Simultaneous Interpenetrating Networks Based on Castor Oil Elastomers and Polystyrene. V. Behavioral Trends and Analysis

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Synopsis

The morphology and/or mechanical properties of simultaneous interpenetrating networks, SINs, based on castor oil elastomers and crosslinked polystyrene, were studied by electron microscopy, stress–strain analysis, and/or Izod impact tests. Several synthetic details were changed systematically and the concomitant changes in morphology or particular properties observed. The toughness of elastomer SINs increased with decreasing domain size of the polystyrene dispersed phase. The use of a prepolymer for the elastomer network synthesis promotes the formation of larger polystyrene domains. The impact resistance of the SINs increased with the total elastomer content. Properly crosslinked and postcured compositions developed impact energies of about 60–70 J/m. SINs based on castor oil-derived elastomers and crosslinked polystyrenes form prototype engineering materials which already compared satisfactorily to commercial polymers in terms of mechanical behavior.

INTRODUCTION

The toughening of brittle plastics by the incorporation of a finely divided elastomeric phase has become increasingly important technologically.[1] The rubber-toughening principles developed for thermoplastics have now been successfully applied to thermosetting resins.[2–4] The challenge in the manufacture of thermoset polyblends consists in learning how to control the homopolymer properties, morphology, and process conditions in order to achieve a balance in properties, with significant improvements in toughening.

The preceding papers discussed the synthesis, morphology, and mechanical properties of simultaneous interpenetrating networks (SINs) based on castor oil elastomers and crosslinked polystyrene.[5–8] The discussion was focused mainly on the role of the elastomer phase characteristics such as reaction kinetics, phase domain morphology, and glass transition temperatures, while other important parameters such as COOH/OH ratio, polystyrene crosslink density, and extent of polymerization of the elastomer network components were kept constant. Besides those parameters mentioned above, setting the composition of the SINs at 10% and 40% elastomer content as reference points allowed both prototype toughened plastics and reinforced elastomers to be studied, respectively.

This paper describes a series of experiments in which some parameters previously held constant were changed systematically to observe their effect on particular aspects of the morphology or mechanical properties. The results obtained serve to identify behavioral trends and the key parameters requiring

control in order to obtain a desired change in morphology or properties. They also serve to complete the mapping of the synthesis–morphology–behavior relationships of these novel SIN-type polyblends, and therefore are useful in gaining an improved understanding of their characteristics.

EXPERIMENTAL

Materials and Synthesis Conditions

The general synthetic procedures were described in the previous papers in this series.[6,7] As before, the following symbols are employed: COPEN represents a castor oil–polyester network; COPUN, a castor oil–urethane network; COPEUN, a castor oil–poly(ester–urethane) mixed network; and PSN, a polystyrene network. See Table I for overall details.

The composition dependence of the morphologic features for the COPEN/PSN system was studied at 5% and 15% elastomer contents, in addition to the 10% elastomer composition previously characterized.[5–8] Sample 1 in Table I, the 5/95 COPEN/PSN SIN, was synthesized under the same experimental conditions employed for sample 8 in reference 8, the 10/90 COPEN/PSN SIN. The synthesis of the 15/85 COPEN/PSN SIN, sample 14 in Table I, employed a route similar to sample 13, the 40/60 COPEN/PSN SIN described elsewhere.[7,8]

Briefly, equivalent weights of castor oil and sebacic acid were allowed to react at 200°C until the acid value[9] fell to 33–36. The viscous prepolymer thus obtained (COPEP1) was dissolved in the styrene mixture previously formed by adding 1% divinylbenzene (55% purity) and 0.4% benzoyl peroxide to the freshly distilled monomer. The SIN containing 5% elastomer was polymerized for 120 min with stirring at 80°C prior to pouring into the molds. Sample 14 was polymerized in the molds without stirring after initial mixing. After 30 hr at 80°C, both samples were postcured at 180°C for 24 hr at 10^5 Pa pressure, followed by 24 hr at 3 kPa pressure.

