

## Phase Separation of Some Clear Polyblends\*

B. D. GESNER, *Bell Telephone Laboratories, Incorporated,  
Murray Hill, New Jersey*

### Synopsis

By using variations of elution and precipitation techniques, a clear ABS resin is found to be a mixture of a styrene-butadiene rubbery copolymer, a methyl methacrylate-styrene-acrylonitrile copolymer, and a graft of the methyl methacrylate-styrene-acrylonitrile copolymer onto the styrene-butadiene rubber. A clear impact acrylic is separated into a methyl methacrylate-styrene-acrylonitrile copolymer and a methyl methacrylate-butadiene rubbery copolymer. Photomicrographs indicate that clarity in the clear ABS and impact acrylic is achieved by matching refractive indices of the continuous and dispersed polymer phases.

### Introduction

One of the more striking disadvantages of commercial polyblends is their opacity, which arises in these two-phase systems from a scattering of visible light at phase interfaces. Lowering the size of dispersed particles below that of the wavelengths of visible light will reduce scattering to an extent that the material will appear transparent. Unfortunately, there is a limiting particle size below which the mechanism of toughening apparently does not take effect.<sup>1</sup> Some compromise between toughness and clarity must be met if control of particle size is a means of obtaining clear polyblends. Perfect matching of refractive indices eliminates light scattering but requires severe modification in both phases. With matching of refractive indices a compromise must be met between extent of phase compositional modification and degree of clarity.

Recently several clear varieties of one of the most popular of commercial polyblends—ABS plastics—were announced, and are now marketed as potential candidates for the bottling industry. The striking similarity of the infrared spectra (Figs. 5 and 6) and the physical properties (Table I) of one such clear ABS resin and a clear impact acrylic, and the possibility that these resins may hold advantages over the present ABS materials led us to investigate their composition.

### Experimental

Physical properties of the clear polyblends studied are listed in Table I. Photomicrographs (Figs. 1-3), taken at a magnification of 20,000, of an

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TABLE I  
Physical Properties of the Clear Impact Plastics

Properties	Clear ABS	Clear impact acrylic
Tensile strength (73°F.), lb./in. <sup>2</sup>	6,400	5,900
Flexural modulus (73°F.), lb./in. <sup>2</sup>	326,000	312,000
Rockwell hardness (R Scale)	102	102
Impact strength, ft.-lb./in. notch		
73°F.	3.2	3.6
-40°F.	1.5	1.6

ABS-poly(methyl methacrylate) blend, a clear ABS resin, and a clear impact acrylic showed that the dispersed particles in all three were approximately the same in size (0.1-0.8  $\mu$ ). Infrared spectra (Figs. 4-6) of the ABS-poly(methyl methacrylate) blend, the clear ABS, and the clear impact acrylic were all qualitatively identical. Chloroform suspensions (4%) of the clear ABS, the clear impact acrylic, styrene-acrylonitrile copolymer, and poly(methyl methacrylate) were treated with one-quarter volumes of a 5% solution of bromine in chloroform. The first two polymer dispersions turned colorless on mixing; the other two remained orange overnight. Methyl methacrylate and styrene were evolved from both clear polyblends on vacuum pyrolysis.

The most satisfactory separations of the clear resins were accomplished with benzene, petroleum ether, and acetone in the order indicated in Figure 7 and outlined here for the clear ABS. On adding cold pentane to a stirred solution of the clear ABS resin in benzene, precipitation of the polymer occurred. After filtering, addition of more pentane, refiltering, and evaporating the filtrate to dryness, a tacky substance was isolated.

