Studies on Heterogeneous Polymeric Systems.
II.   Polyblends Containing Saturated Rubbers

MASSIMO BAER, *Monsanto Co., Hydrocarbons and Polymers Division, Springfield, Massachusetts 01051*

Synopsis

Saturated rubbers composed of ethylene–propylene or ethylene–vinyl acetate copolymers and terpolymers were used in the mass polymerization of high-impact styrene or styrene–acrylonitrile polyblends.   Conventional polymerization procedures lead to blends of inferior mechanical properties.   The cause for the poor performance was traced to the inability of the rubber-phase particles to preserve the desired size and particularity during processing.
   Polymeric blends of saturated rubbers having mechanical properties comparable to those obtainable with polybutadiene rubbers are prepared by (1) controlling the rubber-particle size during prepolymerization and (2) preserving such size by crosslinking and grafting of the rubber following phase inversion.   Extensive crosslinking of the rubber in the final blend must take place prior to processing to resist rubber particle deformation and disintegration during mechanical working.   Rubber vulcanization is realized by the presence of peroxides in the final stages of polymerization; pendant unsaturation in the rubber is also needed or helpful.   The reactivity and number of unsaturated groups in the rubber must be controlled to avoid excessive grafting prior to phase inversion and to permit efficient crosslinking following phase inversion.

INTRODUCTION

The poor weathering resistance of high-impact polystyrene and ABS blends, resulting from photo-oxidative attack on the unsaturated rubbers, greatly limits the outdoor use of these blends.   High-impact polystyrene (PS) or styrene–acrylonitrile (SAN) blends containing saturated rubbers have, therefore, become of interest because of their improved weathering resistance.

Polystyrene blends containing saturated rubbers consisting of copolymers or terpolymers of ethylene and propylene have been reported in the literature.[1–4]   These blends, however, are found to have mechanical properties greatly inferior to those obtained with butadiene rubbers.

The purpose of our study was to understand and correct the cause for the inefficient reinforcing action of saturated rubbers.

EXPERIMENTAL

Materials Used

Ethylene–Propylene Rubber Copolymer (EPR).   Enjay 404 of about 43E/57P composition by weight and of 2.1 dl/g intrinsic viscosity at 25°C

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in toluene was used. Hydroperoxidation of EPR was accomplished by the method of Beati et al.[5,6] by passing oxygen and *tert*-butyl hydroperoxide vapors at 90°C on 0.015-in. calendered films of the rubber. Peroxidation was accompanied by drastic reduction in intrinsic viscosity of the rubber without gel formation.

Ethylene–Propylene–Diene Monomer (EPDM). du Pont's Nordel 1040 of intrinsic viscosity 1.68 in toluene at 25°C was used.

Ethylene–Vinyl Acetate Copolymer (EVA). Bayer's Levaprene 5020 containing a weight ratio of 55E/45VA and of 1.24 dl/g intrinsic viscosity in toluene at 25°C was used. In order to introduce pendant unsaturation for purpose of grafting and crosslinking, EVA was chemically modified by acyl interchange between VA and acrylic acid. Ester interchange was conducted by dissolving 120 g EVA in 400 ml toluene and by reacting with 250 g acrylic acid in the presence of 36 ml 12.5N aqueous H_2SO_4 and 0.15 g hydroquinone as polymerization inhibitor. The reaction was carried out by stirring at 50–60°C for about 4 hr. The solution was diluted with MEK and the polymer was recovered by precipitation into methanol. After careful purification, the polymer was analyzed by saponification followed by chromatographic determination of acrylic acid, and was found to contain 0.11% acrylic acid ester by weight and to have an intrinsic viscosity in toluene at 25°C of 1.02 dl/g. Longer reaction times or dissolution of EVA in acrylic acid and reaction in the absence of solvents resulted in modified EVA of higher vinyl acrylate content.

