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Weathering of a Thermoplastic Elastomer

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ABSTRACT

A styrene-butadiene-styrene thermoplastic elastomer was compounded with several different types and amounts of fillers and antidegradants. Molded sheets of the resulting compounds were exposed outdoors in Melbourne, Australia, for up to 12 months. The effects of filler loading on the stress/strain properties of the compounds both before and after weathering were evaluated. The compound which showed the best overall resistance to weathering contained about 2% of carbon black. The best white compound, which contained titanium dioxide (2% approx) and an ultraviolet stabilizer, was almost as resistant to weathering as the black compound.

INTRODUCTION

Thermoplastic elastomers combine the ease of forming associated with thermoplastics with the flexibility and toughness typical of vulcanized elastomers. They are finding an increasing number of applications where resistance to heat is not required. Thermoplastic elastomers require less energy for fabrication than vulcanized elastomers, and scrap material may be recycled. These laboratories have been concerned with the weathering of elastomers for many years [1], and it was therefore of interest to examine the factors

affecting the weathering of a styrene-butadiene-styrene (SBS) thermoplastic elastomer.

OBJECTIVES

Three consecutive weathering trials were arranged with exposure of the specimens outdoors in Melbourne as described in the experimental section. The objectives of the trials were as follows:

(a) Determination of the effects of carbon black on the stress/strain properties of the elastomer
(b) Evaluation of the effects of weathering on the stress/strain properties
(c) Investigation of the stress/strain properties of recycled material
(d) Determination of those additives which produced weathering resistant compounds especially in light-colored elastomers

EXPERIMENTAL

Materials

The materials used and their suppliers are listed in Table 1.

Compounding

The compounds were all prepared on a steam heated two roll laboratory mill (300 mm × 150 mm) to the formulations shown in Table 2. The thermoplastic elastomer was allowed to form a band on the front roll at a steam inlet temperature of 120°C and the required additives were then incorporated. Care was taken to ensure thorough dispersion of all ingredients in the compounds by following recommended mixing procedures [2].

Molding

The compounded elastomers were molded between sheets of polytetrafluoroethylene/glass release cloth in a single cavity mold in an electrically heated press at 150°C. A pressure of 8 MPa was maintained for 5 min and the mold was cooled by circulating cold water before removal of the finished sheets (150 mm × 150 mm × 2 mm).

TABLE 1. TABLE 1. Compounding Ingredients

Material	Trade name	Supplier
Antioxidant, zinc mercaptobenzothiazole	ZMB	Bayer Australia Pty. Ltd.
Antiozonant	AFD	Bayer Australia Pty. Ltd.
Calcium carbonate	Winnofil S	ICI Australia Pty. Ltd.
Carbon black N219, particle size 23 μm	Acarb	Australian Carbon Black Pty. Ltd.
Clay	Kaolin 37	ACI Minerals Pty. Ltd.
Iron Oxide		A. C. Hatrick Pty. Ltd.
Silica	Neosyl	Crossfield Pty. Ltd.
Thermoplastic elastomer	Tufprene	R. Bryce and Co. Ltd.
Titanium dioxide A	Austiox RSM	Australian Titan Products Pty. Ltd.
" " B	Tioxide R-CR2	Tioxide Australia Pty. Ltd.
" " C	Tioxide R-PP5	" " " "
" " D	Tioxide R-SM2	" " " "
" " E	Tioxide A-PP2	" " " "
UV Stabilizer A, 2(2'-hydroxy-5'-methylphenyl) benzotriazole	Tinuvin P	Ciba-Geigy Australia Pty. Ltd.
UV Stabilizer B, 2-hydroxy-4-methoxy-benzophenone	Cyasorb UV9	Cyanamid Australia Pty. Ltd.

(continued)

TABLE 1 (continued)

Material	Trade name	Supplier
UV Stabilizer C, 2-2'-thiobis(4-t-octylphenolato)-n-butylamine nickel	Cyasorb UV 1084	Cyanamid Australia Pty. Ltd.
UV Stabilizer D, bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate	Tinuvin 770	Ciba-Geigy Australia Pty. Ltd.
UV Stabilizer E, 2-hydroxy-4-n-octyoxy-benzophenone	Cyasorb UV 531	Cyanamid Australia Pty. Ltd.
Wax	110	Bayer Australia Pty. Ltd.

Outdoor Exposure

Strips of each compound (150 mm × 30 mm × 2 mm) were mounted in aluminum frames which were then fastened to exposure racks facing north at an inclination of 45° to the horizontal at Materials Research Laboratories, Melbourne.

