

Synthesis and Structure–Property Relationships of a New Class of Rubber-Toughened PMMA

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SYNOPSIS

In the present work, blends between poly(methyl methacrylate) (PMMA) and poly(ethylene-co-vinyl acetate) (EVA) rubbers obtained by *in situ* polymerization of the acrylic monomer in the presence of the rubber have been investigated by linear elastic fracture mechanics (LEFM), by Charpy impact tests, and by scanning electron microscopy (SEM). Particularly, a correlation among molecular weight and composition of the EVA rubbers, phase structure development, and, consequently, mechanical impact properties of the resulting blends has been drawn.

INTRODUCTION

Tough, transparent poly(methyl methacrylate) (PMMA) is industrially produced by a multistage process of incorporation of rubbery particles in a methacrylic matrix.^{1,2} The rubbers are obtained by a suspension process in which a shell of cross-linked rubbery butyl acrylate–styrene copolymer is polymerized around a core of PMMA. The rubber is then added in the melt to a PMMA matrix. The core-shell structure (Fig. 1) is necessary to assure a good stress transfer between the phases and, at the same time, a better matching of the refractive indices of the two phases in order to get a transparent material. To achieve the desired level of toughening, high amounts of rubber (20–30% by weight) are necessary, with an unavoidable diminution of elastic moduli. In a previous paper,³ we reported the synthesis and impact behavior of PMMA blends in which an ethylene–vinyl acetate copolymer (EVA) was used as rubbery component. We have shown that it is possible to polymerize the methyl methacrylate (MMA) by a radical-initiated process in the presence of the preformed rubber. The EVA rubber is characterized by the fact that it is soluble in the MMA monomer at temperatures > 60°C, while it is immiscible with PMMA. As a conse-

quence, the growing of a PMMA phase, can, in principle, give rise to a complex morphology with the separation of a minor phase constituted by EVA droplets trapping some PMMA particles. The final microstructure that then might develop, schematically represented in Figure 2, can be described as a multicore shell structure, very similar to that industrially realized. We have demonstrated that the addition of as much as 7% of rubber is sufficient to cause a high improvement of the impact properties without a significant loss of tensile modulus, while the optical transparency, typical of methacrylic matrices, is maintained. The synthetic process followed by us is somewhat similar to that industrially used for the toughening of polystyrene by an elastomer, usually polybutadiene (HIPS).^{4,5} In the present paper, we report on the influence of molecular weight and composition of the EVA rubbers on the impact properties of the PMMA/EVA blends and on the resulting morphological appearance of the fracture surfaces. We also carried on some experiments devoted to ascertain the morphological development of the blends during the process of synthesis.

EXPERIMENTAL

Materials

The samples of EVA copolymers, kindly supplied by Dupont, have different contents of vinyl acetate

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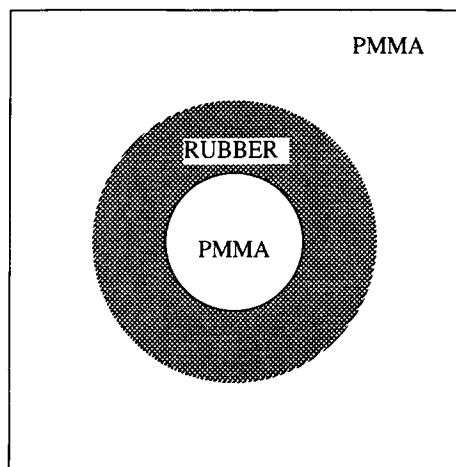


Figure 1 Schematic representation of the core-shell structure in commercial high-impact PMMA.

(from 10% to 40% by weight) and also different molecular weights. Codes, compositions, and η_{inh} of the used EVA are reported in Table I. Poly(vinyl acetate) is an Aldrich product reported as of medium molecular weight, MMA monomer (Fluka product) was used as received, and PMMA was prepared by a conventional radical process initiated by organic peroxide (0.2 wt %) and characterized by viscosimetric analysis.

