

Castor-Oil-Based Interpenetrating Polymer Networks: Synthesis and Characterization

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Synopsis

Castor oil was polymerized and crosslinked with sulfur or diisocyanates to form the vulcanized and urethane derivatives, respectively. Both types were swollen with a plastic-forming monomer plus crosslinker, and a second polymerization was carried out in situ. Polyblends were also made by emulsion polymerization of styrene and methyl methacrylate employing hydrolyzed castor oil as the soap. In all three polymerizations, a wide range of compositions was obtained. The resulting interpenetrating polymer networks were characterized using electron microscopy, modulus-temperature measurements, and stress-strain analysis. The polystyrene phase size of the castor oil-urethane/polystyrene IPN was shown to decrease with increased crosslinking of the castor oil component and with increased polystyrene contents. The modulus-temperature study showed two distinct glass transitions in all cases, with evidence of significant mixing of the two components in many cases. The stress-strain results show that some of the IPN's behave as reinforced, highly extensible elastomers at low polystyrene levels, and as rubber-toughened plastics at high levels of polystyrene or crosslinking.

INTRODUCTION

Many plastics, such as polystyrene, are rather brittle as homopolymers. Even modest shocks, impact blows, or stresses may cause failure in application. Such plastics may be toughened by the incorporation of judicious quantities of an elastomeric material.¹⁻⁶ The elastomer must have a low enough glass temperature to be soft under impact loading conditions⁵ and must present a finely divided structure in order to effectively stop craze/crack growth and subsequent failure. While mechanical blending¹ and graft copolymerization techniques^{1,4} have provided the highly improved commercial products of today, the use of crosslinking in both components to form interpenetrating polymer networks (IPN's) leads to novel engineering materials.⁷⁻¹⁰ The use of IPN's offers potentially improved behavior, because the crosslinking level controls both the size of the rubbery domains and the phase continuity of the plastic component.^{9,11} Thus, a new mode of controlling the morphology to optimize mechanical behavior becomes available. From the scientific point of view, the use of crosslinking in these polymers provides a unique approach to a better theoretical understanding of the thermodynamics and molecular mechanics of phase separation in two

polymer systems. The present paper describes the use of castor oil polymers as the elastomeric component in rubber-toughened IPN plastics.

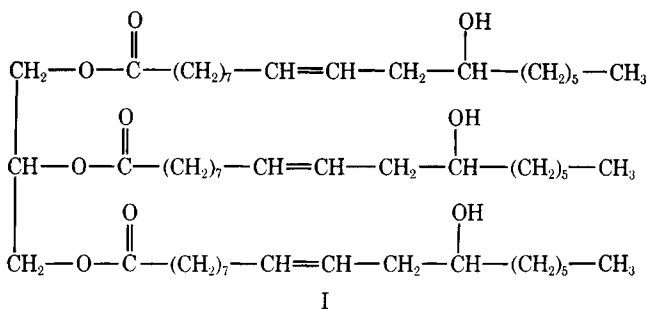
The largest single use of castor oil involves the alkaline pyrolysis of the oil to yield sebacic acid and capryl alcohol.¹²⁻¹⁵ Another important use of castor oil is in the synthesis of nylon 11 through a series of steps involving alcoholysis, cracking, and animation,^{16,17} followed by polymerization.

Castor oil may also be used as a comonomer. Cassidy and Schwank,¹⁸ for example, employed dehydrated castor oil with styrene to form a random copolymer.

Castor oil-based polyurethanes form a variety of elastomers and plastics, useful for potting compounds, encapsulation, and other materials.¹⁷ The chemistry and applications have recently been reviewed.¹⁸⁻²¹

The central concept of the present paper involves the synthesis, characterization, and engineering evaluation of polymerized and crosslinked castor oil as a rubbery toughening element in otherwise brittle plastics such as polystyrene. As will be explained below, the castor oil is polymerized first, followed by the plastic component.

Castor oil consists mainly of the triglyceride of ricinoleic acid (90%); the structural formula is as follows:



Polymerization and crosslinking may be effected in several ways, for example: (1) by the addition of sulfur or peroxides, followed by thermal curing to induce crosslinking through the double bonds; (2) by the addition of diisocyanates to form polyurethanes through reaction with the hydroxyl groups.²²⁻²⁴ As will be shown, both synthetic methods typically lead to rather soft elastomers.