Mechanical Testing

The mechanical properties were determined according to standard procedures [3, 4]. Tensile strength and elongation at break were measured on an Amsler tensile testing machine.

RESULTS AND DISCUSSION

Influence of Carbon Black Loading

Formulations 1 to 4 inclusive (Table 2) were used for the compounds for the investigations into the influence of carbon black loading. The exposed strips were withdrawn from outdoor exposure after 1, 2, 3, and 4 months and their mechanical properties were determined.

The changes in the stress/strain properties of the elastomer resulting from incorporation of carbon black can be seen in Fig. 1. The stiffness of the elastomer was increased by the addition of increasingly large amounts of carbon black as expected. The "S" shaped character of the curve, typical of an unfilled elastomer, was progressively reduced as the carbon black content increased. The elastomeric properties of the compounds, which involve large extensions for small increase in applied force, were therefore reduced as the amount of carbon black was increased.

The tensile strengths of the compounds after weathering are shown in Fig. 2. The weathered specimens were granulated after mechanical testing and remolded and their mechanical properties were again measured. The broken lines in Fig. 2 indicate the values found for the remilled specimens. The results suggest that surface cracking and crazing due to weathering may initiate mechanical failure when tested. Incorporation of the degraded layer into the compound and production of a new surface appeared to lead to some recovery of the lost mechanical properties. The greatest reduction in tensile strength on weathering was shown by the compound which contained 60 phr (parts per hundred parts of rubber) of carbon black. The compound containing no carbon black was affected slightly less, and the compounds with 20 phr or 40 phr were affected the least by weathering.

TABLE 2. Formulations

All formulations 1-22 contained the following ingredients:	
	Parts by weight
Thermoplastic elastomer	100.0
Antioxidant	2.0
Stearic acid	0.5
Antiozonant	2.0
Wax	3.0

Additional ingredients were as shown below:

Formulation no.	Additional ingredients	Parts, wt/ 100 parts elastomer
1	Nil	
2	Carbon black, N219	20.0
3	Carbon black, N219	40.0
4	Carbon black, N219	60.0
5	Titanium dioxide A	20.0
6	Calcium carbonate	20.0
7	Iron oxide	10.0
8	Carbon black, N219	2.0
9	Clay	2.0
10	UV Stabilizer A	1.0
11	" " B	1.0
12	" " C	1.0
13	" " D	1.0
14	" " E	1.0
15	Titanium dioxide A	2.0
	UV Stabilizer D	1.0
16	Silica	2.0
	UV Stabilizer D	1.0

(continued)

TABLE 2 (continued)

Formulation no.	Additional ingredients	Parts, wt/ 100 parts elastomer
17	Clay	2.0
	UV Stabilizer D	1.0
18	Calcium carbonate	2.0
	UV Stabilizer D	1.0
19	Titanium dioxide B	2.0
	UV Stabilizer D	1.0
20	Titanium dioxide C	2.0
	UV Stabilizer D	1.0
21	Titanium dioxide D	2.0
	UV Stabilizer D	1.0
22	Titanium dioxide E	2.0
	UV Stabilizer D	1.0

The complete formulations of numbers 23-27 were as follows:

Formulation no.	23	24	25	26	27
Material	Parts by weight				
Thermoplastic elastomer	100.0	100.0	100.0	100.0	100.0
Antioxidant	-	2.0	-	-	-
Stearic acid	0.5	0.5	0.5	0.5	0.5
Antiozonant	2.0	-	-	-	2.0
Wax	3.0	3.0	3.0	-	-
UV Stabilizer D	1.0	1.0	1.0	1.0	1.0

Influence of Carbon Black Type

The second part of this work was designed to investigate the influence of the type of carbon black on the reduction of mechanical properties due to weathering. Eight different types of carbon black were incorporated at a concentration of 20 phr and one was also used at 15, 10, 2, and 1 phr. The general conclusion was that the type of