Preparation of PMMA/EVA Blends

The PMMA/EVA blends were prepared by dissolving the elastomer EVA in liquid MMA in a ratio 7/100 by weight. The benzoyl peroxide was added to

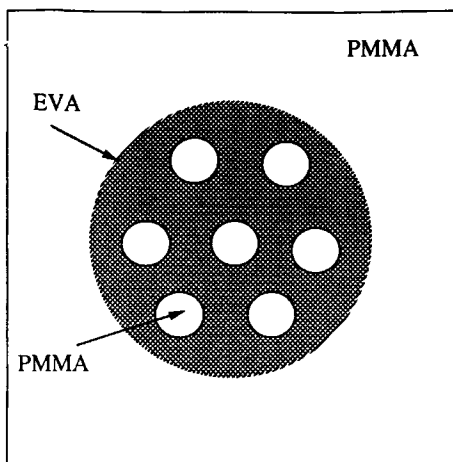


Figure 2 Schematic representation of the multicore-shell structure in PMMA/EVA synthetic blends.

Table I Codes, Composition, and η_{inh}^a of the Used EVA Copolymers and Energy Release Factor (Gc) at 20°C of the Resulting Blends

Code	VA % by Weight	η_{inh} (dL/g)	Gc (20°C)
LMW18	18	0.54	1.3
LMW28	28	0.54	0.9
MMW40	40	0.70	3.4
MMW20	20	0.83	3.5
HMW20	20	1.04	3.6
HMW9	9	1.06	2.3
HMW10	10	1.30	2.5
HMW36	36	1.38	3.2
PMMA	—	—	1.0
PMMA/PVAc	100	—	1.1

^a $c = 0.25$ g/(100 mL toluene) at 30°C.

the solution in quantities of 0.2 wt % and the temperature was raised to 80°C. When the viscosity reached a critical level (normally after about 100 min), the solution was poured into a preheated mold consisting of two glass plates separated by a rubbery gasket and held together by springs. The mold was kept for 12 h in an oven heated to 80°C. Subsequently, the prepared blends and the pure PMMA were compression-molded in a heated press at 200°C and at a pressure of 240 atm to obtain sheets of 3.00 mm thickness.

Techniques

The viscosimetric analysis is effected in toluene ($c = 0.5$ g/100 mL) by a Ubbelohde viscosimeter at 30°C. The impact properties were analyzed according to the linear elastic fracture mechanics (LEFM) approach.⁶ The procedure used for the calculation of the critical strain energy release rate (Gc) and the critical stress intensity factor (Kc) is reported in Ref. 7.

Charpy-type specimens (6.0 mm wide and 60 mm long) were cut by a mill and notched with a fresh razor blade. Then, they were fractured at different temperatures and at an impact speed of 1 m/s by using an instrumented Charpy pendulum.

A Philips 501 scanning electron microscope (SEM) was used for the morphological investigation on the fractured surfaces. The surfaces, prior to observation, were coated with a thin layer of gold/palladium alloy. Some blends were subjected to a smoothing and polishing procedure and observed after exposure to *n*-heptane vapors (20 min) to remove the EVA phase.

RESULTS AND DISCUSSION

Synthesis of Blends

The synthesis of new PMMA-based blends having high impact toughness and good optical transparency has been reported in a patent application,⁸ while a preliminary investigation on the impact behavior and fractographic analysis has been previously reported by us.³ The rubber used in that study was a EVA characterized by a vinyl acetate content of 20% by weight and an inherent viscosity η_{inh} of 0.83 dL/g.

To investigate the influence of the vinyl acetate content and the molecular weight of EVA on the impact resistance and on the morphology of the PMMA-based blends, a series of blends was prepared at a fixed rubber content (i.e., 7 phr) and at different vinyl acetate content and molecular weight (MW) of EVA copolymers.

The blends were obtained by a simple method consisting of the dissolution of EVA copolymers in MMA monomer followed by a first stage of polymerization under efficient stirring for about 100 min and a final curing step effected in a mold kept at 80°C for 12 h. Benzoyl peroxide (0.2% by weight) was used as radical source in all the preparations. It is worth noting that the MMA monomer has not been purified from the inhibitor. As can be observed in Table I, the employed EVA copolymers show a VA content ranging from 9 to 40% by weight with η_{inh} values ranging from 0.5 to 1.4 dL/g. The employed codes refer to low molecular weight (LMW), medium molecular weight (MMW), and high molecular weight (HMW) EVA, followed by the VA content (% by weight). The same codes are hereafter used to identify the prepared blends. The EVA employed in the previous paper³ was of MMW20, which falls in the middle of the investigated range of MW and compositions.

