

Development of AAS Resin by the Emulsion–Suspension Polymerization Method

HISASHI KOHKAME,^{1,*} MASASHI SHITARA,² SEIKICHI TANNO,³ and TADASHI MUROI⁴

¹Organic Chemical Products Division, Hitachi Chemical Co., Ltd., 2-1-1 Nishi-Shinjuku, Shinjuku-ku, Tokyo 163, Japan, ²Goi Works, Hitachi Chemical Co., Ltd., 14 Goi Minami Kaigan, Ichihara, Chiba 290, Japan,

³Hitachi Research Laboratory, Hitachi, Ltd., Kujicho, Hitachi, Ibaraki 319-12, Japan, and

⁴Head Office, Hitachi Chemical Co., Ltd., 2-1-1 Nishi Shinjuku, Shinjuku-ku, Tokyo 163, Japan

SYNOPSIS

In order to improve the weatherability of acrylonitrile–styrene–butadiene rubber graft polymer (ABS resin), an attempt was made to develop a resin (AAS resin) in which acrylic rubber of good weatherability was used instead of butadiene rubber. First, by copolymerizing dicyclopentenyl-methacrylate (DCP-MA, 3%) with butyl acrylate, crosslinked acrylic rubber was obtained. This also introduced grafting sites into the rubber. Next, methods of graft copolymerizing styrene and acrylonitrile with this rubber were examined. An emulsion–suspension polymerization method was developed in which the initial stage of the polymerization, emulsion polymerization, changed into suspension polymerization during the process. By this method of polymerization, rubber particles were combined and enlarged, bringing about a graft-type resin with high impact resistance. This polymerization method is industrially useful because particle-shaped resins are obtained without the need of a salting-out process. The AAS resin, obtained in this way, has much improved weatherability over ABS resin and shows strength equal to that of ABS resin. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Acrylonitrile–styrene–butadiene rubber graft copolymer (ABS resin) is widely used for housings of electric appliances, office automation equipment, and other uses because of its high strength and good moldability. The quantity of this resin used has increased every year. Because the butadiene rubber in the resin has many double bonds, however, the ABS resin has shortcomings, in that it is easily oxidized and it lacks weatherability.^{1,2} The general practice has been to add ultraviolet absorbers to the ABS resin to improve these weak points. Because this is still not adequate to permit long-term outdoor use, products to be subjected to such conditions have been coated with paint that has good weatherability. However, the addition of a painting process is an undesirable extra manufacturing step, and there is an additional problem in that painting sometimes

lowers the strength of resins. The use of saturated rubber instead of butadiene rubber has also been tried in order to overcome the poor weatherability of ABS resin.³ It is generally difficult to crosslink or graft copolymerized saturated rubber in order to increase its strength, however, because it is chemically stable. For this reason, rubber-reinforced resins, with high strength as well as good weatherability, had not been developed before now.

As for the polymerization process, most of the rubber-reinforced resins, such as ABS resins, are obtained by emulsion polymerization. Although the graft polymerization is performed easily, this method has a difficulty in that it requires a coagulating process after the polymerization stage. Therefore, elimination or simplification of this process has been desirable.

The object of this study was to develop resins with strength equal to that of ABS resin, along with good weatherability. First, a saturated rubber with good weatherability was selected instead of butadiene rubber. The latter is considered to be the cause of the inferior weatherability of ABS resin. Next,

* To whom correspondence should be addressed.

the crosslinking and improvement of graft efficiency of this rubber were studied. In addition, the graft copolymerization process, which does not need the coagulating process required for emulsion polymerization, was studied.

PREPARATION OF AAS RESIN

Materials

The names, abbreviations, and grades of the samples used in this study are shown in Table I.

Selection of Rubber Component

Weatherability of ABS Resin

When ABS resin is exposed to open-air conditions, deterioration phenomena appear, such as surface crazing, disappearance of luster, and decrease of impact strength and elongation. Though the cause of the deterioration of ABS resin, which occurs easily, has already been reported,⁴⁻⁷ the weatherability of ABS resin was examined again in this study.

