

NOTE

The Morphology of Poly(2,6-dimethyl-1,4-phenylene oxide)/Natural Rubber Pseudo IPNs and Their Electrically Conductive Behavior upon Doping with Iodine

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a commercially available material (Noryl, General Electric). A series of PPO-related binary IPNs^{1,2} were previously prepared in our laboratory.²⁻⁴ The reason for choosing PPO as one component of the above full IPNs and pseudo (or semi) IPNs (PIPNs) is primarily due to the resistance to chemicals of this industrial resin and also because of its excellent mechanical and thermal properties. Electrically conductive pseudo IPNs have attracted research workers for overcoming the poor miscibility of the majority of polymer blends that are of electrical conductive interest.⁵⁻⁸ We use cross-linked PPO as a good candidate as an insulating host polymer matrix in some conductive polyblends. A number of pseudo IPNs of cross-linked PPO with linear high molecular weight natural rubber (NR) from *Manihot glaziovii* synthesized by Barros et al. all exhibited microphase separation with domain sizes in the range of 1000–4000 nm.³ Yet, by carefully varying the weight ratio of PPO and NR, we found that at some definite compositions of the PIPNs the phase-mixing ability can be greatly improved (domain sizes were below 100 nm). Since NR is of particular interest as a doped conducting polymer with a nonconjugated backbone,^{6,7,9} the uniformity of phase morphology in the PPO/NR PIPNs will play an important role in these doped conducting materials. It was proposed by Wang and Rubner^{5,10} that the improved stability in the conducting materials could be achieved by restricting their chain mobility. We believe that cross-linked PPO matrix can effectively reduce the chain mobility of NR molecules in the more uniform pseudo IPNs because of PPO's high glass transition temperature. In this note, we describe the preparation and morphology of a number of PPO/NR pseudo IPNs and discuss briefly the electrical properties of these iodine-doped materials. The chemical structures of the polymeric materials that we used are shown in Table I.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [$T_g = 210^\circ\text{C}$, $\delta = 9.1$ (cal/cm³)^{1/2}] was supplied by the General Electric Co. It had an intrinsic viscosity of 0.45 dL/g and molecular weights of $\bar{M}_w = 51,327$ and $\bar{M}_n = 22,762$ determined by gel permeation chromatography (GPC). PPO was purified by dissolving it in chloroform and precipitating it with methanol and dried. The dried PPO is a pale yellow solid. Ethylenediamine (EDA) was distilled before use and dried over Linde 4 Å molecular sieves.

Natural rubber (NR) from *Manihot glaziovii* was kindly given to us by Professor G. G. de Barros from the Universidade Brasilia, Brazil. The purified NR had an average molecular weight (\bar{M}_w) of 10^6 .¹¹ *N*-Bromosuccinimide (NBS, 99%, Aldrich) was used as received. All solvents used were of reagent grade and dried over Linde 4 Å molecular sieves.

Preparation of Cross-linked PPO

The purified PPO was brominated by NBS following the procedure described by Frisch and Hua.¹² ¹H-NMR, ¹³C-NMR, and bromine elemental analysis were performed on the methyl-brominated polymer. The analysis showed that the polymer contained a 0.076 Br/repeating unit. The cross-linked reaction was carried out using 2.0 g brominated PPO (Br-PPO) dissolving in 20 mL dry toluene. To the clear solution, a stoichiometric amount of EDA was added to obtain an average molecular weight between cross-links (M_c) of 1.5×10^3 . The solution was stirred at 60°C for 0.5 h, degassed, poured into an aluminum dish, and placed in an oven at 60°C for 24 h under N₂ atmosphere. It was then further dried under vacuum at 60°C for 24 h. The cured films were transparent, relatively stiff, and light yellow in color.

