

# Impact-Resistant Plastics from Blends of Poly(styrene/Acrylonitrile) with $\epsilon$ -Caprolactone Block Copolymers

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## Synopsis

Impact-resistant resins resembling ABS were prepared by hot mixing poly(styrene/acrylonitrile) and rubbery  $\epsilon$ -caprolactone block copolymers in the presence of small amounts of an organic peroxide. Measurements of optical properties and softening temperatures indicate that this discovery is a result of mutual solubility between the poly(styrene/acrylonitrile) and the poly- $\epsilon$ -caprolactone sequences of the block polymer. Advantages of the blend process over latex grafting include lower nonpolymer residue, better color, and more versatility. Disadvantages are slightly lower softening temperature and less surface gloss. Tensile strength, flexural modulus, oil resistance, and melt flow-impact strength relationship are similar. Versatility of the blend process was demonstrated in the development of transparent compositions.

## INTRODUCTION

A mixing procedure for preparing a polymer alloy similar to impact polystyrene was described previously.<sup>1</sup> The procedure consisted of mixing polystyrene with rubbery butadiene-styrene block copolymers in the molten state along with an organic peroxide which generated free radicals during mixing. Morphology and properties of the resultant polymer alloy resembled impact polystyrene.

We now wish to report additional experiments in which poly(styrene/acrylonitrile) (SAN) was mixed with rubbery styrene-butadiene- $\epsilon$ -caprolactone (S-B-CL) block copolymers and an organic peroxide.<sup>2</sup>

## EXPERIMENTAL

### Polymerization

The preparation of rubbery butadiene- $\epsilon$ -caprolactone and styrene-butadiene- $\epsilon$ -caprolactone block copolymers was accomplished by sequential addition of monomers as described by Hsieh.<sup>3</sup> The polymerizations were short-stopped with 2,2'-methylene bis(4-methyl-6-*t*-butylphenol), Cyanox SS (A.O. 2246). Polymers were isolated by coagulation with isopropyl alcohol and vacuum dried at 50°C.

### Blend Preparation

Poly(styrene/acrylonitrile) and styrene-butadiene- $\epsilon$ -caprolactone block copolymers were fluxed in a Brabender Plastograph at 10 rpm, then mixed at 100 rpm for 3 min in a nitrogen atmosphere. Dicumyl peroxide (Hercules Dicumyl 40

C) was then added at 0.01 part level and the mixing chamber evacuated, after which the polymers were mixed at 100 rpm an additional 7 min and dumped. The blends were compression molded and tested by standard methods.<sup>1</sup>

## RESULTS AND DISCUSSION

Styrene-butadiene-caprolactone block polymers are similar in physical properties to styrene-butadiene-styrene block polymers, which result in high impact strength in polystyrene blends without use of peroxide.<sup>4</sup> In preliminary tests, a 25-50-25 styrene-butadiene-caprolactone block polymer was mixed, with or without peroxide, with polystyrene, poly(styrene/acrylonitrile), or poly(methyl methacrylate). The data of Table I show that impact strengths of 10 ft-lb or more were achieved with a 75/25 poly(styrene/acrylonitrile) with or without peroxide. Data in Table I also show that poly(methyl methacrylate) blends were brittle and polystyrene blends were lower in tensile and impact strength than blends with poly(styrene/acrylonitrile).

The influence of various properties of  $\epsilon$ -caprolactone block polymers on properties of blends with poly(styrene/acrylonitrile) are described in the following sections.

### Antioxidant and Peroxide

The effects of antioxidant content of the rubbery  $\epsilon$ -caprolactone block polymer and peroxide level in blends with poly(styrene/acrylonitrile) are shown in Figure 1. The antioxidant levels are approximate values due to uncertainty in analysis. In this particular set of experiments, an optimum of 0.05% dicumyl peroxide for 0.2 part antioxidant in the rubber was found. Since antioxidant decreases the effectiveness of dicumyl peroxide to crosslink the rubber phase, peroxide requirements were lower at lower antioxidant levels. With no antioxidant in the rubber, high impact strength was produced without peroxide. Thermal crosslinking probably takes place under these conditions.

