

Graft Polymerization of Some Vinyl Monomers onto Acrylic Rubber. II. Mechanical Properties of Graft Polymers

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Synopsis

Some mechanical properties of styrene and acrylonitrile copolymers grafted onto acrylic rubber are investigated. The impact strength of graft polymers depended upon the nature and the concentration of the catalyst, the composition and the intrinsic viscosity of the rubber, and the acrylonitrile content in the rigid matrix. The most desirable result was obtained when benzoyl peroxide as the catalyst, *n*-butyl acrylate-acrylonitrile copolymer of 7-10% acrylonitrile content, and about 0-5% acrylonitrile in the rigid matrix were used. Dynamic mechanical tests show the increase in efficiency of rubber modification by the grafted chains. The better weathering resistance of these graft polymers, as compared with commercial ABS plastics, was confirmed.

INTRODUCTION

The mechanism of grafting reactions of vinyl monomers onto acrylic rubber was described in the preceding paper.¹ The rubber-modified vinyl polymers are important thermoplastic materials. The major interest in these two-phase systems centers on the ability of dispersed particles of a rubber phase to improve the impact strength of a glassy matrix without corresponding plasticization. A number of studies have been reported with respect to the impact properties of two-phase plastics^{2,4} and the mechanism of the formation of rubber particles.^{5,6}

The purpose of the present work is to elucidate the correlation between the molecular structure and some mechanical properties of graft polymers of acrylic rubber with styrene-acrylonitrile comonomer.

EXPERIMENTAL

The monomers *n*-butyl acrylate (BA), 2-ethylhexyl acrylate (2EHA), acrylonitrile (AN), and styrene (St) were purified and distilled. Benzoyl peroxide (BPO) and 2,2-azobisisobutyronitrile (AIBN) were purified by recrystallization from chloroform and ethanol, respectively.

The same methods described in the preceding paper¹ were used for the preparation of acrylic rubber and graft polymers. The conversion of graft polymerizations was kept over 98%. In order to remove a small amount of

remaining monomers, products were dissolved in methyl ethyl ketone, precipitated by pouring into methanol, and dried in vacuo.

These polymers, which were mixtures of vinyl polymers, pure graft polymers, and unreacted rubber, were molded to flat sheets of 3-mm thickness by compression molding at 230°C under 100 kg/cm² pressure for 5 min. The impact strength was measured according to the falling weight test, which was made by dropping a steel ball of given weight and dimensions from a predetermined height on a fixed specimen.

Dynamic viscoelastic properties were investigated with a commercial apparatus made by Toyo-Sokki Co. Ltd. (Vibron DDV-1), and dynamic modulus and loss modulus were measured at 138 c/s over a temperature range from -100° to 140°C.

The accelerated weathering test was carried out with a carbon-arc weather meter. After the required time of exposure, the impact strength of the compression-molded flat sheet of 2-mm thickness was measured according to the Dynstat Impact Test in which the specimen was held as a vertical cantilever sheet and was broken by a blow delivered at a fixed distance from the edge of the specimen clamp.

RESULTS AND DISCUSSION

Impact Strength

Figure 1 shows the effect of the catalyst concentration on the impact strength of samples of 80/20 styrene/acrylonitrile copolymers grafted onto 93/7 *n*-butyl acrylate/acrylonitrile copolymers. The impact strength of graft polymers catalyzed by BPO was higher than that catalyzed by AIBN. The high grafting efficiency in the BPO system, as shown previously,¹ seems to be the main factor of the high impact strength. A maximum was observed at 0.3–0.5% BPO. The desirable molecular weight of the styrene-acrylonitrile copolymer may be responsible for the high impact strength.

TABLE I
Effect of Compositions of Rubber on Impact Strength of Graft Polymers^a

BA/AN wt. ratio	Impact strength, ^b cm	BA/St, wt. ratio	Impact strength, ^b cm	2EHA/AN, wt. ratio	Impact strength, ^b cm
100/0	65	100/0	70	100/0	55
97/3	70	95/5	190	95/5	70
95/5	85	90/10	180	90/10	75
90/10	110	85/15	170	85/15	100
85/15	95	80/20	105	80/20	85
80/20	60	75/25	55	75/25	80

^a The rubber concentration was 20 wt-%; monomer, St/AN = 80/20; catalyst, 0.3 wt-% BPO.

