

Environmental Surface Effects on ABS Resins

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Synopsis

Spectroscopic analyses of weathered samples and thermal oxidation of the various phases found in ABS resins indicate that these plastics deteriorate most readily through their polybutadiene component. The change in physical properties and color of these resins with age can be correlated with the decomposition of the polybutadiene-containing phases.

Introduction

ABS (acrylonitrile-butadiene-styrene) resins are tough, moderately rigid, readily processible thermoplastics made up of a styrene-acrylonitrile plastic continuous phase and a highly dispersed rubber phase.¹ These gum-plasticized resins retain most of the base plastic's outstanding tensile properties and, because of the rubber modification, possess a high degree of toughness. In addition, because of low cost raw materials and relatively inexpensive processing methods, ABS resins command a sizeable economic advantage over the common tough plastics (Table I).

TABLE I
Physical Properties of Some Tough Plastics

	Notched Izod impact, ft.-lb./in. at 73°F.	Flexural modulus, lb./in. ² × 10 ⁻⁵ at 73°F.	Cost, ¢/in. ^{3a}
Polyacetal	1.7	4.5	3.3
Nylon 66	2.2	4.0	4.0
Polycarbonate	14.0	3.8	4.6
ABS	4.0	3.0	1.5

^a Data of Sittig.²

Unfortunately, the great improvements for ABS plastics over their base resin are not retained under all environmental conditions.

Experimental

An ABS resin was prepared according to a modification of the procedure of Daly.³ Styrene and acrylonitrile were copolymerized in the presence of

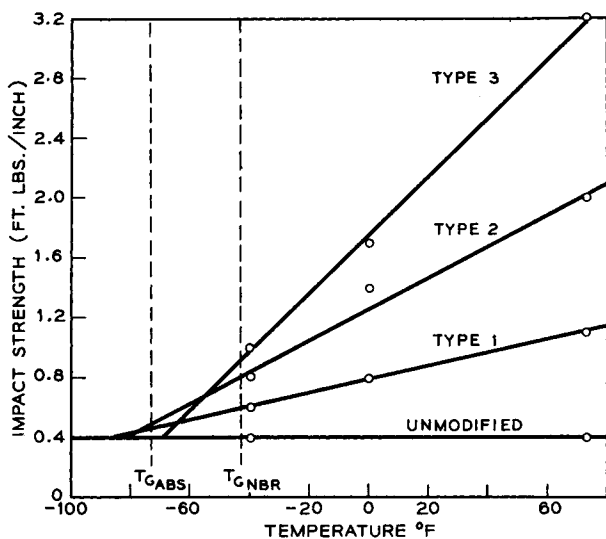


Fig. 1. Codependence of impact strength and glass transition temperature for ABS plastics.

cis-1,4-polybutadiene latex. After coagulation the uninhibited resin was filtered, washed with water, and air-dried under ambient conditions. The glass transition temperature of the resin, as measured on a duPont 900 differential thermal analyzer, was -73°F . A 1-mil film was molded from this material and exposed in a modified Atlas X1A Weatherometer for approximately 1000 hr. Periodically the specimen was removed and its infrared spectrum recorded on a Beckman IR 8 spectrophotometer (Fig. 2). A portion of the prepared resin was separated into its component parts⁴ and the oxygen uptake at 120°C . of each of the phases and the resin itself was studied (Fig. 3). Styrene and methacrylonitrile were copolymerized in the presence of *cis*-1,4-polybutadiene latex and the oxygen uptake at 120°C . of the resulting uninhibited resin was also studied. All of the oxidized samples were examined after 1000 hr. exposure.

Three commercial ABS resins (A, B, and C) were molded into $0.030 \times \frac{1}{2} \times 4$ in. test bars and aged in Yuma, Arizona. Periodically, test bars were removed and their modulus properties examined (Fig. 4).

Discussion

The thickness of the samples used in the study were such that the observed results are more characteristic of surface effects.