Phase Inversion

To study the morphological development of phases in our blends, we prepared smoothed and polished surfaces of selected samples and observed them by scanning electron microscopy (SEM) after *n*-heptane extraction. The final morphology of a blend having medium-viscosity EVA is reported in Figure 3. It is evident that the morphology revealed by the extraction of EVA is very complex. Particularly, the PMMA constitutes the matrix while large regions of EVA with subincluded PMMA particles are clearly evident. High-viscosity EVA blends show the

same final morphology depicted in Figure 3. The revealed morphology is very similar to that reported for HIPS.^{1,2} For HIPS, it is also reported that the absence of stirring leads to a "not inverted" morphology, in which a matrix of rubber surrounds large spherical polystyrene domains, even if the rubber represents only 7% of the total polymeric material. This situation was obtained also by us and is shown in Figure 4, where the same blend of Figure 3 was polymerized under stirring for only 90 min, i.e., before the attainment of the proper viscosity for "phase inversion." Upon etching with *n*-heptane, the tiny network of rubber that surrounded PMMA particles is removed. It is evident that PMMA, although present in a proportion larger than 90%, nevertheless constitutes the dispersed phase embedded in a continuous network of EVA copolymer.

The above results clearly show that a so-called phase inversion process must occur during the polymerization; the final morphology then strongly depends upon the stirring conditions. For low-viscosity EVA, even after 110 min of stirring, the morphology of the cured blend, reported in Figure 5, after smoothing and etching with *n*-heptane shows a "not inverted" situation, with large domains of PMMA surrounded by a tiny shell of EVA. This demonstrates that the MW of the rubber also plays an important role in the development of the final morphology.

Impact Behavior and Fractographic Analysis

The prepared blends have been investigated by the application of the linear elastic fracture mechanics (LEFM) analysis in Charpy impact tests. For simplicity, the impact values can be collected into three groups as function of the molecular characteristic of employed EVA, i.e.:

- (a) Blends containing low-viscosity EVA (η_{inh} = 0.54 dL/g).
- (b) Blends containing medium-viscosity EVA (η_{inh} = 0.7–0.83 dL/g).
- (c) Blends containing high-viscosity EVA (η_{inh} = 1.04–1.38 dL/g).

In Figures 6–8, the values of G_c (energy release factor) vs. temperature are reported for, respectively, low-, medium-, and high-viscosity EVA.

As can be observed from the impact data, the blends obtained with low-viscosity EVA are characterized by G_c values similar to, or worse than, that of pure PMMA, in all the ranges of investigated temperatures.

Going to medium-viscosity EVA (see Fig. 7), the behavior of blends is definitely more satisfactory. In fact, the values of G_c for both kinds of copolymers are well above the values of PMMA for all the investigated temperatures. The major improvement is observed at temperatures higher than -10°C , where PMMA still behaves as a brittle material, while the blends undergo brittle-to-ductile transition. The dif-

ferences in the G_c values of the two blends are relevant at temperatures below 0°C , while their curves tend to overlap at room temperature.

A similar trend is observed for the blends reported in Figure 8, having EVA copolymers with the highest molecular weights. Another important variable that we have studied is the vinyl acetate (VA) content. In Table I, together with codes and compositions of