Injection moldings of ABS resin were irradiated by a xenon-type weathering apparatus and the degree of deterioration of the resin surface was observed by means of infrared absorption spectrum. One specimen was given 600 h of irradiation by the weathering apparatus. Absorption at 920 and 960 cm^{-1} , caused by the double bond of butadiene rubber (BR), shown in Figure 1, decreased remarkably as compared with that before irradiation, while absorption caused by C=O at 1720 cm^{-1} and OH at 3400 cm^{-1} had appeared. These results indicate clearly that the double bonds of the BR component in the ABS resin were oxidized and that OH or OOH and C=O were formed. This is assumed to be due to the fact that ABS resin is inferior in weatherability. This conclusion led to the use of saturated rubber (without double bonds) instead of the BR component to improve the weatherability over that of ABS resin.

Selection of Saturated Rubber

In order to judge roughly whether various kinds of saturated rubber would be suitable for the rubber

Table I Specimen

Item	Specimen	Symbol	Quality
Monomer	Styrene	ST	Distilled industrial grade
	Acrylonitrile	AN	Distilled industrial grade
	Butyl acrylate	BA	Distilled industrial grade
Crosslinking agent	Divinyl benzene	—	Reagent grade
	Ethylene glycol dimethacrylate	EGDM	Reagent grade
	Propylene glycol dimethacrylate	PGDM	Reagent grade
	Bicyclopentadiene	BCHD	Distilled industrial grade
	Dicyclopentenyl methacrylate	DCP-MA	Distilled industrial grade
Initiator	Lauroyl peroxide	LPO	Grade 1 reagent grade
	Benzoyl peroxide	BPO	Grade 1 reagent grade
	Potassium persulfate	KPS	Grade 1 reagent grade
Emulsifier and suspension agent	Sodium soap of partially hydrogenated tallow fatty acid	NS soap	Industrial grade (Kao Co.)
	Polyvinyl alcohol	PVA	Industrial grade (KH017, Nippon Gosei Kagaku Co.)
Others	<i>t</i> -Dodecyl mercaptan	<i>t</i> -DM	Reagent grade
	Sodium sulphite	Na ₂ SO ₃	Special reagent grade
	ABS resin		Industrial grade (Vitax V1200, Hitachi Chemical Co.)

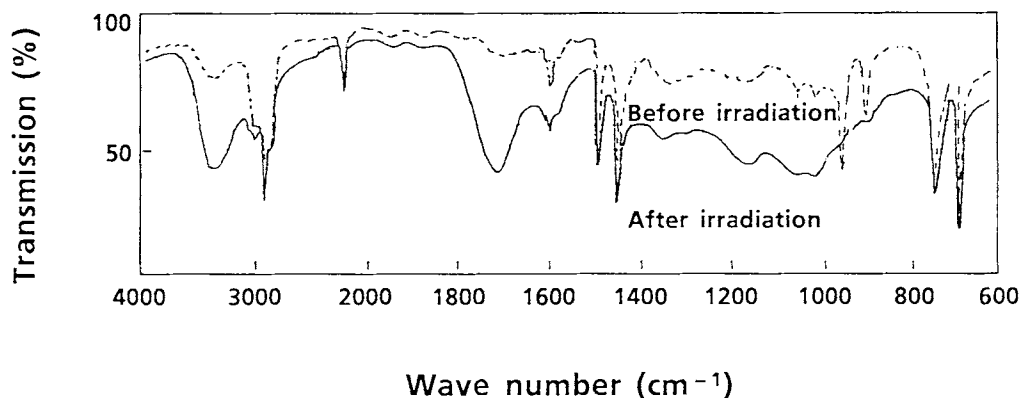


Figure 1 Infrared spectrum of ABS resin irradiated by weathermeter (600 angstrom).

component of a rubber-reinforced resin, the following comparisons were made:

1. Ease of introducing crosslinking and radical grafting sites: Observation of the structure of a rubber-reinforced type of resin with a transmission electron microscope shows rubber particles dispersed within the matrix of the acrylonitrile-styrene copolymer (AS copolymer).⁸⁻¹⁰ Good affinity between the rubber particles and the AS copolymer is required for this resin to have high strength. For this purpose, the AS copolymer is generally graft-polymerized with rubber particles.

