Morphologic Changes on Processing of Polyblends of Saturated Rubber-Reinforced Plastics

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Synopsis

Laminar peeling is often observed on the injection-molded surface of the saturated rubber-modified plastics (EVASTAN), which are prepared by copolymerizing styrene and acrylonitrile in the presence of ethylene–vinylacetate copolymer (EVA). However, the delamination rarely occurs upon higher grafting and crosslinking EVASTAN with preactivated EVA, which has pendent unsaturation. The microstructure of these EVASTAN resins was observed by electron microscopy at the end of polymerization and after processing. It was found that the delamination is caused by the agglomeration and deformation of the EVA particles and is prevented by increasing the stability of the particles by grafting and crosslinking.

INTRODUCTION

Rubber-modified plastics such as ABS resin and high-impact polystyrene exhibit excellent impact resistance, while such plastics containing polybutadiene or butadiene copolymer have poor weathering property because of photo-oxidative attack on double bonds and have great limitations for outdoor uses.

It has been reported that plastics with saturated rubbers consisting of ethylene–vinylacetate copolymer (EVA), ethylene–propylene copolymer or terpolymer, and acrylate polymer improve weather resistance.[1-5] However, these saturated elastomer-modified plastics have inferior impact resistance compared with butadiene rubber-modified plastics, and especially show laminar peeling on the surface of injection moldings. The laminar peeling causes inferior appearance and poor mechanical property of the injection moldings.

For ABS resin, it has been reported[6] that the molding anisotropy of rubber particles is caused by the difference of the material flow inside the mold in the injection process. This phenomenon on the plastics at a two-phase system is very interesting.

The purpose of this study is to clarify the reason why laminar peeling takes place in the injection molding of saturated rubber-modified plastics composed of ethylene–vinylacetate/styrene–acrylonitrile blend (EVASTAN) prepared by copolymerizing styrene and acrylonitrile in the presence of EVA copolymer.

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EXPERIMENTAL

Materials

Ethylene–Vinyl Acetate Copolymer (EVA). EVA copolymers used in this work were UE634 (melt index, 3.6 g/10 min; VAc cont. 24 wt-%) and UE633 (melt index, 19 g/10 min; VAc cont., 19 wt-%), which were supplied by Toyo Soda Manufacturing Co., Ltd.

Preactivated EVA. In order to introduce pendent unsaturation for the purpose of increasing grafting, EVA was chemically modified by ester interchange with methyl methacrylate (MMA). Ester interchange was carried out by dissolving 60 g EVA in 630 g toluene and by reacting with 75 g MMA in the presence of 3.0 ml of 28 wt-% sodium methylate–methanol solution and 0.0075 g hydroquinone as the polymerization inhibitor. The reaction was carried out with agitation at 60°C for 1 hr. The polymer was obtained by precipitation into methanol and dried at room temperature in vacuo. The polymer was analyzed by iodine titration of methacrylic acid after hydrolysis by potassium hydroxide, and found to contain 0.9×10^{-4} mole methacrylic acid/g EVA.

Polymerization Procedure

Various EVASTAN resins were prepared by the following procedures.

Suspension Polymerization. In a 2-liter stainless-steel autoclave fitted with an agitator, 120 g EVA was dissolved in 360 g styrene and 120 g acrylonitrile. The batch was charged with 1.56 g tert-dodecyl mercaptan (t-DDM), 4.4 g benzoyl peroxide, and 1020 g of 0.5 wt-% poly(vinyl alcohol) ($\bar{P}$, 2400; degree of hydrolysis, 88%) aqueous solution, and polymerization was carried out with agitation at 89°C for 4 hr. The resulting polymer was washed with water and dried in vacuo.

Bulk-Suspension Polymerization. In a glass reactor with an agitator, a reflux condenser, and a nitrogen inlet tube, 45 g EVA or preactivated EVA was dissolved in 180 g styrene and 60 g acrylonitrile. The batch was charged with 0.6 g t-DDM and 0.6 g of tert-butyl peroxypivalate, and polymerization was carried out at 60°C. Bulk polymerization was continued for 2.2–2.4 hr. Phase inversion occurred after 1.5 hr (at about 15% conversion). Then, 510 g of the above-mentioned suspending agent aqueous solution was charged to obtain a suspension, and polymerization was continued at 60–75°C for 3–5.5 hr. The resulting polymers were washed with water and dried in vacuo.