The effect of elastomer crosslink density on the morphology of a 5/95 COPEN/PSN SIN was studied by changing the COOH/OH ratio of the prepolymer (COPEP2) to 0.9. The synthesis procedure for sample 2 was the same as described above for sample 1.

Also, sample 4 (5/95 COPEUN/PSN) and sample 5 (5/95 COPUN/PSN) SINs were prepared employing synthesis conditions similar to those used for their counterpart 10/90 SINs.[7,8] In brief, the synthesis of sample 4 involved the preparation of a polyester prepolymer (COPEP4) having terminal OH groups, which were further reacted with 2,4-tolylene diisocyanate (TDI) dissolved in the styrene comonomer mixture. For sample 5, the synthetic procedure involved as a first step the preparation of an NCO-terminated prepolymer (COPUP1) by reacting 2.2. equivalents of TDI with one equivalent of castor oil. The prepolymer was dissolved in the styrene mixture and then castor oil was added to give a final NCO/OH ratio of unity. Both SINs were polymerized at 80°C with stirring for 60 to 70 min, then poured between Teflon-lined glass plates and the polymerization continued at 80°C for 30 hr.

Three additional samples were synthesized in which only the elastomer was crosslinked, forming materials known as semi-IPNs.[10] The absence of the crosslinker divinylbenzene in the styrene solution yielded thermoplastic materials

TABLE I
Composition and Synthetic Conditions for Castor Oil Elastomer/Polystyrene Materials

Sample No.	Composition	(NCH + COOH)/OH	Elastomer Components[b]	Plastic Components	
1	5/95 COPEN/PSN	1.0	COPEP1	styrene + DVB	[a]
2	5/95 COPEN/PSN	0.9	COPEP2	styrene + DVB	[a]
3	3/97 COPE/PS	0.6	COPEP4	styrene	synthesized in Colombia
4	5/95 COPEUN/PSN	1.0	COPEP4 + TDI	styrene + DVB	[a]
5	5/95 COPUN/PSN	1.0	COPUP1 + castor oil	styrene + DVB	[a]
6	10/90 COPE/PSN	1.0	COPEP1	styrene + DVB	not postcured
7	10/90 COPEN/PSN	1.0	COPEP1	styrene + DVB	postcured 24 hr
8	10/90 COPEN/PSN	1.0	COPEP1	styrene + DVB	postcured 48 hr
9	10/90 COPEN/PSN	1.0	COPEP1	styrene + DVB	postcured 72 hr
10	10/90 COPEN/PS	1.0	COPEP1	styrene	[a]
11	10/90 COPEN/PS	1.0	COPEP1	styrene	remolded
12	10/90 COPEUN/PS	1.0	COPEP4 + TDI	styrene	sample 4 from ref. 8
13	40/60 COPEN/PSN	1.0	COPEP1	styrene + DVB	[a]
14	15/85 COPEN/PSN	1.0	COPEP1	styrene + DVB	[a]
15	40/60 COPEN/PSN	0.9	Sebacyl chloride–castor oil	styrene + DVB	[a]
16	40/60 COPEN/PSN	0.9	COCl prep + castor oil	styrene + DVB	[a]
17	40/60 COPEN/PSN	0.9	COCl prep + castor oil	styrene + DVB	[a]
18	COPEN	0.9	COCl prep + OH prep	none	[a]
19	PSN		none	styrene + DVB	[a]

[a] See text for synthesis details.
[b] prep = Prepolymer.

when polystyrene formed the continuous phase. Samples 10 and 11 (10/90 COPEN/PS) and sample 12 (10/90 COPEUN/PS) were synthesized following a similar synthesis procedure to that used for their corresponding SINs. Since phase inversion did not occur at 90 min for sample 10, polymerization was continued with stirring for 180 min prior to pouring into the molds. As a test of the thermoplastic nature of these materials, sample 11 was pulverized and pressure molded at 150°C and 18.0 MPa pressure.

In order to study the effect of postcuring time on the impact resistance of the COPEN/PSN system, a series of 10/90 composition samples were synthesized and postcured at 180°C ± 5°C and at a pressure of 3 kPa for different periods of time, namely, 0, 24, 48, and 72 hr (samples 6 to 9).