Table I The Chemical Structure of Polymeric Materials

Polymer	Structure
PPO	
Br-PPO	
Linear natural rubber (NR)	
Cross-linked PPO	

Preparation of Pseudo IPNs

The pseudo IPN was prepared by dissolving proportional amounts of linear Br-PPO in 5% NR toluene solution to give the desired composition by weight of Br-PPO and NR. The mixture was vigorously stirred at 50°C under N₂ atmosphere to a clear solution; then, the cross-linking agent for Br-PPO, EDA, was added with stirring for 15 min. The reaction procedure was the same as that described for cross-linked PPO. Also, as a comparison, the linear blend was prepared for a 65–35% Br-PPO–NR composition in the same manner as for the pseudo IPN except that the cross-linking agent was omitted.

Measurements

Calorimetric Measurements. The glass transitions (T_g 's) were measured by differential scanning calorimetry (DSC, DuPont 2000). Measurements were carried out from -100 to 250°C under nitrogen at a scanning rate of 20°C/min. Specimen sizes were of the order of 15 mg.

Electron Microscopy. The phase morphological characteristics of the samples were studied by scanning electron microscopy (SEM). The specimens for SEM were frozen in liquid nitrogen, fractured, mounted on a stub with silver paint, and coated with gold in a Blazers SCD-004 sputter coater. They were then observed with a digital scanning microscope (DSM 940, Zeiss, Germany) operating at middle voltage.

Conductivity Measurements. The conductivities of

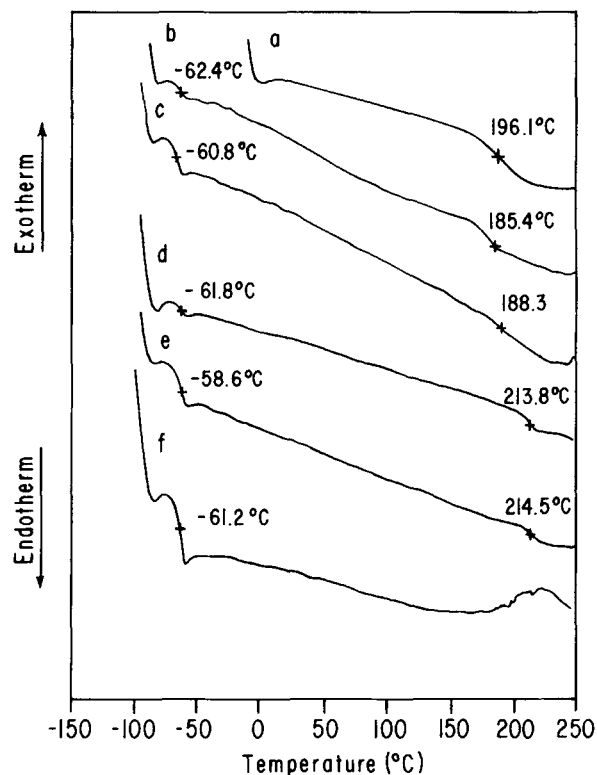
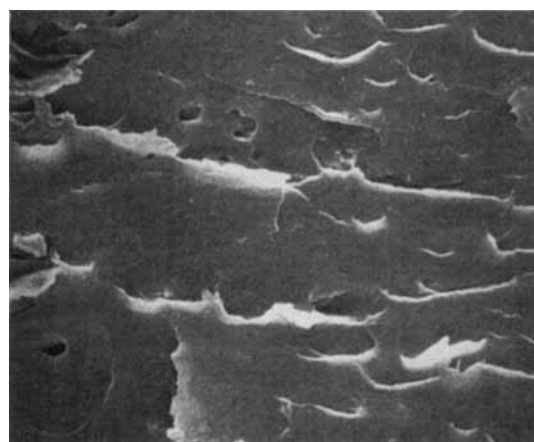
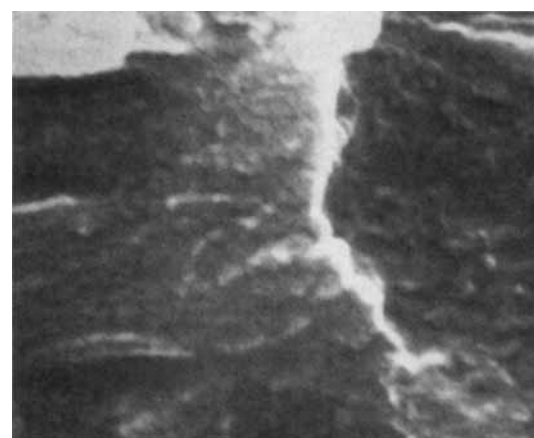


