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Environmental Stability of ABS Plastics

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Synopsis

Experiments with different ABS resins indicate that thermal stability in this class of polymers is dependent upon the ratio of styrene–acrylonitrile copolymer to polybutadiene rubber in the graft phase; resins containing more highly grafted rubber are more resistant to thermal oxidation. It is also found that in outdoor aging there is a minimum carbon black loading for these resins below which light screening is not effective.

Introduction

Polymers can be stabilized to some degree by the addition of antioxidants for thermal processes and carbon black for both thermal and outdoor processes. We will show that in addition to these stabilizing techniques, ABS resins can be further stabilized by modifying the structure of the graft phase.

Experimental

All the samples studied are commercially available. Their physical properties are listed in Table I. Specimens were injection-molded by using a Lester Phoenix 4-oz. injection machine. Cylinder and die temperatures of 221°C. and 66°C., respectively, and a cycle of 12 sec. injection, 18 sec. delay, and 2 sec. open time were used. Specimens were exposed outdoors at Murray Hill, N. J. at a 45° angle facing south, starting in February 1965. Resin 5 was started in December 1965. Previously published methods were used for thermal oxidation.[1] Measurements of angle at break were made on exposed specimens by the Stiffness in Flexure test (ASTM D747).

Natural resins 1, 3, and 5 (Table II) were separated into their phases by a solvent-elution technique.[2] Elemental analysis of the separated phases was used to calculate acrylonitrile, butadiene, and styrene contents in the whole resin. These values were then used with appropriate optical densities to construct infrared calibration curves. The acrylonitrile, butadiene and styrene percentages in the black compounds (2, 4, and 6) were then estimated from their infrared spectra. Graft contents were approximated from butadiene values. This analysis showed that resins 4 and 6 were

TABLE I
Initial Properties of ABS Plastics

Resin	Type	Impact strength, ft.-lb./in.	Melt flow rate, g./10 min.[a]	Flexural modulus, psi	Tensile strength, psi
1	Natural	4.3	2.9	351,000	6,400
2	Black	3.1	2.5	329,000	5,600
3	Natural	3.5	7.3	354,000	5,600
4	Black	3.0	6.0	366,000	5,100
5	Natural	3.7	10.1	363,000	5,300
6	Black	3.4	10.7	352,000	5,000

[a] Measured at 210°C., 5000 g. load, 7 g. charge.

TABLE II
Composition of ABS Plastic Studied

Resin	Additives, %	Styrene–acrylonitrile copolymer, %	Graft and free rubber, %	Graft SAN/rubber	Carbon black, %
1	4	65	31	45/55	—
3	4	64	32	32/68	—
5	5	75	20	45/55	—
2					2.5
4					2.0
6					0.5

based on 3 and 5, respectively. Resin 2, though similar to resin 1, had a greater amount of diene. This difference is small enough to consider resin 2 a black counterpart of resin 1 in this work.

Carbon black loadings (Table II) were estimated by Jarrel Ash microphotometric comparison of the black ABS's with standards. Antioxidants were removed from the base resin by methanol extraction. Analysis of these extracts indicated that resins 1 and 3 have the same antioxidant system, a thiobisphenol–tris(alkylaryl)phosphite type; resin 5 contains a hindered bisphenol–dialkylthiodiester–tris(alkylaryl)phosphite type. The x-ray fluorescence analysis showed that the black counterparts had the same levels of phosphorus and sulfur as their natural resins and therefore the same antioxidant loadings.

Discussion of Results

The initial properties of the ABS plastics (Table I) are of the same order. In each case the black resin suffers a decrease in impact strength proportional to the amount of carbon black present. The increase in melt flow rates from natural resins 1–5 follows an increase in the infrared absorption band at 3.0 μ. This points to the addition of an amide-type flow control agent, although systems with lower graft loading, such as resins 5 and 6, should have improved flow properties.

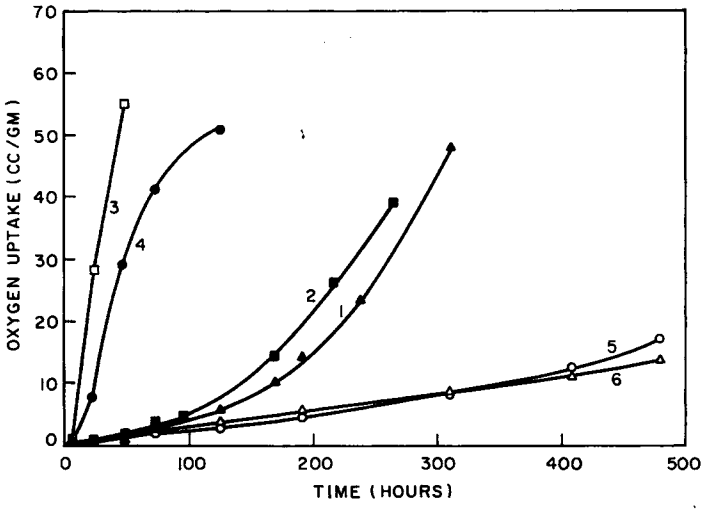

Fig. 1. Thermal oxidation of ABS plastics at 110°C. Numbers refer to resins 1–6.