The synthesis of the 40/60 COPEN/PSN SINs using the highly reactive sebacyl chloride as a crosslinking monomer for the castor oil involved three different synthetic routes. In the first one, all SIN components were mixed in their monomeric state, sample 15. The synthesis of sample 16 involved the preparation of a OH-terminated polyester prepolymer (initial COOH/OH = 0.6), followed by mixing with the styrene comonomer mixture containing dissolved sebacyl chloride to finish the elastomer network formation. Sample 17 of this series was prepared by dissolving two opposite prepolymer compositions having initial COCl/OH ratios of 1.64 and 0.58, respectively, in the styrene comonomer mixture. All samples had an overall COOH/OH ratio of 0.9 and were polymerized at 80°C for 72 hr. For sample 18, pure elastomer network was synthesized by mixing the opposite prepolymer compositions described above and cured at 23°C under vacuum for 72 hr. For sample 19, the PSN was polymerized 24 hr at 80°C, followed by 12 hr at 110°C.

Instrumental Techniques

Electron Microscopy

The elastomer phase was selectively stained dark by using the osmium tetroxide technique by Kato.[11] Samples were exposed to OsO_4 vapors for a week, embedded in epoxy resin, and cut to a thickness of 60–80 nm with a Porter–Blum MT-2 ultramicrotome equipped with a diamond knife. The transmission electron micrographs were obtained by direct observation of the stained microtomed sections under a Philips 300 electron microscope.

Tensile Tests

Tensile behavior was studied on an Instron Universal Test Instrument Model TTL, at ambient conditions. Samples were cut according to standard dimensions,[12] polished to remove all visible flaws, and tested at a cross-head speed of 8.47×10^{-5} m/sec; a minimum of three specimens were tested for each sample and average values reported.

Impact Tests

Impact resistance tests were conducted using a Baldwin impact tester, which is a simple beam set in a Izod-type mode of test. Samples were notched and conditioned prior to test according to standard methods.[13]

RESULTS

Effect of Composition on Morphology

Figure 1 shows the morphology of the 5/95 COPEN/PSN SIN, sample 1, at two levels of magnification. Such electron micrographs indicated elastomer domain sizes ranging from 200 to 1400 nm, with an average of 730 nm. PSN cellular domains within the elastomer phase averaged 90 nm, with an estimated maximum to minimum domain size ratio of 2.0. The elastomer phase (including the PSN domains) constitutes 8.1% by volume, with the PSN domain content in the elastomer phase calculated at 38% by comparison with the stoichiometric composition.

The effect of increasing PSN content from 60% to 85% on the morphology of COPEN/PSN SINs in the absence of stirring beyond mixing is illustrated in Figure 2. PSN domains up to 4500 nm are formed and constitute the 70% by volume of the sample. Like with their counterpart polybutadiene-containing high-impact polystyrene (HIPS) materials,[14,15] lack of stirring causes the elastomer phase to remain continuous. The morphology in Figure 2(a) should be compared with Figure 9 in reference 6, showing the effects of stirring on phase continuity in this system.
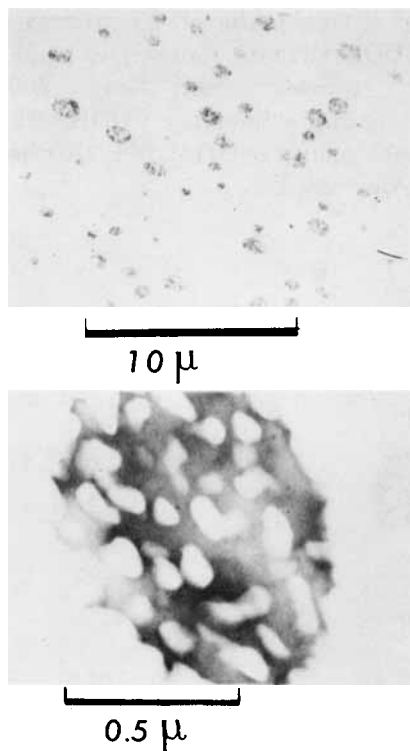

Fig. 1. Morphology of sample 1, a 5/95 COPEN/PSN SIN stirred for 120 min before pouring, shown at two magnifications. Micrograph at the bottom shows the structure within an elastomer domain.