PREPARATION OF BLENDS BY MASS POLYMERIZATION

Initial Polymerization (Prepolymerization)

Eight parts rubber are dissolved in 92 parts styrene in a glass reactor fitted with an agitator, a reflux condenser, and a nitrogen inlet tube. The batch is charged with 0.035% *tert*-butyl peracetate (TBPA) and 0.025% to 0.05% *tert*-dodecyl mercaptan (TDDM), and polymerization is conducted with agitation at 95–105°C.

The course of the polymerization reaction was followed by determining conversion by refractive index and by studying morphologic changes by phase-contrast microscopy. Phase inversion normally occurred after 2–3 hr (at about 15% conversion) with the rubber phase becoming the dispersed phase. Polymerization was generally continued for 1–2 hr after completion of phase inversion to reach about 25% conversion. At the end of this time (prior to suspension polymerization), di-*tert*-butyl-peroxide (DTBP), 0.2% to 0.43%, was added to the batch.

For the mass polymerization of rubbers dissolved in styrene and acrylonitrile (70S/30AN), similar procedures were used, except for the use of a pressure reactor to prevent distillation of AN during polymerization at 95°C. Terpinolene (0.085%) was used as the chain-transfer agent together with 0.01% to 0.03% TBPA and 0.04% DTBP as initiators. A post-

addition of 0.1% to 0.4% DTBP was made at the end of the prepolymerization cycle.

When using EPDM rubbers in S/AN mass polymerization, it was found necessary (in order to avoid precipitation of the rubber) to dissolve the rubber in styrene and to add to this solution at 80°C an equal weight of AN and heptane. The batch was heated to 95°C and maintained at this temperature for 3.5 hr.

Suspension Polymerization

The prepolymerization syrup is charged to a pressure reactor together with water, suspending agents, and surfactants. Polymerization is conducted by heating with good agitation to prevent agglomeration of the suspension. The polymerization cycles used for suspension polymerization are reported in the tables.

At the end of the heating cycle, the suspension is cooled to 25°C while good agitation is maintained. The resulting suspension beads are washed with water and dried.

Processing and Molding

The suspension beads containing 8% rubber were dry-blended with 0.3% di-*tert*-butyl paracresol (Ionol) and 0.2% zinc stearate, extruded at 220°C, and compression molded into a flat sheet. Tensile and tensile-impact test specimens were prepared by cutting the sheet into strips which were placed in a multiple-cavity flash mold die. Compression molding was conducted at 210°C.

Analytic Procedures

Refer to part I.[7]

DISCUSSION

Polyblends prepared by polymerizing a monomer or a mixture of monomers in the presence of a saturated rubber or a hydroperoxidized EPR rubber are described in the technical or patent literature. However, the resulting blends display poor mechanical properties and make very inefficient use of the rubber as shown by their inferior toughness, low elongation, and small area under a stress–strain curve.

Polyblends of saturated rubbers prepared by conventional mass polymerization can be made to contain rubber-phase particles of the desired size and discreteness at the end of the polymerization cycle (Table I). If the blends so obtained are not exposed to mechanical working, it is found that they are capable of displaying toughness and elongation in tension. However, when exposed to the high-intensity mixing and heating encountered in conventional processing operations, it is found that the mechanical properties of the blends suffer a very large decrease in impact strength and elongation in tension.

TABLE I

Mass-Polymerization Blends of Polystyrene and EPR Rubbers (8% Rubber in Blends)

Rubber used	Intrinsic viscosity of rubber[a]	Time to phase inversion (hr)	Particle-size diameter of rubber phase, μ		Rubber graft		Blend properties[d]	
			In suspension bead[b]	After processing	D.G.[c]	% Gel	% Elong. at fail	Tensile impact, ft lb/in.[2]
EPR (Enjay 404)	2.10	>6	>100	0.5-1	44	~15	5	7.1
EPR-1 hydroperoxidized	1.70	<1	0.5-3	—	—	<10	4	3.5
EPR-2 hydroperoxidized	1.38	<1	1-10	≪1	60	<10	2	3.2
90% EPR / 10% EPR-2	—	0.5	1.5-12	0.5-2	61	—	—	4.0

[a] Intrinsic viscosity in toluene at 25°C.

