Fracture Behavior of Rubber-Modified Thermoplastics after Aging

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Synopsis

Experiments show that the effects of outdoor aging on rubber-modified thermoplastics can be reproduced by laminating a layer of a glassy polymer onto the surface of unaged specimens. This technique is used to study the effects of fracture temperature, specimen geometry, and polymer composition on the impact strength of aged HIPS and ABS. Aging reduces the energy of crack initiation, so that the impact strength is determined by the crack-propagation energy, which is in turn governed by the nature and concentration of the rubber and by the fracture temperature.

Most rubber-modified thermoplastics become brittle after a few months, or even weeks, out of doors. This tendency is one of the most serious limitations of these materials, since it excludes them from a wide range of applications for which they are otherwise suitable. Several papers have been published on the subject in recent years,[1-3] but these have been concerned mainly with the chemistry of the aging process, and very little attention has been paid to the physical factors affecting the serviceability of aged articles. The aim of this paper is to show, with particular reference to acrylonitrile–butadiene–styrene (ABS) and high impact polystyrene, (HIPS), how the impact strength of aged specimens is related to the fracture behavior of the rubber modified polymer over a range of test conditions.

Brittle-Layer Technique

Aging studies present two problems experimentally: the time factor, and the difficulty of defining standard exposure conditions. Even when accelerated aging equipment is employed, it may take many weeks to complete an experiment. We therefore began our investigation by seeking quicker and more reproducible methods for studying the effects of aging on impact behavior. The reasoning behind this approach was that the embrittlement brought about by aging is limited to the surface of the rubber-modified thermoplastic, and that relevant experiments could therefore be carried out on unaged specimens which had been coated with a layer of a brittle polymer.

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There is ample evidence that aging of HIPS and ABS is a surface effect; it is well known, for example, that the original properties of the polymer can be restored completely by machining away the exposed surfaces of aged specimens; further evidence to support this view is provided in the present paper. The basic cause of aging appears to be photo-oxidation of the rubber particles,[1] a reaction that proceeds particularly rapidly in the presence of ultraviolet light; embrittlement is therefore limited to those regions that are penetrated by ultraviolet light.

We found that the fracture behavior of aged specimens could be reproduced by laminating polystyrene onto HIPS, or styrene–acrylonitrile copolymer (SAN), onto ABS. The type of specimen illustrated in Figure 1

Fig. 1. Brittle-layer impact specimen. The 0.020-in. brittle layer is shown on the right-hand side.

was evolved in a series of trials, and was used in most of the experiments described below. It consists of a standard $1/_4 \times 1/_2 \times 2^1/_2$ in. Izod bar with a central notch of 0.040 in. radius; the brittle glassy polymer forms a layer 0.020 in. deep on one broad face of the specimen. In order to prepare these specimens a 0.020-in. sheet of the glassy polymer and a 0.230-in. sheet of the rubber-modified polymer were compression-molded separately and then laminated together in a steam press; the resulting sheet was then sawn into bars and notched in the usual way. It might appear preferable to have the brittle layer along the base of the notch rather than at the side, but this is more difficult to achieve reproducibly, and offers little real advantage.

Specimens of ABS prepared in this way, with an SAN brittle layer, were compared with ordinary compression-molded specimens of the same ABS which had been aged either out of doors or under a xenon lamp. Outdoor aging was carried out at these laboratories between 29 March and 14 July 1967 (686 hr. sunshine; blue cloth 6 faded to 4 on geometric grey scale).
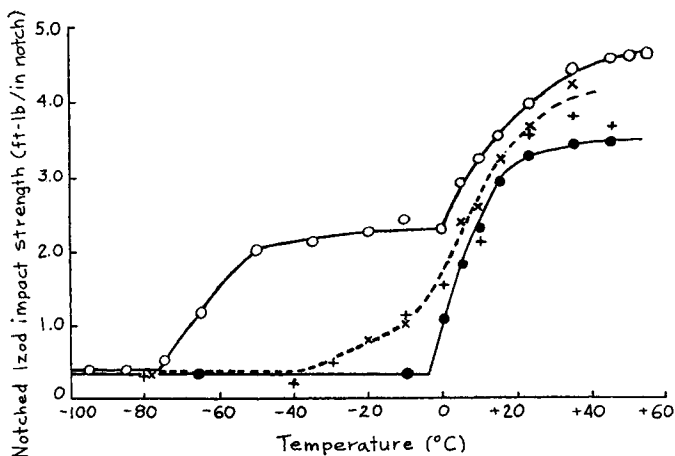
Fig. 2. Impact strength of ABS as a function of temperature: (O) unaged; (×) 635 hr. xenon lamp; (+) 3½ months outdoors; (●) brittle-layer specimens.