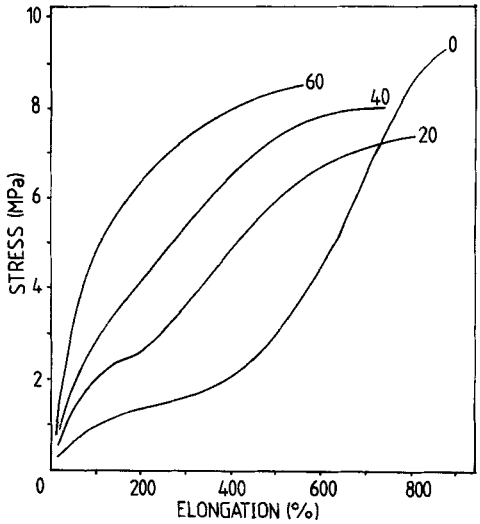

FIG. 1. Stress-strain curves for thermoplastic elastomers containing different amounts of carbon black, indicated as parts of carbon black by weight per hundred parts of base elastomer.

carbon black did not greatly affect the change in properties at a given carbon black concentration. Another observation was that low levels of carbon black, 1 or 2 phr, produced compounds which retained their properties well on exposure.

Formulations Resistant to Weathering

The third exposure test consisted of compounds containing small amounts of fillers (2 phr) or ultraviolet stabilizers (1 phr) or combinations of fillers and UV stabilizers. This part of the work was directed toward the development of white compounds which would have good resistance to weathering. The mechanical properties of the compounds after 13, 26, 39, and 52 weeks were measured. The percentage changes of the properties compared to the control for each compound after exposure for 52 weeks were calculated. The compound showing the least percentage change was allocated a rating of 1 and the ratings so derived are shown in Table 3. In each column the best weathering resistance is denoted by the lowest number. An overall rating was then derived from the three mechanical property ratings and this is also shown in Table 3. Compounds with the lowest overall ratings should have the highest resistance to weathering.

The compound with the best performance contained 2 phr of carbon

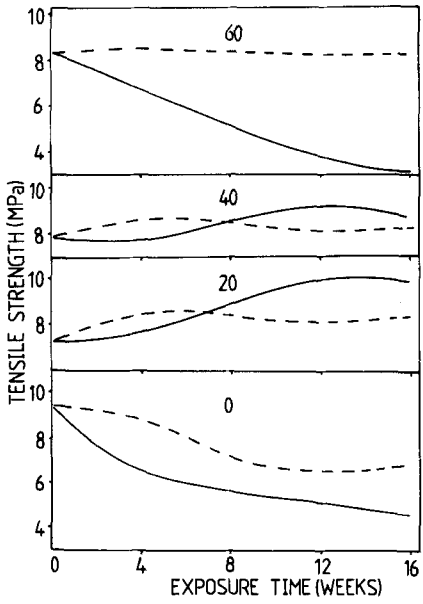

FIG. 2. Tensile strengths of thermoplastic elastomers after outdoor exposure as shown. Carbon black content of each elastomer, in parts by weight per hundred parts of base elastomer indicated on each graph.

black, the next highest performance was from a compound containing titanium dioxide (2 phr) and UV stabilizer D bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (1 phr). There appeared to be a synergistic effect operating as compounds with titanium dioxide or UV stabilizer D alone each had a rating of 7. Compounds without an antioxidant performed very poorly with the worst rating overall being for Compound No. 25 which contained only stearic acid, wax, and UV stabilizer D. The stress/strain properties of the best compound (No. 8), the worst overall (No. 25), and the unfilled compound (No. 1) are shown in Figs. 3, 4, and 5, respectively. Titanium dioxide was the most effective white filler and there appeared to be little difference between the performance of a rutile type (Nos. 15, 19, 20, and 21) and an anatase type (No. 22) in the presence of the UV stabilizer.

The effects of compounding ingredients on the weathering of the SBS thermoplastic elastomer are in agreement with the mechanisms for oxidation of diene rubbers [5]. The antioxidant used in the present work, zinc mercaptobenzthiazole, was recently shown [6] to be a much better antioxidant than mercaptobenzthiazole itself in paraffin oil at 140°. An antioxidant was necessary to prevent loss of mechanical

TABLE 3. Ratings[a] of Weathering Resistance Derived from 52-Week Exposure Results of Third Trial

Formulation no.	Tensile strength rating	Elongation at break rating	Hardness rating	Overall rating
1	17	14	13	14
5	8	8	11	7
6	18	15	6	11
7	4	3	9	3
8	5	2	1	1
9	16	16	12	14
10	15	20	21	19
11	21	19	4	14
12	13	12	20	15
13	9	10	8	7
14	20	17	14	17
15	3	5	2	2
16	11	9	15	8
17	14	13	16	13
18	12	11	13	9
19	6	1	12	5
20	7	4	14	6
21	2	6	17	6
22	1	7	10	4
23	23	22	7	18
24	10	9	19	10
25	22	24	18	20
26	24	21	6	17
27	21	23	5	16

[a]In any column, rating 1 denotes least change after 52 weeks exposure.