^b Falling weight test with 198-g steel ball.

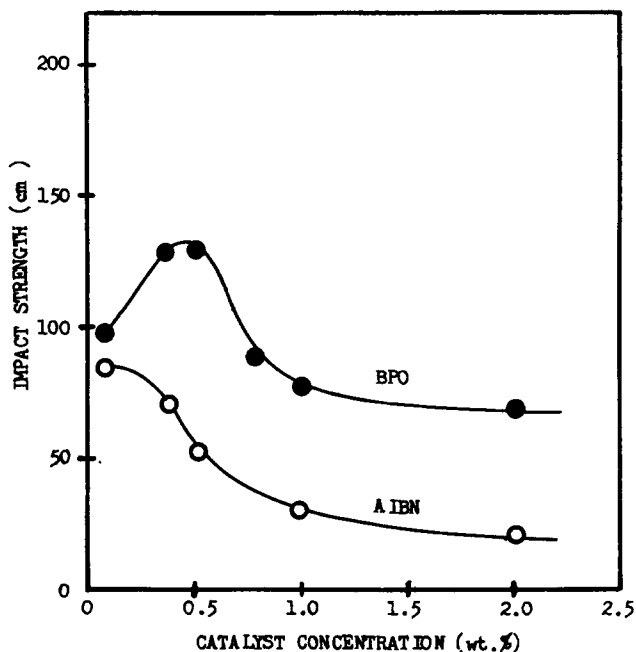


Fig. 1. Effect of catalyst concentration on impact strength of 80/20 styrene/acrylonitrile copolymers grafted onto 25 wt-% rubber of 93/7 *n*-butyl acrylate/acrylonitrile copolymers. Falling weight test with 198-g steel ball.

The impact strength of some samples of 80/20 styrene/acrylonitrile copolymers grafted onto various acrylic rubber such as *n*-butyl acrylate-acrylonitrile (BA-AN), *n*-butyl acrylate-styrene (BA-St), and 2-ethylhexyl acrylate-acrylonitrile (2EHA-AN) copolymers is summarized in Table I. The highest impact strength was observed in the BA-St system. Other copolymers, however, have excellent properties as rubber components, for example, the heat resistance of BA-AN copolymers and the impact resistance at low temperature of 2EHA-AN copolymers, respectively.

Table II reveals that the impact strength decreased with increasing acrylonitrile content in the comonomer and was remarkably high at 0-3% acrylonitrile. Styrene-acrylonitrile copolymer is noted as an excellent thermoplastic material which is superior to unmodified polystyrene in the impact resistance. Ziemda et al.⁷ reported that 20-35% acrylonitrile in the copolymer is the most desirable. In our laboratory, the graft polymers prepared by the emulsion polymerization of styrene and acrylonitrile in the presence of acrylic rubber were also studied, and it was proved that the impact strength was highest at 25-30% acrylonitrile in the rigid matrix. Adequate explanation could not be offered for the difference of the most desirable acrylonitrile content between polymers made by bulk polymerizations and those made by emulsion polymerizations. However, some peculiar effects of the high grafting efficiency in bulk polymerizations may be

TABLE II
Effect of Compositions of Styrene-Acrylonitrile on
Impact Strength of Graft Polymers^a

Monomer St/AN, wt. ratio	Impact strength, cm		
	198.0-g steel ball	286.0-g steel ball	439.5-g steel ball
100/0	over ^b	145	100
97/3	over	175	130
95/5	over	110	70
90/10	120	65	below ^c
85/15	105	45	below
80/20	90	40	below
75/25	80	below	below
70/30	75	below	below
75/35	65	below	below

^a The rubber concentration was 20 wt-%, BA/AN = 93/7; catalyst, 0.3 wt-% BPO.

^b Over 220 cm.