The accelerated aging consisted of 635 hr. exposure at a distance of 13½ in. from an Osram XBF6000 W/1 6kW xenon lamp fitted with an ultraviolet-transmissive cooling jacket.

Impact strengths were measured over a wide range of temperatures; the specimens were heated or cooled to the required temperature for at least 15 min. and then transferred to the test apparatus and broken within 5 sec.

Results for a commercial ABS polymer are shown in Figure 2. It is clear that the brittle-layer specimens are very similar in impact strength to both naturally weathered and artificially aged samples over the whole range of temperatures studied.
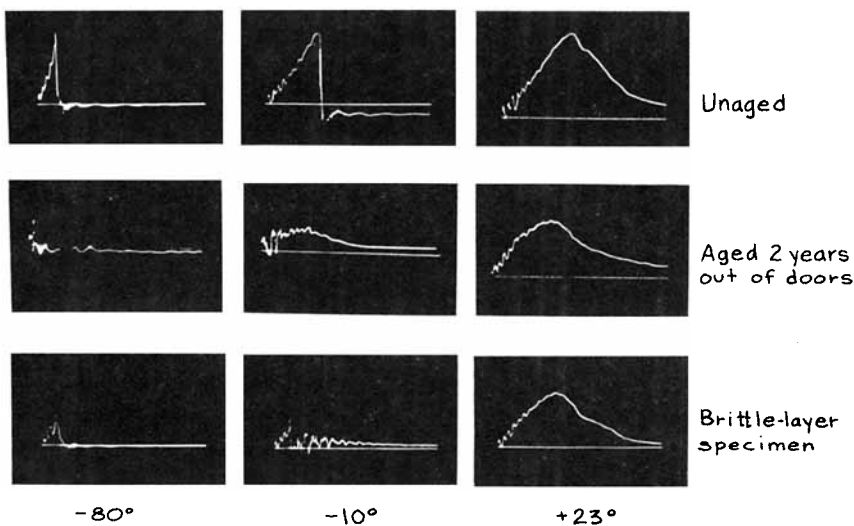

Fig. 3. Oscilloscope traces of impact force as a function of time for ABS Izod specimens fractured at −80, −10, and +23°C. Base lines = 3 msec.
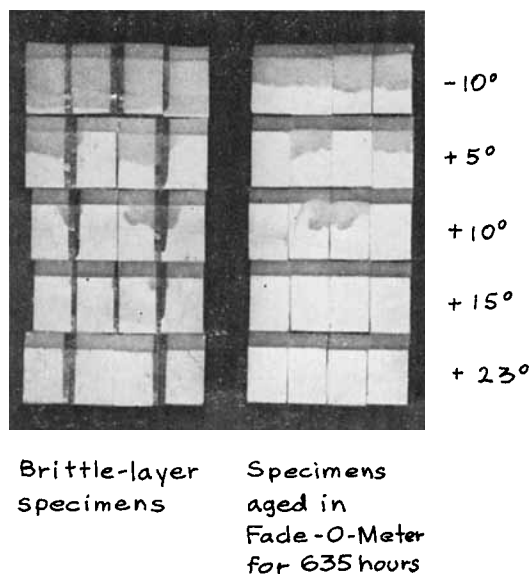
Fig. 4. Fracture surfaces of ABS Izod specimens broken at various temperatures, showing nonwhitened and stress-whitened areas. Notches are uppermost in the photograph.

Instrumented impact tests on the same ABS polymer also showed a similarity in fracture behavior between brittle-layer specimens and conventionally aged samples. In these tests, which are described more fully in a previous paper,[4] the impact force acting on the specimen was recorded as a function of time by clamping a pressure transducer to the specimen and feeding the signal to an oscilloscope; the oscilloscope trace was recorded photographically. Figure 3 shows the results obtained at −80, −10, and +23°C. At −80°C., aging reduces the peak height without altering the essential shape of the trace. At −10°C., the shape of the trace changes from a steady rise and sharp fall in the case of the unaged specimen, to a long low curve with some vertical breaks in the case of the aged specimen. At +23°C., the trace for the aged specimen is again simply a smaller version of the one for the unaged specimen. Brittle-layer specimens give essentially similar results to aged specimens at all three temperatures.

