highest composition of Br-PPO (90 wt %) showed cavities observed previously for some IPNs and attributed to the reaction conditions.^{7,13} In general, however, the material appears to have no phase separation (Fig. 3a). In contrast, the full IPN in the composition of 50 wt % Br-PPO showed a diffused particulate morphology, made up of a visible phase of separated large domains in the range of 1000–4000 nm (Fig. 3b). Similar morphologies are observed for the pseudo IPN at 50 wt % Br-PPO and the blend at the same composition (Figs. 4a and 4b).

DISCUSSION

The theoretical thermodynamic stability of binary simultaneous IPNs, discussed by Binder and Frisch,

Table V Glass Transition Temperatures, T_g , Solubility Parameters and Values of Dispersive (d), Polar (p), and Hydrogen Bonding (h) Contributions to the Total Solubility Parameters^{8,10,12}

Linear Polymer	Solubility Parameters				$\Delta\delta$ (cal/cm ³) ^{1/2}	T_g (°C)	ΔT_g (°C)
	δ^a	(δ_d	δ_p	δ_h)			
PPO	9.1	(8.6	3.0	2.0)	0	210	0
PS	9.1	(8.6	3.0	2.0)	0	100	106
PMMA	9.3	(9.2	5.0	4.2)	0.2	105	111
PUA	9.1				0	< 56	< 155
PB	8.38	(8.8	2.5	1.2)	0.72	-95	306
PDMS		7.6-7.3			1.5-1.8	-127	338
NR		8.3-7.9			0.8-1.2	-55	266

^a δ in (cal/cm³)^{1/2}, $\Delta T_g = T_{g(\text{PPO})} - T_{g(\text{linear polymer})}$, $\Delta\delta = (\delta_{\text{PPO}} - \delta_{\text{linear polymer}})$

can be achieved despite differences between the two solubility parameters of the IPN components with no visible of microphase separation.¹ Binary simultaneous IPNs using PPO as one of the components exhibit fully miscible IPNs despite the difference in the solubility parameters (δ , δ_d , δ_p , δ_h) of the pure components (Table V). In these cases, differences between the T_g values of the components reached values of approximately 100°C. However, when the solubility parameter difference attained relatively large values [> 0.72 (cal/cm³)^{1/2}], together with a

large difference between the T_g values ($> 300^\circ\text{C}$), microphase separation occurs.⁶ This is the case of the system PPO/PDMS,^{11,14,15,17} which shows single phase materials only at high compositions of PDMS or PPO (Table VI). In a similar way, the results presented here show that it is possible to produce full IPNs exhibiting a single phase only at the highest composition of one of the constituents of the system NR/Br-PPO (90, 70 wt % NR or 90 wt % Br-PPO). At intermediate compositions, microphase separation was observed for full IPNs and all

Table VI Comparison of Compatibility of Binary Simultaneous IPNs Systems of PPO⁶ and NR/Br-PPO Systems

System	Method of Miscibility Determination	Compatibility			Range Domain of Microphase (nm)	Reference
		Full IPN	Pseudo IPN	Blend		
PPO/PS	DSC TEM	C	C	C	—	2
PPO/PMMA	DSC TEM	C	I	I	—	3
PPO/PUA	DSC TEM	C	C	I	—	4
PPO/PB	DSC TEM	C	Miscible at 90 wt % Br-PPO	I	—	7
PPO/PB	DSC	Miscible at 90 wt % Br-PPO and 20 wt % Br-PPO	I	I	—	16
PPO/PDMS	DSC TEM	Miscible at 90 wt % Br-PPO and 10 wt % Br-PPO	I	I	10-200	14
PPO/PDMS	DSC SEM	Miscible at 90 wt % to 60 wt % Br-PPO	I	—	1000-1000	11, 15
PPO/PDMS	DSC TEM	I	—	—	10,000-50,000	17
PPO/NR	DSC SEM	Miscible at 90 wt % and 10-30 wt % PPO	I	I	1000-4000	

C, Compatible; I, Incompatible.

pseudo IPNs and blends. Like the system PPO/PDMS, this system shows large differences between the solubility parameters and between the T_g values of the pure constituents ($\geq 0.8 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ and 226°C). In this case, the two phased materials exhibit intermediate domain sizes as compared to the domain size in the incompatible PPO/PDMS systems (Table VI).

A complete explanation for this behavior may not be possible at this time, but we suggest possibilities as previously suggested by Huang et al.,¹⁴ such as two-step network formation and/or the contributions of the elastic free energy of the IPNs not being sufficiently favorable. These possibilities could be acting as the main limiting factors for the control of mutual miscibility of these systems.

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