[b] Suspension polymerization cycle: 1 hr at 110°C, 2 hr at 140°C, and 1 hr at 155°C.

[c] Parts of PS chemically attached to 100 parts rubber.

[d] Properties after extrusion and compression molding.

The reason for this loss in properties on processing can be traced to the inability of the rubber-phase particles to preserve the desired size and particularly as shown in Table I and Figure 1. The rubber particles not being crosslinked, or being insufficiently crosslinked, are broken up, often into submicron particles, and are deformed during processing. They also
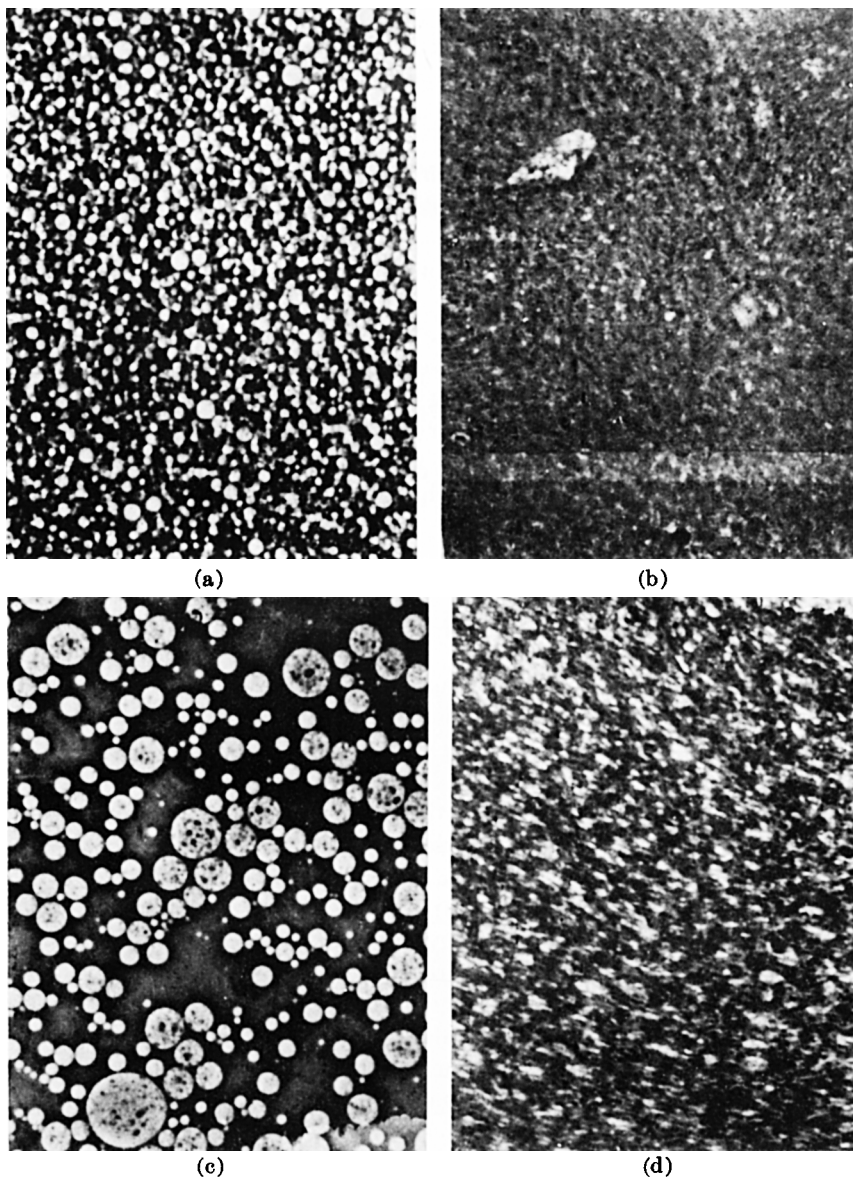

(a)   (b)

(c)   (d)

Fig. 1. Internal structure of blends at end of prepolymerization and after extrusion (640×): (a) prepolymer of EVA in SAN; (b) EVA in SAN after blend extrusion; (c) prepolymer of EPR in PS; (d) EPR in PS after blend extrusion.

appear to flatten out, perhaps in the form of thin lamellae, with no well-defined shape and structure.