Crosslinking of the rubber component is required to some extent to minimize deformation of the rubber particles in the rubber-reinforced resin by injection molding because this would cause the strength to vary directionally. In the case of ABS resin, the rubber component BR has one double bond for each monomer unit ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$). Therefore, the hydrogen radical, bonded to each of the carbon atoms connected to this double bond, can be removed easily. Thus, each of these carbon atoms becomes a grafting site and also a crosslinking site, resulting in a resin with high strength. On the other hand, it is difficult to crosslink or graft polymerize a saturated rubber to increase the rubber strength because it has no functional radicals, such as double bonds. It became necessary to introduce the functional group, which would become the sites for crosslinking or graft polymerization, in order to solve this problem. It was decided to copolymerize a small amount of diene type monomer with

the resin. Therefore, the ability to copolymerize with the selected monomer is required.

2. Ease of emulsifying: In a rubber-reinforced type resin, such as ABS resin, rubber particles of about 0.1 to 1.0 μm diameter were dispersed in the matrix of the AS polymer. As mentioned above, these resins were generally prepared by emulsion polymerization, so it is generally desired that the rubber be prepared by emulsion polymerization.
3. Ease of handling: From the viewpoint of industrial production, it is desirable to be able to obtain the rubber by radical polymerization with simple equipment and processing conditions.

As shown in Table II, acrylic rubber (AR) satisfies these conditions. The reasons are as follows:

1. The raw material, butyl acrylate (BA), copolymerizes easily with diene type monomers so crosslinking is easily effected. Also, a grafting site is easy to introduce into the rubber thus formed.
2. BA is easy to emulsify and can be prepared into rubber by emulsion polymerization.
3. BA is easy to radical-polymerize and easy to handle, because it is liquid at room temperatures. For these reasons, AR was considered to be suitable for the rubber component of the rubber-reinforced resin. In the following polymerization experiment, crosslinking and graft copolymerization sites were introduced by polymerizing the AR with BA together with a diene-type monomer. Subsequently, graft-copolymerization of styrene (ST) and

Table II Selection of Saturated Rubbers Suitable to Rubber Reinforced Plastics

Saturated Rubber		Crosslinking and Grafting Sites ^a	Ease of Emulsifying ^b	Workability ^c
Popular Name	Chemical Name			
Butyl rubber	Isobutylene-isoprene copolymer	△	×	×
Acrylic rubber	Buthyl acrylate acrylonitrile copolymer	○	○	○
Hyparon	Chlorosulfonated polyethylene	△	×	×
Elvax	Ethylene vinyl acetate copolymer	△	△	×
Bistrenex	Polyisobutylene	×	×	×
EPT	Ethylene-propylene-diene terpolymer	○	△	×
Chlorinated polyethylene	Same	△	×	×

^a Copolymer with diene group monomer should be formed easily.

^b Rubber can be prepared by emulsion polymerization.

^c Monomer is liquid at room temperature.

(○) Easy, (△) Middle, (×) Difficult.

acrylonitrile (AN) with this modified AR was studied.

Preparation of AAS Resin

Crosslinking and Grafting of Acrylic Rubber

1. Crosslinking of AR and preparation of BA emulsion: First, in order to make radical sites for crosslinking and graft-copolymerization on the AR, a small number of double bonds was introduced by copolymerizing a small quantity of a diene type monomer with BA in emulsion. The method was to dissolve NS soap, KPS, and Na₂SO₃ in water. BA and a diene-type monomer were then added to the solution and mixed. The mixture was heated and polymerized in a nitrogen gas atmosphere.

As shown in Table III, various diene-type monomers were copolymerized with BA and matter insoluble in toluene was determined. The degree of swelling of the product was also measured by weight gain after a 24 h immersion in toluene. As a result, every diene-type monomer, except divinylbenzene, produced insoluble matter and 90% or more of the AR could be made insoluble. A radical initiator, BPO, was also effective in crosslinking the AR. The degree of swelling, which expresses

the density of crosslinking, was especially small (crosslinking density is large) for EGDM and PGDM, while BCHD and DCP-MA, with cyclic double bonds, did not show such small values.