Processing and Testing

One hundred parts of the EVASTAN resin were dry-blended with 0.5 parts alkylaryl phosphate, 0.5 parts barium stearate, 0.05 parts Ionol, and 0.5 parts hydrogenated custer oil. The dry-blended polymers were pelletized with a 40-mm-ϕ extruder (Ikegai Tekko Co., Ltd.) under the following conditions:

Position	Temperature
zone 1	170°C
zone 2	175°C
zone 3	185°C
die	180°C

The pellets were injected into a cup by a 10-oz injection machine (Yamashiro Seiki Co., Ltd.) under the following conditions:

Temperature, °C		Cycle time, sec	
zone 1	200	inject	5
zone 2	210	hold	30
nozzle	210		
mold	60	pressure	50 kg/cm²

Test specimens for the measurements of mechanical properties, such as tensile strength and Izod impact strength, were obtained by compression molding at 200°C after mill rolling at 180°C.

Degree of Grafting

The degree of grafting was obtained by alternate extraction in acetone and cyclohexane. Acetone is a solvent for acrylonitrile–styrene (AS) copolymer but a nonsolvent for EVA, and cyclohexane is a solvent for EVA but a nonsolvent for AS copolymer. The pellets after extrusion were extracted in acetone for one day with a Soxhlet extractor. The residue was dried in vacuo to constant weight. The residue was then extracted in cyclohexane for one day with the Soxhlet extractor. The residue was dried in vacuo. IR spectra show no existence of EVA in acetone-extracted solution nor of AS copolymer in cyclohexane-extracted solution. The degree of grafting is defined by two numbers. One is the value of the weight of grafted AS copolymer divided by the weight of total AS copolymer; the other is the value of the weight of nonextracted EVA divided by the weight of total EVA. It is suggested that the latter value indicates the ratio of grafted EVA plus crosslinked EVA to total EVA.

Electron Microscopy

The microstructure of the EVASTAN resins was observed at the end of polymerization and after each processing. Thin sections were cut from these samples and were dipped with 4 wt–% sodium hydroxide–methanol solution for three days at room temperature. After hydrolysis, the thin sections were washed thoroughly with water and stained with osmium tetroxide (usually 1 wt–% aqueous solution) vapor. Sections as thin as several hundred Å were cut from these on an ordinary rotary microtome and observed by the electron microscope of Akashi Seisakusho Co., Ltd. The heterogeneous structures could be observed as the phase of EVA was dyed to a deep black.

RESULTS AND DISCUSSION

The characteristics of the EVASTAN resins used in this work and the degree of laminar peeling of the injection moldings are presented in Table I. Strong delamination occurs in EVASTAN with nontreated EVA in both the suspension (polymer A) and the bulk-suspension procedure (polymer B). It occurs, however, occasionally only upon injection molding of the EVASTAN resin with activated EVA (polymer C). Polymer C is more highly grafted than polymers A and B. However, the fact that polymer B contains 20% nonextracted EVA in spite of the low grafting efficiency of AS copolymer shows that even polymer B

TABLE I
Blend Properties and Degree of Delamination on Injection Molding

| Polymer no. | Polymerization procedure | Rubber | Rubber content, wt-% | Degree of grafting[a] | | Degree of delam- ination[b] | Mechanical properties[c] | | | | |
				Grafted AS, total AS %	Grafted and crosslinked EVA, total EVA %		Tensile strength,[d] kg/cm²	Izod impact strength,[e] kg·cm/cm²	Elonga- tion,[d] %	Modulus,[f] 10⁶ kg/cm²
A	suspension	UE634	20.1	3.7	30	strong	295	23	42	1.4
B	bulk suspension	UE634	16.7	0.3	20	strong	330	5	45	1.5
C	bulk suspension	preactivated UE633	16.2	8.8	89	occasional	310	11	30	1.7