15/85 COPEN / PSN   40/60 COPEN/PSN
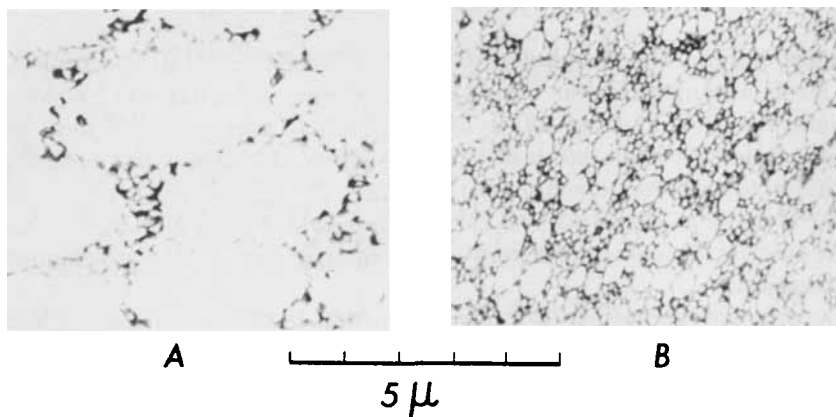

A   5 μ   B

Fig. 2. Effect of composition on morphology for COPEN/PSN SINs polymerized without stirring. Micrographs A and B correspond to samples 14 and 13 in Table I, respectively.

Effect of Elastomer COOH/OH Ratio on Morphology

Figure 3 illustrates the changes in the cellular structure of the elastomer phase due to changes in the COOH/OH ratio for samples 1 and 2 (5/95 COPEN/PSN SIN). For comparison purposes, the morphology of 3/97 COPE/PS graft copolymer, sample 3, having approximately a COOH/OH ratio of 0.6, has been included. The polystyrene cellular content within the elastomer phase increases as the COOH/OH ratio decreased.

5/95 COPEN/PSN   5/95 COPEN/PSN   3/97 COPE/PS

COOH/OH : 1.0   0.9   0.6

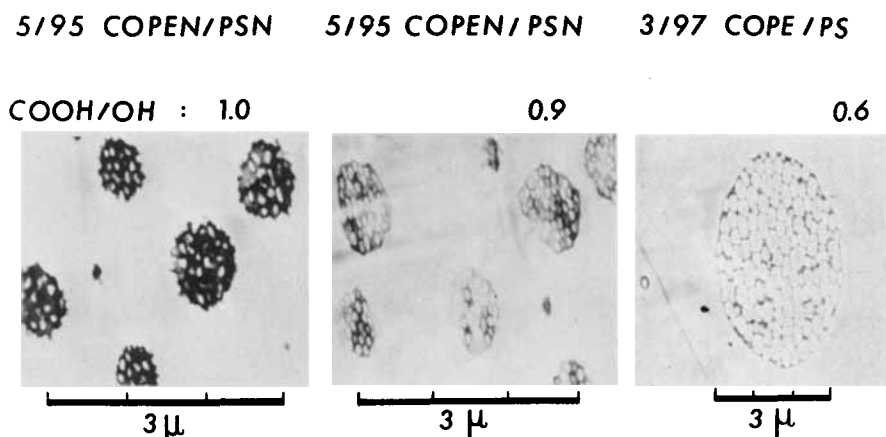

3 μ   3 μ   3 μ

Fig. 3. Effect of COOH/OH ratio of elastomer phase on cellular structure. Samples 1 and 2 at left and center, respectively, are SINs; sample 3 at right is a graft copolymer of similar components.