^c Below 40 cm.

responsible. Taking into account these results, we investigated the impact strength of various samples of polystyrene grafted onto acrylic rubber. Figure 2, as well as Figure 1, shows a maximum at 0.3–0.5% BPO. The

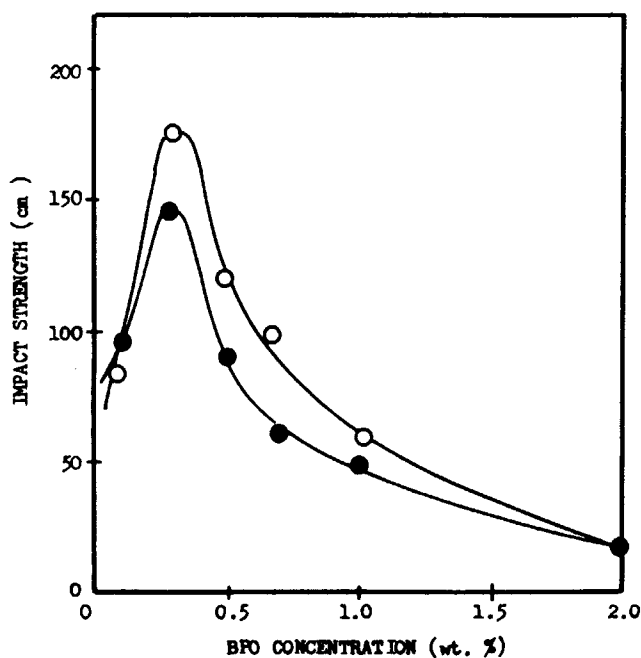


Fig. 2. Effect of catalyst concentration on impact strength of polystyrene (●) and 97/3 styrene/acrylonitrile copolymers (○) grafted onto 25 wt-% rubber of 93/7 *n*-butyl acrylate/acrylonitrile copolymers. Falling weight test with 286-g steel ball.

TABLE III
Effect of Compositions of Rubber on Impact Strength of Graft Polymers^a

BA/AN, wt. ratio	Impact strength, ^b cm	BA/St, wt. ratio	Impact strength, ^b cm	EHA/AN, wt. ratio	Impact strength, ^b cm
100/0	95	100/0	125	100/0	75
97/3	135	95/5	180	95/5	135
95/5	200	90/10	155	90/10	145
93/7	145 ^c	85/15	125	85/15	180
90/10	120 ^c	80/20	115	80/20	125
85/15	170	75/25	100	75/25	115
80/20	155	70/30	75	70/30	100
70/30	110	65/35	50	65/35	

^a The rubber concentration was 20 wt-%; monomer, St; catalyst, 0.3 wt-% BPO.

^b Falling weight test with 198-g steel ball.

^c Falling weight test with 286-g steel ball.

effects of the composition of acrylic rubber on the impact strength are shown in Table III. The impact strength was considerably higher as compared with the 80/20 styrene/acrylonitrile system (Table I) and was remarkably high in the system of polystyrene grafted onto the 97/3 *n*-butyl acrylate/acrylonitrile copolymer.

TABLE IV
Effect of Intrinsic Viscosity of Rubber
on Impact Strength of Graft Polymers^a

RSH ^b	[η] of rubber ^c	Impact strength, ^d cm	
		Monomer A	Monomer B
0	8.14	140	135
0.025	4.51	160	170
0.050	1.56	150	200
0.075	1.48	120	185
0.100	1.36	95	175
0.125	1.20	90	—
0.150	1.12	80	140
0.200	0.77	—	140

^a The rubber concentration was 20 wt-%; BA/AN = 93/7; monomers, St/AN = 80/20; Monomer B, St; catalyst, 0.3 wt-% BPO.

^b *n*-Lauryl mercaptan in parts per 100 parts BA/AN monomers.

^c Determined in methyl ethyl ketone at 30°C.

^d Falling weight test with 198-g (A) and 286-g (B) steel ball.

Table IV reveals that the addition of *n*-dodecyl mercaptan in the emulsion polymerization of *n*-butyl acrylate and acrylonitrile sharply reduced the intrinsic viscosity of the copolymer and shows the maximum impact strength at 0.05% *n*-dodecyl mercaptan.