[a] Obtained by extrusion molding.
[b] Obtained by injection molding.
[c] Obtained by compression molding.
[d] ASTM D 638.
[e] ASTM D 256.
[f] ASTM D 747.
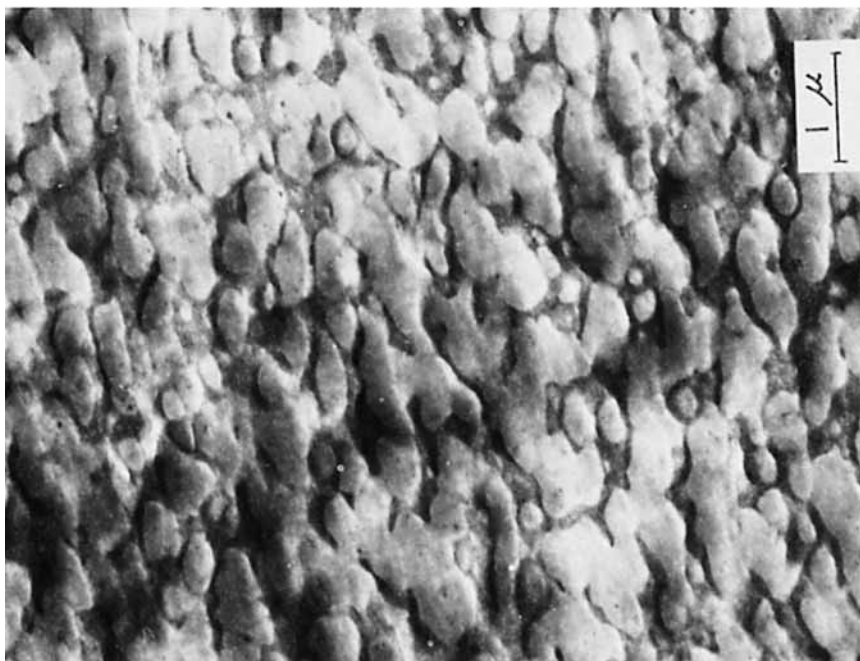
Fig. 1 (continued)
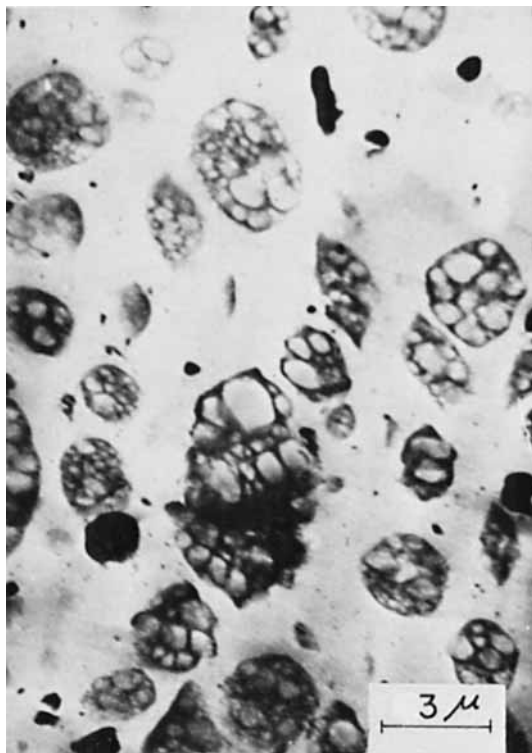
(c)

Fig. 1. The microstructures of EVASTAN's at the end of polymerization (no processing):
(a) polymer A; (b) polymer B; (c) polymer C.

contains fairly crosslinked EVA. So, it is expected that polymer C, which con-
tains 89% nonextracted EVA, is more highly crosslinked than polymers A and B.
These results suggest that there is close correlation between the laminar peeling
and grafting and crosslinking.

Figure 1 shows the microstructure of the samples at the end of polymerization
without any exposure to mechanical work. In the bulk-suspension procedure
(1B and 1C), rubber particles are dispersed completely in acrylonitrile–styrene
(AS) copolymer, but an opposite phase structure is shown in the suspension
procedure (1A). The microstructure of the product in the suspension procedure
indicates lack of phase inversion during the polymerization, which is expected in
the bulk polymerization procedure without agitation.[7] This suggests that the
rubber of suspended particles of polymer solution in the suspension procedure re-
ceived little shear stress.

The microstructure of sample 1C with activated EVA is apparently different
from the one with EVA in the bulk-suspension procedure. In sample 1C, the
rubber particles involve large amounts of occluded AS copolymer, and the
particle size is larger than 1B. It is expected that these phenomena are due to
the increase in compatibility between EVA and AS copolymer by higher grafting.

