

NOTE

Pseudo Interpenetrating Polymer Networks of High Molecular Weight Polychloroprene and *cis*-1,4-Polybutadiene

INTRODUCTION

Interpenetrating polymer networks (IPNs)¹⁻³ are more or less intimate mixtures of two or more distinct cross-linked polymers mutually held together by permanent entanglements, containing essentially no covalent bonds or grafts between them. If only one of the polymers in any IPN is cross-linked, the material is referred to as a pseudo-IPN (PIPn) or semi-IPN. PIPNs normally exhibit varying degrees of phase separation.

Polychloroprene rubber (CR) has the distinction of being the earliest commercially successful synthetic rubber.⁴ The vulcanizates of CR possess excellent oil resistance, chemical resistance, weather resistance, and non-flammability. Although CR provides a very useful all-around balance of properties, there are many applications for which one particular property of CR is insufficiently developed: For some applications, the resistance of CR to high temperature or very low temperature may be insufficient. *cis*-1,4-Polybutadiene (PB), which is also a synthetic rubber, has the excellent low-temperature and heat buildup performance and possesses high abrasion resistance.^{5,6} PB rubber can be used as a replacement for natural rubber in such applications as tires and industrial products.⁶ But it has already been noted that pure gum vulcanizates from PB do not show high tensile strength and the processing behavior of butadiene rubber alone is poor.⁴ For general-purpose applications, butadiene rubbers are normally used as blends with other rubbers. To improve technical properties and achieve better processing and lower compound cost, blending of two or more rubbers is usually carried out in the rubber industry.⁵ Such rubber/rubber blends that undergo subsequent vulcanizations constitute a specialized type of IPN.³ Unsaturated diene polymers can be cross-linked using a number of well-established techniques involving different kinds of cross-linking agents.⁷ However, of particular interest to this work was our⁸ recently developed novel low-temperature cross-linking method for high molecular weight CR. Here we report on the synthesis and characterization of a novel simultaneous PIPn based on cross-linked CR that was cross-linked using the same method as the one in Ref. 8 and PB.

EXPERIMENTAL

Materials

The original white elastic polychloroprene (CR) (10% *cis*; 85% *trans*; $M_w = 2.9 \times 10^6$; $\rho = 1.23 \text{ g/cm}^3$; $T_g, -48^\circ\text{C}$; $T_m, 115^\circ\text{C}$) and *cis*-1,4-polybutadiene (PB) (98% *cis*; $M_w = 2 \times 10^6$ – 3×10^6 ; $\rho = 1.01 \text{ g/cm}^3$; $T_g, -102^\circ\text{C}$; $\delta = 6.3 \text{ [cal/cm}^3\text{]}^{1/2}$) were purchased from Aldrich Chemical Co. The PB is a soft, transparent, nearly colorless, and easily soluble elastomer. No color change was observed in the CR raw material under storage in the dark. The expected structures of the polymers were confirmed by FTIR spectra. "DYTEK" A amine (2-methylpentamethylenediamine, 98.5%) was a gift from the DuPont Co. It is a colorless liquid with a weak ammonia odor. ACS-certified potassium iodide KI (Fisher Scientific), which was used in the experiment, is a white crystalline solid. All chemicals were used as received. All solvents used were of reagent grade and dried over Linde 4 Å molecular sieves.

Preparation of Cross-linked CR

The cross-linking reaction of CR with bifunctional "DYTEK" A amine and the pure network characterization followed the same procedure described in our previous work.⁸ Chlorine analyses (the elemental analyses were performed by M-H-W Laboratories in Phoenix) were carried out on both linear and cross-linked CR samples. The results of chlorine content obtained were in excellent agreement with the estimated values.