Dynamic Viscoelastic Properties

The effect of temperature on the dynamic modulus E' and the loss modulus E'' determined for the mixtures of polystyrene and BA-AN copolymers are shown in Figure 3. The mixtures were recovered from the mixed solu-

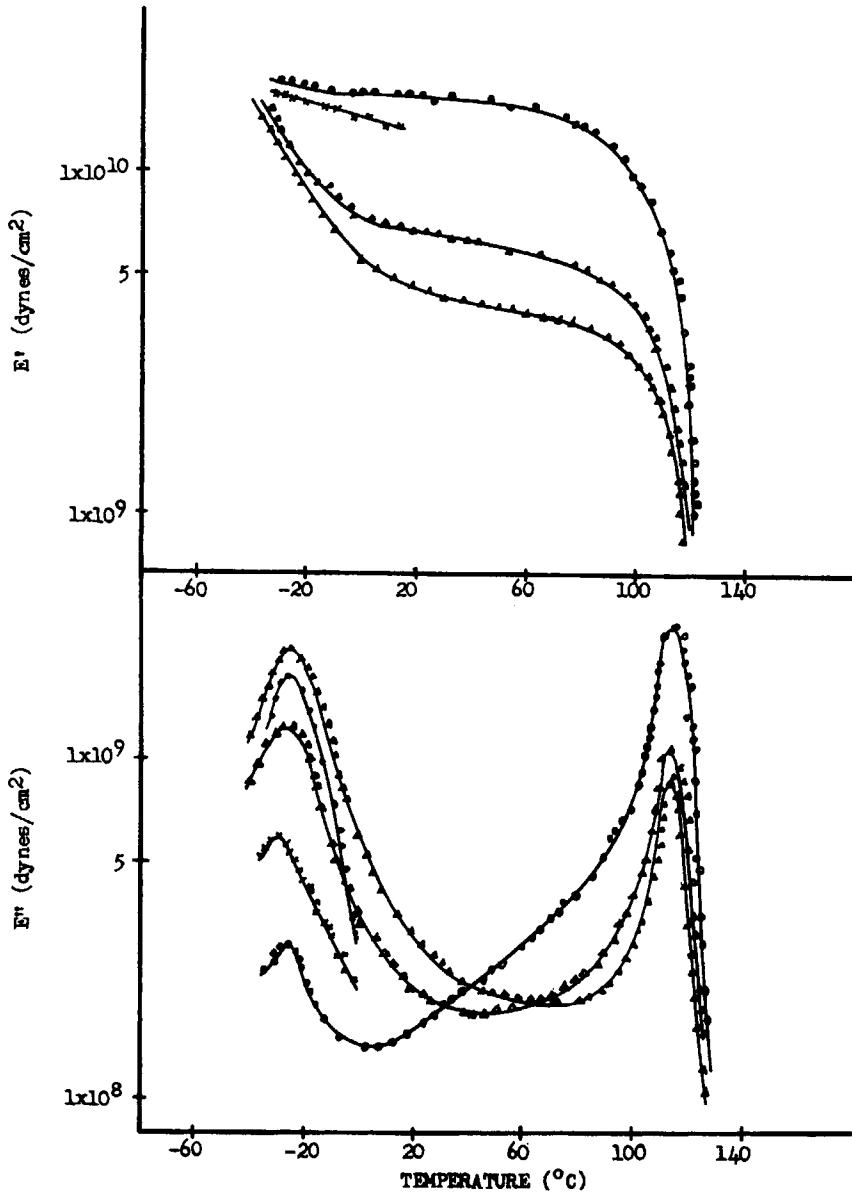


Fig. 3. Dynamic modulus and loss modulus in mixtures of polystyrene and 90/10 *n*-butyl acrylate/acrylonitrile copolymers: (O) 17 wt-%; (X) 20 wt-%; (Δ) 35 wt-%; (\bullet) 40 wt-%; (\blacktriangle) 50 wt-% BA-AN copolymer.