Figure 2 shows the microstructure of extrusion-molded EVASTAN's. Photo-
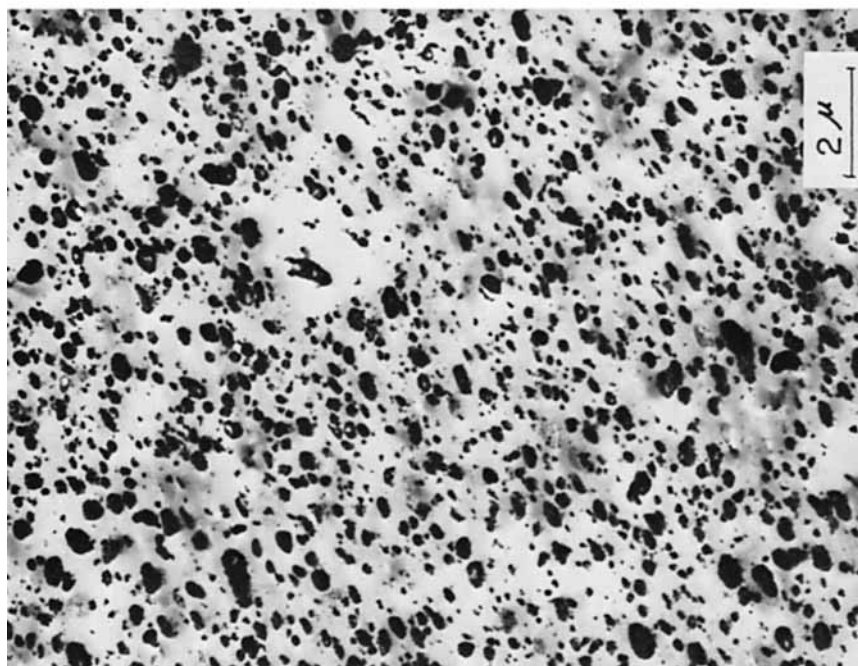graphs of samples 2A and 2B are similar, whereas samples 1A and 1B of Figure 1
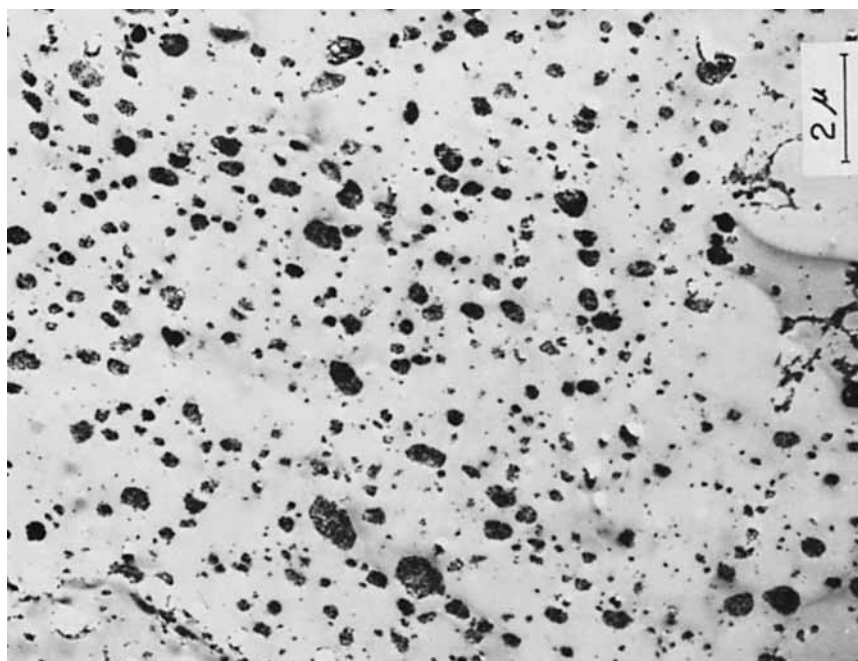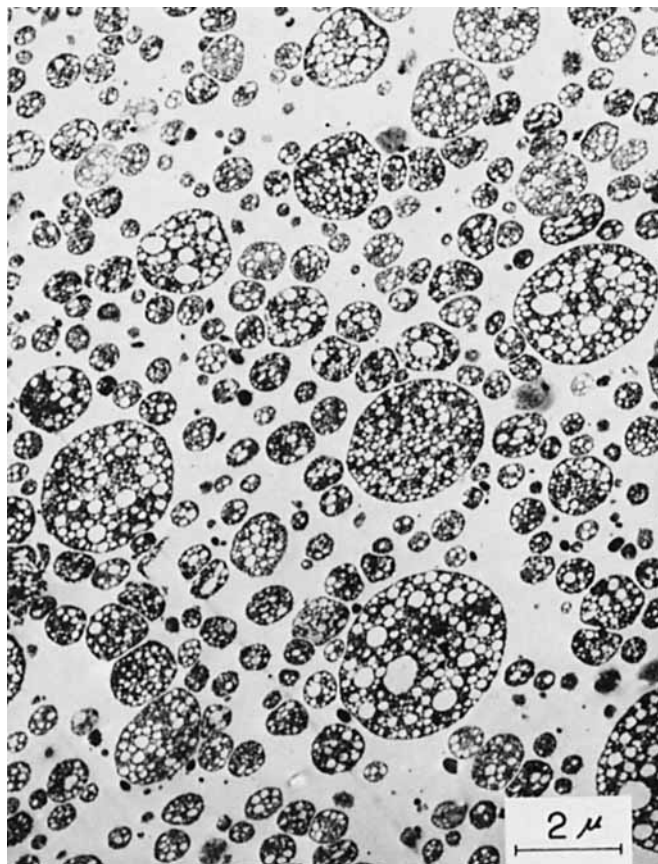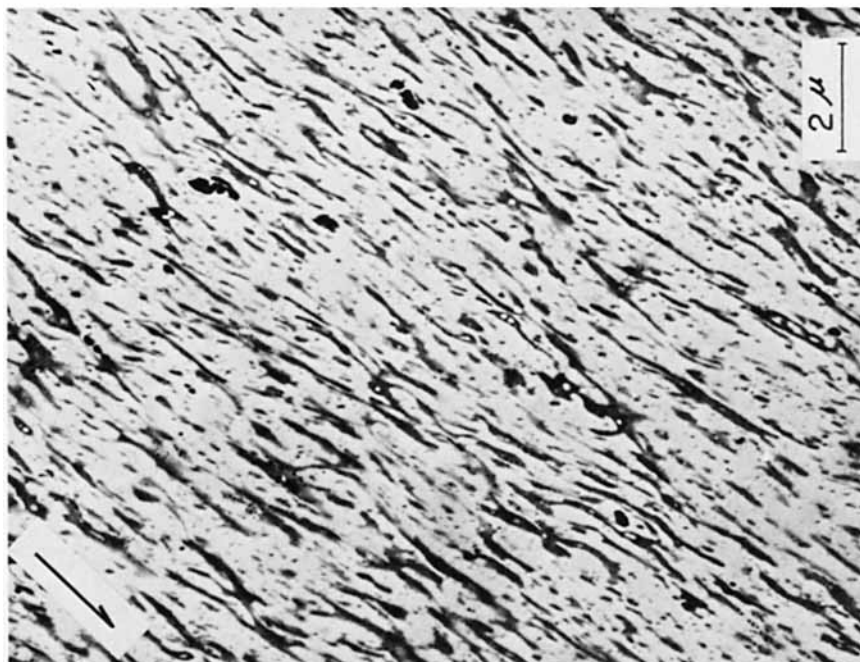
Fig. 2 (continued)