Effect of Composition on Impact Resistance

The Izod impact energy of SINs containg 5% of elastomer shows the polyester elastomer as the most effective material for imparting toughening under high rates of loading. Table II summarizes the results, including data for the SINs containing 10% elastomer from the previous paper in this series.[8]

Sample 12, the 10/90 COPEUN/PS, yielded the best impact resistance of the semi-IPNs, 39.2 J/m, very close to that of the 10/90 COPEUN/PSN SINs.

Effect of Postcuring Time on Impact Resistance

Table III lists impact resistance data for several materials, showing that postcuring is required for the development of impact resistance in the COPEN/PSN system but that postcuring time beyond 24 hr introduces very little change in impact resistance. The postcuring reaction completes the crosslinking of the elastomer phase.

Effect of Extent of Prepolymerization on the Elastomer Network Components on the Morphology and Stress–Strain Behavior

The use of unreacted monomers instead of prepolymers as elastomer network synthetic components during the synthesis of 40/60 COPEN/PSN SINs, sample 15, resulted in the morphologic differences illustrated in Figure 4. All materials exhibited a PSN cellular structure and a continuous elastomer phase, with the disperse PSN domains showing multimodal size distributions. As the extent

TABLE II
Effect of Composition on Impact Resistance for SIN Based on Castor Oil Elastomers and Polystyrene

Sample No.	Composition	Impact resistance,[b] J/m
	PSN	13.3
[a]	10/90 COPEN/PSN	67.8
[a]	10/90 COPEUN/PSN	44.8
[a]	10/90 COPUN/PSN	24.6
1	5/95 COPEN/PSN	46.6
4	5/95 COPEUN/PSN	36.4
5	5/95 COPUN/PSN	16.6
12	10/90 COPEUN/PS	39.2

[a] Reproduced from ref. 8.
[b] 1 J/m = 0.0187 lb-ft/in.

TABLE III
Effect of Postcuring Time on Impact Resistance for a 10/90 COPEN/PSN SIN

Sample No.	Postcuring Time, hr	Impact Strength, J/m
6	0	16.6
7	24	64.1
8	48	68.1
9	72	67.6

SEBACYL   CHLORIDE

SEBACYL   CHLORIDE
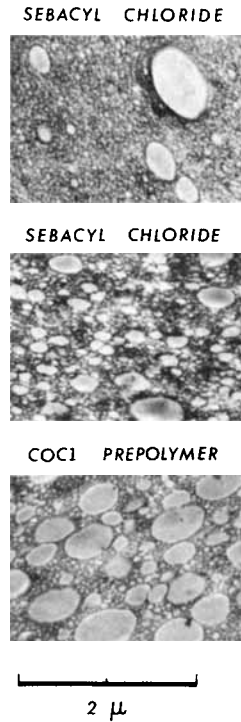
COCl   PREPOLYMER

2 μ

Fig. 4. Morphologic dependence of 40/60 COPEN/PSN SINs on extent of prepolymerization of elastomer network components. Transmission electron micrographs on top, middle, and bottom were taken from samples 15, 16, and 17, respectively. Reaction conditions: 80°C without stirring; overall COCl/OH ratio 0.9.

of prepolymerization of the elastomer network components was increased, the PSN tended for form larger domains preferentially. Tensile properties of the material such as modulus, ultimate strength, elongation to break, and toughness decreased as the extent of prepolymerization increased, as illustrated in Figure 5.
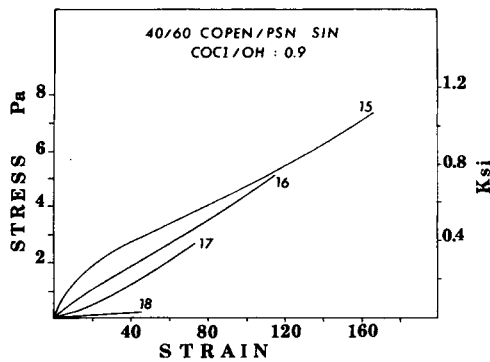
40/60 COPEN/PSN SIN
COCl/OH : 0.9

Fig. 5. Effect of synthetic details on stress–strain behavior. Samples corresponding to the morphology shown in Fig. 4:   15, OH monomer + COCl monomer; 16, OH prepolymer + COCl monomer; 17, OH prepolymer + COCl prepolymer; 18 COPEN.