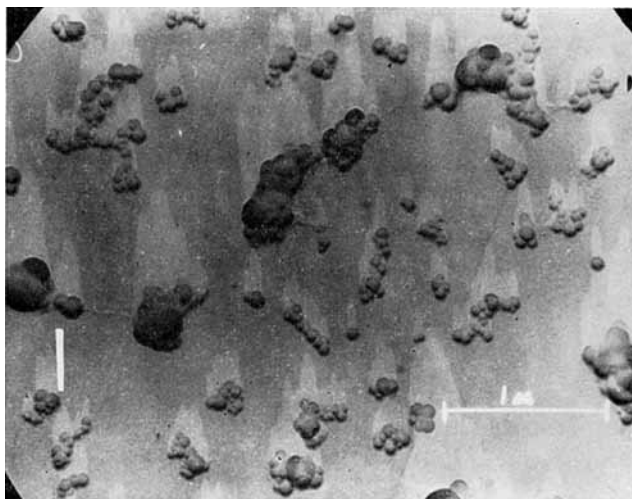


Fig. 1. Electron micrograph of the ABS-poly(methyl methacrylate) blend.

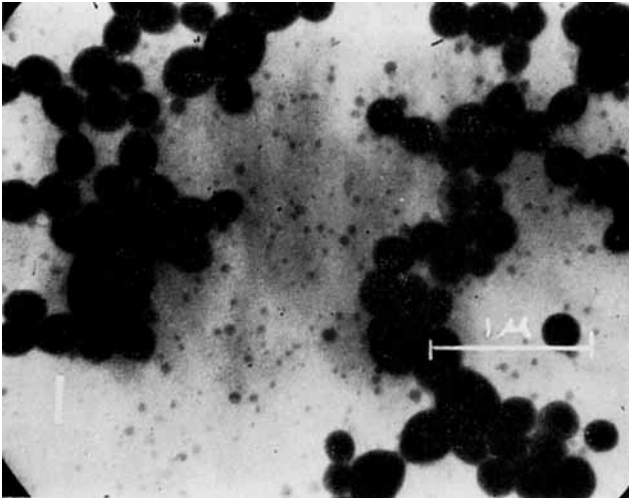


Fig. 2. Electron micrograph of the clear ABS resin.

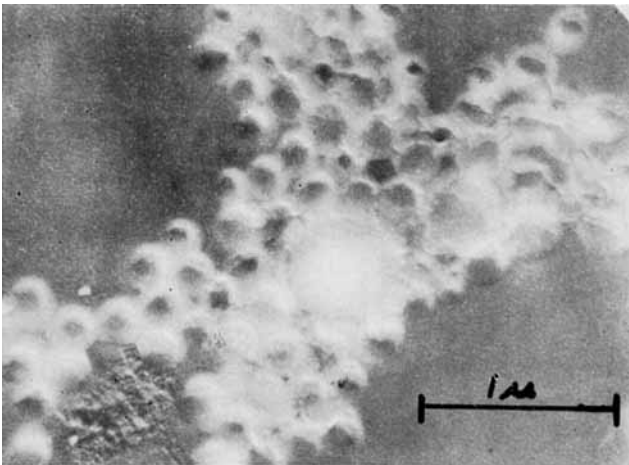


Fig. 3. Electron micrograph of the clear impact acrylic.

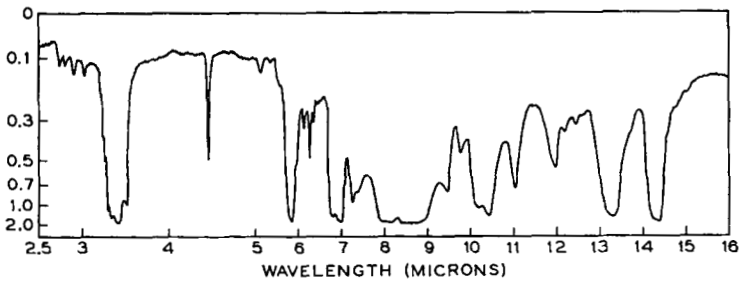


Fig. 4. Infrared spectrum of the ABS-poly(methyl methacrylate) blend (55:45).

The infrared spectrum indicated that this material was largely a mixture of rosin acid and butadiene with lesser amounts of styrene and an amide. From a basic alumina column, petroleum ether eluted a material whose infrared spectrum was identical with that of styrene-butadiene rubber ( $\sim 27:73$ ).<sup>2</sup> In the case of the acrylic multipolymer, benzene and acetone eluted a material whose infrared spectrum was similar to that for methyl methacrylate-butadiene copolymer.