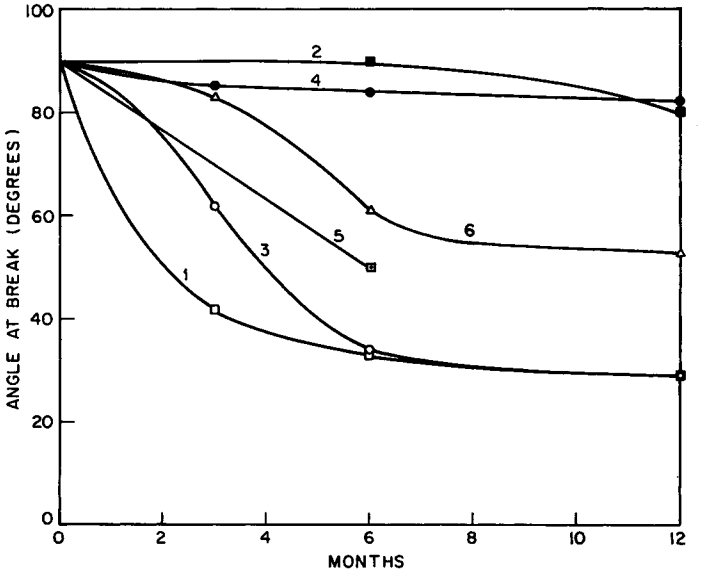

Fig. 2. Effect of angle at break on outdoor exposure of ABS plastics. Numbers refer to resins 1–6.

The behavior observed in the thermal oxidation experiments at 110°C. (Fig. 1) can be rationalized on the basis of the structures (Table II) and antioxidant systems found in these resins. The effect of carbon black is not noticeable in this thermal process. It has been previously shown[3] that in ABS resins, the rubber is the critical material as regards oxidation. The only difference between resins 1 and 3 is the graft structure. Resin 3 with

the less grafted rubber oxidizes more rapidly. Oxidation must then be a function of the degree of grafting; graft phases with the higher SAN to rubber ratios are more stable. The only differences between resins 1 and 5 are the amount of graft in the composite and the type of antioxidants. Since graft loading does not alter the induction period appreciably, the antioxidant system in resin 5 must be superior to that in resin 1. The thermal oxidation results are confirmed by the behavior of these materials on oven aging at 70°C. as measured by changes in elongation, Izod impact strength, and angle at break. These results also show that carbon black provides added stability for resins 1 and 3.

Based on the values at angle at break (Fig. 2), resin 6 is not significantly better than its natural counterpart (resin 5) on outdoor aging. The carbon black loading in resin 6 is too low to provide a suitable screening effect such as that observed with resins 2 and 4. There is little difference in the light aging characteristics of resins 1 and 3. The degree of increased thermal stability of the more heavily grafted material appears to be overshadowed by the higher energy of the photo-oxidation process.

Conclusion

ABS resins suffer a decrease in initial impact strength proportional to their carbon black contents. Conversely, a minimum carbon black loading exists, below which the advantage of light screening is not felt. Consequently, a compromise must be met in preparing black compounds to optimize the initial impact strength and minimize outdoor instability.

In thermal aging processes, ABS resins containing the more heavily grafted rubber possess greater stability. Unfortunately, as grafting increases, the amount of rubber available for toughening decreases. A balance must be obtained here also to insure the proper combination of impact strength and thermal stability.

References

1. W. L. Hawkins, R. H. Hansen, W. Matreyek, and F. H. Winslow, *J. Appl. Polymer Sci.*, **1**, 37 (1959).
2. B. D. Gesner, *J. Polymer Sci. A*, **3**, 3825 (1965).
3. B. D. Gesner, *J. Appl. Polymer Sci.*, **9**, 3701 (1965).

Résumé

Une étude sur les effets du vieillissement dû à l'environnement sur de nombreux composés naturels et de composés à base d'acrylonitrile–butadiène–styrène a été effectuée. Le vieillissement peut être relié à la composition et la quantité de phase greffée de la résine avec le type d'antioxydant utilisé et avec la quantité de noir de carbone présent dans le mélange.

Zusammenfassung

Eine Untersuchung des Einflusses der milieu-bedingten Alterung auf einige ungefüllte und russ-gefüllte Acrylnitril–Butadien–Styrol-Plastomere wurde durchgeführt. Die Alterung kann zur Zusammensetzung und Menge der Pfropfungsphase des Harzes, zum Typ des verwendeten Antioxydans oder zur Menge des eingebrachten Russes in Korrelation gebracht werden.

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