2. Graft polymerization of AN and ST with AR: Graft copolymerization was performed by the ordinary emulsion method used for ABS resin. That is, KPS was dissolved in water and then AR emulsion, previously polymerized, was mixed into the solution. ST, AN, and a chain transfer agent, *t*-DM, were then added to cause the solution to polymerize. The graft efficiency of ST and AN was then measured on the resin obtained. As shown in Table III, all resins for which diene-type monomers with cyclic double bonds were used had a high graft efficiency. In particular, DCP-MA, which has both chain and cyclic double bonds with different reaction rates, showed a graft efficiency as high as 16%. On the other hand, EGDM and PGDM, with two similarly reactive chain double bonds, showed a low graft efficiency. It was supposed that the quantity of residual double bonds of EGDM and PGDM was small at the end of the rubber polymerization step, while those of DCP-MA were 13 to 15% of the initial quantity. These residual double bonds were believed to have been used for the graft co-

Table III Crosslinking of Acrylic Rubbers by Diene Group Monomer and Mechanical Properties of Graft Polymer With Use of Crosslinked Rubber

Acrylic Rubber ^a				Graft Polymer ^b		
Diene Group Monomer		Matter Insoluble in Toluene (%)	Swelling (%)	Graft Efficiency (%)	Mechanical Properties	
Type	Proportion (%)				Impact Values (J/m)	Tensile Strength (MPa)
Divinyl	4	3	—	3	<20	27
Benzene	8	7	—	5	<20	28
EGDM	4	93	23	6	40	31
	8	95	21	4	50	35
PGDM	4	93	22	5	50	31
	8	94	21	8	50	34
BCHD	4	91	25	8	100	45
	8	93	24	8	100	48
DCP-MA	4	91	28	14	120	43
	8	94	22	16	110	44
BPO	0.5	92	26	9	50	35
	1.0	95	20	10	50	41
LPO	0.5	0	—	0	<20	25
	1.0	0	—	0	<20	26

^a Polymerization conditions: Water: 400 g; BA: 20 g; NS soap: 4.4 g; KPS: 1.0 g; Na₂SO₃: 0.2 g; Polymerization time: 4 to 10 h.

^b Polymerization conditions: Acrylic rubber latex: 120 g (rubber content 40 g); ST: 60 g; AN: 40 g; LPO: 0.25 g; polyvinyl alcohol: 1.8 g; water: 220 cc. Temperature: 70°C.

polymerization of ST and AN. Next, the relation of both the degree of swelling and graft efficiency with strength of the graft copolymers was examined. The tendency was that the smaller the degree of swelling, the larger the tensile strength, but no such tendency was found for the impact value. A good correlation was found between graft efficiency and Izod impact value (ASTM D256). Specifically, it was found that Izod impact value increased with improvement in graft efficiency, and that DCP-MA, with high graft efficiency, showed the highest impact value.

These findings indicate that DCP-MA, with both chain and cyclic double bonds, is best suited for use as the diene-type monomer.

Control of the Size of Rubber Particles by Emulsion-Suspension Polymerization Method

Observation of rubber particles in ABS resin with a transmission electron microscope showed dispersed particles with a range of diameters 0.1–1.0 μm .^{8–10} This range is generally believed to be required for satisfying both high impact value and high elasticity.^{8–10} Preparation of AAS resin by the emulsion

polymerization method with the previously described emulsion, however, produces particles of AR in the resin of only 0.03–0.1 μm diameter, considerably smaller than those of BR in ABS resin. A method is available to produce AR particles as large as the BR particles of ABS resin. First, an emulsion of small particles of AR 0.03–0.1 μm in diameter was produced by ordinary polymerization; BA was then added to this emulsion, which caused the polymerized particles to act as seeds and to increase in size. This method of enlarging the particle diameter by seed polymerization was attempted as part of this study, but the addition of BA made the emulsion system unstable and, moreover, slowed the reaction noticeably. Although the emulsion polymerization method was suitable for graft copolymerization, it has the shortcoming of requiring a coagulation process after completion of polymerization. Therefore, the removal or simplification of this process would be desirable. Accordingly, a new polymerization method to replace emulsion polymerization was tried, as described in this study.