As seen in structure I, the number of double bonds exactly equals the number of hydroxyl groups. Thus, it becomes of interest to compare the sulfur and diisocyanate syntheses and their products. Ideally, the same limiting level of crosslinking ought to be attainable in each case.

EXPERIMENTAL

The synthesis of the castor oil IPN's has been described via previously.²⁶ In brief, three experiments were carried out:

1. The castor oil was crosslinked with sulfur, followed by swelling in of methyl methacrylate plus tetraethylene glycol dimethacrylate as crosslinker, followed by polymerization.

2. The castor oil was crosslinked by reaction with 2,4-tolylene diisocyanate (TDI), followed by swelling in of styrene plus 1% divinylbenzene and 0.4% ben-

TABLE I
Castor Oil-Urethane Elastomers

Designation	Wt. TDI, g	Wt. castor oil, first addition, g	Prepolymer composition NCO/OH	Wt. castor oil, second addition, g	Final NCO/OH ratio
A	10	15.47	2.3	22.0	0.95
B	10	16.17	2.2	25.7	0.85
C	10	16.94	2.1	30.5	0.75

TABLE II
IPN Compositions

Sample no.	NCO/OH ratio	Composition castor oil-urethane/PS
1	0.95	32/68
2	0.95	40/60
3	0.95	53/47
4	0.85	36/64
5	0.85	40/60
6	0.85	50/50
7	0.75	29/71
8	0.75	36/64
9	0.75	50/50

zoin. A photopolymerization of the styrene produced the IPN. The several samples are described in Tables I and II.

3. Sodium ricinoleate, the soap prepared from castor oil, was used as an emulsifier for the emulsion polymerization of styrene. After the polymerization of the styrene, castor oil and sulfur were added to some of the samples, which produced a semi-IPN of the second kind upon heating. The latexes described in Table III were then mixed in various proportions (as described below), and the samples were compression molded.

Instrumentation and Measurements

A Philips 300 electron microscope equipped with a high-resolution stage was employed for all microscopy work.

To produce contrast between the phase domains, the osmium tetroxide technique of Kato²⁵ was employed. Samples were exposed to OsO₄ vapor for one week, during which time they darkened due to selective staining of residual double bonds. The samples were then embedded in an epoxy resin to ensure rigidity and cut to a thickness of not more than 600 Å with a Porter-Blum MT-2 ultramicrotome equipped with a diamond knife.

A Gehman torsion stiffness tester^{27,28} was used to measure the shear modulus G as a function of temperature. For easy comparison with other published data, E was also calculated using the Young's modulus approximation $E \approx 3G$.

Stress-strain measurements were conducted on an Instron tester at room temperature; a cross-head speed of 0.2 in./min was used. The force required

TABLE III
Synthesis of Latexes

Product	Water, ml	Styrene, ml	Initiator ($K_2S_2O_8$), g	Emulsifier	Polystyrene latex	Castor oil, ml	Sulfur, g	Reaction temp., °C	Reaction time, hr
Latex 1	600	120	0.3	Sodium Ricinoleate, 10 gm	—	—	—	70	3
Latex 2	600	120	0.3	Sodium Stearate, 10 gm	—	—	—	70	3
Latex 3	—	—	—	—	172 ml latex 1	6.34	1.22	160	3
Latex 4	—	—	—	—	200 ml latex 2	6.34	1.22	160	3

to break the sample and the displacement at this point were recorded and the yield and tensile strengths and elongation at break calculated.

The specimens were cut in an hourglass shape, with minimum widths of 7.0–14.0 mm, thicknesses of about 1.0 mm, and gauge lengths of 30–50 mm. The results reported are an average of four specimens for each composition.

The impact resistance measurements were conducted using a Baldwin impact tester, which is a simple beam (Charpy type) instrument.²⁹

RESULTS AND DISCUSSION

IPN's are synthesized by swelling a crosslinked polymer I with monomer II, complete with its own crosslinking agent and activator. After polymerization *in situ* of the second component, two continuous networks exist throughout the bulk material. Because the deliberately introduced crosslinks outnumber accidentally introduced graft sites, a new class of polymer material emerges in which phase domain size is controlled by the level of crosslinking. The term IPN was originally adopted because, in the limiting case of high compatibility, the two networks could be visualized as being interpenetrating and continuous throughout the macroscopic sample. However, if both components consist of chemically distinct polymers, incompatibility and some degree of phase separation usually result.^{7,9,25} Even under these conditions, the two components are forced to remain intimately mixed. If one polymer is elastomeric and one polymer plastic at use temperatures, the combination tends to behave synergistically, and either reinforced elastomers or impact resistant plastics result, depending upon which phase predominates.