An examination of fracture surfaces revealed a further similarity between brittle-layer specimens and conventionally aged samples: the fracture surfaces of unaged specimens broken at temperatures above about 0°C. are fully stress-whitened, but on aged specimens the stress whitening is often incomplete, and extensive smooth, shiny areas are observed near the notch; the extent of these shiny areas decreases as the fracture temperature is raised. A similar pattern of behavior is observed in brittle-layer specimens, as shown in Figure 4.

These observations all support the view that aging is purely a surface effect in rubber-modified thermoplastics, and is equivalent to replacing the surface layer with a layer of the corresponding glassy polymer. A more

important conclusion to be drawn from this work, however, is that the long-term aging behavior of rubber-modified thermoplastics can be predicted by tests on suitable specimens coated with a brittle surface layer. This means that a wide range of material and test parameters can be studied in a relatively short time without resorting to conventional aging trials.

Fracture Temperature

It is clear from Figure 2 that the impact strength of ABS, both aged and unaged, is critically dependent upon the test temperature. A similar dependence is observed in HIPS and other rubber-modified thermoplastics. The extent to which the impact strength falls on aging is also dependent upon test temperature: in Figure 2, for example, the distance between the upper and lower curves is very much smaller at 15°C. than it is at −40°C. This point is well illustrated by Figure 5, which shows impact strength as a function of Fade-O-Meter exposure for two identical sets of HIPS specimens; the set tested at 23°C. shows very little loss of impact strength on aging, whereas the set tested at −10°C. shows an immediate drastic drop in impact strength, which continues to fall with further exposure. These observations have an important bearing on standard aging trials, since the retention of impact strength after exposure to ultraviolet light is often taken to indicate that no aging has taken place; evidence of this sort is obviously not sufficient in its own right to substantiate such a conclusion.

The relationship between impact strength and temperature in unaged samples is discussed in an earlier paper.[4] Energy absorption occurs through the formation of craze dislocations,[5,6] and is governed by two temperature-activated stress-relaxation processes: the relaxation of the rubber particles, and the initiation of crazes in the resulting inhomogeneous stress field. The rate of craze formation, and hence the impact strength, therefore rises with temperature as these processes are activated. The rise takes place in two steps, the first representing an increase in crack-initiation energy, the second an increase in crack-propagation energy. The
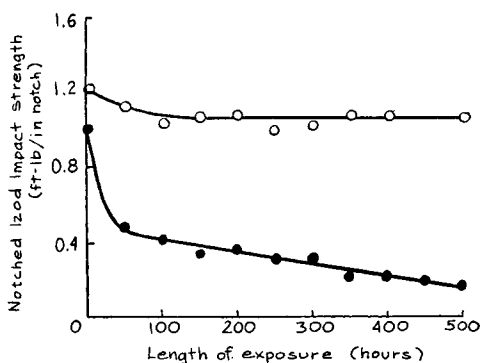

Fig. 5. Effect of fracture temperature on the impact strength of HIPS aged in the Fade-O-Meter; (O) fractured at 23°C.; (●) fractured at −10°C.

initial rise in crack-initiation energy occurs at much lower temperatures than the initial rise in crack-propagation energy because the maximum rates of strain imposed on the polymer before a crack is formed are much lower than those operating at the crack tip while the crack is propagating. Thus in Figure 2 the unaged ABS is able to delay crack initiation at −75°C. by crazing at the base of the notch, but does not abstract energy from the propagating crack by this mechanism until the temperature reaches 0°C.

In the case of aged samples there is only one step in the curve, corresponding to a rise in propagation energy. It is clear from Figure 2 that neither aged nor brittle-layer specimens offer much resistance to crack initiation, so that the impact strength is determined by the ability of the unaged material below the surface to abstract energy by crazing ahead of the propagating crack.

At first sight it is surprising that there is so little difference in impact strength, within the temperature range 0–60°C., between the aged and unaged specimens illustrated in Figure 2. The reason is that initiation and propagation energy are not additive quantities; most of the energy imparted to the unaged specimen at the initiation stage is converted to elastic strain energy, which reappears as kinetic energy of the broken half-specimen if the temperature is below 0°C. and as propagation energy if the temperature is above 0°C. The rise observed at 0°C. in the impact strength of unaged ABS indicates that this source of energy is insufficient for crack propagation, and has to be supplemented by the pendulum. The amount of energy abstracted from the pendulum at each stage of fracture can be deduced from an examination of the oscilloscope traces, and valuable supporting evidence can be obtained from a study of fracture surfaces.