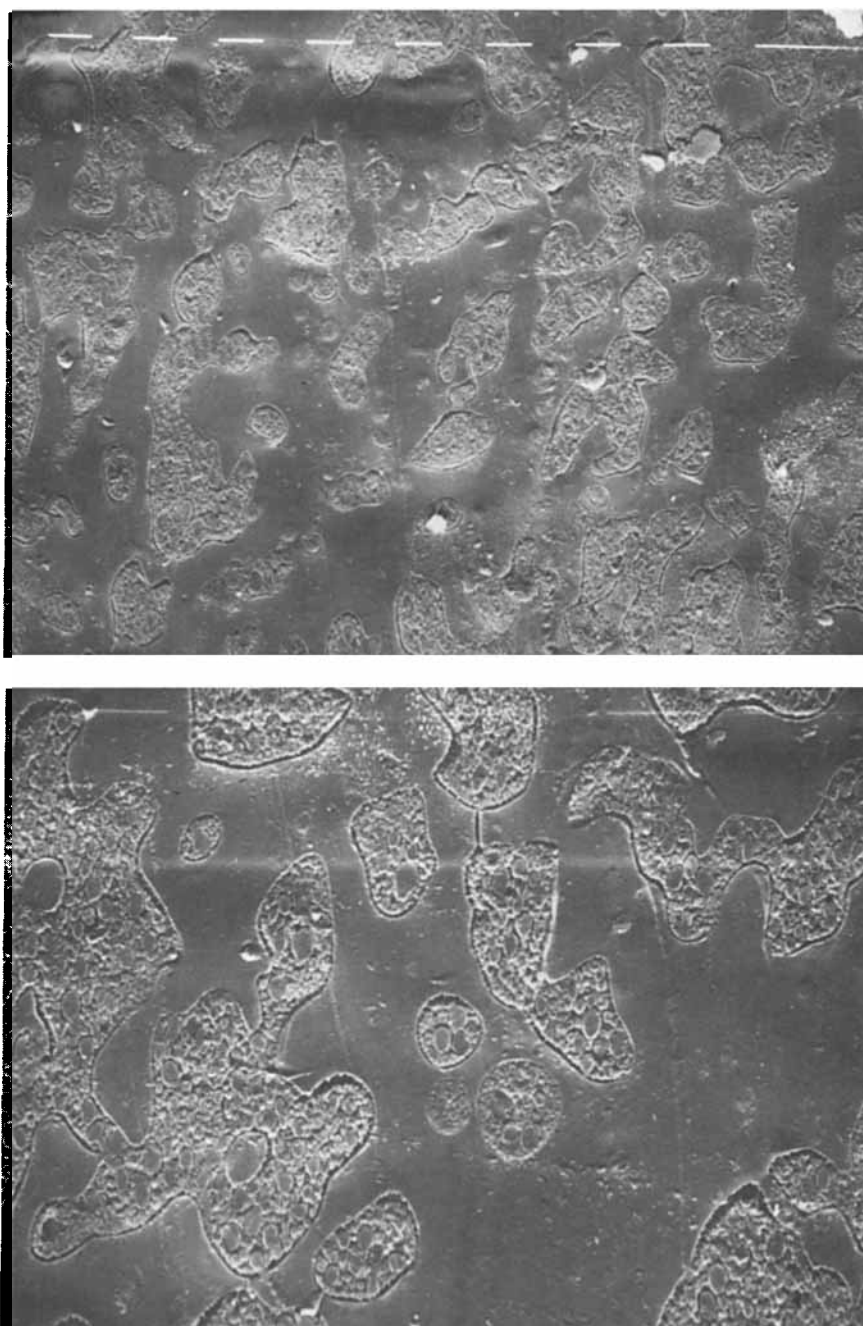


Figure 3 SEM micrograph of a smoothed surface of MMW20 blend after etching with *n*-heptane (a = 640 \times ; b = 1250 \times).