In order to obtain blends capable of developing good toughness and capable of preserving it on processing, it is necessary that the bulk of the rubber and rubber–graft in the final blend be sufficiently tightly cross-linked to resist disintegration and deformation.

Grafting of the rubber backbone with branches soluble in the matrix is necessary to impart sufficient adhesion between the dispersed rubber phase and the rigid matrix. The grafted branches also function as a protective interlayer discouraging agglomeration or disintegration of rubber particles during processing.

When soluble butadiene rubbers are used in mass polymerization with styrene or styrene–acrylonitrile, it is found that the rubber is crosslinked in the final stages of polymerization, and that grafting efficiency can be made very high.[7] This is the result of the high unsaturation of the rubbers and the fair reactivity of macroradicals formed by either alpha-hydrogen abstraction or by addition across the double bonds. The particle size of the rubber phase obtained after phase inversion is fully preserved because of this high grafting and crosslinking efficiency in the final stages of poly-merization. With butadiene rubber blends, therefore, one is not faced with the problem of fixing and preserving the desired rubber-phase mor-phology in order to obtain good mechanical properties. This, however, is not the case with saturated rubbers.

Grafting and Crosslinking of the Saturated Rubbers by Mass Polymerization

Essentially gel-free rubbers were used in our mass-suspension process in order to permit their complete solution in the monomers to be polymerized. It was essential for the rubber to remain soluble during the initial stages of mass polymerization to permit phase inversion to occur without diffi-culty. Crosslinking of the rubber, therefore, must take place after phase inversion when a well-defined dispersed rubber phase has formed.

The concentration and reactivity of the pendant unsaturation in the rubber markedly influence the control of the desired grafting and cross-linking reactions and the morphology of the resulting blend. The double bonds must be of sufficiently low reactivity to avoid excessive grafting prior to phase inversion. High degree of rubber grafting, prior to phase inversion, can lead to excessively small rubber-phase particle size because of the strong peptizing effects of the rubber graft. The double bonds in the rubber, however, must be sufficiently reactive and numerous to readily crosslink the rubber after phase inversion and prior to processing, so as to fix and preserve the desired rubber size.

Grafting and crosslinking reactions are not exclusively determined by reactivity and concentration of available double bonds. They are also significantly affected by selection of type of initiators and their time of

TABLE II

Polyblends Containing a Polystyrene Matrix and EPDM Rubbers (8% EPDM by Weight)[a]

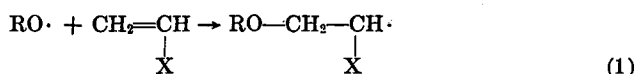| Blend	Initial polymerization[b] % DTBP Initial	% DTBP Post-addition	% TDDM	Suspension cycle[c]	Rubber particle-size[d] diameter Initial	Extrudate	Rubber graft[e] D.G.	% Gel	Blend properties Tensile, psi Yield	Fail	% Elongation at fail	Tensile Impact[f] ft·lb/in.²
1	0.1	—	0.05	1	30–200	1–4	69	—	3940	3140	6	14
2	0.1	—	0.05	1	20–80	0.5–3	82	19	3600	2900	3	32
3	0.1	—	0.025	3	5–40	1–30	95	30	4300	2980	10	26
4	—	0.2	0.025	3	30–100	5–40	104	59	3460	3240	46	64
5	—	0.2	—	3	2–15	4–20	108	66	3640	3200	43	47
6	—	0.2	0.025	3	—	10	90	72	2900	2250	19	31
7	0.1	0.36	0.025	3	13	13	103	90	2560	2600	34	55
High-impact PS (6.5% PBD)					1–6	1–6	170	98	2700	3200	45	53