(c)

Fig. 2. The microstructures of EVASTAN's after extrusion: (a) polymer A; (b) polymer B:
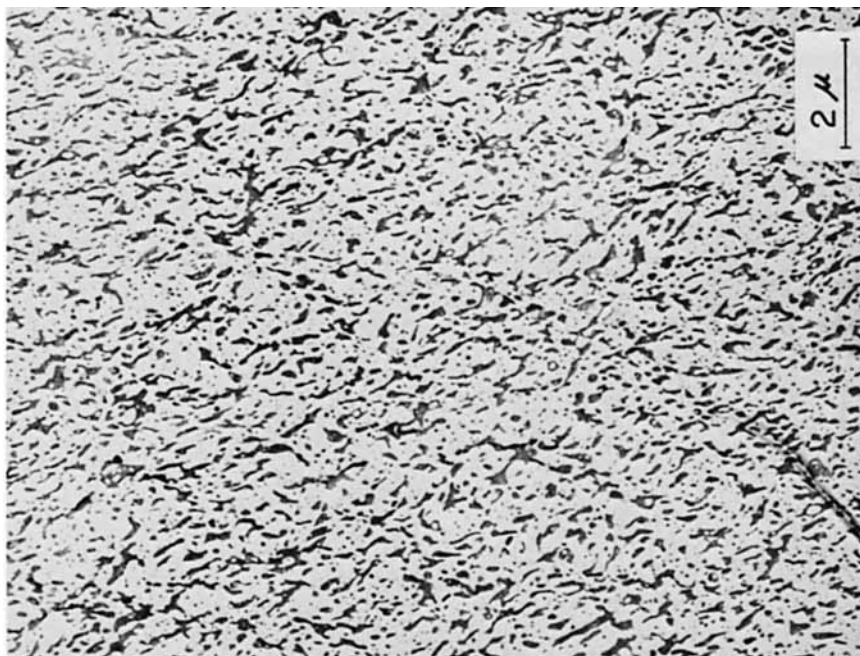(c) polymer C.

are quite different.   This shows that phase inversion in polymer A occurs on extrusion.   The particles of polymer B in Figure 2B are deformed and are small compared with those of Figure 1B.   When activated EVA is used, the microstructure of extrusion-molded polymer (2C) is similar to that observed at the end of the polymerization.   From these results, it is evident that the phase structure when EVA is in the dispersed phase is more stable and that the stability of EVA particles is greatly affected by grafting and crosslinking.