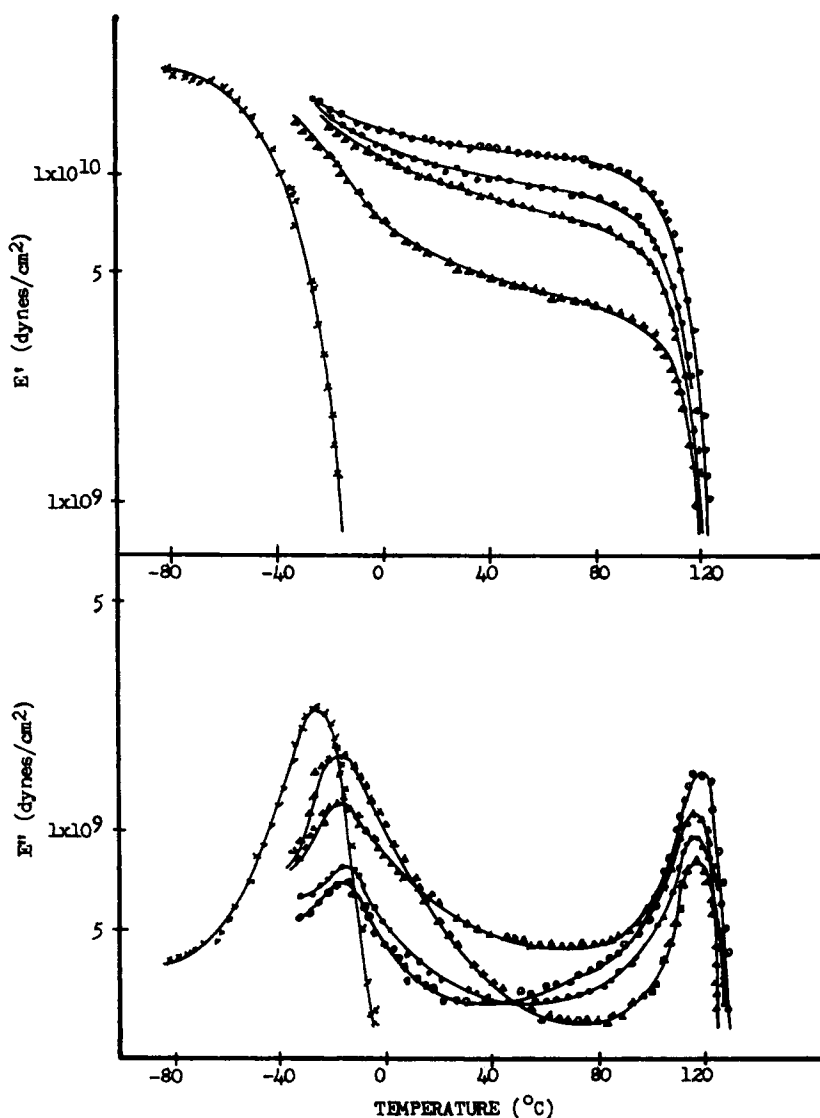


Fig. 4. Dynamic modulus and loss modulus in polystyrene grafted onto 90/10 *n*-butyl acrylate/acrylonitrile copolymers: (O) 15 wt-%; (●) 20 wt-%; (▲) 25 wt-%; (Δ) 30 wt-%; (X) 100 wt-% BA-AN copolymer.

tion of the two components in methyl ethyl ketone, with methanol as the precipitant. The loss modulus-versus-temperature curves for all the examined samples show two maxima, the first at -25°C due to the absorption of acrylic rubber, and the second at 115°C due to the absorption of polystyrene. On changing the ratio of the two components in the mixtures, the maximum points of E'' were observed to remain practically unchanged. The heights of E'' maxima at the lower temperature increased with increas-

ing acrylic rubber content, which was due to a softening effect of the rubber. This effect was also observed at the higher temperature as the decrease of dynamic modulus E' with increasing rubber content.

Similar behavior is shown in Figure 4, in which the dynamic modulus and the loss modulus were investigated for polystyrene grafted onto BA-AN copolymers. A comparison of these curves with those corresponding to mixtures of the same components shows that while the maximum points of E'' at the higher temperature remained practically unchanged, those at the lower temperature were shifted toward a little higher temperature. In a graft polymer, the maximum point of E'' at the higher temperature is known to be shifted toward a lower temperature. These samples in Figure 4, however, are not pure graft polymer fractionated from crude products.

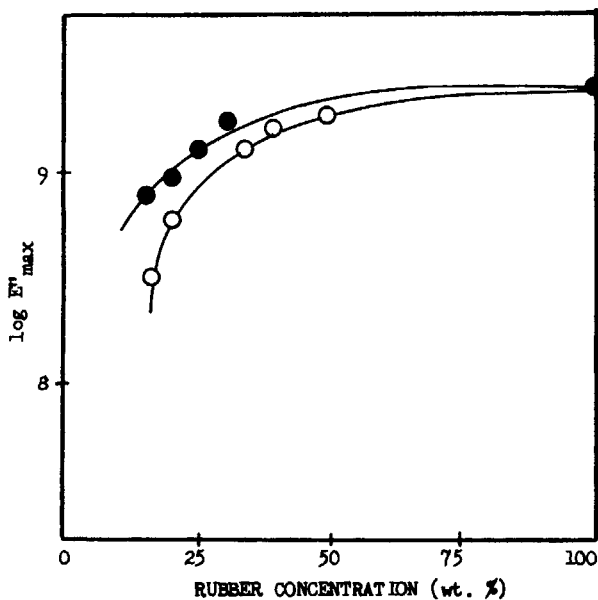


Fig. 5. Effect of rubber concentration on loss modulus E'' maxima: (●) polystyrene grafted onto BA-AN copolymers; (○) mixtures of polystyrene and BA-AN copolymers.