Morphology

Transmission electron microscopy studies were made on the nine samples shown in Table II; the results are summarized in Figure 1. The sizes of the phases are seen to range from 300 Å to 500 Å, which is rather small, compared to the SBR/PS IPN's of Donatelli,^{9,11} which exhibited phase sizes of 800–1000 Å, and reflects the dense crosslinking developed in the castor oil–urethane network. In general, the sizes of the PS phases are seen to decrease with increasing crosslink density of the castor oil network, as indicated by the greater NCO/OH ratio. Also, the phase size of the polystyrene decreases with increasing polystyrene content.

Modulus–Temperature Behavior

Sulfur–Castor Oil IPN's

Shear modulus (10-sec)-versus-temperature data are presented in Figure 2. The following observations can be made:

1. Both the PMMA and the vulcanized oil have clear, well-defined glass transitions near 100°C and near –80°C, respectively.

2. The very low modulus of the vulcanized oil in the rubbery state, and the fact that its glass temperature changes to higher temperatures with increasing PMMA, both suggest somewhat incomplete network formation. This conclusion is consistent with the fact that a rather small amount of sulfur was used in the

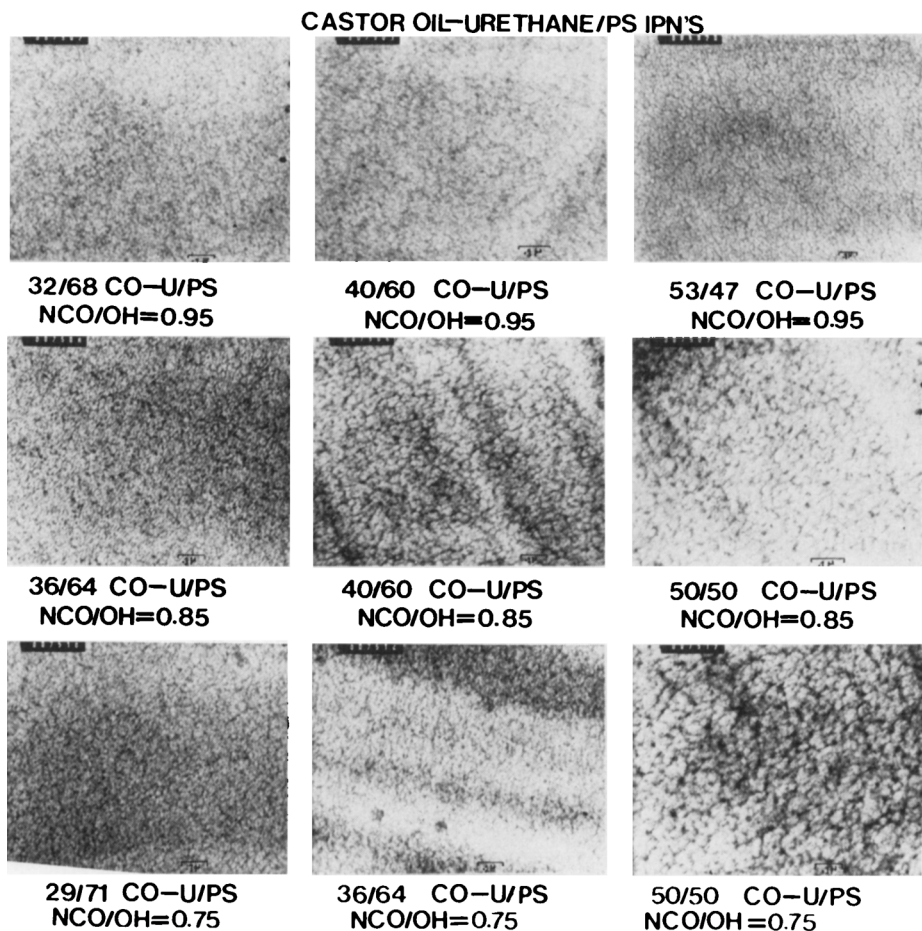


Fig. 1. Morphology of castor oil-urethane/polystyrene IPN's. Transmission electron microscopy, osmium tetroxide staining of the castor oil component.

vulcanized oil synthesis, about 2 g sulfur per 100 ml castor oil. Apparently, much low molecular weight material remains unincorporated in the sulfur-cured network.