TABLE I  
Blends of  $\epsilon$ -Caprolactone Block Polymers with Various Thermoplastics<sup>c</sup>

Thermoplastic	Dicumyl peroxide, %	Tensile, psi	Elongation, %	Flexural modulus, $\text{psi} \times 10^{-3}$	Melt <sup>a</sup> flow, g/10 min	Notched Izod impact, ft-lb/in.
Polystyrene	0	2370	16	172	1.46	5.0
Poly(methyl methacrylate)	0	2040	5	118	0.64	0.7
Poly(styrene/acrylonitrile) <sup>b</sup>	0	2870	35	189	1.32	11.8
Polystyrene	0.1	2520	25	205	1.16	1.3
Poly(methyl methacrylate)	0.1	2830	12	180	0.20	0.7
Poly(styrene/acrylonitrile)	0.1	3160	42	219	0.52	10.4

<sup>a</sup> Conditions: 200°C and 5 kg.

<sup>b</sup> Ratio 75/25.

<sup>c</sup> Blend recipe: 62.5 parts thermoplastic and 37.5 parts 25-50-25 styrene-butadiene-caprolactone block polymer.

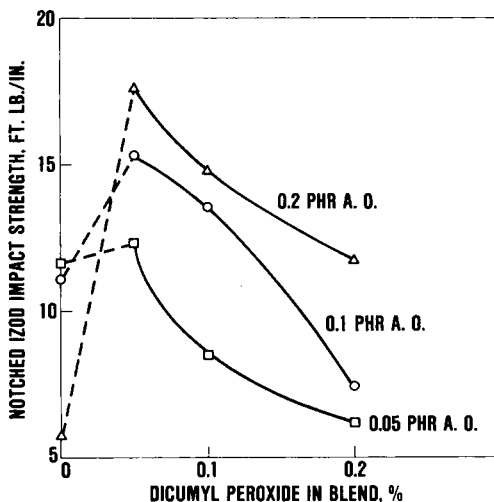


Fig. 1. Influence of antioxidant and peroxide levels on impact strength. Blends are 62.5% SAN (75/25) and 37.5% S-B-CL (25-50-25).

### Composition

The effect of blend composition on flexural modulus and tensile strength is shown in Figure 2. Flexural modulus and tensile strength are reduced as rubber content of the blend is raised. On the other hand, impact strength rises with increasing rubber content particularly rapidly near 20% rubber (Fig. 3). To maintain modulus and tensile strength at levels comparable to ABS polymers, most of the blends were prepared with 22.5% rubber. If modulus and tensile strength are held constant, impact strength and melt flow are then indications of toughness and processability. Minimum rubber content consistent with high impact strength is considered desirable for oxidative stability and oil resistance.

The effect of poly(styrene/acrylonitrile) composition on properties of blends is shown in Table II. Three commercial resins and three laboratory resins of

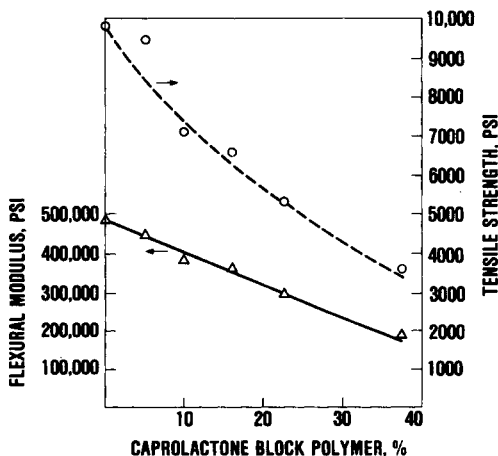


Fig. 2. Influence of blend composition on tensile strength and flexural modulus. Blends were prepared with 75/25 SAN and 25-50-25 S-B-CL.