The heights of E'' maxima increased by grafting, as is evident from Figure 5. Similar results have been reported in a dynamic mechanical study of rubber-modified polystyrene by Turley,⁸ who explained the increase in efficiency of rubber modification by the existence of grafted chains as follows. Grafted chains, providing direct mechanical coupling between the rigid polymer matrix and the flexible rubber phase, may possibly serve as pathways for leading the impact energy from the polystyrene matrix into the rubber network. On the other hand, the mixtures of two components have a distinct boundary between the rubber particle and the rigid matrix. This results in a discontinuous change in the energy transmission, and the impact energy is likely to be reflected. This is in agreement with the fact

that the impact strength of the simple mixture of two components was lower than that of graft polymers.

Viscoelastic behaviors of the mixtures of rubber and plastics were examined in connection with the compatibility of two component polymers by Takayanagi.⁹ The mixing types of two components were classified as systems consisting of two separate phases, partially miscible system or molecularly mixed system. Close agreement was obtained between the observed values of E' and E'' of each types of model specimens and the values calculated by equations, in which the volume fraction and the construction form were taken into consideration. The shapes of the temperature dispersion E' and absorption E'' curves became loose and broad with increasing compatibility of the two components, respectively. This is in agreement with the results shown in Figures 3 and 4. The existence of grafted chains increased the compatibility, and the shape of the dispersion and absorption curves were more loose and broad in graft polymers as compared with the simple mixtures of two components.

Weathering Resistance

The changes in the impact strength during exposure in the weathermeter were determined for the polystyrene and the 80/20 styrene/acrylonitrile copolymer grafted onto the 97/3 *n*-butyl acrylate/acrylonitrile copolymer and for commercial ABS plastics. Antioxidants or UV stabilizers were not added to the grafted acrylic polymers. Figure 6 shows a definite embrittle-

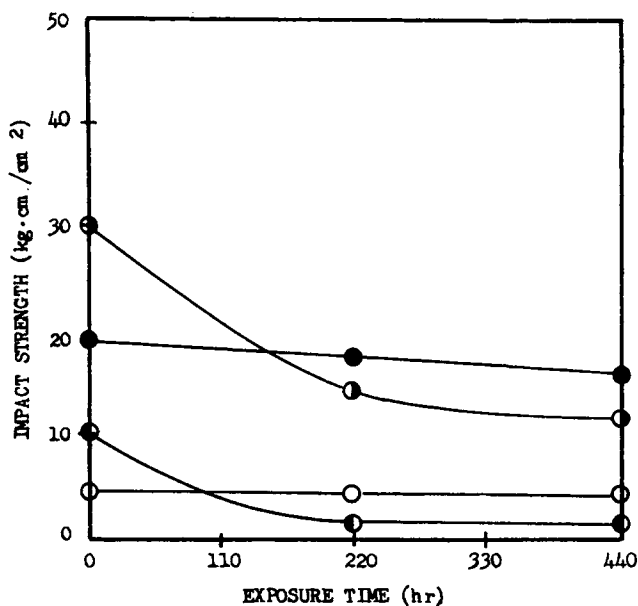


Fig. 6. Changes in impact strength during exposure: (●) polystyrene grafted onto 20 wt-% BA/AN = 97/3; (○) 80/20 St-AN grafted onto 20 wt-% BA/AN = 97/3; (⊙) commercial ABS-C; (⊖) commercial ABS-L.

ment of the commercial ABS plastics which contain unsaturated bonds in the rubber components. The graft polymers of vinyl monomers with BA-AN copolymers, which has no unsaturated bond in the rubber components, indicated the better weathering resistance. In the present study, the accelerated weathering test after 440 hr was not carried out, and it is not at all clear whether the 440-hr exposure time is sufficient to terminate the test. This point is being investigated.

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