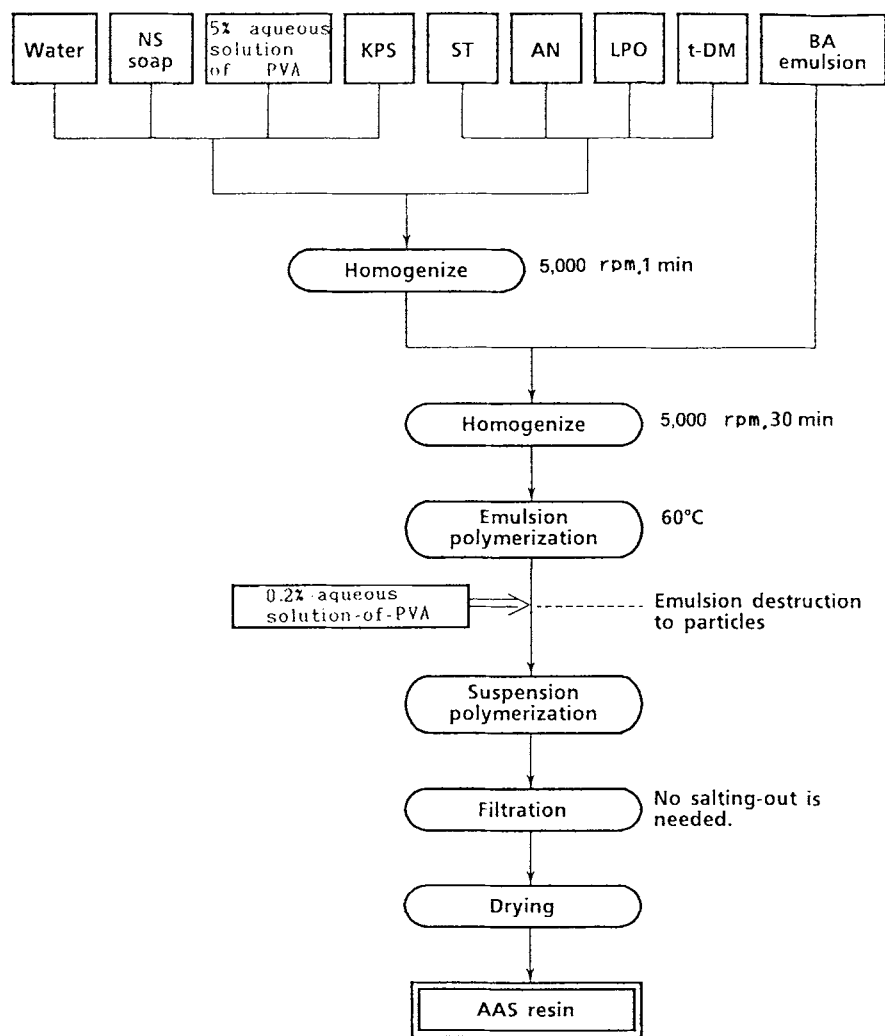
1. Preparation by suspension polymerization: First, AAS resin was prepared as follows by a method based on suspension polymerization (using an oil soluble initiator), which does

Table IV Properties of AAS Resin Polymerized Using Oil-Soluble Initiator

Item	Unit	Suspension Polymerized AAS Resin	Emulsion Polymerized AAS Resin Using BPO as Initiator	ABS Resin
Izod impact value, roll to press	J/m	250	200	250
Izod impact value, extrusion to injection	J/m	60	60	240
Tensile strength	MPa	39	41	46
Tensile modulus	MPa	1900	2000	2200
Rockwell hardness	R Scale	92	93	105
Heat distortion temperature	°C	79	80	85

not need a coagulation process. A monomer solution was created by dissolving SBR, *t*-DM, and LPO in ST and AN. A 0.2% PVA solution in water was then prepared and

mixed with the monomer solution. The mixture was heated to promote polymerization. This method enabled production of resins with high impact resistance, as shown by the

