Acrylonitrile–Styrene Copolymer Grafted onto Ethylene–Propylene–Diene Terpolymer

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Synopsis

The two-phase structure of the acrylonitrile–styrene copolymer grafted onto ethylene–propylene–diene terpolymer (EPDM) was investigated using an electron microscope. It was found that the microstructure depends on the solvent system for graft copolymerization, separation of the graft copolymer, and the processing procedure. The graft EPDM phase forms the discontinuous phase in chlorobenzene and in the toluene–ethyl acetate mixed solvent, whereas it is the continuous phase in the hexane–ethyl acetate mixed solvent. The phase inversion of the rubber phase in the case of the latter is carried out partially in the separation procedure and completely in the processing procedure.

INTRODUCTION

It is generally known that EPDM is superior in weather resistivity and thermal stability because of its lower residual unsaturated content. The application of EPDM to plastics was predicted to lead to new material having interesting physical properties. Acrylonitrile–styrene copolymer grafted onto butadiene (ABS), because of its balance of mechanical properties and processability, is a very popular, high-impact rubber-modified plastic. One serious deficiency of this material, however, is that it exhibits poor aging characteristics when exposed to outdoor conditions. Thus, intensive studies were carried out to improve the aging properties, aimed at producing a good-weathering ABS-type plastic. One such work centered around the use of an EPDM rubber in place of the polybutadiene or SBR rubber of ABS.

The varying polymerization process was studied to synthesize the acrylonitrile–styrene graft EPDM (AES). The solution-polymerization method was selected in view of the balanced qualities on the physical properties of AES resins.

It was most important to fix the solvent system because the solvent was the influential parameter on the physical properties of AES resins. As a consequence, mixed-solvent systems which comprise the aromatic hydrocarbon and the polar solvent, or the aliphatic hydrocarbon and the polar solvent, were developed for the solution polymerization of AES resins.

While developing the solvent system, interesting results were obtained concerning the microstructure of AES resins comprising a two-phase system of grafted EPDM and styrene–acrylonitrile copolymer (SAN). An objective of this article is to provide the microstructure of AES resins affected by the solvent system, a separation procedure for a graft copolymer, and a processing procedure.

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EXPERIMENTAL

EPDM, acrylonitrile, and styrene were supplied by Sumitomo Chemical Co. Solvents and benzoyl peroxide (Wako) were received at reagent grade, except for toluene, ethylene dichloride, and methanol, which were supplied by Sumitomo.

SAN was supplied by Sumitomo Naugatuck Co. in the form of kralastic (acrylonitrile content: 27.5 wt %; $[\eta]$ in methyl ethyl ketone at 25°C: 0.53).

Characteristics of the supplied EPDM for graft copolymerization are shown in Table I.

Solubility Test of EPDM or SAN in Organic Solvents

A solvent was added to the polymer in an amount ten times the weight of the latter and the mixture was allowed to stand for 24 hr. After the whole system had become homogeneous, or the degree of swelling of the polymer was 200% or more even if the system was homogeneous, the system was judged to be dissolved.

Acrylonitrile–Styrene Graft Copolymerization on EPDM[1–4]

In α g of hydrocarbon solvent, placed in a 2-liter separable flask provided with a Dimroth condenser, a thermometer, a glass tube for bubbling a gas, a Hopkins cooler, and a stirrer with low-turbine-type blades, 45 g of EPDM were dissolved throughly. Added to the solution in the flask were 292.5 g of styrene, 97.5 g of acrylonitrile diluted with 50 g of a hydrocarbon solvent, and 3.9 g of benzoyl peroxide diluted with 50 g of hydrocarbon solvent. While rotating the stirrer at 600 rpm, polymerization was allowed to proceed under an atmosphere of argon at 70°C. When conversion reached 15%, β g of a polar solvent was added dropwise and the reaction was continued until conversion reached 80% or higher. After completion of the reaction, the reaction mixture was poured into methanol or was gradually vaporized at room temperature to separate the graft copolymer. The separated copolymer was dried at reduced pressure at 110°C for 3 hr, in the form of a cast film or powder.

TABLE I
Characteristics of Supplied EPDM[a]

	ML_{1+4}^{100}	C_3, wt %	I_2V	$[\eta]$, dl/g	Third component
EPDM B-238	52	30.2	18.1	1.38	ENB
EPDM F-113	75	44	16	—	ENB

[a] ENB: ethylidenenorbornene, ML_{1+4}^{100}, Mooney viscosity, C_3, propylene content, I_2V, iodine value. Intrinsic viscosity was measured in xylene at 70°C.