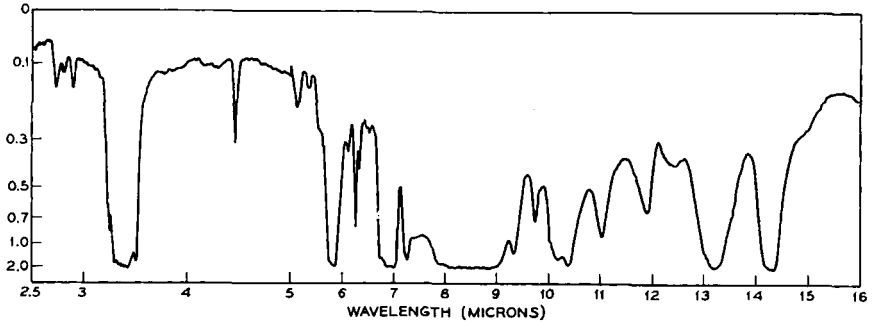


Fig. 5. Infrared spectrum of the clear ABS resin.

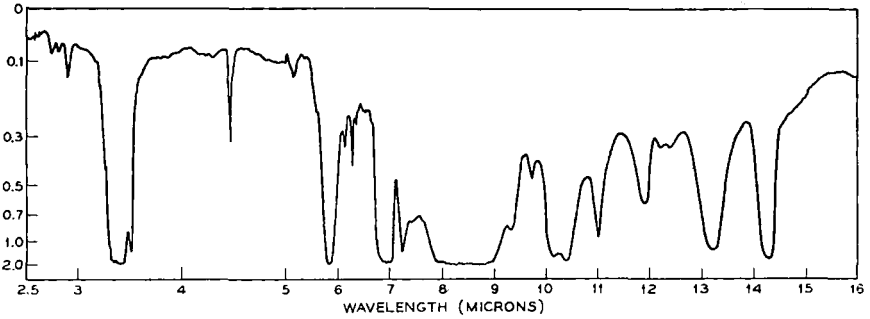


Fig. 6. Infrared spectrum of the clear impact acrylic.

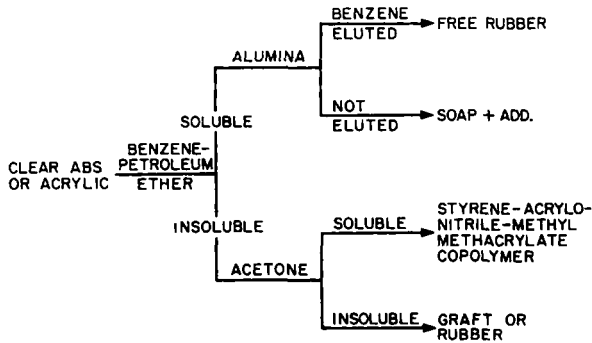


Fig. 7. Separation scheme for clear impact plastics.

Aliquots of acetone-dispersed solutions of the two benzene-petroleum ether treated polymers were centrifuged at 20,000 rpm on a Beckman Model L ultracentrifuge for 10 min. The supernatant liquids and precipitants were separately evaporated to dryness and weighed. Table II

TABLE II  
Solvent-Extracted Phases

	Alumina		Acetone	
	Wt.-% eluted	Wt.-% not eluted	Wt.-% soluble	Wt.-% insoluble
Clear ABS	1.0	1.0	70.3	27.7
Acrylic	0.3	2.0	76.9	20.8

TABLE III  
Elemental Analysis of Sols and Gels

	C, %	H, %	O, %	N, %
Clear ABS				
Sol	73.26	8.06	17.12	1.92
Gel	81.67	9.18	8.16	0.79
Acrylic				
Sol	67.45	7.91	21.90	2.70
Gel	82.23	10.23	6.58	Trace

TABLE IV  
Compositional Analysis of the Separated Phases

	Refractive index*	Methyl meth- acrylate, %	Styrene, %	Butadiene, %	Acrylo- nitrile, %	Additive, %
Clear ABS						
Sol	1.529	53.4	39.4	0.0	7.2	—
Gel	1.527	21.1	30.8	44.9	3.2	—
Free Rubber	1.527	0.0	27.0	73.0	0.0	—
Total	—	43.4	36.5	13.1	6.0	1.0
Acrylic						
Sol	1.516	65.4	22.6	0.0	12.0	—
Gel	1.513	13.7	0.0	86.3	0.0	—
Total	—	53.1	17.4	18.3	9.2	2.0

\* Calculated.

contains a list of fraction weight-per cents for each of the polymers. Elemental analysis (Midwest Microanalytical Laboratory) of the important fractions are listed in Table III. The compositions of the isolated phases calculated from elemental analysis are listed in Table IV.