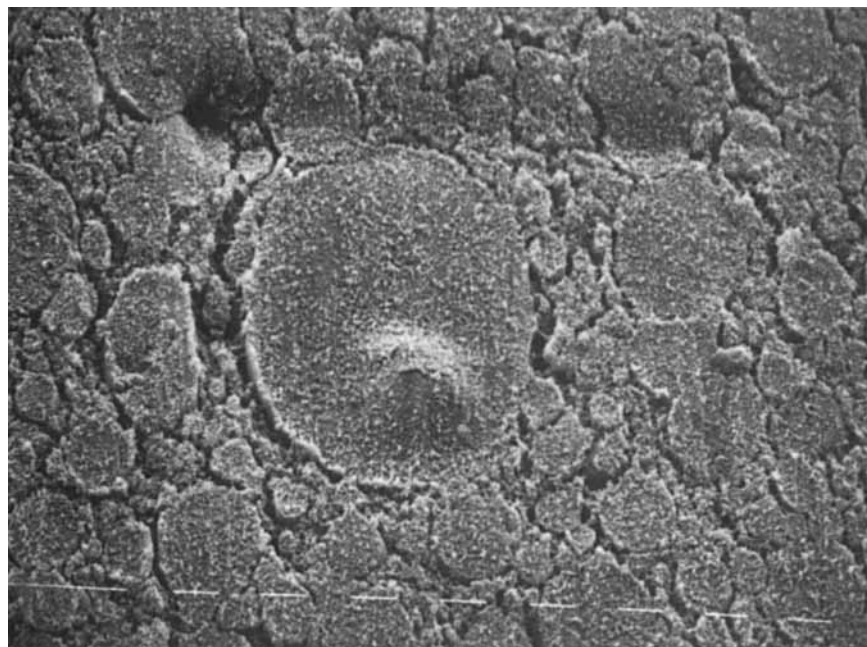


Figure 4 SEM micrograph of a smoothed surface of MMW20 blend (90 min of stirring) after etching with *n*-heptane (640 \times).

the employed EVA, the G_c values at 20 $^{\circ}$ C are reported. For blends with low MW EVA, the G_c diminishes, increasing the VA content, but at high MW EVA (i.e., $\eta_{inh} > 1$ dL/g), the G_c goes through a maximum.

The fractographic analysis of PMMA and PMMA blends surfaces after impact testing at room temperature is reported in Figures 9–13. For all the figures, the notch front is on the left-hand side.

The fracture surface of PMMA (Fig. 9) shows a

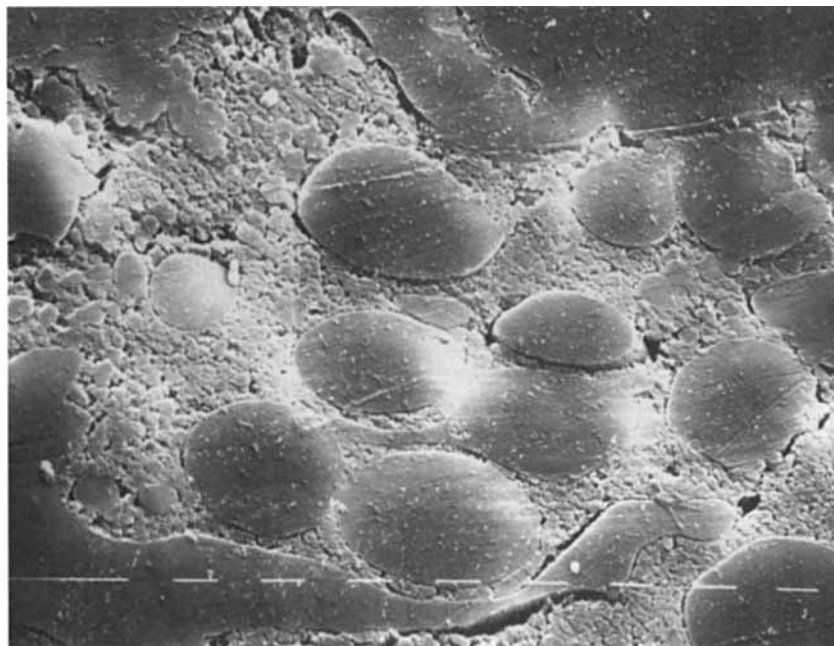


Figure 5 SEM micrograph of a smoothed surface of LMW18 blend after etching with *n*-heptane (640 \times).