[a] EPDM = ethylene–propylene–diene monomer.
[b] DTBP = di-tert-butyl peroxide; TDDM = tert-dodecyl mercaptan; postaddition = addition at end of prepolymerization cycle.
[c] Suspension cycle 1: 1 hr at 110°C; 2 hr at 140°C; 1 hr at 155°C. Cycle 2: 1 hr at 120°C; 2 hr at 140°C; 3 hr at 155°C.
[d] Initial = particle size at end of prepolymerization cycle; extrudate = particle size in extruded ribbon.
[e] DG = degree of grafting = parts of PS chemically combined with 100 parts EPDM in final blend.
[f] ASTM D-1822.

addition, reactivity of the monomers, rubber concentration, polymerization cycle, and chemical composition of the rubber substrate.
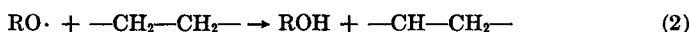
The final extent of grafting is found (Table II) to be moderately increased by increasing concentrations of high-temperature initiators (DTBP). The crosslinking reaction, however, is greatly enhanced by increasing DTBP concentration and by longer heating cycles at higher temperatures during suspension polymerization.

In the competitive reactions of the catalyst radical $RO\cdot$ for (1) addition to monomer, (2) hydrogen abstraction from the rubber backbone, and (3) addition to pendant unsaturation in the rubber, reactions (2) and (3), leading to grafting and crosslinking, become more favorable as the concentration of the monomer decreases with increasing conversion in the later stages of suspension polymerization. Probability of attack on rubber backbone and on rubber unsaturation increases greatly as the population of double bonds of the more mobile and reactive monomer decreases with conversion. High temperatures may also favor these reactions because of the larger activation energy of hydrogen abstraction by a radical compared to monomer addition:
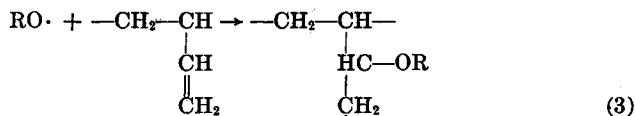
Propagation:
$$RO\cdot + CH_2{=}CH \rightarrow RO{-}CH_2{-}CH\cdot$$
$$\quad\quad\quad\quad\quad\;\; |\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad X\quad\quad\quad\quad\quad\quad X \quad\quad\quad\quad (1)$$

Hydrogen abstraction:
$$RO\cdot + {-}CH_2{-}CH_2{-} \rightarrow ROH + {-}\overset{\cdot}{C}H{-}CH_2{-} \quad\quad (2)$$

Addition to pendant unsaturation:
$$RO\cdot + {-}CH_2{-}CH \rightarrow {-}CH_2{-}CH{-}$$
$$\quad\quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad CH \quad\quad\quad\quad\quad HC{-}OR$$
$$\quad\quad\quad\quad\quad\quad \| \quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad\quad\quad CH_2 \quad\quad\quad\quad\quad \overset{\cdot}{C}H_2 \quad\quad (3)$$

Blends of Polystyrene and EPR Rubbers

The EPR rubbers in mass-polymerized styrene blends gave a very retarded and poorly defined phase inversion. The high intrinsic viscosity of the rubbers resulted in a high rubber solution viscosity in styrene monomer and was responsible for delayed phase inversion and formation of large rubber-phase particle size during prepolymerization. The rubber-phase particles were readily disintegrated by mild processing conditions into submicron particles, yielding blends of poor toughness and low elongation (Fig. 1,c and d).

Grafting of styrene on EPR, investigated by Natta et al.,[1,2] resulted in blends in which the rubber graft was lightly crosslinked and had a high swelling index. The mechanical properties of the blends displayed only moderate toughness and very low ultimate elongation in tension.

Hydroperoxidation of EPR, as described by Beati et al.[5,6] for other saturated rubbers, results in the expected extensive rubber degradation.

As shown in Table I, hydroperoxidation of EPR results in a higher degree of grafting but in a lower gel content.