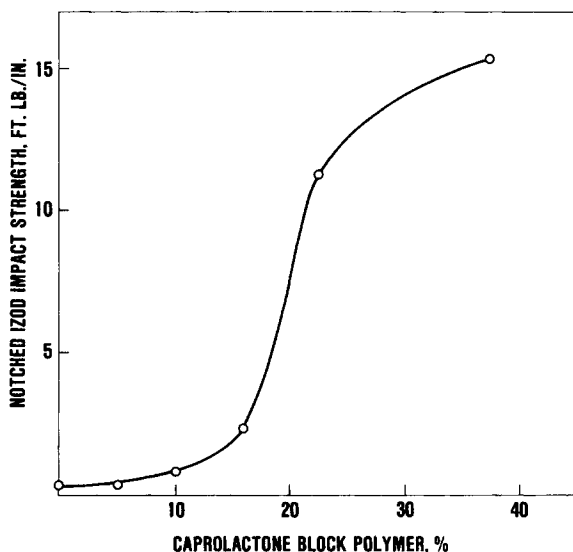


Fig. 3. Influence of blend composition on impact strength. Blends were prepared with 75/25 SAN and 25-50-25 S-B-CL.

TABLE II  
Influence of Poly(Styrene/Acrylonitrile) Composition on Properties of Blends<sup>a</sup>

Composition, styrene/acrylonitrile	Tensile, psi	Elonga- tion, %	Flexural modulus, psi $\times 10^{-3}$	Melt <sup>b</sup> flow, g/10 min	Notched Izod impact, ft.-lb/in.
76.5/23.5 (Tyril 760)	5630	31	303	0.65	10.4
75.4/24.6 (Tyril 767)	5610	37	298	0.29	11.1
71.2/28.8 (Tyril 780)	5010	60	277	0.39	7.8
81.4/18.6	4770	17	288	0.17	7.9
73.9/26.1	4640	45	296	0.22	8.6
69.3/30.7	4740	34	305	0.01	2.4

<sup>a</sup> Blend recipe: 77.5 parts poly(styrene/acrylonitrile), 22.5 parts of a 25-50-25 styrene-butadiene-caprolactone block polymer and 0.1 part dicumyl peroxide.

<sup>b</sup> Conditions: 200°C and 5 kg.

varying styrene/acrylonitrile ratios were used. The data show that a 75/25 styrene/acrylonitrile ratio is about optimum for impact strength.

The effect of caprolactone block polymer composition on blend properties is shown in Table III. All blends were formulated to contain 11.25% polybutadiene except those with 0-60-40, 0-20-80 and 20-20-60 styrene-butadiene- $\epsilon$ -caprolactone block polymers. The blend with 0-60-40 block polymer contains 13.5% polybutadiene, which accounts for the high Izod impact, and the blends with 0-20-80 and 20-20-60 block polymers contain 4.5% polybutadiene. In general, tensile strength and modulus decrease as the amount of  $\epsilon$ -caprolactone increases in the rubbery component. Highest impact strengths were achieved with 0-75-25 and 25-50-25 styrene-butadiene- $\epsilon$ -caprolactone block polymers.

Block polymers containing 25% styrene, 50% butadiene, and 25%  $\epsilon$ -caprolactone were also prepared in different sequence distributions. One was a true block polymer with compositionally pure monomer sequences, S-B-CL; and the other

TABLE III  
Influence of Caprolactone Block Polymer Composition on Properties of Blends with 75/25 Poly(Styrene/Acrylonitrile)