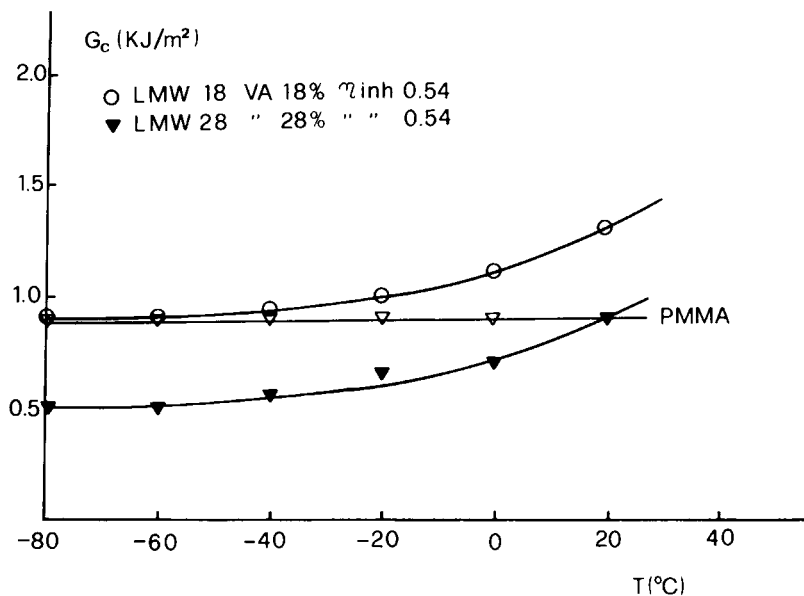


Figure 6 Energy-release factor G_c of plain PMMA and of PMMA/low-viscosity EVA blends as function of the testing temperature.

series of brittle fracture bands or striations, oriented perpendicular to the crack propagation. The formation of these bands is because, above a certain crack speed, the craze preceding the crack front undergoes branching.⁹ At sufficiently high stress levels, these crazes undergo fracture, causing surface roughening (bands), a deceleration of the crack, and a drop in the stress amplitude around the crack tip

that is below that necessary to initiate branching crazes. The fracture then reverts back, the crack speed rises again, and branching reoccurs. The repetition of this process gives rise to the banded appearance of the fracture surface. Figure 10 shows the fracture morphology of a blend containing low-viscosity EVA copolymer. This blend is characterized by a major-phase PMMA dispersed in the shape

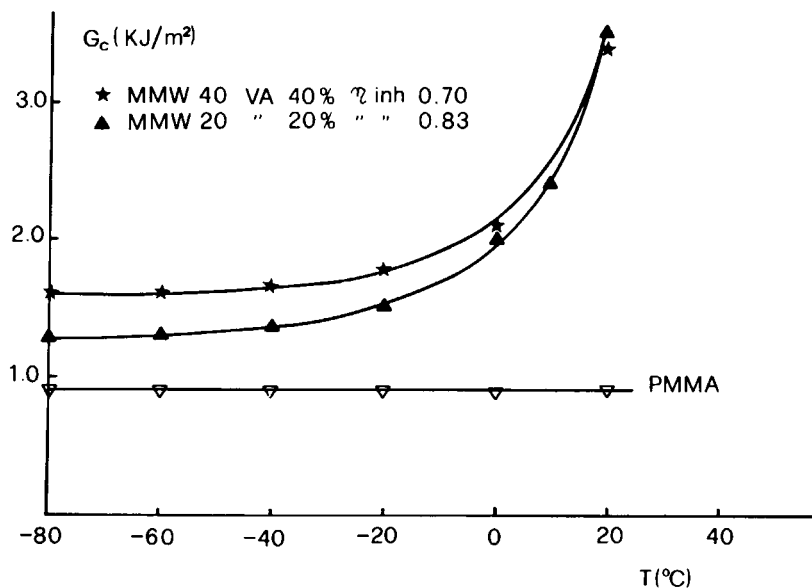


Figure 7 Energy-release factor G_c of plain PMMA and of PMMA/medium viscosity EVA blends as function of the testing temperature.