In injection molding, the intensity of mixing is much greater than that obtained on extrusion.   Figure 3 shows the microstructure of a surface portion of the injection-molded cup from which specimens were cut parallel and vertical to the injection direction.   The microstructure of EVASTAN with nontreated EVA (3A and 3C) is greatly changed: it is emphasized that all EVA particles are agglomerated and elongated in the flow direction, while the rubber particles of preactivated EVA-modified EVASTAN (3E) are moderately agglomerated and are a little extended.

These results indicate that the increase in the stability of dispersed particles by grafting and crosslinking decreases delamination in the injection process.   It
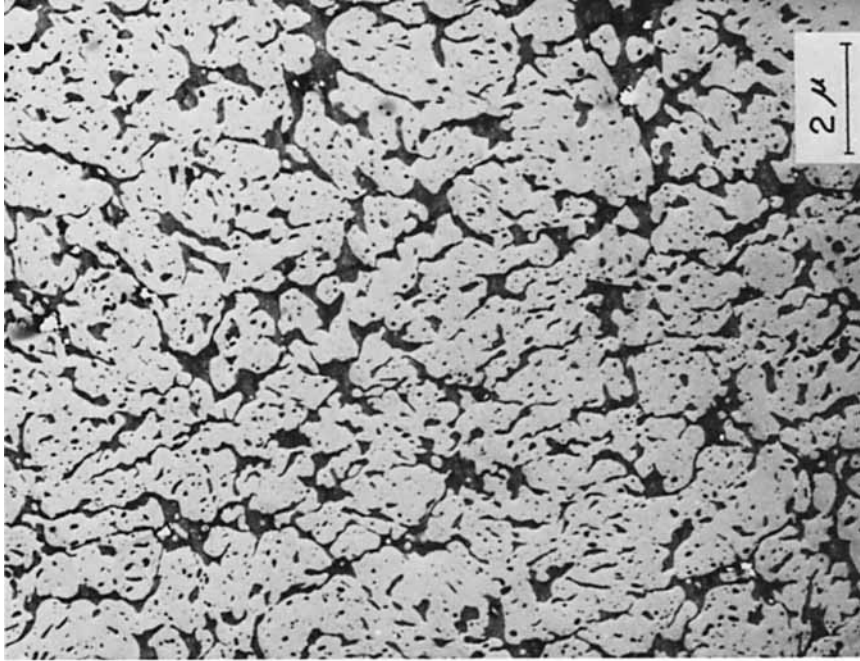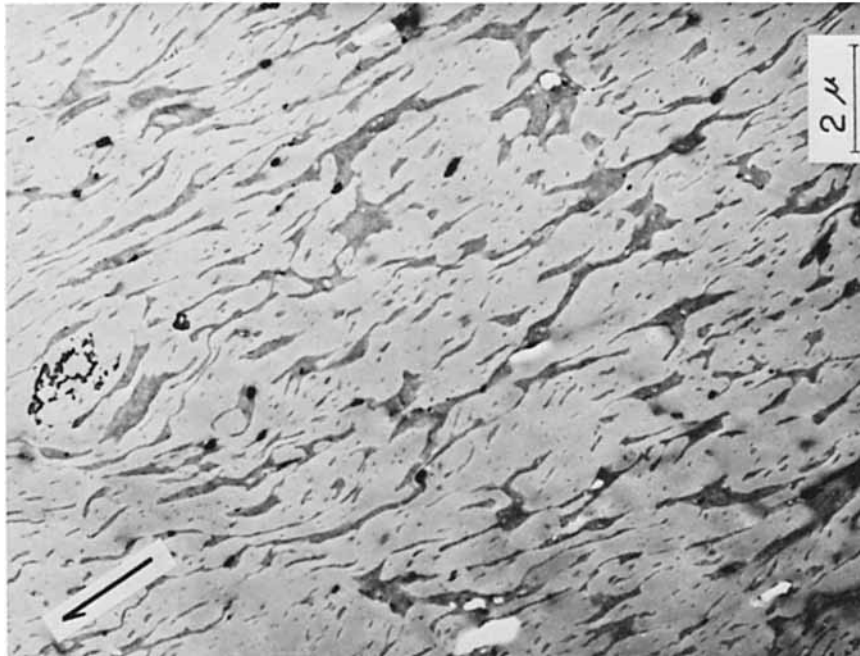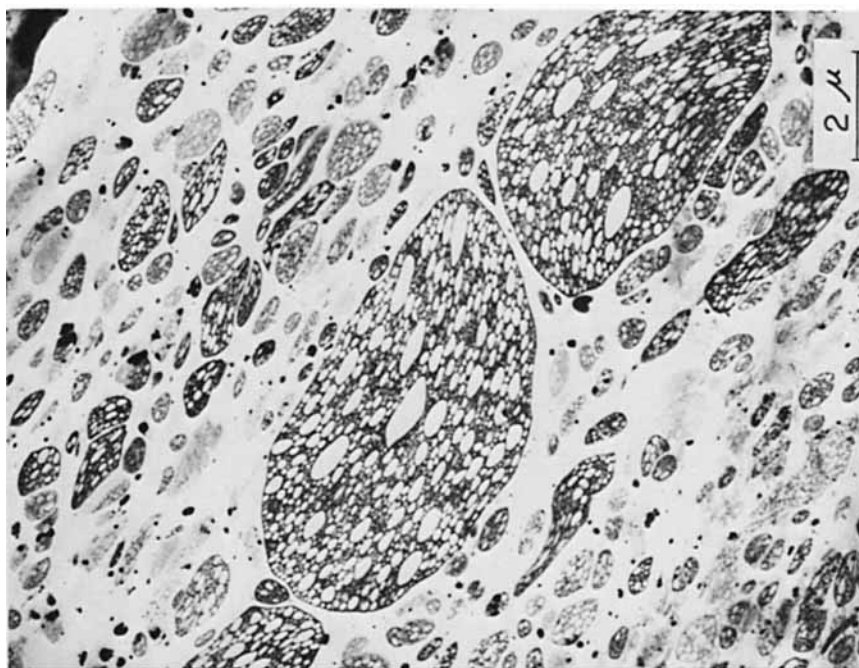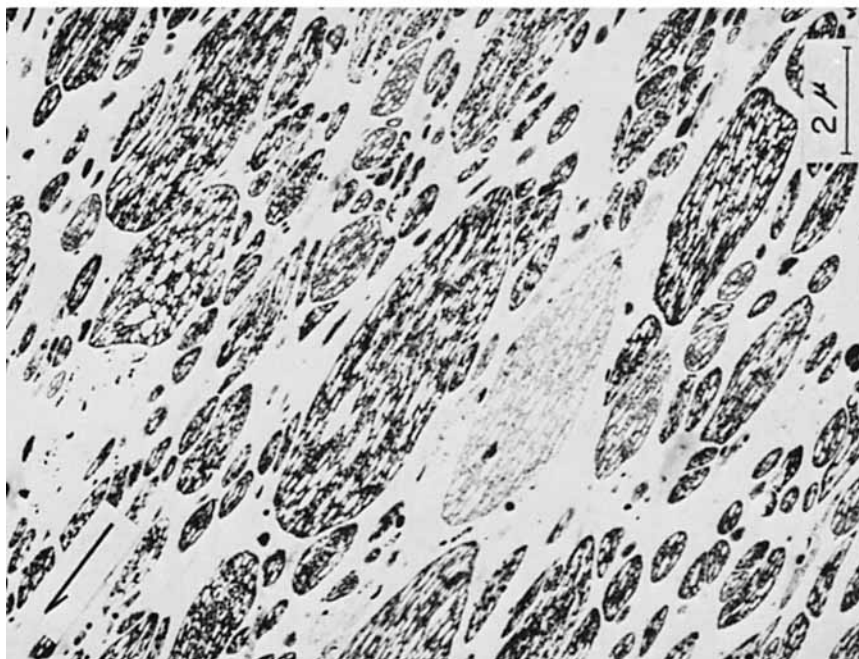
Fig. 3 (continued)