Rubbery block S-B-CL	Blend SAN/rubber	Tensile, psi	Elongation, %	Flexural modulus, psi $\times 10^{-3}$	Melt flow, <sup>a</sup> g/10 min	Notched Izod impact, ft-lb/in.
0-85-15	87/13	5510	29	368	0.43	1.7
0-80-20	86/14	5640	31	333	0.30	6.2
0-75-25	85/15	5640	40	339	0.25	9.1
0-65-35	83/17	5510	19	315	0.31	8.8
0-60-40	77.5/22.5	4940	28	285	0.32	10.3
0-40-60	72/28	4600	48	262	0.11	3.8
0-20-80	77.5/22.5	6560	78	334	0.78	0.4
25-50-25	77.5/22.5	5500	49	312	0.17	11.4
15-60-25	81/19	5540	30	326	0.23	10.0
5-70-25	84/16	5900	40	330	0.19	4.6
15-45-40	75/25	5190	18	292	0.16	0.4
20-20-60	77.5/22.5	6660	156	341	0.46	0.4

<sup>a</sup> Conditions: 200°C and 5 kg.

contained a block of completely random butadiene and styrene units. Both were blended with poly(styrene/acrylonitrile) in the same recipe. As shown in Table IV, all blends had low melt flow. However, modulus and tensile strength decreased when the styrene/butadiene portion became random, and the elongation and notched izod impact strength increased. These are the expected trends for increasing rubber content.

### Melt Flow

Melt flow of poly(styrene/acrylonitrile) is reduced sharply by addition of rubber and treatment with peroxide. Since the poly(styrene/acrylonitrile) used in most of this study had a melt flow of 2, most of the compounds had melt flow values between 0.2 and 0.5. Conventional plasticizers are generally detrimental to tensile strength and are consequently of limited use. An effective method of raising melt flow is to raise the melt flow of the poly(styrene/acrylonitrile) even though this causes a reduction in impact strength. The relationship between melt flow and impact strength of blends prepared with poly(styrene/acrylonitrile) of varying melt is illustrated in Figure 4.

The primary result of raising molecular weight of the rubbery component is

TABLE IV  
Influence of Caprolactone Block Polymer Sequence Distribution on Properties of Blends with 75/25 Poly(Styrene/Acrylonitrile)

Sequence distribution of 25-50-25 styrene-butadiene-caprolactone	Blend SAN/rubber	Tensile, psi	Elongation, %	Flexural modulus, psi $\times 10^{-3}$	Melt flow, <sup>a</sup> g/10 min	Notched Izod impact, ft-lb/in.
True block (S-B-CL)	77.5/22.5	5500	49	312	0.17	11.4
Random (B/S-CL)	75/25	4600	79	249	0.35	15.0

<sup>a</sup> Conditions 200°C and 5 kg.

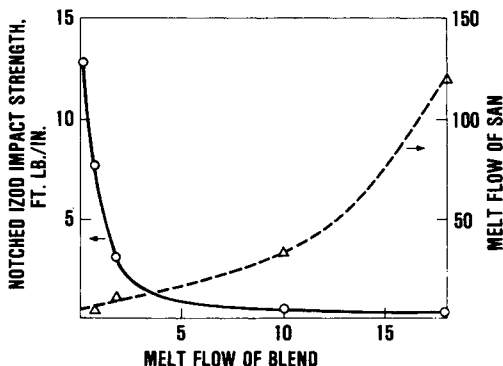


Fig. 4. Influence of poly(styrene/acrylonitrile) melt flow on blend melt flow and impact strength. Blends contain 77.5 parts (75/25) SAN, 22.5 parts (25-50-25) S-B-CL, and 0.05 parts dicumyl peroxide.

an increase in impact strength. A slight reduction in melt flow of the blend also accompanies this change, as shown in Figures 5 and 6 for terblock and simple block copolymers. These results show that high molecular weight block polymers are desirable for toughness with the melt flow of the poly(styrene/acrylonitrile) being selected to meet the desired melt flow of the blend.

### Transparency

One of the inherent properties of ABS polymers is their opacity, which arises from scattering of visible light by the rubbery inclusions. Lowering the size of dispersed particles below that of the wavelengths of visible light will reduce scattering to such an extent that the material will appear transparent. The mechanism of toughening, however, does not function well with small particles. Matching of refractive indices of the two phases eliminates light scattering even in a coarse dispersion<sup>5</sup> and results in a transparent blend. Table V shows that transparency, measured as percent haze, is indeed a function of rubber composition.