**Figure 2** Emulsion-suspension polymerization process.

main characteristics in Table IV. However, the problem with these resins was that the impact value varied with the molding conditions. Next, an-oil soluble initiator, instead of the water-soluble initiator, was added to the rubber emulsion prepared before. The results obtained by this method, in which suspension polymerization was conducted in an emulsion system, are shown in Table IV. As can be seen, the impact value of the resins that were produced also varied with molding conditions. This was because the rubber component in the polymerized material was extensively crosslinked and has one set of properties, while the molding process was believed to result in smaller particles of elongated shape (typically 0.5–3 mm long and 0.05–0.3 mm in diameter), which have different properties.

Preparation by emulsion-suspension polymerization method: Because it appeared to be difficult to produce resins with consistent mechanical properties using a suspension system, a new polymerization method was examined. This method began mainly with polymerization in an emulsion system, then changed to a suspension system, thus making the best use of the advantages of both emulsion and suspension polymerization. This process is shown in Figure 2. Water, NS soap,

PVA solution in water, and KPS were mixed. To this mixture (2) AN, LPO, and *t*-DM solution were added and then the mixture was agitated with a TK Homomixer (Tokushu Kika Kogyo; M type). To this emulsion liquid (3) the acrylic rubber emulsion described earlier was added and the mixture was agitated with a TK Homomixer. By this operation, a part of the rubber particles were combined and the particles enlarged. This mixture was heated and polymerized in a nitrogen atmosphere. At the beginning of polymerization, emulsion polymerization and suspension polymerization proceeded concurrently, but the emulsion became unstable and coagulated at polymerization ratios of 30–60%. Addition of a 0.2% PVA solution in water converted the emulsion to a suspension system that did not coagulate. After completion of polymerization, the polymer produced was filtered and dried. For polymerization by this method, it was necessary to use an oil soluble initiator (required for suspension polymerization) as well as a water soluble initiator (required for emulsion polymerization). This method is hereafter called the emulsion-suspension polymerization method.

The emulsion-suspension polymerization method has advantages over traditional emulsion polymer-

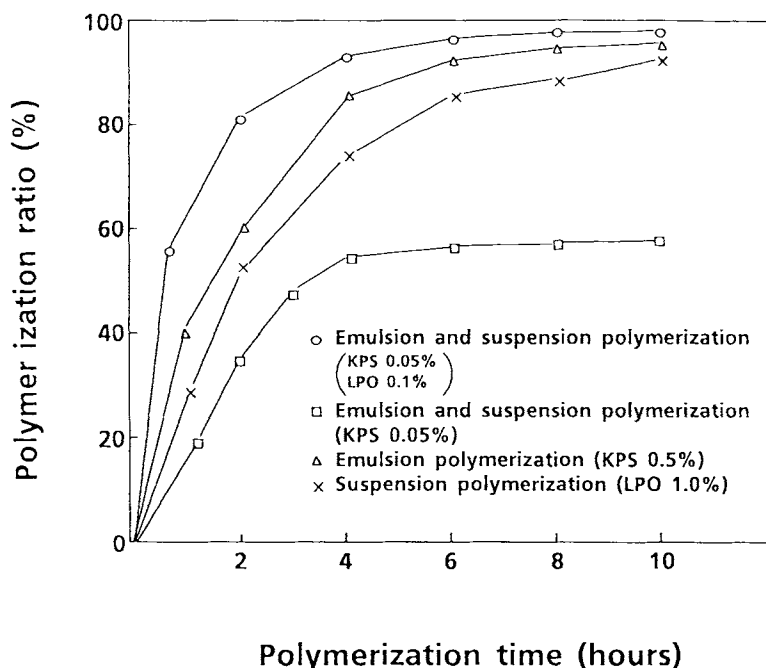


Figure 3 Polymerization processes and polymerization times.