3. The flattening and slight drift of the PMMA T_g with increasing vulcanized oil level (note especially the 78% PMMA curve) suggest either extensive grafting or slight extents of molecular mixing, or both.

Castor Oil-Urethane/Polystyrene IPN's

The castor oil-urethane elastomer was soft and tough, with little or no free castor oil remaining. The polymerized castor oil is mixed with a second monomer to form an interpenetrating polymer network (IPN).

IPN's prepared from the urethane elastomers with polystyrene were nearly clear, and tough. Depending on composition, either tough plastics or reinforced elastomers were made, as illustrated in Figure 3. The castor oil-urethane homopolymer is seen to have a glass temperature near -25°C . Significant but

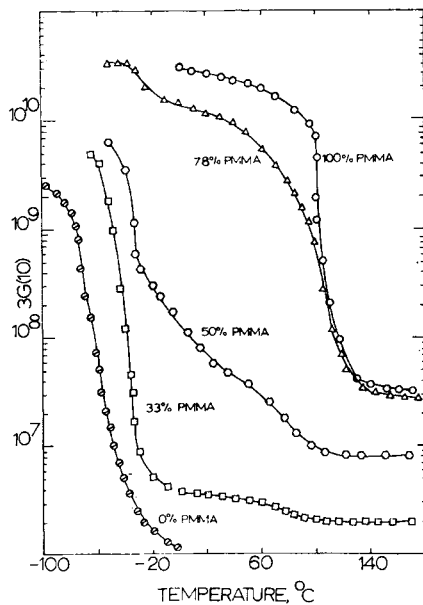


Fig. 2. 10-sec shear modulus vs. temperature for polymerized castor oil-based IPN's. The castor oil was crosslinked with 6.7% sulfur and the poly(methyl methacrylate), with 0.5% tetraethyl glycol dimethacrylate.

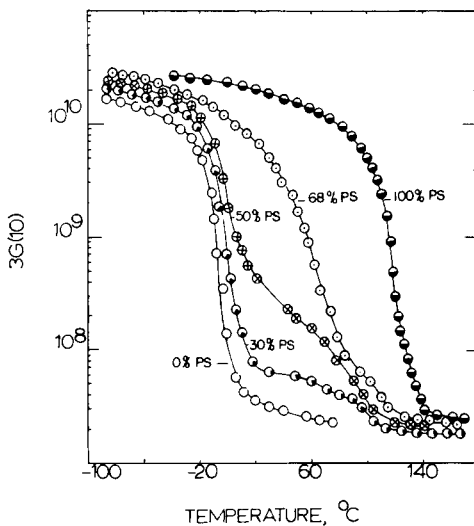


Fig. 3. Glass-rubber transition behavior of castor oil-polyurethane/polystyrene IPN's.

incomplete phase separation, perhaps of a complex nature, must result, as illustrated by the shape of the transition of the intermediate compositions. The 50/50 composition, for example, shows one transition near the castor oil elastomer transition temperature, and another transition at a temperature intermediate between the T_g 's of the castor oil-urethane polymer and polystyrene. Significant but incomplete mixing of the two components is indicated, thus confirming and