The blend containing a 47.5-27.5-25 styrene-butadiene- $\epsilon$ -caprolactone block polymer has 7.5 ft-lb/in. notched Izod impact strength along with 5% haze. Refractive indices of the homopolymers and selected copolymers are also shown in Table V. The refractive indices of the copolymers and polymeric solutions

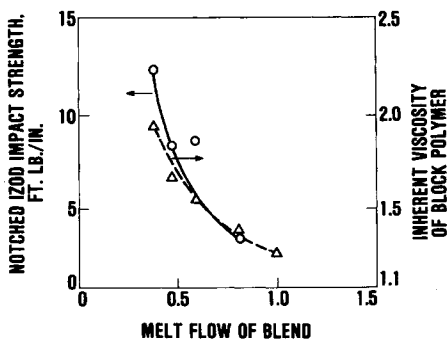


Fig. 5. Influence of block polymer inherent viscosity on impact strength and melt flow. Blends contain 77.5 parts (75/25) SAN, 22.5 parts (25-50-25) S-B-CL, and 0.05 parts dicumyl peroxide.

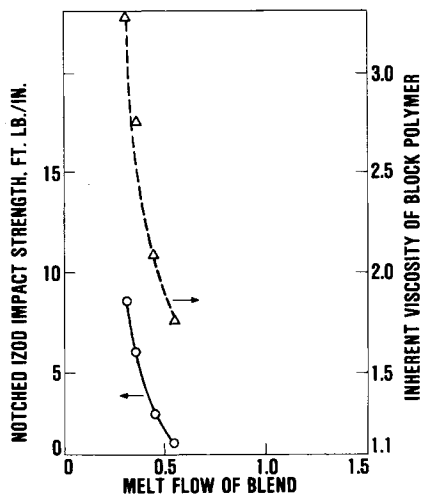


Fig. 6. Influence of block polymer inherent viscosity on impact strength and melt flow. Blends contain 85 parts (75/25) SAN, 15 parts (75-25) B-CL, and 0.1 part dicumyl peroxide.

were calculated assuming additivity by weight. As can be seen, refractive indices of all the styrene-butadiene- $\epsilon$ -caprolactone polymers are less than that of poly(styrene/acrylonitrile). However, if one assumes the  $\epsilon$ -caprolactone block to be soluble in the poly(styrene/acrylonitrile), a refractive index can be calculated for this solution and, as is shown, closely matches that of the styrene-butadiene portion for blends having low haze. These results are consistent with compatibility between poly- $\epsilon$ -caprolactone and poly(styrene/acrylonitrile).<sup>6</sup>

In another test of compatibility, varying amounts of poly- $\epsilon$ -caprolactone were hot mixed with poly(styrene/acrylonitrile) (Table VI). These blends exhibited constant clarity, increasing melt flow and elongation, and decreasing modulus, tensile strength, and heat distortion with no improvement in impact strength as the amount of poly- $\epsilon$ -caprolactone increased. These are the expected trends for compatibility. The 50/50 blend was clear immediately after molding but became opaque in less than 24 hr, evidently the result of crystallization of poly- $\epsilon$ -caprolactone.

Dynamic measurements were made on these same blends as well as on  $\epsilon$ -caprolactone homopolymer and poly(styrene/acrylonitrile) using a Vibron Dynamic Viscoelastometer. Poly- $\epsilon$ -caprolactone shows two transition regions, the glass transition at  $-40^{\circ}\text{C}$  and a crystalline melting region at approximately  $60^{\circ}\text{C}$ . Poly(styrene/acrylonitrile) shows only a glassy transition at  $104^{\circ}\text{C}$ . The blends show one glassy transition each, the major peaks in Figure 7, which yield a straight line when  $1/T_{\text{max}}$  is plotted against composition (Fig. 8). This is the Mandelkern rule for the  $T_g$  of a random copolymer in terms of the  $T_g$  values of the homopolymers,<sup>7</sup> further confirming compatibility of the two polymers.