Processing Procedure for Graft Copolymers[1–4]

Graft copolymers were mixed on a 7-in. $\phi \times$ 16-in. roll mill at 170°C for 10 min and pressed at 200°C for 10 min to prepare a sheet.

Microstructure of Graft Copolymers

A Hitachi HV11E transmission electron microscope was used to determine the microstructure. The osmium tetroxide procedure[5] was adapted to make it possible to cut ultrathin sections, and to obtain electron micrographs with excellent contrast and definition. The sample used to prepare specimens to determine the microstructure is shown in Table II.

RESULTS

The results of the solubility test in the varying organic solvents are given in Table III. While EPDM is soluble in a hydrocarbon solvent, SAN is soluble in a polar solvent such as group IV. This behavior is reasonably understood in terms of the solubility parameter. It should be noted that SAN swells in the aromatic solvent of group II, without reaching an absolute solubilizing state.

Electron micrographs of AES samples, obtained by the varying after-treatment procedures as a function of the organic solvents for copolymerization, are summarized in Figures 1–3. The effect of the mixing ratio of a polar solvent content to an aliphatic hydrocarbon solvent content on the phase separation is illustrated in Figure 4.

All electron micrographs of sections are positives, where the osmium-stained rubber phase appears dark against the brighter SAN resin matrix. It is observed that the size of the rubber phase isolated in the resin matrix as compared to the samples copolymerized in chlorobenzene and a mixed solvent of toluene and ethyl acetate is approximately 0.1 μm, independent of after-treatment procedure, as shown in Figures 1 and 2. On the other hand, the electron micrographs of AES samples, copolymerized in a mixed solvent of hexane and ethylacetate, are notable for indicating the absolutely different patterns in a cast film, and for forming a continuous phase of rubber and a discontinuous phase of SAN plastics. But AES samples treated by methanol precipitation and a roll-mill processing procedure give the electron micrographs of an isolated rubber phase in the SAN resin matrix through phase inversion (Fig. 3).

The state of the phase separation of a cast film is shown as a function of ratio of the ethyl acetate content to the hexane content in Figure 4. The rubber phase forms a continuous phase comprising the network structure in the ratio of hexane/ethyl acetate = 1:1. It forms a continuous and discontinuous phases comprising the isolated rubber phase, including the numerous resin particles in the case of hexane/ethyl acetate = 4:6. It is noted that the absolute phase inversion is not yet observed in hexane/ethyl acetate = 2:8, although the isolation of the rubber phase in the resin matrix definitely appears with increasing ethylacetate content in the system.

TABLE II
Polymerization Conditions

	Hydrocarbon solvent, α + 100 g	Polar solvent, βg	EPDM	Time, hr	Conversion, %	Separation procedure[a]
ASE-1336	chlorobenzene 1200	0	F-113	19	86.0	MeOH or cast
AES-1302	toluene 600	ethyl acetate 600	B-238	25	86.4	MeOH or cast
AES-1322	hexane 600	ethyl acetate 600	F-113	15	84.5	MeOH or cast
AES-1401	hexane 480	ethyl acetate 720	F-113	20	76.6	MeOH or cast
AES-1403	hexane 240	ethyl acetate 960	F-113	29	71.5	MeOH or cast

[a] MeOH, methanol precipitation; cast, vaporization of solvent at room temperature.

TABLE III
Solubility Test of EPDM and SAN

Group	Solvents	EPDM[a]	SAN[a]
I	tetrahydrofuran, chloroform	O	O
II	benzene, toluene, chlorobenzene	O	O
III	hexane, heptane	O	X
IV	ethylene dichloride, ethyl acetate, dioxane, acetone, methyl ethyl ketone, acetonitrile	X	O
V	methanol, ethanol	X	X

[a] O, solubilizing; X insolubilizing.

DISCUSSION

Rubber modification requires a two-phase system which must have some compatibility between the phases and an optimum distribution of the elastomer within the plastic matrix.   The physical properties of the rubber-modified plastics are significantly improved when grafted rubber is used as the discontinuous phase.