The observed degree of grafting of about 60 parts polystyrene per 100 parts rubber backbone would be expected to be sufficient to impart the necessary adhesion between matrix and rubber.   (This degree of grafting level is in fact found to be adequate with butadiene-rich rubbers.[9]) The degree of crosslinking of the rubber grafts in the final blend, however, is too low to preserve the integrity of the rubber particles on processing and results in blends of inferior properties because of excessively small rubber particle size.   Blends of only moderate toughness were also obtained by Natta et al.[1,2] by grafting styrene on hydroperoxidized polyolefin rubbers.

Hydroperoxidation of EPR is very effective in promoting fast phase inversion and in reducing rubber-particle size during prepolymerization. Even if only 10% of the rubber charged is composed of hydroperoxidized EPR, one observes a rapid phase inversion and a rubber-phase particle size in the desirable range of 2–12 microns.   The observed effects are probably the result of more efficient formation of grafts, prior to phase inversion, through hydroperoxide decomposition.   The grafted rubber thus behaves, as expected, as a dispersing agent for the rubber phase by collecting at the interphase.

Blends of EPDM Rubbers

The EPDM rubbers used were soluble in styrene monomer but were precipitated out of solution by addition of acrylonitrile, even when this addition was made stepwise at 80–85°C

Heptane (21.6% by weight based on the total weight of the charge) was used to prevent precipitation from solution when a 70S/30AN monomer charge was used.   The function of the hydrocarbon diluent is to reduce the solubility parameter of S/AN mixed monomers and to more closely match it to that of EPDM.   In the absence of heptane as a diluent, the resulting SAN blends had inferior properties.

With PS blends (Table II and Fig. 2,a,b, and c), it is found that conditions leading to more extensive crosslinking and grafting of the rubber in the final blend lead to concurrent better preservation of morphology and improved mechanical properties.   By crosslinking the rubber after phase inversion, by means of peroxides at a sufficiently high temperature, it becomes possible to prevent extensive disintegration and deformation of the rubber phase on processing.   Blends are thus obtained with tensile and toughness properties comparable to those obtainable with butadiene rubbers.

With an SAN blend (Table III), the same trend of improving mechanical properties with more extensive crosslinking appears to apply.   Because of the presence of heptane in the charge, the rubber-phase particle size obtained at the end of prepolymerization is never preserved in the final blend after processing.   Heptane, being a good solvent for the rubber

TABLE III
Polyblends Containing a 70 S/30 an Matrix and EPDM Rubbers (8% EPDM by Weight)[a]

Blend[b]	Postaddition,[c] % DTBP	Rubber-phase particle size diameter, μ		Rubber graft		Tensile, psi		% Elongation Fail	Tensile impact, ft lb/in.[2]
		Initial	Extrudate	D.G.	% Gel	Yield	Fail		
1	0.08	2–10	~1	54	20	—	—	—	38
2	0.16	2–7	~1	43	32	5600	5100	26	40
3	0.16	2–7	~1	45	76	5970	6030	19	49
4	0.36	2–7	~1	61	59	5400	5010	33	61
ABS (8% PBD)		~1	~1	60	97	6700	5770	28	45

[a] See Table II for abbreviations and column headings.
[b] All blends contain in the initial charge 0.01% TBPA, 0.04% DTBP, 0.085% terpinolene, and 21.6% heptane.
[c] At end of polymerization, 0.2% terpinolene and the tabulated % DTBP are added. The suspension polymerization cycle is 2 hrs at 130°C, 1 hr at 140°C, and 3 hr at 150°C.

TABLE IV

Polyblends Containing A 70S/30AN Matrix and EVA Rubber (8% EVA by Weight)[a]

Blend[b]	Postaddition,[c] % DTBP	Rubber-Phase particle size diameter, μ		Rubber graft		Tensile psi		% Elongation at Fail	Tensile impact, ft. lb/in.[2]
		Initial	Extrudate	D.G.[d]	% Gel	Yield	Fail		
1	0.16	1–20	<1–2	4	Very low	—	9200	7	15
2	0.36	1–6	1–6	—	—	7390	6450	14	38
3	0.36	—	1–20	30	78	8010	6050	20	49
4[e]	0.16	0.5–4	0.5–1.5	41	36	7400	6600	22	22
5[e]	0.40	0.5–2	1–4	20	76	7560	6660	20	—