(d)

(c)

Fig. 3 (continued)

(e)

(f)

Fig. 3. The microstructure of a surface portion of injection-molded polymer specimen: (a) polymer A cut to injection direction; (b) polymer A cut to transverse direction; (c) polymer B cut to injection direction; (d) polymer B cut to transverse direction; (e) polymer C cut to injection direction; (f) polymer C cut to transverse direction. Arrow shows injection direction.

is suggested that occasional delamination of polymer C is caused by a little deformation of rubber particles.

Figure 4 shows the microstructure of a middle portion of the injection-molded cup of polymer C. Deformation and elongation of rubber particles is less compared with Figure 3E.

In the case of ABS resins, it is reported that delamination is often caused in the injection process under the severe conditions of lower molding temperature and higher molding speed, because rubber particles appear to be aligned one after another along the flow line.[6] But Figures 3 and 4 do not show that rubber particles appear to be aligned.

It is concluded that delamination of molding surfaces with saturated rubbers in the injection process is caused by agglomeration and deformation of the rubber particles and is prevented by grafting and crosslinking.

The mechanical properties of these plastics are also listed in Table I. Highly grafted polymer C shows more excellent impact resistance than polymer B, although the glass transition temperature of rubber of polymer C is higher than polymer B. It is suggested that polymer A shows the most excellent impact resistance because the rubber content in polymer A is highest.
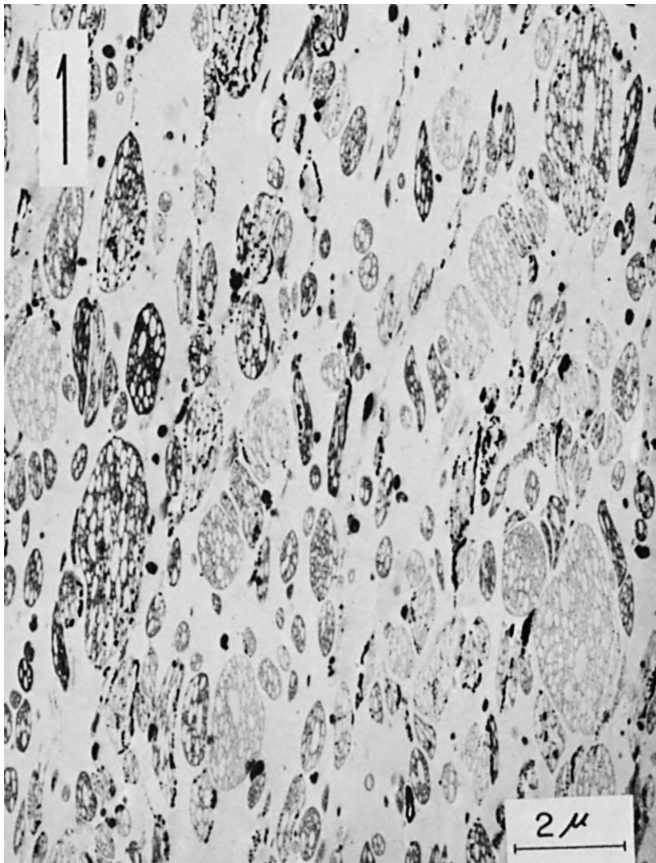
(a)

Fig. 4 (continued)
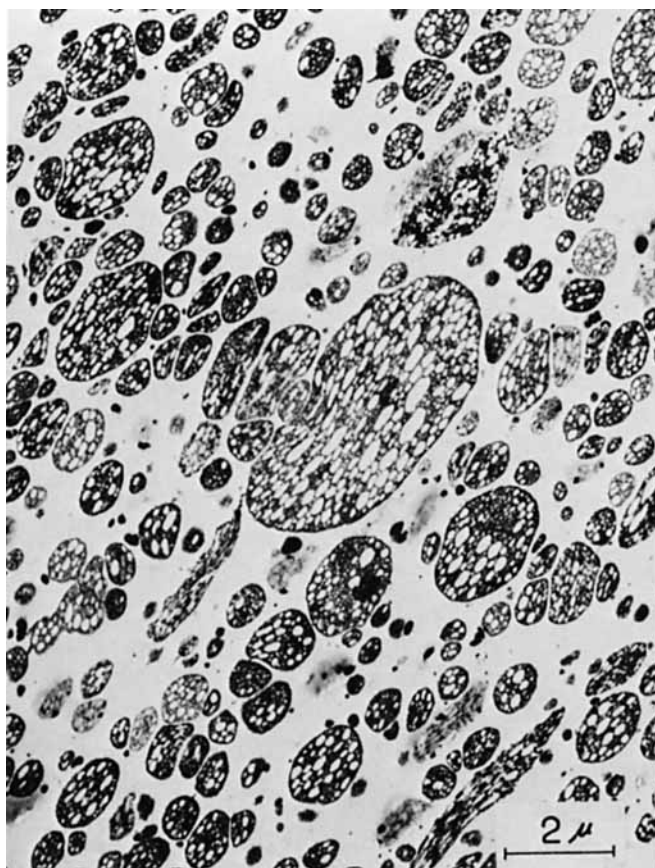
(b)

Fig. 4. Microstructure of a middle portion of injection-molded polymer of polymer C: (a) cut parallel to the flow; (b) cut vertical to the flow. Arrow shows injection direction.

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