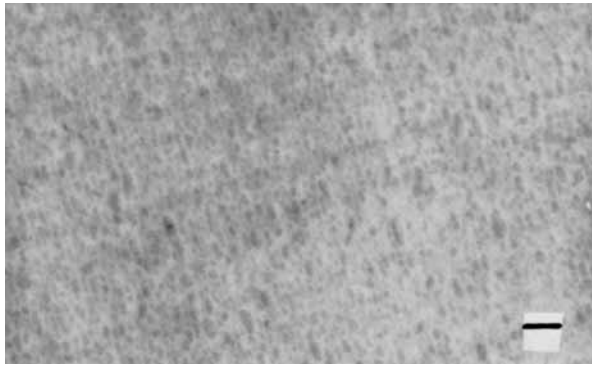It has been reported that the mixed aromatic–aliphatic solvents are an ex-
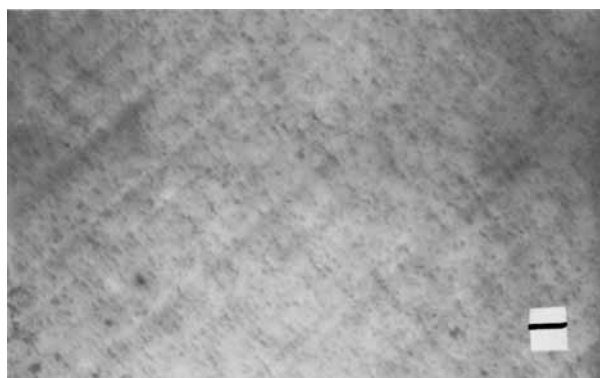
MeOH

Cast

Fig. 1. Electron micrograph of AES synthesized in toluene/ethyl acetate mixed solvent: AES-1302 (bar = 1 μm).
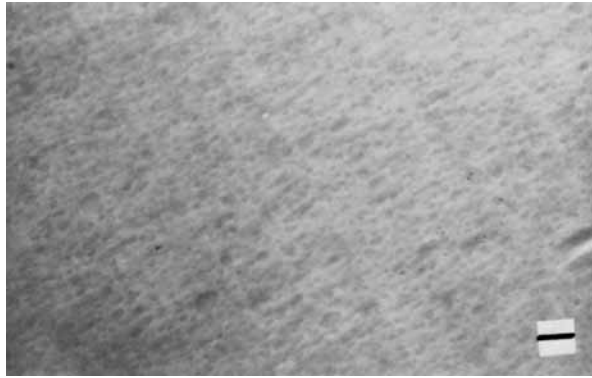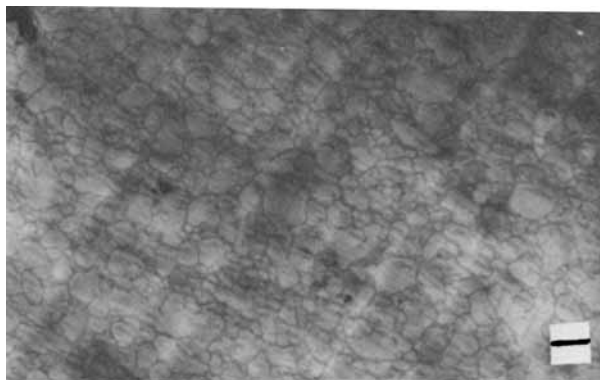
MeOH

Cast

Fig. 2. Electron micrograph of AES synthesized in chlorobenzene solvent: AES-1336 (bar = 1 μm).

tremely efficient medium in which to carry out the graft copolymerization of styrene and acrylonitrile onto EPDM.[6-8]

It is expected that a two-phase structure depends on the varying graft co-polymerization conditions, the separation procedures of a graft copolymer, and the processing procedures. The processing stability concerning the two-phase structure is one of the most important properties in evaluating the physical properties of rubber-modified plastics. A solvent system for graft copolymerization is extremely interesting from the standpoint of a two-phase structure.