[a] See Table II for abbreviations and column headings.
[b] All blends contain in the initial charge 0.01% TBPA, 0.04% DTBP, and 0.085% terpinolene.
[c] At the end of prepolymerization are added 0.2% terpinolene and the tabulated % DTBP. Suspension polymerization cycle is 2 hr at 130°C, 1 hr at 140°C, and 3 hr at 150°C.
[d] DMF is used as the solvent.
[e] EVA contains 0.11% acrylate ester.

and a nonsolvent for SAN, must concentrate in the rubber phase and leave a spongy and weak rubber structure on being expelled during drying and processing. The rubber particles, however, appear particulate rather than smeared, and the properties of the blends are similar to those obtained with a mass-polymerized ABS of equivalent rubber concentration.

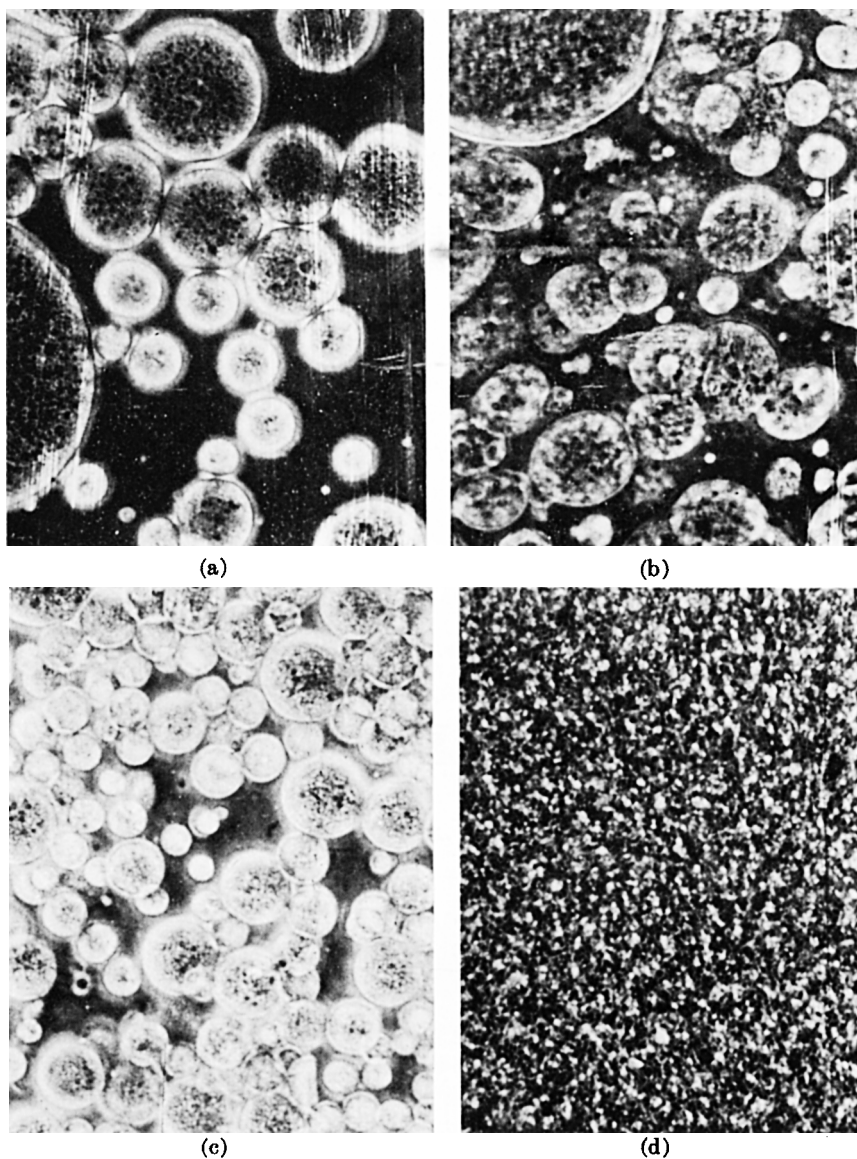The observed reduction in particle size (Fig. 2d) may not be damaging

