

Aging of Polyblends

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Synopsis

Methyl methacrylate-styrene-acrylonitrile copolymers, alone and with polybutadiene modification, were examined for changes in impact strength and yellowness after thermal and light aging. The copolymer displayed no change in strength or clarity, while the butadiene-modified material showed increase in yellowness and loss in impact resistance. It is apparent that these changes are primarily due to the decomposition of the butadiene phase in the impact material, and this conclusion might be applied to diene-containing blends in general.

Introduction

Because of their good weather resistance compared to other thermoplastic materials, acrylic polymers are preferred for most outdoor applications. Unfortunately, these plastics possess low impact strength and, until the recent development of rubber-modified acrylic polymers, could not be used where toughness was required. The purpose of this work is to compare the effects of aging on an acrylic plastic and its polybutadiene modification.

Experimental

Specimens of a methyl methacrylate-styrene-acrylonitrile copolymer and its clear butadiene-modified counterpart were injection-molded at a stock temperature of $221 \pm 2^\circ\text{C}$. Izod impact resistance (ASTM D256, Method A) and yellowness index (ASTM D1925) were used to determine changes caused by natural weathering and heat aging at 71°C . The similarity between the acrylate and the clear impact material was not apparent from manufacturer's data or from routine spectroscopic measurements. It was not until the impact material was separated into its continuous and dispersed phases that the relation between the two resins was discovered. Elemental analyses (Table I), performed by Midwest Micro-analytical Laboratories, showed that the acrylic multipolymer and the continuous phase (sol) for the clear impact acrylic multipolymer are the same. This fact was used in analyzing the aging data.

Results and Discussion

The most interesting result of this work is the yellowing of the rubber-modified material. Regardless of environment, the impact material dis-

TABLE I
Analysis of Plastics

Material	Analysis				Impact strength
	C, %	H, %	O, %	N, %	
Acrylic multipolymer Clear impact acrylate, total	67.78	7.91	21.86	2.94	0.3
Clear impact acrylate Sol ^a	71.85	8.36	17.33	2.46	3.6
	67.45	7.91	21.90	2.70	—

^a Data of Gesner.¹

colors at a greater rate than the base acrylate. After 12 months' outdoor aging (Fig. 1), the impact acrylate reaches a yellowness index plateau, while in thermal aging (Fig. 2) the same acrylate continues to increase in yellowness index even after 24 months' exposure. In the outdoor process the oxidation leading to discoloring is complete after about 12 months. The reaction must be confined to polymer surface perhaps because of oxygen diffusion and/or because of a light filtering effect by the yellow surface. In the thermal process oxidation continues even after 24 months, and the discoloring index is a factor of two greater. The oxidation in this case does not depend upon diffusion and the degradative process involves the total polymer. Thermal motion of polymer must lower the barrier to oxygen diffusion. Both processes give rise to truncated S-shaped curves typical of autocatalytic reactions.² In the photodegradation, initiation is rapid, and therefore the lower part of the curve is not observed. In the thermal process, consumption of the polymer reactant is not complete over the time interval of the experiment; hence, the upper part of the curve has not been reached.

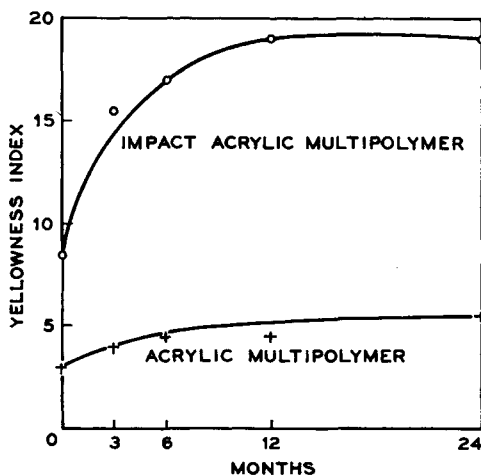


Fig. 1. Effect of outdoor aging on yellowness index.

The fact that the change in color of the impact acrylate during thermal exposure proceeds by an autocatalytic process whereas loss in strength does not (Fig. 4), indicates that the mechanisms for the two loss processes are not the same, albeit both depend on polymer oxidation. Strength properties of polymers usually change rapidly with slight degradation; discoloring

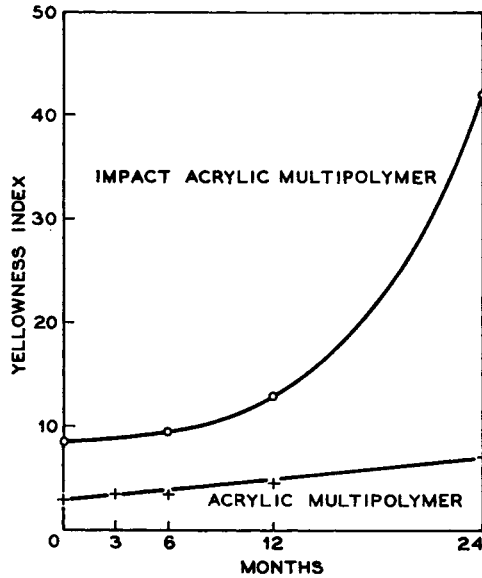


Fig. 2. Effect of heat aging at 71°C. on yellowness index.