Initially, EPDM dissolves in the solvents and monomers, leading to a completely homogeneous solution. After the reaction proceeds for a few minutes, the copolymerization mixture becomes turbid, and, in the space of a few additional minutes, it becomes opaque white, very similar in appearance to that of a normal emulsion polymerization. It is known as the polymeric oil in oil-(POO)-type polymerization. In this reaction, the styrene–acrylonitrile copolymer is evidently insolubilized in the form of monomeric droplets.
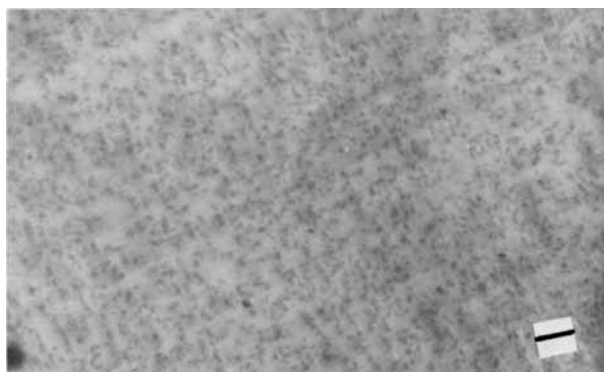
Early in the polymerization, EPDM dissolves in the solvent system as a continuous phase. It is extremely interesting to see whether the phase inversion could be carried out by way of the graft copolymerization process, the separation
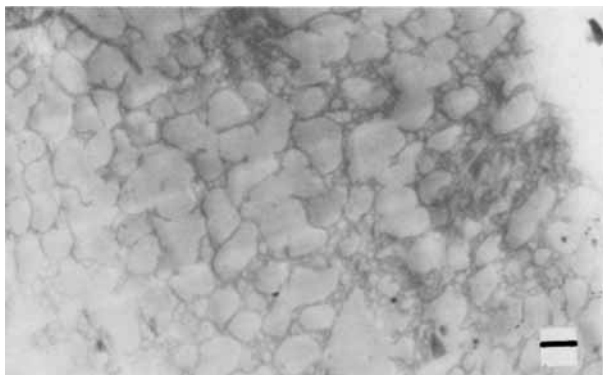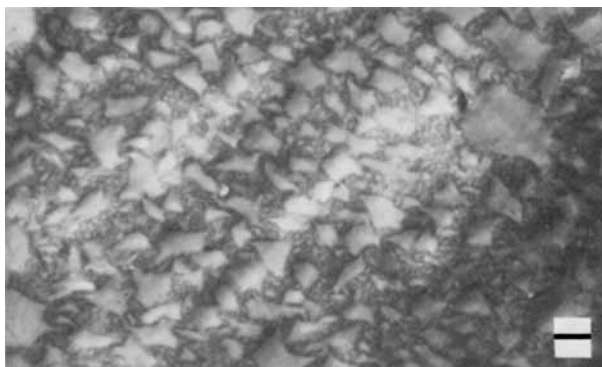
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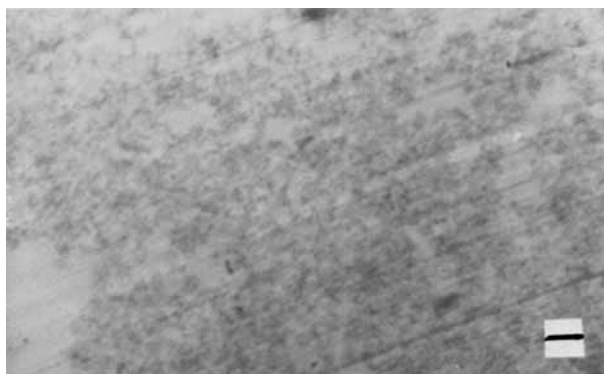
MeOH

Roll-Milling

Fig. 3. Electron micrograph of AES synthesized in hexane/ethyl acetate (1:1) mixed solvent: AES-1322 (bar = 1 μm).

Cast: AES-1401

Cast: AES-1403

Fig. 4. Electron micrograph of AES synthesized in hexane/ethyl acetate (4:6, 2:8) mixed solvent: AES-1401 and AES-1403 (bar = 1 μm).

procedure of a graft copolymer, or the processing procedure. It is clear that the phase inversion in chlorobenzene or toluene/ethylacetate is executed in the graft copolymerization process.

In contrast with Figures 1 and 2, Figure 3 shows that the phase inversion of the sample copolymerized in hexane/ethyl acetate is carried out partially in the methanol precipitation procedure and completely in the processing procedure. In whole graft copolymerization, most of the SAN compolymer precipitates from the hexane/ethyl acetate mixed solvent, whereas grafted EPDM is distributed homogeneously in the mixed solvent system. In the final product, the SAN copolymer must be the discontinuous phase and the grafted EPDM the contin- uous phase. This might be attributed to the differences in the solvation power between the SAN phase and the grafted EPDM phase in the hexane/ethyl acetate mixed solvent system.

The phase inversion of a cast film advances by increasing the ratio of ethyl acetate to hexane, while it is not enough to reach the complete phase inversion in hexane/ethylacetate = 2:8. The methanol precipitation procedure is under- stood to accelerate the phase inversion in the hexane/ethyl acetate mixed-solvent system. This could be due to the differences in the phase separation effect of

methanol against the SAN phase and the grafted EPDM phase.   The rubber phase is absolutely isolated in the SAN plastics matrix, being the discontinuous phase of about 0.1 μm in size owing to the processing procedure, and because of mechanical shear stress and the softening effect at high temperature.

CONCLUSIONS

The two-phase structure of the AES resins was found to depend on the graft copolymerization solvent system, the separation procedure of the graft copolymer, and the processing procedure.   The phase inversion of the graft EPDM (initially the continuous phase but finally the discontinuous phase) was carried out by graft copolymerization, in the case of chlorobenzene and toluene:ethyl acetate.   The rubber phase of AES obtained in hexane/ethylacetate forms the continuous phase, while phase inversion is done partially in the methanol precipitation procedure and completely in the processing procedure.

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