Preparation of PIPNs

The PIPNs were prepared by mixing proportional amounts of linear CR (KI pretreated in benzene and dimethyl sulfoxide mixed solvent) and PB (which was dissolved in dry benzene) to give the desired compositions followed by addition of the diamine cross-linking agent for CR in the same proportion as in the pure cross-linked CR. Subsequently, the mixtures were stirred intensively at room temperature overnight under a nitrogen atmosphere. The

Table I Results of DSC Measurements

Sample	Composition of CR/PB (Wt %)	T_g (°C)	T_m (°C)	Remarks on the Sample
Linear CR	100/0	-37.7	38.6	TU, PY, soft
Cross-linked CR	100/0	-38.8	—	TU, DB, rubbery
Linear PB	0/100	-97.9	-5.6	TP, colorless, soft
PIP-1	75/25	-98.8, -35.9	-6.9	OP, DB, soft, tough film was nonsmooth-surfaced
PIP-2	50/50	-99.4, -37.3	-7.3	TU, B, soft, tough film was smooth-surfaced
PIP-3	25/75	-98.2, -37.1	-6.7	TU, LB, soft, tough film was smooth-surfaced

TU = translucent, PY = pale yellow, DB = deep brown, TP = transparent, OP = opaque, B = brown, LB = light brown.

sufficiently stirred solutions were carefully poured into aluminum dishes and placed in an oven maintained at 60°C for 24 h under a nitrogen atmosphere. The solidified films were further dried at 60°C under vacuum for another 24 h. The final products were from deep brown to light brown, opaque to translucent solids depending on the composition. The average thickness of the product films was 0.55 mm.

MEASUREMENTS

Calorimetric Measurements

The glass transitions (T_g 's) were measured by differential scanning calorimetry (DSC, DuPont 2000). Measurements were carried out from -120 to 80°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. The electron images were recorded directly from the cathode ray tube on Polaroid 55 film.

Ultimate Properties

The tensile strength (TS) and elongation at break were measured at room temperature on an Instron tester (ASTM D1708) with a crosshead speed of 5 in. per min. Specimens were 0.22 in.-wide dumbbells.

RESULTS AND DISCUSSION

The reaction of KI-treated CR with "DYTEK" A amine at a low temperature of 60°C yielded a deep brown, translucent, and soft elastomer. Unlike some CR vulcanizates that undergo degradation gradually, even when stored in a desiccator under vacuum,^{9,10} no observable change was found for this cross-linked CR after being exposed in air for several months. Its high stability to the environment was presumably due to the reactive sites based on the highly reactive tertiary allylic chlorine atoms of the 1,2 units present in the polymer chain being used up and no new reactive sites being generated during the cross-linking process employed.

The results of DSC measurements for linear CR, pure cross-linked CR, linear PB, and PIPNs of CR/PB are listed in Table I. Both linear polymers have melting points

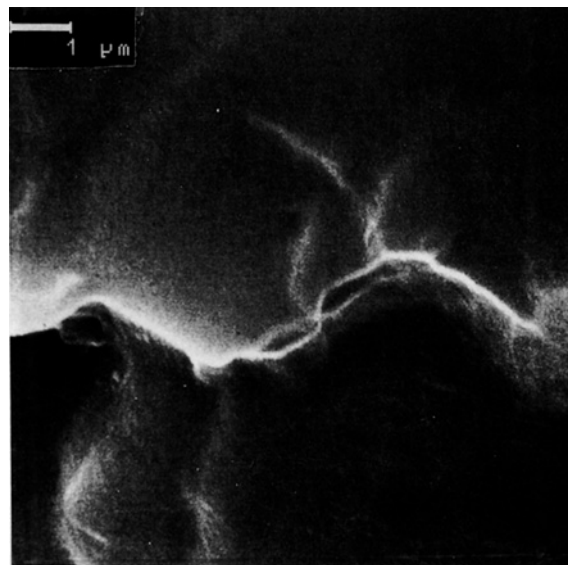


Figure 1 SEM of the cross-linked CR. Magnification 10,000×.

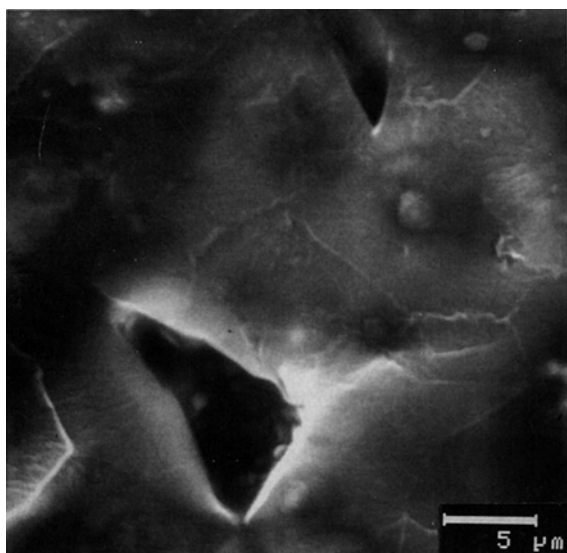


Figure 2 SEM of PIPN-1 (CR/PB = 75 : 25). Magnification 3000 \times .