(a)   (b)

(c)   (d)

Fig. 2. Internal structure of EPDM rubber blends (1280✕): (a) prepolymer in PS, and (b) after blend extrusion; (c) PS blend after extrusion; (d) SAN blend after extrusion (640✕).

to properties since with in SAN matrix a considerably smaller rubber particle size than with a polystyrene matrix can be tolerated, without damage to properties.

Blends of EVA and SAN (Table IV)

Since EVA (55E/45VA) rubber is soluble in S/AN mixed monomers, no diluents are required to keep the rubber in solution.

In the absence of sufficient rubber crosslinking and grafting in the final blend, the morphology obtained at the end of prepolymerization could not be preserved (Fig. 1,a and b), and poor blend properties were obtained.

Two approaches were used to enhance grafting and crosslinking of EVA: (1) relatively high peroxide concentrations in conjunction with
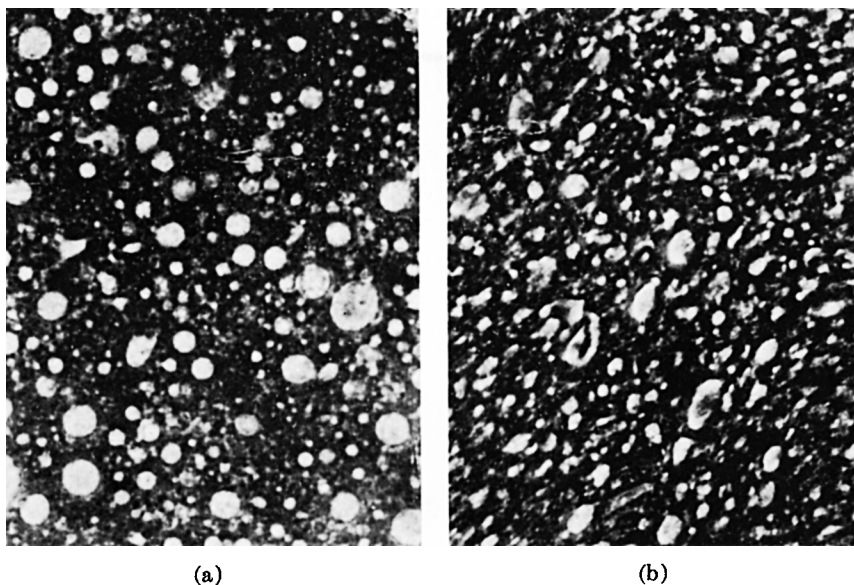

(a)   (b)

Fig. 3. Internal structure of EVA in SAN (640X): (a) at end of prepolymerization; (b) after blend extrusion.

high temperature in the finishing stages of polymerization and (2) introduction of pendant unsaturation in EVA.

Polyblends of good mechanical properties were obtained by approach (1). However, high peroxide concentration coupled with high temperatures caused poor color with SAN blends in the presence of EVA (carbonyl groups tend to induce color with AN polymers). Approach (2) permitted the use of more moderate peroxide concentrations and temperatures without sacrificing preservation of rubber particle size (Fig. 3, a and b). Blends of improved color are thus obtained without, however, any advantage in mechanical properties.

Attempts to use EVA rubbers of higher degree of unsaturation (0.6% acrylate ester) resulted in excessively high degrees of grafting and cross-

linking after inversion and in the final blends. More favorable results would be expected by using pendant unsaturation of lower reactivity than an acrylate.

The rather low grafting efficiency of EVA is somewhat surprising, since one would not predict it in consideration of (a) the greater lability of hydrogens in EVA compared to EPR,[8] which should favor hydrogen abstraction by initiator or polymeric radicals, and (b) the expected high reactivity of EVA macroradicals toward addition of styrene or acrylonitrile monomers.

References

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