### Discussion

Although small compared to Bender's 1–10  $\mu$  range for microgel particles in impact polystyrene,<sup>3</sup> the 0.1–0.8  $\mu$  range for the two clear impact plastics is of the normal order for ABS resins. It appears, then, that clarity in both clear impact plastics has been achieved by matching refractive indices of the two contributing phases rather than by use of a small molecular size butadiene latex in the grafting reaction. Calculated on the assumption that there is a linear relationship between the refractive indices of two homopolymers and their mixtures as random copolymers, the refractive indices for the gel, sol, and free rubber of the clear ABS are 1.529, 1.527, and 1.527, respectively, while those for the clear impact acrylic are 1.516 and 1.513 (Table IV), respectively. The good agreement of these values indicates that the calculations on composition, based on elemental analysis, are sound.

The poly(methyl methacrylate)–ABS blend is included in this study to show the problems associated with infrared analysis of these complex polyblend systems. The striking similarities of the infrared spectra (Figs. 4–6) of the three mixed polymers, each of which phase separation shows to be quite different, indicates convincingly that infrared spectroscopy cannot distinguish between the different forms in which the four monomer units could possibly be assembled. In all three materials, infrared bands for styrene appear at 6.2, 13.2, and 14.2  $\mu$ , nitrile at 4.5  $\mu$ , diene at 6.4  $\mu$ , and ester (identified by pyrolysis as methyl methacrylate) at 5.8, 7.8, and 9.0  $\mu$ . The spectrum of the normal ABS (Fig. 8) has all but the ester bands.

The two resins are readily separated by solution techniques (Fig. 7). In addition to the styrene–butadiene rubber, the clear ABS contains an acetone-soluble fraction, the infrared spectrum of which is identical with that for styrene–acrylonitrile–methyl methacrylate copolymer and an acetone-insoluble fraction which contains styrene, acrylonitrile, methyl methacrylate, and butadiene units. The unit per cent composition of both materials (Table IV) can be calculated with reasonable accuracy from

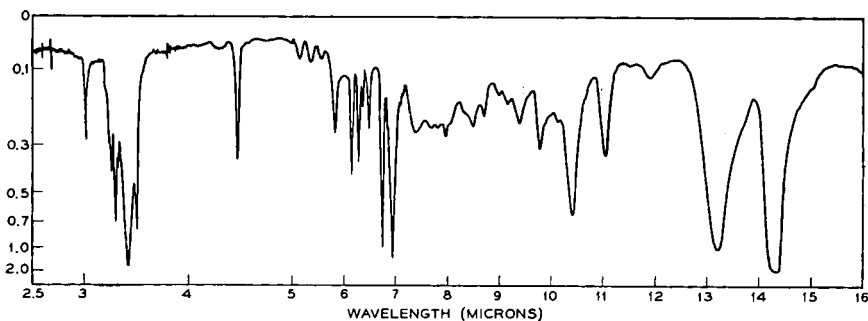


Fig. 8. Infrared spectrum of a typical ABS resin.

elemental analysis (Table III). Because of the free styrene-butadiene rubber found in the composite and because of the composition of the acetone-soluble fraction, the gel is believed to be a graft of styrene-acrylonitrile-methylmethacrylate copolymer onto styrene-butadiene rubber.

Some questions might arise as to whether the free rubber isolated is chemically cleaved during extraction or is actually present as a free material in the composite. The solution temperatures necessary for phase separation are quite mild compared to those necessary to cause chain scission, as in, for instance, vacuum pyrolysis. As far as phase analysis is concerned, the method of extraction is not critical, and the most important implication is that as such the isolated rubber must serve as the grafting backbone.