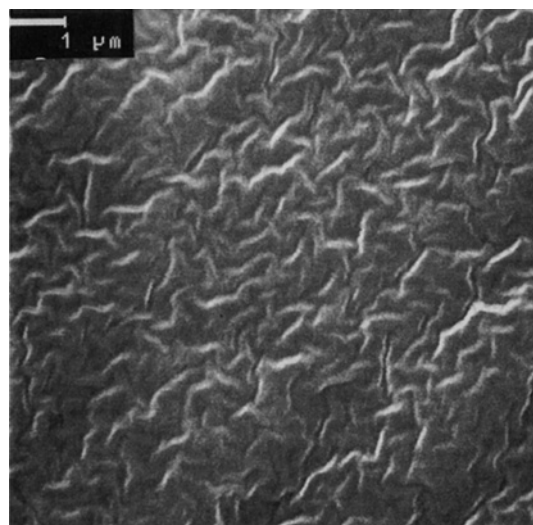
exhibiting their partial crystalline features. All PIPNs studied revealed two distinct glass transitions and a melting point that corresponded to the linear PB component. These results suggest microphase separation in the PIPNs. SEM micrographs for the cross-linked CR network and three PIPNs are shown in Figures 1-3. SEM studies exhibiting the fractured surface of the pure CR network and PIPNs confirm the results obtained by the DSC measurements listed in Table I. Pure cross-linked CR exhibits a uniform morphology (Fig. 1). PIPN-1 showed a complex morphology with a small number of micrometer-sized disperse spherical domains and some large irregular "holes" (Fig. 2). This material also possesses a nonsmooth surfaced appearance. PIPN-2 and PIPN-3 showed interesting wormlike disperse fibrous domains that were also found in some rubber blends.¹¹ The average thickness of the disperse fibrous domains decreases as the weight fraction of PB component increases (Fig. 3). The appearance of PIPN-3 film is optically much clearer.

The data obtained from the measurements of ultimate mechanical properties of the PIPNs, i.e., tensile strength

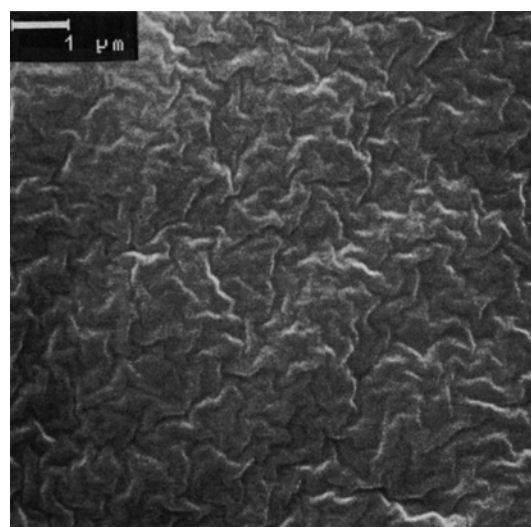
Table II Ultimate Mechanical Properties of the PIPNs

Sample	Percent by Weight Composition (CR/PB)	Tensile Strength (psi)	Elongation at Break (%)
Cross-linked CR	100/0	960	851
PIPN-1	75/25	872	700
PIPN-2	50/50	536	662
PIPN-3	25/75	305	629

and elongation at break, are shown in Table II. In Figure 4, these tensile strengths and elongations at break are plotted against the weight percentage of linear PB in the CR/PB PIPNs. The points follow straight lines over the composition range studied, within the rather large experimental error characteristic of tensile strength measurements.¹² The considerable decrease in tensile strength with the increase of weight fraction of the PB component implies that the main contribution to the tensile strength of the PIPNs is made by the cross-linked CR component, and the linear PB chains that did not enter the cross-linking reaction acted as a "diluent"¹² in the cross-linked



(a)



(b)

Figure 3 SEM of PIPNs: (a) PIPN-2 (CR/PB = 50 : 50). Magnification 10,000 \times . (b) PIPN-3 (CR/PB = 25 : 75). Magnification 10,000 \times .