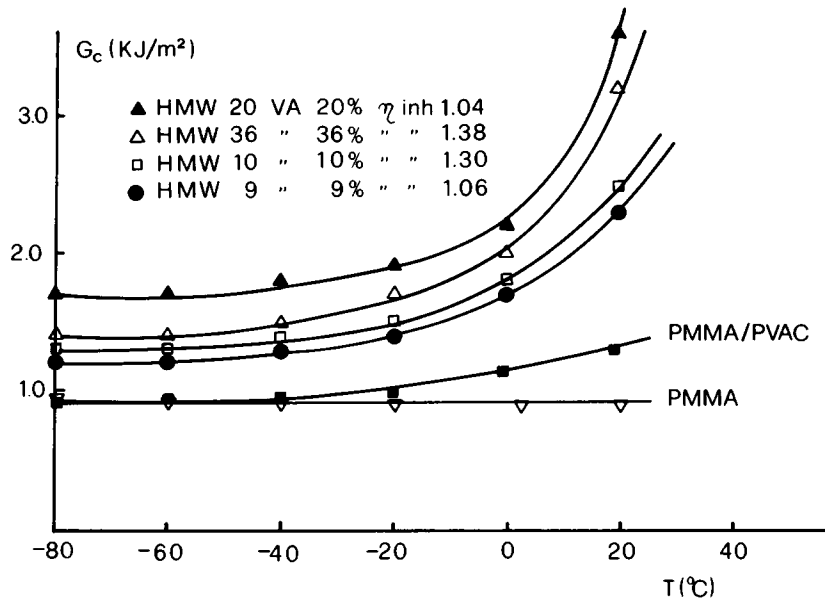


Figure 8 Energy-release factor G_c of plain PMMA, of PMMA/high-viscosity EVA, and of PMMA/PVAc blends as function of the testing temperature.

of very large domains in a matrix of a tiny layer of EVA copolymer. A similar structure, as already mentioned, is consistent with the absence of phase inversion during the radical polymerization of MMA. Apart from this observation, the fracture surface does not reveal any fractographic feature

distinctive of plastic deformation mechanisms (crazes and/or shear bands) from which crack development can take place. Completely different are the fracture surfaces of blends containing medium- and high-viscosity EVA copolymers, as can be seen from the micrographs of Figures 11 and 12, respec-

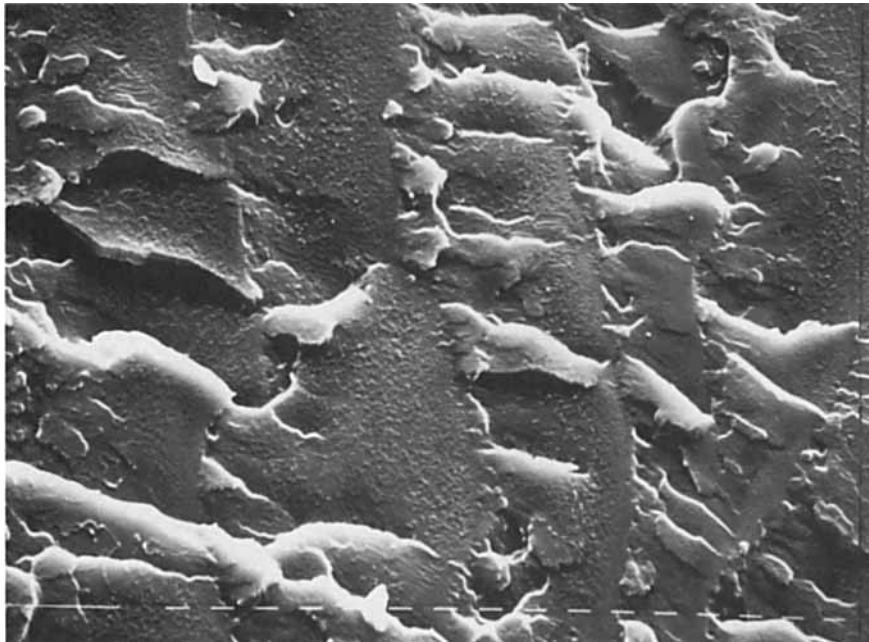


Figure 9 SEM micrograph of fracture surface at room temperature of plain PMMA (320 \times).