#### Oil Resistance

Impact polystyrene is seriously weakened by contact with edible fats and oils while ABS has good resistance to these materials.<sup>8</sup> A test devised to measure this property involves measuring time to failure at constant stress for plastics coated with household oils. Two commercial resins, Tyril 767, a SAN resin, and Cylolac TD, an ABS resin, were included for comparison purposes.

TABLE V  
Influence of Rubber Composition on Blend Transparency

Rubber	Refractive Index	Blend ratio, <sup>b</sup> SAN/rubber	Calculated refractive indices <sup>a</sup>				Melt flow, <sup>c</sup> g/10 min	Flexural modulus, psi X 10 <sup>-3</sup>	Tensile, psi	Elongation, %	Notched Izod impact, ft-lb/in.
			Continuous phase: CL block in SAN	S-B Rubber phase: part of rubber	Haze, %	Flexural modulus, psi X 10 <sup>-3</sup>					
S-B-CL											
25-50-25	1.529	82/18	1.575	1.545	47	0.32	330	5910	50	6.6	
37.5-37.5-25	1.539	76/24	1.572	1.559	27	0.29	310	5290	93	7.4	
47.5-27.5-25	1.547	67.3/32.7	1.569	1.569	5	0.15	295	4880	45	7.5	
52.5-22.5-25	1.551	60/40	1.565	1.575	4	0.04	270	4330	31	0.7	

<sup>a</sup> Based on following refractive index values: polystyrene—1.600; polybutadiene—1.518; polyacrylonitrile—1.519; poly-ε-caprolactone—1.480; poly(styrene/acrylonitrile)—1.580.

<sup>b</sup> All blends contain 9% polybutadiene as a block.

<sup>c</sup> Conditions: 200°C and 5 kg.



TABLE VI  
Blends of Poly- $\epsilon$ -caprolactone and Poly(Styrene/Acrylonitrile)

Blend ratio SAN/CL	Tensile, psi	Elongation, %	Flexural modulus, psi $\times 10^{-3}$	Melt flow, <sup>a</sup> g/10 min	Notched Izod impact, ft-lb/in.	Heat distortion, °C	Haze, %
100/0	8790	3	491	1.6	0.3	101.1	1.0
95/5	8270	4	472	2.9	0.4	78.3	1.4
85/15	7870	4	417	6.0	0.4	63.3	1.0
75/25	5650	50	312	10.8	0.4	50.0	1.0
50/50	2110	470	155	25.6	0.5	—	—

<sup>a</sup> Conditions: 200°C and 5 kg.

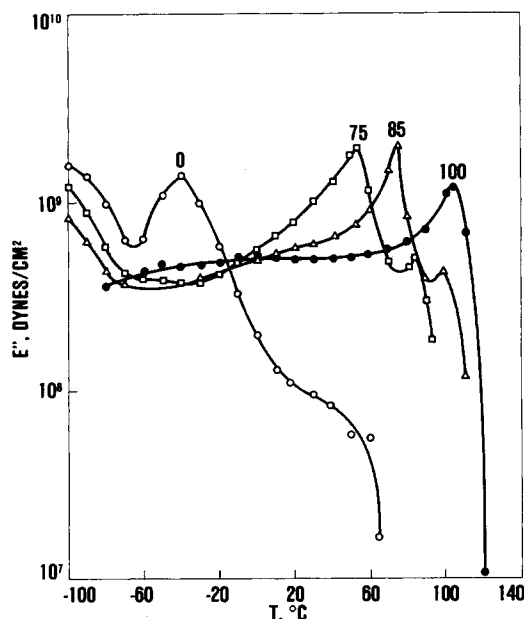


Fig. 7. Loss modulus for poly- $\epsilon$ -caprolactone/poly(styrene/acrylonitrile) blends. Numbers are percent SAN.