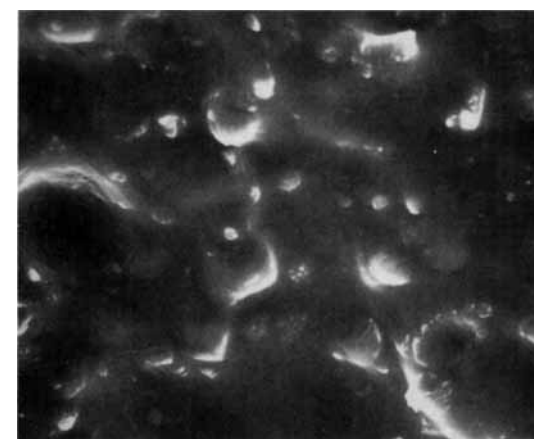
Figure 1 DSC thermograms of PPO/NR system: (a) cross-linked PPO; (b) pseudo IPN1 (PPO/NR = 80 : 20); (c) pseudo IPN2 (PPO/NR = 65 : 35); (d) linear blend of PPO and NR (65 : 35); (e) pseudo IPN3 (PPO/NR = 50 : 50); (f) LNR.



a)



b)

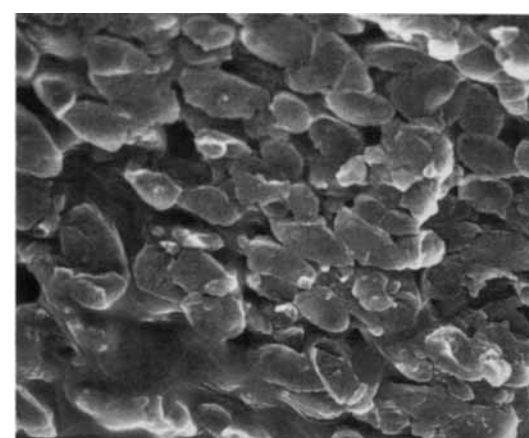


c)

Figure 2 SEM micrographs: (a) cross-linked PPO, bar = 2 μm ; (b) PIPN1, bar = 500 nm; (c) PIPN3, bar = 10 μm .



a)



b)



c)

Figure 3 SEM micrographs: (a) PIPN2, bar = 500 nm; (b) linear blend of PPO and NR (65 : 35), bar = 10 μm ; (c) iodine-doped PIPN2, bar = 500 nm.

Table II Results of DSC Measurements (T_g) and Phase Domains

Sample	Composition of PPO/NR (Wt %)	T_g ($^{\circ}$ C)	Phase Domain	Remarks on the Sample
Linear NR	0/100	-61.2	—	TP, PY
Cross-linked PPO	100/0	196.1	Nonresolvable by SEM up to 5000 \times	TP, LY, stiff
PIP1	80/20	-62.4, 185.4	Average 80 nm resolved by SEM	TU, LY, tough
PIP2	65/35	-60.8, 188.3	Nonresolvable by SEM up to 20,000 \times	TU, LY, tough
PIP3	50/50	-58.6, 214.5	Average 4 μ m resolved by SEM	OP, Y, soft
L-PPO/L-NR	65/35	-61.8, 213.8	Average 10 μ m resolved by SEM	OP, PY, film has many cracks

TP = transparent, PY = pale yellow, LY = light yellow, TU = translucent, OP = opaque, Y = yellow.

samples were measured following the procedure described in Ref. 6. The sample was placed in the two-probe glass cell and two platinum wires were attached to the film using an Electrodag 502 paste. Vapor-phase iodine doping was used (under vacuum $\sim 10^{-4}$ Torr). The resistance of the film was monitored periodically with the iodine uptake until the film was saturated with iodine at room temperature (~ 6 –10 days). A Keithley 617 digital electrometer was used for the measurements.