DISCUSSION

A detailed knowledge of the interrelationships among the synthetic variables, the resulting morphology, and concomitant properties of a polyblend constitutes the key to improved engineering materials. The experiments and results described above reveal significant trends useful in the understanding of such relationships for a novel set of polyblends, i.e., the SINs based in castor oil elastomers and crosslinked polystyrene.

The morphologic characteristics of sample 1 (5/95 COPEN/PSN SIN, Fig. 1) suggest that lower elastomer content and a higher stirring input energy after phase inversion tend to decrease the elastomer domain size and the PSN domain content of the elastomer phase and to render a more homogeneous elastomer domain size distribution. These results are in agreement with those found by Wagner and Robeson[16] for the polybutadiene–polystyrene system.

Impact resistance of the SINs containing 5% elastomer, Table II, followed the same trend exhibited by those containing 10% elastomer. As discussed in part of this series,[8] the trend yielding the castor oil polyester as the best toughening agent suggests that the glass transition temperature of the elastomer phase is perhaps the most important factor controlling the development of impact resistance in these materials.

The tests conducted on semi-I IPNs[10] explored the possibility of manufacturing thermoplastic materials with good impact resistance. The impact resistance of the 10/90 COPEUN/PS thermoplastic was close to that obtained in the corresponding SIN material (39.2 and 44.8 J/m, respectively.

With regard to SINs in which the elastomer phase forms the continuous phase and therefore exhibits elastomeric or leathery behavior, the polystyrene domain size controls the tensile behavior of the material. Similar to the results reported previously for other systems such as graft copolymer[14,15] and semi-IPNs of the second kind prepared without stirring,[17,18] materials exhibiting morphology similar to that shown in Figure 2(a) have extremely poor mechanical properties. On the other hand, the 40/60 composition shown in Figure 2(b) illustrates the prototype morphology expected of reinforced elastomers. This structure resembled the PS latex-reinforced elastomers reported by Kraus et al.[19]

The number and size of the large PSN domains in the elastomer series can be reduced by decreasing the polystyrene content, Figure 2, or by increasing the actual crosslinking density of the elastomer phase before or during the styrene polymerization. Figure 4 supports this latter observation for the 40/60 COPEN/PSN SIN. As the size of the PSN domains decreases, the initial modulus, the elongation to break, and the ultimate strength increase (Fig. 5). Tougher materials also are manufactured by promoting controlled molecular mixing between the two network components, as illustrated in the previous papers.[7,8]

Figure 4 also supports observations regarding the mechanism of PSN domain formation in SINs described previously.[8] The use of the highly reactive sebacyl chloride as a crosslinker for the castor oil caused the elastomer network to form very quickly. Samples reached the gel point only after 10 to 15 min, while the onset of turbidity was observed 30 to 50 min later. The existence of large PSN domains can be explained by a microsyneresis process occurring as the crosslink density of the elastomer network increases due reaction[8] and/or as the styrene polymerizes.

As a result of the lower thermodynamic ability of the network to hold the monomer, the concentration of the styrene mixture increases locally in some regions and eventually phase separation occurs. The styrene monomer pockets that form first will grow bigger than the finer structures that form later, and the latter are controlled by the network characteristics to a greater extent than the former.