The 100-hr failure stress of samples coated with vegetable shortening is given in Table VII. When rubber was reduced or acrylonitrile increased, the 100-hr failure stress increased. Clarity of blends was unrelated to failure stress. Very high amounts of poly- $\epsilon$ -caprolactone and very high melt flow poly(styrene/acrylonitrile) lowered the failure stress significantly. In general, the blends described here have 100-hr oil resistance in the range of 1200–1300 psi.

### Scale-Up

Several large batches of  $\epsilon$ -caprolactone block copolymers were made in order to prepare sufficient stock of SAN/S-B-CL blends for evaluation in sheeting, thermoforming, and injection molding. Blends were prepared in a 5-lb Banbury using 25–50–25 S-B-CL and 75–25 B-CL block polymers. Banbury blends are compared with smaller laboratory blends (values in parentheses) in Table VIII. The higher melt flow and lower tensile strength and elongation of the blends

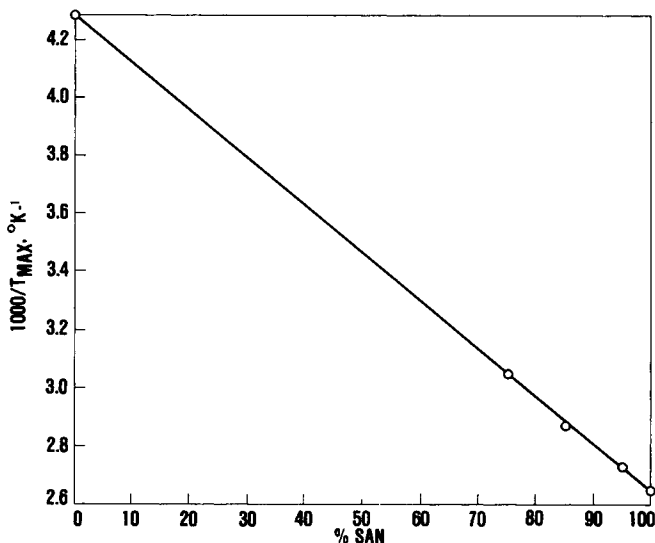


Fig. 8. Position of loss maxima vs composition.

prepared in the Banbury are probably due to increased antioxidant level (2%), which acts as a plasticizer. However, impact strength is not affected. The sheet made from these blends had good surface gloss, and the material thermoformed well although there was some streaking and nonuniform thickness. Injection-molded articles look good.

### Blends with Other Polymers

Some unsuccessful attempts to extend this development to other polymers will be mentioned for completeness. Blends (77.5/22.5) of poly(styrene/acrylonitrile) with styrene-butadiene-2,2,4-trimethyl-2-hydroxy-3-pentenoic acid beta-lactone block polymers of various composition were prepared in an attempt to raise heat distortion, but the high-melting lactone block polymers were ineffective in producing high impact strength. Blends with polycarbonate had reasonably good strength and toughness but zero melt flow, and blends of poly(styrene/acrylonitrile)/ $\epsilon$ -caprolactone block polymer/low unsaturation rubber (70/20/10) produced only 1 ft-lb/in. notched Izod impact strength at a modulus of 250,000 psi.

### CONCLUSIONS

A polymer alloy with properties resembling ABS has been prepared by hot mixing poly(styrene/acrylonitrile) with rubbery  $\epsilon$ -caprolactone block copolymers and organic peroxide, with the amount of peroxide being dependent on the amount of antioxidant in the polymers. A 25-50-25 S-B-CL block copolymer hot mixed with 75/25 poly(styrene/acrylonitrile) resulted in highest notched Izod impact strength while maintaining good modulus and tensile strength, and the melt flow of the poly(styrene/acrylonitrile) had the most influence on the melt flow of the blend. Evidence was also presented for the mutual solubility of poly- $\epsilon$ -caprolactone and poly(styrene/acrylonitrile) which increased the versa-

TABLE VII  
Environmental Resistance to Vegetable Shortening (Crisco)