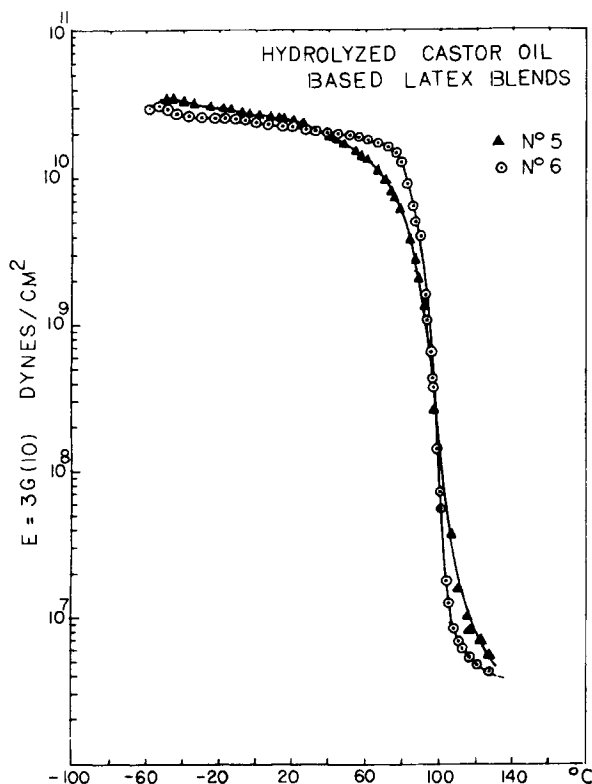


Fig. 4. Modulus-temperature studies on emulsion-synthesized materials: No. 5, hydrolyzed castor oil used as an emulsifier for styrene monomer; No. 6, sodium stearate emulsifier (see text for details).

extending conclusions drawn from electron microscopy study. The sample containing 68% PS resembles high-impact polystyrene in behavior.

Latex-Derived Samples

Modulus-temperature results of the synthesis in latex form are shown in Figure 4 for samples 5 and 6. Sample 5 was made by mixing latexes 1 and 3 followed by coagulation, drying, and molding. Sample 6 was similarly made from latexes 2 and 4. Sample 5, which employed castor oil-based soap as the emulsifier, appears to be slightly plasticized in comparison with the stearate synthesized product. However, the difference appears minor. (In a paper to be published separately, various proportions of castor oil were also added after the polystyrene syntheses. The sodium ricinoleate-castor oil-sulfur portion then is polymerized on the surface of the latex particle.)

The blend-type materials constitute extremely tough plastics that exhibit extensive stress whitening during failure. Two possible mechanisms for the toughening include the fine dispersal of the rubbery phase, poly(sodium ricinoleate), and/or the ionic nature of this polymer, which may impart ionomer characteristics to the blend.

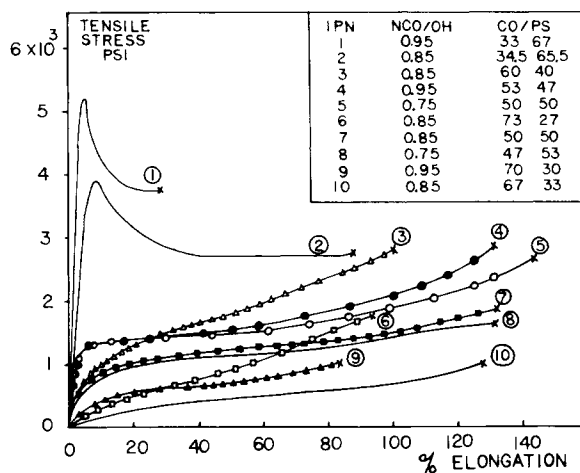


Fig. 5. Stress-strain studies on ten castor oil-urethane/polystyrene IPN's.

Stress-Strain Analysis

Figure 5 shows the stress-strain behavior of three compositions of castor oil-urethane IPN's, mainly varying in NCO/OH ratio. The sample having a NCO/OH ratio of 0.75 is clearly elastomeric, and apparently has only one continuous phase. With increasing crosslink level, however, the sample becomes stiffer and stronger, and the degree of phase continuity of the plastic polystyrene component apparently increases. A similar result was found by Donatelli et al.,¹¹ who showed that an increase in the crosslink level of polymer I resulted in an increase in the degree of phase continuity of polymer II. The fact that yield points were found for the compositions 1 and 2 suggests considerable toughness, the area under the stress-strain curve being large compared with that of polystyrene homopolymer, which normally fails at 1–2% extension. In this respect, these specimens resemble high-impact polystyrene (HIPS).

Stress-strain curves for the latex-based materials are shown in Figure 6. For comparison, a stress-strain curve for high-impact polystyrene is included. At levels of 8% sulfur-cured sodium ricinoleate, the best properties were obtained, with extensions of 6–7% being obtained. While these materials lack optimization, the clear presence of a yield point and of increased extension point to their potential capabilities.