Specimen Geometry

A notch reduces the energy required to initiate a crack, so that the propagation energy may represent a major proportion of the total impact strength. In unnotched specimens, on the other hand, the energy absorbed at the initiation stage is usually far in excess of that required for crack propagation, so that aging has a far greater effect on impact strength than it does in notched specimens.

Similar principles apply to specimens coated with a brittle layer of polymer. Figure 6 shows the drop-weight impact strength of 0.170-in. extruded HIPS sheet coated with a 0.001-in. layer of glassy polystyrene. Testing with the foil upwards corresponds to testing unaged sheet; testing with the foil downwards corresponds to testing aged sheet. The curves are similar to those obtained for notched Izod specimens, with a rise in initiation energy at about −70°C. and a rise in propagation energy at 10°C. The difference is that the propagation energy for the sheet is only a fraction of the total impact strength, even at the most favorable temperatures.

These experiments show that the effects of aging upon impact strength depend upon the geometry of the specimen, and that care is necessary in
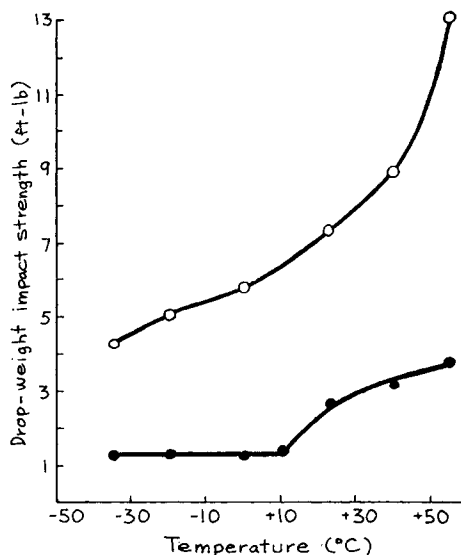
Fig. 6. Drop weight impact strength of foil-coated HIPS sheet: (O) foil upwards; (●) foil downwards.

translating results from one type of specimen to specimens of a different shape. Nevertheless, in a limited series of tests we have found a good correlation between the fracture resistance of aged commercial moldings and the performance of the polymer in the brittle-layer test, thus demonstrating that the propagation energy can be high enough to affect the serviceability of molded articles in practical applications.

Polymer Structure

Crack propagation energies are presumably governed by the same characteristics of the polymer as determine overall impact strength, viz., the method of manufacture; the nature, molecular weight, and molecular weight distribution of the rigid matrix; the nature, concentration, dispersion, degree of crosslinking, and relaxation behavior of the rubber; the extent of grafting between the two phases; and the nature and concentration of pigments, plasticizers, and other additives. In the present study, the effects of polymer structure were demonstrated by carrying out brittle-layer tests on polymers containing polybutadiene and GR-S in varying proportions.

Since the glass temperature of polybutadiene lies about 50C.° below that of GR-S, the craze mechanism for energy absorption can operate at lower temperatures in polymers containing polybutadiene than in those containing GR-S; it was shown in a previous paper that both the initiation and propagation stages of fracture are affected by this difference in glass temperature.[4] The effect is illustrated in Figure 7, which compares the

brittle-layer impact strengths of two HIPS materials, one based on poly-
butadiene, the other on GR-S.

Increasing the rubber content of the polymer raises the crack propagation
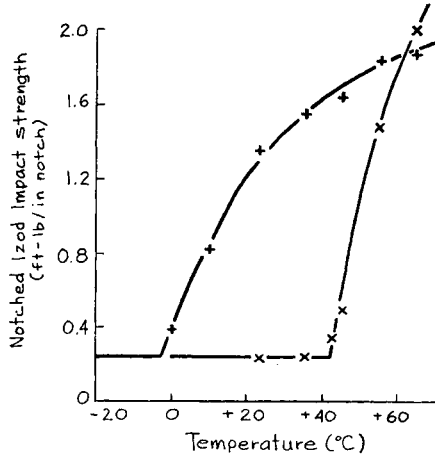energy in two related ways: firstly, the number of crazes formed in a given