Table V Properties of AAS Resin Prepared by Emulsion–Suspension Polymerization

Item	Unit	AAS Resin		
		Emulsion–Suspension ^a Polymerization	Emulsion Polymerization	ABS Resin
Izod impact value	J/m	100	60	250
Tensile strength	MPa	43	47	46
Tensile modulus	MPa	2300	2400	2200
Rockwell hardness	R scale	103	104	105
Heat distortion temperature	°C	84	87	85

^a Polymerization conditions: Acrylic rubber, DCP–MA: 5% (10 g); *t*-DM: 0.2% (0.4 g). Other polymerization conditions the same as in Table III. Graft polymer, Same as in Table III.

ization because it readily achieves enlargement of rubber particles (0.2–1.5 μm long and 0.05–0.2 μm in diameter) during the homogenizing process before graft copolymerization, and because it does not require the coagulating process of emulsion polymerization. Moreover, large variation of impact value of the resin, due to different molding methods, was not observed, although variations were observed in resin produced by suspension polymerization.

Figure 3 shows the polymerization rates of emulsion polymerization, suspension polymerization, and emulsion–suspension polymerization achieved in this study. As shown in Figure 3, it was found that emulsion–suspension polymerization requires joint use of a small amount of a water soluble initiator (KPS) and an oil-soluble initiator (LPO). The high

polymerization rate of an emulsion–suspension system is believed to be due to the fact that emulsion polymerization proceeds both in micells and on small polymer particles that polymerized in micells while emulsion–suspension polymerization proceeds in oil droplets.

EVALUATION OF AAS RESIN

General Properties

The general properties of the AAS resin, obtained by emulsion–suspension polymerization, are shown in Table V.

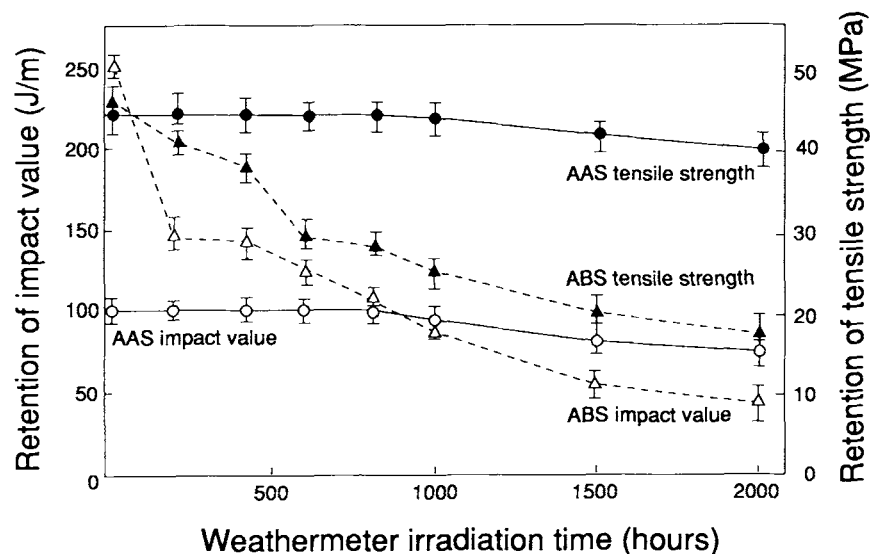


Figure 4 Weather resistance of AAS resin (change in mechanical properties).