The low-temperature impact strengths of all rubber-modified plastics are influenced to some degree by the glass transition temperature of the rubber.⁵ In the cases of nitrile rubber (31% acrylonitrile) and a specific grafted polybutadiene rubber, both of which are used in styrene-acrylonitrile gum plasticization,⁴ the glass transitions are -41 and -73°F . respectively (Table II).⁶ The nitrile rubber-modified styrene-acrylonitrile

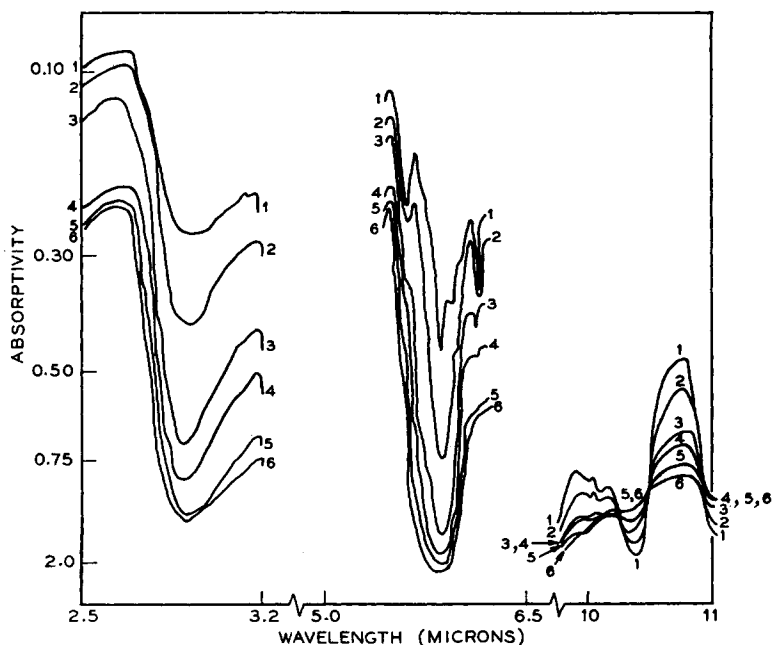


Fig. 2. Infrared spectra of an oxidized uninhibited ABS resin at different degrees of Fadeometer aging: (1) unaged; (2) 21 hr.; (3) 113 hr.; (4) 282 hr.; (5) 669 hr.; (6) 1049 hr.

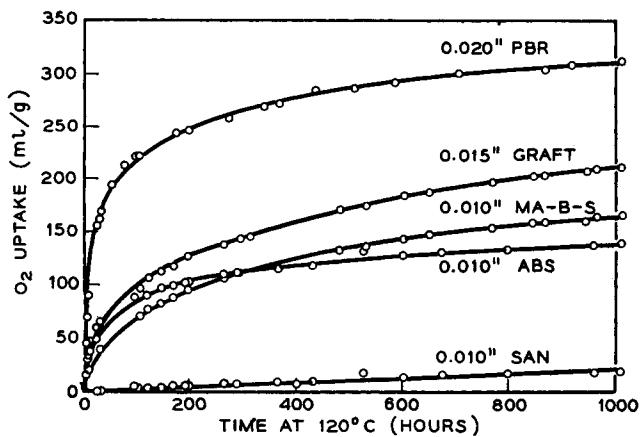


Fig. 3. Oxygen uptakes for polybutadiene rubber (PBR), grafted polybutadiene rubber (GRAFT); methacrylonitrile-butadiene-styrene resin (MA-B-S), acrylonitrile-butadiene styrene resin (ABS), and styrene-acrylonitrile copolymer (SAN).

resin demonstrates low temperature brittleness (impact strength approaches that of the base resin, Table II), whereas the grafted polybutadiene-modified resin retains an appreciable amount of low temperature toughness.

A plot of impact strength versus temperature for a series of ABS resins⁷

TABLE II
Impact Strengths of Graft and Rubber-Modified Styrene-Acrylonitrile Copolymers

	Rubber- modified	Graft- modified	Unmodified
Rubber glass transition temperature °F.	-41	-73	—
Notched Izod impact strength, ft.-lb./in.			
At 73°F.	6.0	4.0	0.4
At -40°F.	0.5	1.0	0.4

(Fig. 1) shows a very interesting codependence of impact strength on rubber content and the glass transition temperature of modifying grafted rubber. Every resin tends to the same value as the unmodified resin at or near the glass transition temperature. This effect is qualitatively predicted by Merz et al.,⁸ since, as the temperature is lowered the efficiency of the rubber to absorb mechanical energy becomes proportionally reduced until a point is reached where the rubber has no impact-improving effect on the resin. From such a relationship can be obtained glass transition temperatures by extrapolation and low-temperature impact strengths by interpolation.