The best elastomers for SINs are obtained by an overall composition similar to that approximating equilibrium swelling of the elastomer network by the styrene. This condition closely resembles the sequential mode of synthesis used by several workers.[20-23]

Although electron microscopy studies did not reveal substantial differences in the elastomer domain size distribution for 5/95 COPEN/PSN SINs with different COOH/OH ratios, Figure 3 shows that the polystyrene cellular content within the elastomer phase increases as the COOH/OH ratio decreases. For comparison purposes, an electron micrograph of a graft copolymer formed by polymerizing a solution of a fully reacted polyester prepolymer (COOH/OH 0.64) in styrene monomer with stirring was also included in Figure 3. Since crosslinking of the elastomer phase domains occurs after PSN domain formation, PSN domain size differences might also arise from different solubilities of the styrene monomer in the prepolymer at the phase inversion point. It is suggested that the higher the COOH/OH ratio, the higher the number of the free carboxyl groups in the prepolymer. The existence of these highly polar groups along the polyester chains could decrease solubility of the styrene monomer in these domains. This observation insinuates yet another key parameter in controlling the cellular structure of the elastomer domains, namely differences in polarity between prepolymer I and monomer or prepolymer II.

In order to explore the potential uses of the SINs based on castor oil elastomers and crosslinked polystyrene as reinforced elastomers or high impact plastics, a comparison with commercial type materials is presented in Table IV and Figure 6. The tensile behavior of the SINs containing 40% elastomer compares satisfactorily with three commercial reinforced rubbers (Fig. 6). The tensile strengths of the SINs in this study are higher, although they tend to break at lower elongations. The energy to break C1, C2, and C3 materials, as indicated by the area under the stress–strain curves, was found to be 17.0, 10.7, and 12.5 J/m^3. Values of 16.85, 4.47, and 2.2 J/m^3 were reported earlier[8] for SIN compositions containing 40% COPUN, COPEUN, and COPEN elastomers, respectively. These results indicate that the SINs have considerable toughness. Since the SINs shown in Figure 6 are research materials without any attempt at optimization, the comparision at least yields encouraging results.

CONCLUSIONS

The experimental results presented above identify trends in morphology and properties of the SINs based on castor oil elastomers and polystyrene as the synthesis parameters are systematically changed. Impact resistance increases with elastomer content and with the polyester content of the elastomer phase. Crosslinking of the elastomer phase is required to achieve impact resistance. Postcuring times of 24 hr are sufficient to develop good impact resistance in the COPEN/PSN SINs containing 5–10% elastomer.

TABLE IV
Mechanical Properties for Styrene-Based Plastics[a]

Property	PS	Medium HIPS	High HIPS	Super HIPS	COPEN/PSN-1	COPEN/PSN-7	COPEUN/PSN-12
Elastomer, %	0	3.4	5.1	14.5	5	10	10
Tensile Yield, MPa	35.1	25.5	20.7	13.8	37.2	31.1	22.1
Elongation Rupture, %	0.9	1.4	35-45	17[b]	7	16	15
Modulus, 10^5 MPa	3980	3282	2400	1746	1886	1520	1090
Izod Impact Strength, J/m[c]	13.9	32.0	69.4	240.2	47.0	67.8	39.2

[a] Commercial materials data from ref. 24.
[b] Localized whitening and flow, nonuniform extension.
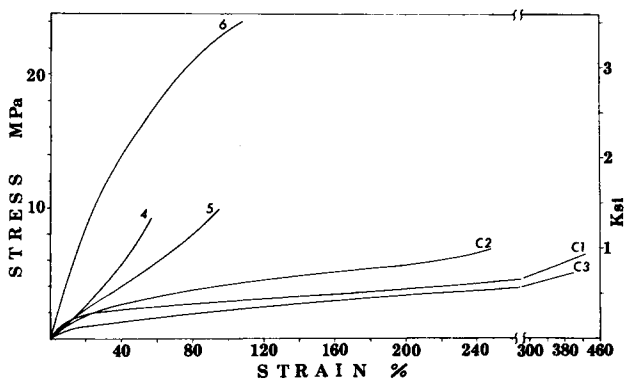[c] Conversion factor: 1 J/m = 0.0187 lb-ft/in.

Fig. 6. Stress–strain curves for experimental and commercial reinforced elastomers. Curves 4, 5, and 6 were adapted from the corresponding samples in ref. 8. C1, C2, and C3 represent commercial shoe heel materials: 4, 40/60 COPEN/PSN; 5, 40/60 COPEUN/PSN; 6, 40/60 COPUN/PSN.