Fig. 7. Impact strength of HIPS brittle-layer specimens: (+) toughened with poly-
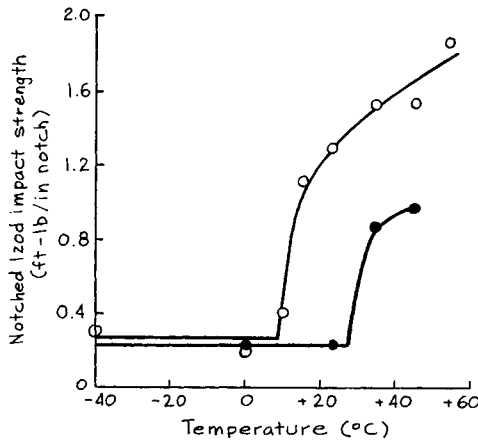butadiene; (×) toughened with GR-S.

Fig. 8. Impact strength of HIPS brittle-layer specimens: (○) 10% rubber; (●) 7%
rubber.

time is increased; and secondly the crack speed is progressively reduced as
energy is abstracted from the system, so that more time is available for
craze formation. Because of the interaction of these two effects, doubling
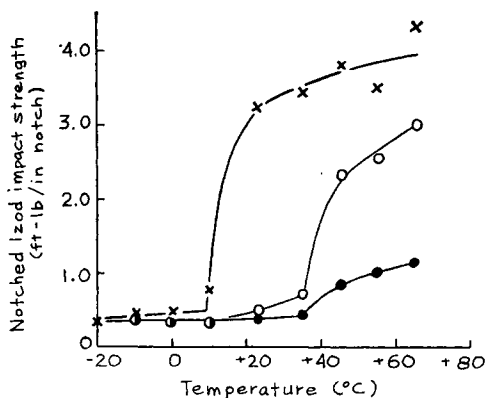the rubber content more than doubles the propagation energy. Typical

Fig. 9. Impact strength of ABS brittle-layer specimens: (×) 20% rubber; (○) 15% rubber; (●) 10% rubber.

relationships between rubber content and brittle-layer impact strength in HIPS and ABS are illustrated in Figures 8 and 9.

Discussion and Conclusions

The brittle-layer test described in this paper is complementary to conventional outdoor and accelerated-aging tests. It provides a rapid and convenient method for measuring the effects of surface embrittlement on the impact strength of the polymer, and as such is a valuable tool in any aging study. However, it remains for conventional exposure tests to determine whether such embrittlement takes place, and to what extent. The performance of the material may be better than that predicted by the brittle-layer test because of the presence of pigments,[7] which limit the penetration of ultraviolet light, or antioxidants, which retard the oxidation reaction; these factors are outside the scope of the present study.

The rubbers used for the manufacture of ABS and HIPS are almost invariably polymers or copolymers of butadiene, and as such are extremely susceptible to oxidation under the severe conditions imposed during outdoor exposure. Attempts have been made to replace them with more inert rubbers such as polyisobutylene and EPR,[8] but this approach has met with little success on a commercial scale. The problem is a difficult one, since the rubber is required to swell in styrene or other monomers and to undergo considerable grafting and crosslinking during polymerization, a requirement that is apparently incompatible with oxidation resistance. For the moment, therefore, it seems that the best answer to the aging problem in HIPS and ABS is to select polymers that have a high fracture resistance as measured by the brittle-layer test.

References

1. B. D. Gesner, *J. Appl. Polymer Sci.*, **9**, 3701 (1965).

2. G. P. Fratkina, E. I. Kirillova, Yu. A. Glagoleva, and K. A. Leitman, *Soviet Plastics*, **1966**, No. 9, 54.

3. E. I. Kirillova, E. N. Matveeva, L. D. Zavitaeva, Yu. A. Glagoleva, K. A. Leitman, and G. P. Fratkina, *Soviet Plastics*, **1967**, No. 2, 48.

4. C. B. Bucknall and D. G. Street, *S. C. I. Monograph No. 26*, Society of Chemical Industry, London, 1967, p. 272.

5. C. B. Bucknall and R. R. Smith, *Polymer*, **6**, 437 (1965).

6. C. B. Bucknall, *Brit. Plastics*, **40**(11), 118; **40**(12), 84 (1967).

7. J. A. Laird, *Brit. Plastics*, **32**, 32 (1959).

8. G. Natta, *Chim. Ind. (Milan)*, **47**, 384 (1965); *Rubber Chem. Technol.*, **39**, 1667 (1966).