During the stress-strain studies, all the samples were observed to stress whiten. This indicates failure arising from a crazing mechanism. Multiple crazes, brought about by the castor oil elastomer domains, increase toughness by increasing the fracture energy dissipations. Compositions 1 and 2 in Figure 5 are plastic in behavior; compositions 3 through 10 are more elastomeric. Note the yield point obtained in compositions 1 and 2, suggesting toughening. Polystyrene homopolymer fails at about 2% elongation.

A comparison of Figures 2 and 3 reveals important differences between the sulfur-cured castor oil IPN's and the urethane counterpart derivatives. Above the glass transition temperature, the sulfur-cured product is much softer. Employing the modulus-temperature relationship³⁰ for elastomers,

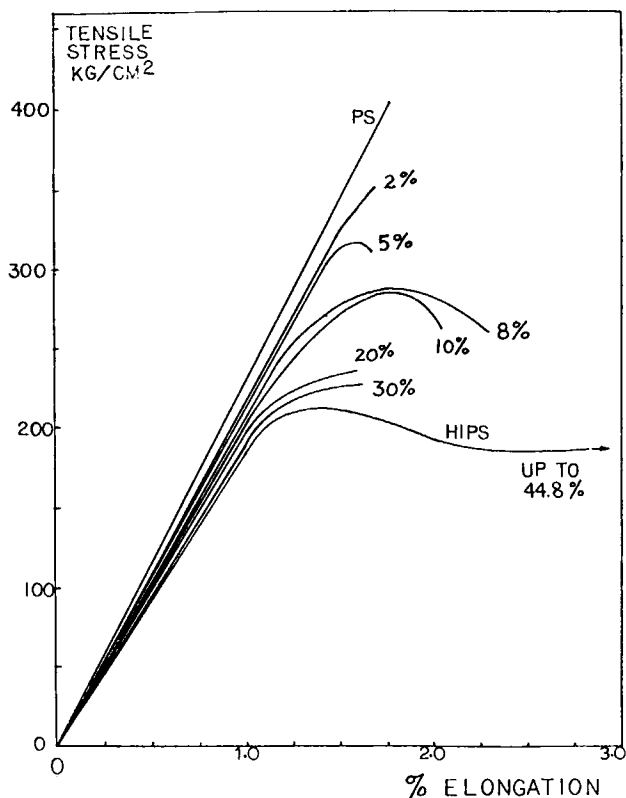


Fig. 6. Stress-strain behavior of polystyrene/sulfur vulcanized sodium ricinoleate latexes, at different levels of sodium ricinoleate.

$$G = nRT \quad (1)$$

the number of network effective chains, n , can be deduced for the two castor oil homopolymer elastomers. The results are 4.0×10^{-5} moles/cc and 8.0×10^{-4} moles/cc for the sulfur product and the urethane derivative, respectively. Thus, the sulfur-cured product has a much more open network. This is quite consistent with the fact that sulfur unfortunately interferes with the polymerization of monomer II, both it and its compounds behaving as chain transfer agents. Thus, only limited amounts of sulfur could be introduced if a reasonable IPN is to be produced. Methyl methacrylate was less susceptible to chain transfer than styrene, and hence the former was used with the sulfur-cured castor oil. The use of TDI to prepare the urethane produced both an elastomer with superior physical properties and a material that does not interfere with the second polymerization. Thus, most of the work reported herein employed the isocyanate-cured castor oil.

The electron micrographs in Figure 1 show that the phase domains are significantly smaller than counterpart morphologies of the SBR/PS IPN.^{9,11} Lowering the crosslink level of the castor oil component (down) or increasing the castor oil content (left to right) causes the phase domain size of the polystyrene to increase. According to current theories on rubber-toughened plastics,¹⁻⁶ these domains are probably too small for optimum mechanical behavior.

Reduced crosslinking levels in the castor oil-urethane should produce still better products, although even the nonoptimized products reported herein are surprisingly tough.

The authors wish to thank the National Science Foundation for support under Grant No. GF-42712, and Colciencias in Colombia. The authors also wish to thank Mr. F. C. Naughton of the N. L. Industries for his many helpful discussions.

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Received January 21, 1976

Revised March 24, 1976