In the synthesis of reinforced elastomers, toughness improves with decreasing the PS domain size; this can be accomplished by using styrene weight fractions below the equilibrium swelling of the pure elastomer network, monomer mixtures preferentially to prepolymers, and a high formation rate of the elastomer network.

Since this is the last paper in the series dealing with SINs based on castor oil elastomers and crosslinked polystyrene, a summary of the main results and conclusions of this study follow:

1. A 100% natural polymer based entirely on agricultural products, the polyester elastomer obtained by reacting castor oil with a castor oil derivative, sebacic acid, was the basis for the synthesis of SINs.

2. Based on castor oil-derived elastomers and crosslinked polystyrene, a simultaneous mode of polymerization can be successfully employed to synthesize prototype engineering materials such as tough, impact-resistant plastics and reinforced elastomers.

3. All of the SINs studied formed two-phase systems with tensile properties similar to the continuous-phase component but exhibiting a substantial improvement in toughness arising from the characteristics of the disperse phase. The SINs required higher fracture energies than either polymer component, indicating a synergistic mechanism.

4. At lower elastomer contents, the presence of stirring during the early stages of the polymerization induces morphologic changes similar to those observed in the bulk synthesis of the commerical high-impact polystyrenes (HIPS), finally evoking a material bearing a close resemblance to the morphology of commercial HIPS. The polystyrene forms the continuous phase, while the elastomer forms domains ranging from 100 to 5000 nm in size and contain polystyrene subinclusions. The total energy input and the shear conditions introduced by stirring during polymerization and the rate of elastomer network formation in the time interval between phase inversion and gelation seems to determine the elastomer domain size distribution of such materials.

The cellular structure within the elastomer domains seems to be controlled mainly by the rate of elastomer network formation and the solubility of the polystyrene in the elastomer. Pouring into the molds must be done in the time

(or conversion) interval between phase inversion and gelation. Such time intervals decreased as the elastomer concentration increased because the higher polystyrene conversions were required for phase inversion. Thus, a critical "window" exists for stopping the stirring and pouring into the molds. Pouring too early leads to poor products because of incomplete phase inversion. Pouring too late also yields inferior products because of the onset of gelation.

5. There is a limit in composition, at about 15% elastomer content, at which stirring alone can no longer induce the polystyrene phase to be continuous, and the quality of the mechanical properties of the materials changes drastically.

6. The impact resistance of the SIN plastics increased with elastomer content and polyester content of the elastomer phase.

7. Dynamical mechanical spectroscopy and Izod impact results suggest that the glass transition temperature of the elastomer phase constitutes the most critical parameter in achieving impact resistance in these materials.

8. The modulus, elongation to break, ultimate strength, and toughness of the straight castor oil elastomers increase with increasing amounts of TDI employed as crosslinker. A similar trend was observed in the elastomeric SINs (40% elastomer content) in which the elastomer phase was continuous.

9. While phase separation per se occurs when the free energy of mixing becomes positive, two different mechanisms of phase separation are postulated in the synthesis of SINs. The first one originates in the precipitation of polystyrene chains from the polymerizing solution and seems to occur periodically evolving a multimodal domain size distribution. The second one originates in the reduction of the ability of the still reacting elastomer to hold the styrene monomer mixture. The process is referred to as microsyneresis and occurs mainly when the styrene monomer concentration exceeds that of equilibrium swelling conditions within the elastomer. Microsyneresis appears to be encouraged by the presence of network inhomogeneities, such as local regions of different crosslink density.

10. The morphology and mechanical properties of SINs evolve from a sequence of events, namely, separation of phase 1 from phase 2, separation of phase 2 from phase 1, gelation of polymer 1, gelation of polymer 2, and phase inversion. The crucial criteria center on what happens first and what morphologic changes occur. Variables such as composition, compatibility, reaction rates, and reaction conditions determine the morphologic path followed by the reacting system.

11. Although the materials studied in this research program lack optimization, they already compare satisfactorily to commercial materials in many respects. With reasonable further research and development studies, high-quality tough plastics and reinforced elastomers may be anticipated.

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