The artificial weathering of an uninhibited ABS film was followed with infrared spectroscopy (Fig. 2). The increase in absorptivity in the O—H and C=O regions is to be expected, since oxidation of hydrocarbons ultimately ends in the production of hydroxyl- and carbonyl-containing compounds.⁹ The most striking feature of the spectrum is the parallel decrease in *cis*-1,4-polybutadiene absorbance with increase in hydroxyl and carbonyl absorb-

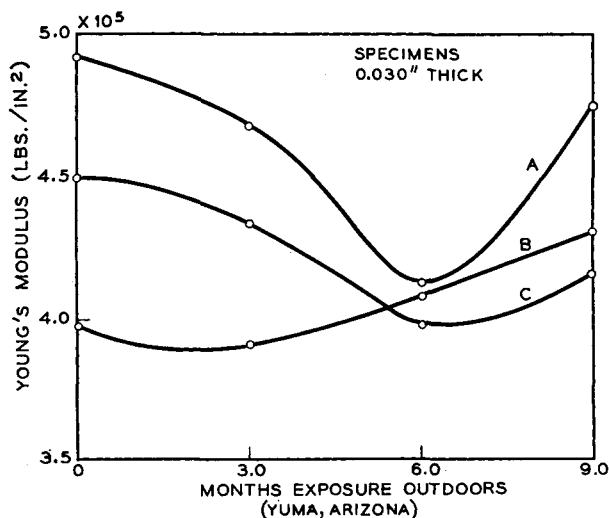


Fig. 4. Effect of weathering on Young's modulus for commercial ABS plastics A, B, and C.

ance. The rubber content has decreased to less than 20% of the initial value after 1000 hr. exposure.

Each of the separated phases contained in graft-modified ABS resins was oxidized for approximately 1000 hr. The oxygen uptake for these phases compared to the same measurement for the whole resin (Fig. 3) substantiates the fact that the grafted rubber is responsible for the bulk of the oxidative degradation. Modification of the resin with methacrylonitrile has little effect on the oxidative process.

On examination the oxidized samples gave further indications as to their degree of contribution to the oxidative scheme. The styrene-acrylonitrile copolymer in this study was completely soluble in acetone and chloroform, showed very little carbonyl and hydroxyl development in its infrared spectrum, and had no noticeable color change. The graft phase and the two resins became extremely brittle and turned red-brown after 1000 hr. oxidation. In view of these facts the problems of both embrittlement and yellowing in ABS resins probably can be attributed for the most part to the graft-containing phase.

Figure 4 shows the influence of outdoor aging on the modulus of elasticity of stabilized natural ABS resins. The initial lowering in modulus is probably due to chain scission which is predominate in the early stages of polybutadiene rubber degradation. As crosslinking becomes important, the material grows harder and stiffer, i.e., modulus increases.⁵

Conclusions

Weathering and thermal oxidation (aging) tend to have the same detrimental bearing on the rubber that low temperatures have. The aging effect, however, is permanent. Since the effect of oxidative degradation on the physical properties of the aged ABS resin corresponds to the effect of low temperature on the properties of unaged resin, it is reasonably safe to assume that the change in modulus and color can be represented by considering only the rubber phase. The other phases must contribute to some degree, particularly since the resin phase absorbs a measurable amount of oxygen. Nonetheless, the most important implication in this work is that of all the structures found in ABS resins, the rubber in itself contributes the most to the ultimate failure of the material with age.

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Résumé

L'analyse spectroscopique des échantillons exposés aux intempéries et à l'oxydation thermique des différentes phases trouvées dans les résines ABS montrent que ces plastiques se détériorent très facilement à cause du polybutadiène dont ils sont partiellement constitués. Lors du vieillissement de ces résines, il se produit des variations dans les propriétés physiques et dans la coloration qui peuvent être mises en relation avec la décomposition des phases contenant le polybutadiène.

Zusammenfassung

Die spektroskopische Analyse bewitterter Proben und die thermische Oxydation der verschiedenen in ABS-Harzen auftretenden Phasen zeigen, dass diese Plaste am stärksten über ihre Polybutadienkomponente angegriffen werden. Die Änderung der physikalischen Eigenschaften und der Farbe dieser Harze mit dem Alter kann zur Zersetzung der Polybutadien enthaltenden Phasen in Korrelation gebracht werden.

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