The clear impact acrylic contains an acetone-soluble fraction identified from its infrared spectrum and elemental analysis as a styrene-acrylonitrile-methyl methacrylate copolymer. The acetone-insoluble material, identified in the same manner, is a methyl methacrylate-butadiene copolymer.

The conclusions from the analysis are that the clear ABS is a grafted rubber-modified styrene-acrylonitrile-methyl methacrylate copolymer; the clear impact acrylic is a crosslinked rubber-modified styrene-acrylonitrile-methyl methacrylate copolymer. This structural relationship is the same as that of the original ABS materials, which are nitrile rubber-modified styrene-acrylonitrile copolymers, and the more recent versions, which are grafted polybutadiene rubber-modified styrene-acrylonitrile copolymers.

The nomenclature used for these materials must have come from the type polymer being modified. For instance, the manufacturer of the clear ABS probably took the necessary steps to attain clarity in an already existing ABS. This effort undoubtedly ended in the finding that by the proper addition of methyl methacrylate units to the matrix and suitably modified (styrene-butadiene rubber backbone) graft phase a clear material—the clear ABS—resulted. On the other hand, the clear impact acrylic manufacturer aimed at improving the toughness, while retaining the clarity, in an existing acrylic material. Their work presumably led to the discovery that a methyl methacrylate-butadiene rubbery copolymer improved toughness and because of its refractive index retained clarity in a suitable acrylic copolymer. The resultant material would be a clear impact acrylic.

In comparing the two clear impact plastics the glass transition of the modifying rubber should be mentioned. The calculated<sup>4</sup>  $T_g$  for the SBR is  $-50^\circ\text{C}$ ., while that for the methyl methacrylate-butadiene copolymer is  $-65^\circ\text{C}$ . Previous results<sup>5</sup> on an empirical basis have indicated that there exists an interdependence between impact strength, rubber content, and  $T_g$ . This perhaps explains why, in spite of the lower rubber loading, the clear impact acrylic attains a greater room temperature impact strength than the clear ABS (Table I). Because of its grafted and therefore partially protected rubber, the clear ABS should have a slight weatherability advantage over the acrylic. However, the higher loading of rubber in the

clear ABS may cancel out this effect. In any event, outdoor use of either of these materials should, because of the clarity, result in a yellowing and loss in tensile properties greater than that for the normal opaque ABS resins. A recent study on the weathering of these materials is consistent with these predictions.<sup>6</sup>

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### References

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### Résumé

En faisant varier les techniques d'éluion et de précipitation, on a pu voir qu'une résine ABS limpide était constituée par le mélange de copolymère caoutchouteux styrène-butadiène, d'un copolymère de méthacrylate de méthyle-styrène-acrylonitrile et d'un copolymère greffé de méthacrylate de méthyle-styrène-acrylonitrile sur un caoutchouc styrène-butadiène. Une résine acrylique transparente à impact a également été séparée en un copolymère méthacrylate de méthyle-styrène-acrylonitrile et un copolymère caoutchouteux méthacrylate de méthyle-butadiène. Les photomicrographies indiquent que la transparence dans l'ABS et dans l'acrylique à impact est obtenue par mélange des indices de réfractions des phases polymériques continues et dispersées.

### Zusammenfassung

Durch Verwendung verschiedener Eluierungs- und Fällungsverfahren wird festgestellt, dass ein klares ABS-Harz aus einer Mischung eines kautschukartigen Styrol-Butadien-copolymeren, eines Methylmethacrylat-Styrol-Acrylnitrilcopolymeren und einer Aufpfropfung des Methylmethacrylat-Styrol-Acrylnitrilcopolymeren auf den Styrol-Butadienkautschuk besteht. Ein klares Schlagfesten Acrylharz uns. Photographische Mikroaufnahmen zeigen, dass die Klarheit von klarem ABS und schlagfesten Acrylharzen durch Angleichung der Brechungsindizes der kontinuierlichen und der dispersion Polymerphase erreicht wird.

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