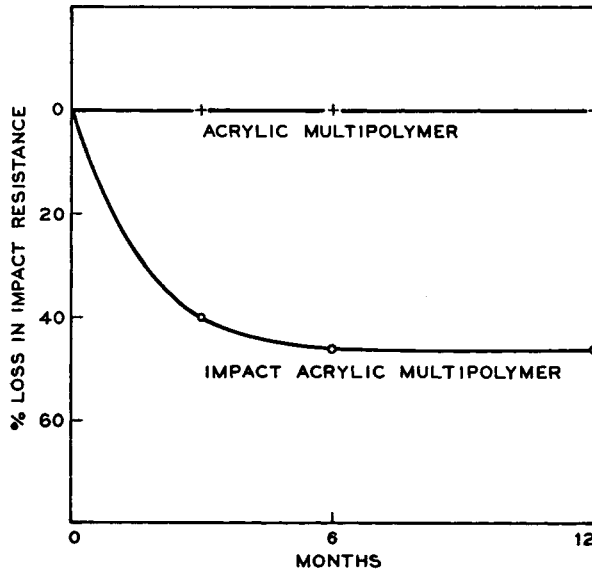


Fig. 3. Effect of outdoor aging on impact resistance.

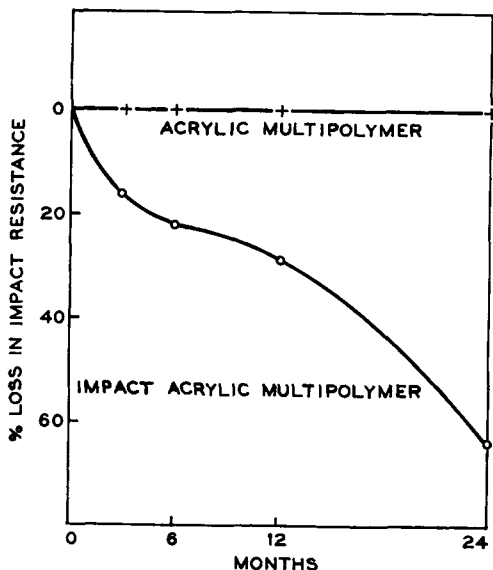


Fig. 4. Effect of heat aging at 71°C. on impact resistance.

follows degradation more linearly. In the outdoor process, rate of oxidation is so much faster that a lag in the change in color cannot be detected and both loss curves (Figs. 1 and 3) appear the same.

Embrittlement of the rubber-modified acrylate increases with outdoor and thermal aging. The acrylic base polymer is unchanged by outdoor exposure, while the clear impact acrylate degrades rapidly to a point where impact strength is approximately one-half its original value (Fig. 3). The leveling off of impact strength for the weathered impact material at a value higher than that of the base polymer indicates that there is a permanent retention of some of the rubbery phase. This is probably due to the formation of an oxidized protective outer layer. The same phenomenon has been observed for other weathered impact plastics.³

Thermal aging at 71°C. has no effect on the impact strength of the base acrylate. The same exposure conditions cause a continuous decrease in the impact strength of the rubber-modified material (Fig. 4). In this instance, however, there is no leveling off of the loss curve. It appears that the thermal process allows sufficient polymer motion so that no barrier to oxygen diffusion, as found in the case of the outdoor process, can be formed.

Because of a corresponding loss of butadiene absorption in the infrared, with loss of strength and increased yellowness in aged ABS resins, one of us concluded that embrittlement and discoloring in the ABS system must be due to oxidation of the graft-containing phase.⁴ In that study the discoloring was attributed to the rubber because of its amber appearance after very short thermal exposure. Under the same conditions, however, the styrene-acrylonitrile copolymer did discolor (approximately a twofold

increase in the yellowness index). In that term of exposure styrene was considered a minor contributor to the discoloring of the composite. The present results show unequivocally that this is indeed the case for the acrylic system studied and probably for all diene-containing polyblends. To prevent discoloring in these systems, therefore, one must be concerned primarily with the rubber.

Conclusion

Oxidation of the rubbery component during natural and thermal aging of a diene rubber-modified acrylic plastic is shown to be the primary process leading to the loss in mechanical strength and change in color for the system.

References

1. B. D. Gesner, *J. Appl. Polymer Sci.*, **11**, 2403 (1967).
2. A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1953, p. 20.
3. P. G. Kelleher, D. J. Boyle, and B. D. Gesner, *J. Appl. Polymer Sci.*, **11**, 1731 (1967).
4. B. D. Gesner, *J. Appl. Polymer Sci.*, **9**, 3701 (1965).

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