RESULTS AND DISCUSSION

DSC thermograms obtained from pure CPPO (cross-linked PPO), pure linear natural rubber (LNR), pseudo IPNs (PIP1, PIP2, and PIP3 having weight percent compositions of PPO/NR of 80/20, 65/35, and 50/50), and the linear blend of PPO and NR (65 : 35) are shown in Figure 1. CPPO exhibited a smooth curve, with the best-adjusted fit for the T_g transition at 196.1 $^{\circ}$ C [curve (a)]. Two pseudo IPNs (PIP1 and PIP3) and the linear blend showed two distinct T_g 's [curves (b), (d), and (e)]. Only one sharp glass transition and a broad second T_g was observed for PIP2 [curve (c)]; the wide broadening of the second transition region presented may reflect better phase mixing. No endotherm peak was observed

for linear NR (LNR) [curve (f)], and this indicates the absence of crystallinity in the rubber material. SEM micrographs for the CPPO network, PIP1, and PIP3 are shown in Figure 2. The CPPO network reveals a morphology with a small number of delamination cavities in the structure, presumably due to solvent evaporation during the cross-linking reaction,^{3,4} but the film itself appears to be homogeneous [Fig. 2(a)]. PIP1 and PIP3 showed apparent SEM resolvable domains [Fig. 2(b) and (c)], but the average domain size of PIP1 is much smaller than that of PIP3. SEM micrographs of PIP2, the linear blend, and iodine-doped PIP2 are shown in Figure 3. No SEM resolvable domains were present in PIP2 at the magnification employed. Some delamination cavities present in the structure could be explained as due to pure CPPO. Large domain sizes present in the linear blend indicates the poor miscibility of the two linear polymers, which resulted in many cracks in the cast film [Fig. 3(b)]. The iodine-doped PIP2 revealed strikingly uniform domain sizes and distribution [Fig. 3(c)]. These small domains (~ 50 nm) were presumably due to clustering of the iodine molecules in the supermolecular structure region of NR. SEM fracture studies of the cross-linked PPO, the pseudo IPNs, and the linear blend of PPO/NR confirm all results obtained by the DSC measurements and these results are listed in Table II.

Table III dc Conductivities of Homopolymers and PIPNs

Sample	Undoped Sample σ (S cm $^{-1}$)	Doped Sample at Saturation σ (S cm $^{-1}$)	Doping Time (Days)
LNR	10^{-12}	1.40×10^{-4}	10
Cross-linked PPO	10^{-13}	10^{-13}	6
PIP1	3×10^{-11}	3.97×10^{-7}	10
PIP2	1×10^{-12}	4.06×10^{-6}	10

All the dc conductivities were calculated from the constant resistance values and are listed in Table III. It can be seen that iodine-doped LNR gave a conductivity of $\sim 10^{-4}$ S cm $^{-1}$, which is eight orders of magnitude higher than the original NR. CPPO was a good insulator both if doped or undoped ($\sigma < 10^{-9}$ S cm $^{-1}$) and these results are in good agreement with the PPO resin upon doping with AsF $_5$.¹³ The incorporation of iodine in CPPO/LNR PIPNs significantly changes the conductivities of these materials. The conductivities are increased four to six orders of magnitude as compared to the undoped materials. PIPN2 (PPO/NR = 65 : 35) had the highest conductivity increased upon iodine doping. The quite uniform domain size and domain distribution as displayed in Figure 3(c) reflects the uniform iodine uptake on doping. The SEM results showed that PIPN2 possessed a morphology with a high level of microphase mixing. Thus, the higher conductivity of this composition can be related to its highly uniform morphology. In this work, a greatly improved morphology of pseudo IPNs of PPO/NR was achieved by composition control. Our conductive polymer materials possess a high degree of molecular mixing, excellent mechanical and thermal properties, good processability, and environmental stability.

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YONGPENG XUE
ZHEFEI CHEN
H. L. FRISCH

State University of New York at Albany, Albany, New York 12222

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