S/AN	S-B-CL	SAN/rubber	Haze, %	Melt flow of SAN, <sup>a</sup> g/10 min	100-Hr failure stress, psi
75/25	25-50-25	62.5/37.5	opaque	2	950
75/25	25-50-25	77.5/22.5	opaque	2	1280
75/25	25-50-25	84/16	opaque	2	1280
76.5/23.5	25-50-25	77.5/22.5	opaque	—	1100
75.4/24.6	25-50-25	77.5/22.5	opaque	—	1280
71.2/28.8	25-50-25	77.5/22.5	opaque	—	1420
75/25	5-70-25	84/16	opaque	2	1280
75/25	0-75-25	85/15	opaque	2	1350
75/25	0-60-40	77.5/22.5	opaque	2	1140
75/25	20-20-60	77.5/22.5	opaque	2	650
75/25	25-50-25	77.5/22.5	40	2	1280
75/25	32.5-42.5-25	77.5/22.5	29	2	1200
75/25	37.5-37.5-25	77.5/22.5	13	2	1390
75/25	42.5-32.5-25	77.5/22.5	8	2	1380
75/25	25-50-25	77.5/22.5	opaque	10.5	860
75/25	25-50-25	77.5/22.5	opaque	4	1150
75/25	25-50-25	77.5/22.5	opaque	2	1280
75/25 <sup>b</sup>	—	—	1.0	2	1850
ABS <sup>c</sup>	—	—	opaque	—	1200

<sup>a</sup> Conditions: 200°C and 5 kg.

<sup>b</sup> Tyril 767.

<sup>c</sup> Cyclocac TD.

TABLE VIII  
Banbury Blending<sup>a</sup>

Sample	A	B	C	D
S-B-CL	0-75-25	0-75-25	0-75-25	25-50-25
Inherent viscosity, dl/g	2.09	2.76	3.29	2.50
SAN <sup>b</sup> /CL copolymer blend	85/15	85/15	85/15	77.5/22.5
Tensile, psi	4750 (5240)	4670 (5530)	4940 (5840)	4620 (5210)
Elongation, %	6 (31)	12 (32)	10 (17)	21 (95)
Flexural modulus, psi × 10 <sup>-3</sup>	349 (319)	349 (325)	343 (314)	294 (268)
Melt flow, <sup>c</sup> g/10 min	0.71 (0.45)	0.50 (0.36)	0.42 (0.31)	0.32 (0.20)
Notched Izod impact, ft-lb/in.	2.9 (3.0)	6.2 (6.1)	8.0 (8.6)	11.3 (11.2)

<sup>a</sup> Properties of Brabender blends are indicated in parentheses.

<sup>b</sup> S/AN ratio is 75/25.

<sup>c</sup> Conditions: 200°C and 5 kg.

tility of this unique system and simplified the preparation of transparent blends by matching refractive indices of matrix and rubbery inclusions.

### References

1. C. W. Childers, G. Kraus, J. T. Gruver, and Earl Clark, *Polym. Prepr.*, **11**, 553 (1970).
2. (a) C. W. Childers and Earl Clark (to Phillips Petroleum Co.), U.S. Pat. 3,649,716 (March 14, 1972); (b) C. W. Childers and Earl Clark (to Phillips Petroleum Co.), U.S. Pat. 3,789,084 (Jan. 29, 1974).
3. H. L. Hsieh, *J. Appl. Polym. Sci.*, in press.
4. C. W. Childers (to Phillips Petroleum Co.), U.S. Pat. 3,429,951 (Feb. 25, 1969).
5. B. D. Gesner, *J. Appl. Polym. Sci.*, **11**, 2499 (1967).
6. D. H. Mullins (to Union Carbide Corp.), U.S. Pat. 3,592,877 (July 13, 1971).
7. L. Mandelkern, *Rubber Chem. Technol.*, **32**, 1392 (1959).
8. H. Keskkula, *Encyclopedia of Polymer Science and Technology*, Vol. 13, N. M. Bikales, Ed., Wiley, New York, 1970.

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