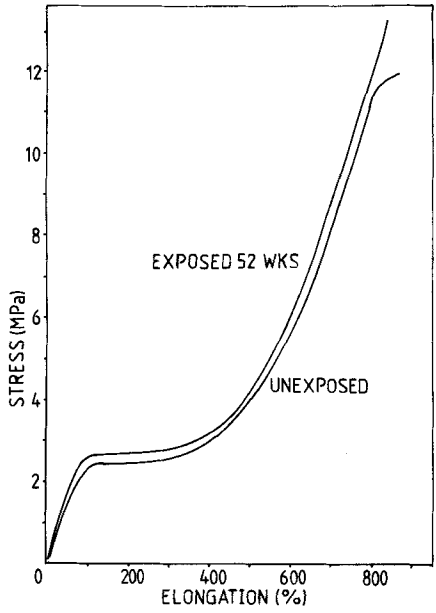

FIG. 3. Stress-strain curves for thermoplastic elastomer (Formulation No. 8) in unexposed condition and after outdoor exposure for 52 weeks.

properties on weathering of the thermoplastic elastomer; UV stabilizers were insufficient by themselves. Photooxidation of high impact polystyrene has been shown [7] to involve hydroperoxide attack on the 1,2-polybutadiene segments of the graft copolymer. Weathering of the SBS thermoplastic elastomer would appear to occur by similar mechanisms, indicating that these materials should be regarded as conventional styrene-butadiene rubbers from an outdoor weathering viewpoint.

CONCLUSIONS

1. Increasing amounts of carbon black progressively reduced the elastomeric properties of the thermoplastic elastomer. The resulting compounds with high loadings of carbon black resembled thermoplastics rather than vulcanized elastomers.

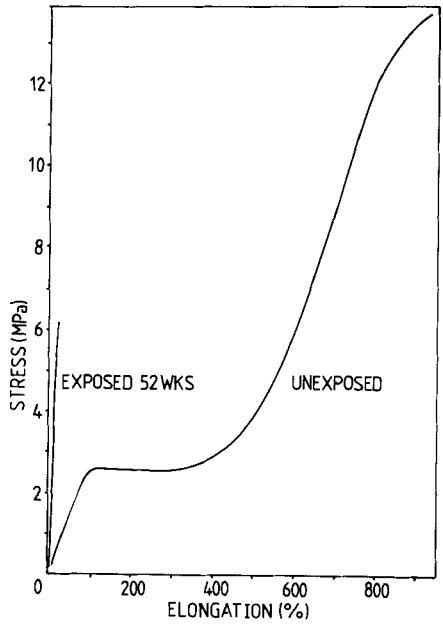

FIG. 4. Stress-strain curves for thermoplastic elastomer (Formulation No. 25) in unexposed condition and after outdoor exposure for 52 weeks.

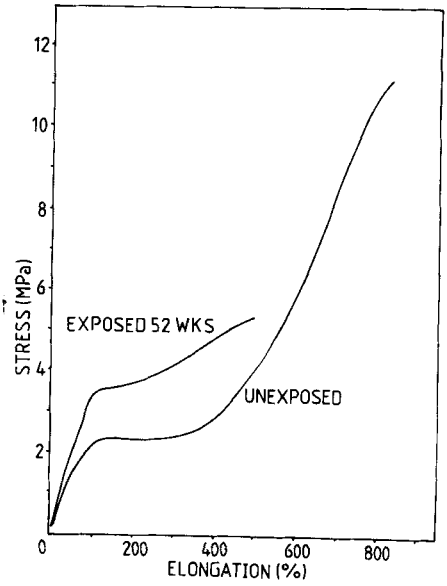

FIG. 5. Stress-strain curves for thermoplastic elastomer (Formulation No. 1) in unexposed condition and after outdoor exposure for 52 weeks.

2. Suitable antidegradants or carbon black must be incorporated into the thermoplastic elastomer to prevent drastic loss of mechanical properties on weathering.

3. The reduction in mechanical properties due to weathering of the compounds was reduced to some extent by granulating and remolding the compounds.

4. The additives which produced the compounds most resistant to weathering were first carbon black (2 phr) and second a combination of titanium dioxide (2 phr) and a UV stabilizer of the hindered amine type (1 phr).

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