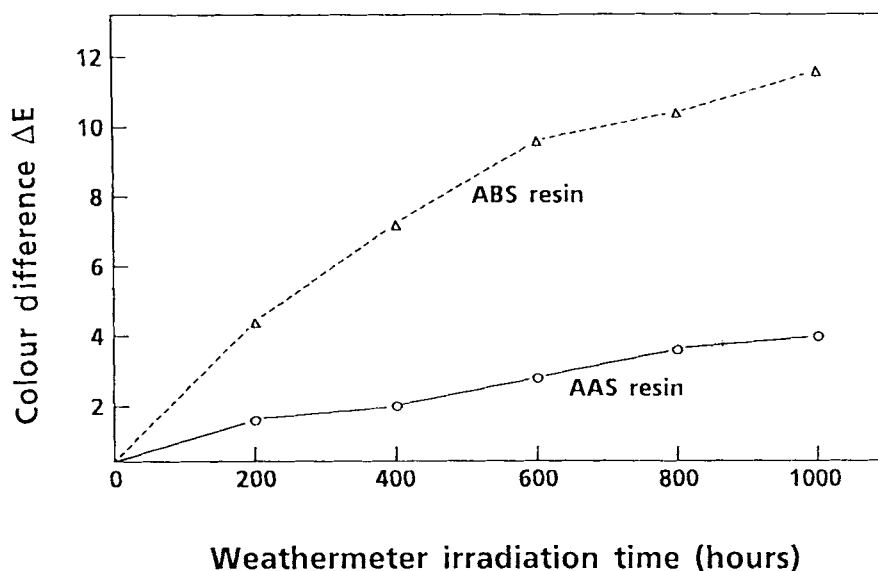


Figure 5 Weather resistance of AAS resin (change in color difference).

Izod impact values of resins produced by this method of polymerization are clearly higher than those produced from emulsion polymerization. Table V also shows that the values of main characteristics are close to those of ABS resin.

Weatherability of AAS Resin

The weatherability of resins produced using emulsion-suspension polymerization was measured. A xenon-type weathering apparatus (made by Toyo Rika Kogyo) was used in this measurement.

Atmosphere temperature apparatus inside: 40–50°C,

Panel temperature: 60–65°C,

Humidity inside apparatus 60–70% RH, and

Spray cycle (ON/OFF) 12 min/48 min.

The change in color was expressed by color difference ΔE , as determined by JIS Z 8730.

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

where ΔL : Change lightness, Δa : Change red-green, and Δb : Change yellow-blue.

Figure 4 shows the change of impact value and tensile strength with exposure to the weathering apparatus. The figure shows that the decrease of both

properties of the AAS resin is clearly smaller than that of ABS resin. The change of color with exposure to the weathering apparatus is shown in Figure 5, which shows that the AAS resin resists degradation. Clearly, the AAS resin developed had good weatherability.

CONCLUSIONS

Development of AAS resin with good weatherability was investigated. The following conclusions were drawn:

1. By copolymerizing dicyclopentenyl-methacrylate (DCP-MA, 3%) with butyl acrylate, graft sites were introduced into the rubber that permitted the production of a crosslinked acrylic rubber.
2. Following the development of the process for graft copolymerizing styrene and acrylonitrile onto this rubber, an emulsion-suspension polymerization method was developed in which the emulsion polymerization stage changed to suspension polymerization. By this method of preparation, the size of rubber particles was enlarged by growth. The result was a graft copolymerization type of resin with high strength and impact resistance. This method was also useful industrially, be-

cause the resin can be separated from the water phase without coagulation.

3. The AAS resin obtained in this study had much better weatherability than ABS resin, and exhibited strengths equal to ABS resin.

REFERENCES

1. P. K. Kelleher, *J. Appl. Polym. Sci.*, **10**, 843 (1966).
2. E. Zahn, *Appl. Polym. Symp.*, **11**, 222 (1967).
3. Monsanto Chemical Co., U.S. Patent 3,118,855 (1964).
4. S. M. McDougle, *SPE Journal*, **22**, 12, 31 (1966).
5. C. B. Bucknal and D. G. Street, *J. Appl. Polym. Sci.*, **12**, 1311 (1968).
6. J. Shimada and K. Kabuki, *J. Appl. Polym. Sci.*, **12**, 655 (1968).
7. J. Shimada and K. Kabuki, *J. Appl. Polym. Sci.*, **12**, 671 (1968).
8. K. Kato, *Polym. Lett.*, **4**, 35 (1966).
9. K. Kato, *Polym. Eng. Sci.*, **7**, 38 (1967).
10. T. Hamazaki, *J. Appl. Polym. Sci.*, **21**, 1569 (1977).

Accepted January 29, 1992