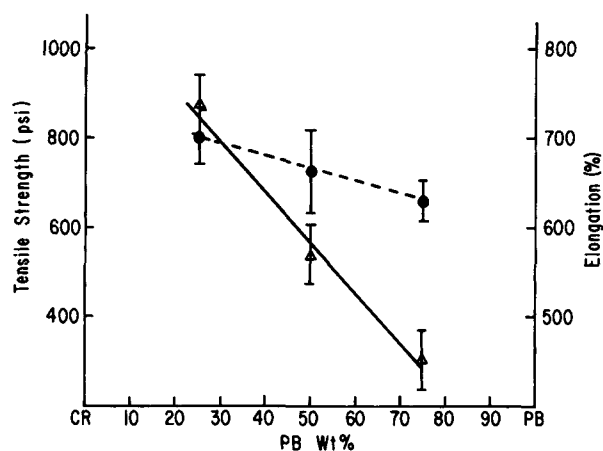


Figure 4 The mechanical properties of the PIPNs of C-CR and PB: (Δ) tensile strength of the PIPNs; (\bullet) elongation of the PIPNs.

CR matrix. The Soxhlet extraction of PIPN-2 (50 : 50) in CHCl_3 for a period of 10 h demonstrated that the weight lost is 51.3%. This result provides evidence that almost all linear PB chains can be released from the cross-linked CR matrix in a good solvent. We conclude that there are essentially no graft bonds between these two diene polymers. It would be difficult to obtain such a material via conventional cross-linking methods for the unsaturated diene macromolecules because of the chemical similarity of the dienes to many chemical reactions.⁷

Some miscible and immiscible CR/rubber blends have been investigated.^{5,13} In the case of miscible blends, another rubber was a modified oligomer by attaching functional groups that provide specific interactions with CR chains. Fortunately, miscibility is not a requirement for most rubber applications. Homogeneity at a fairly fine level is necessary for optimum performance, but some degree of microheterogeneity is usually desirable to preserve the individual properties of the respective polymer components.¹¹ We expect that novel combination properties from high molecular weight CR with other high molecular weight diene polymers can be produced by using the PIPN approach.

We are deeply indebted to Professor K. C. Frisch, Polymer Technologies, Inc., University of Detroit, for help with measurements of mechanical properties and Dr. J. L.

Travis for allowing the use of the electron microscopy laboratory at the Biology Department, State University of New York at Albany. This work was supported by the National Science Foundation Grant DMR 9023541.

References

1. H. L. Frisch, D. Klempner, and K. C. Frisch, *J. Polym. Sci. Part B*, **7**, 775 (1969).
2. D. Klempner, and H. L. Frisch, *J. Polym. Sci. Part B*, **8**, 525 (1970).
3. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum, New York, 1981.
4. D. C. Blackley, *Synthetic Rubbers: Their Chemistry and Technology*, Applied Science, New York, 1983.
5. P. J. Corish, in *Polymer Blends and Mixtures*, D. J. Walsh, J. S. Higgins, and A. Maconnachie, Eds., Martinus Nijhoff, Boston, 1985.
6. L. Sheckman, *Rubber Red Book*, Palmerton, New York, 1966, p. 634.
7. M. A. Golub, in *The Chemistry of Alkenes*, J. Zabicky, Ed., Interscience, New York, 1970.
8. Y. Xue, Z. Chen, and H. L. Frisch, *J. Appl. Polym. Sci.*, to appear.
9. Y. Xue and H. L. Frisch, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 2165 (1993).
10. W. R. Krigbaum and R.-J. Roe, *J. Polym. Sci. A.*, **2**, 4391 (1964).
11. W. M. Hess, C. R. Herd, and P. C. Vegvari, *Rubber Chem. Technol.*, **66**, 329 (1993).
12. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University, Ithaca, NY, 1953, Chap. XI.
13. J. B. Nagode and C. M. Roland, *Polymer*, **32**, 505 (1991).

YONGPENG XUE
ZHEFEI CHEN
H. L. FRISCH

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

Received September 24, 1993

Accepted December 22, 1993