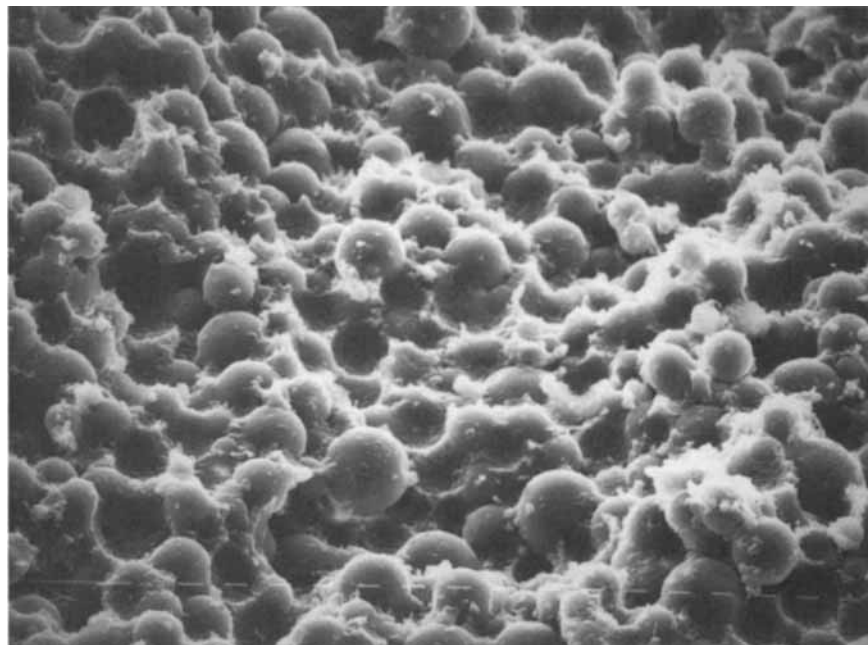


Figure 10 SEM micrograph of fracture surface at room temperature of LMW18 blend (320X).

tively. The overall morphology of these blends seems to be very similar. In fact, both figures reveal domains (less than 1 micron in size) finely dispersed and well embedded in the matrix. Moreover, signs

of an extensive plastic deformation in the matrix are also evident. In view of the intrinsic morphologies revealed by the heptane extraction (see previous paragraph), we may attribute the small par-

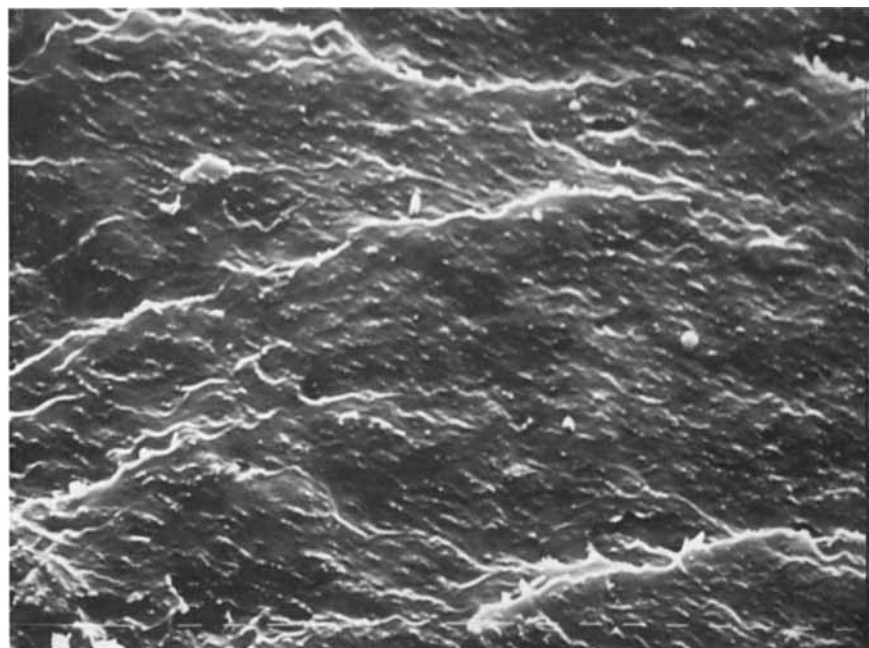


Figure 11 SEM micrograph of fracture surface at room temperature of MMW20 blend (320X).

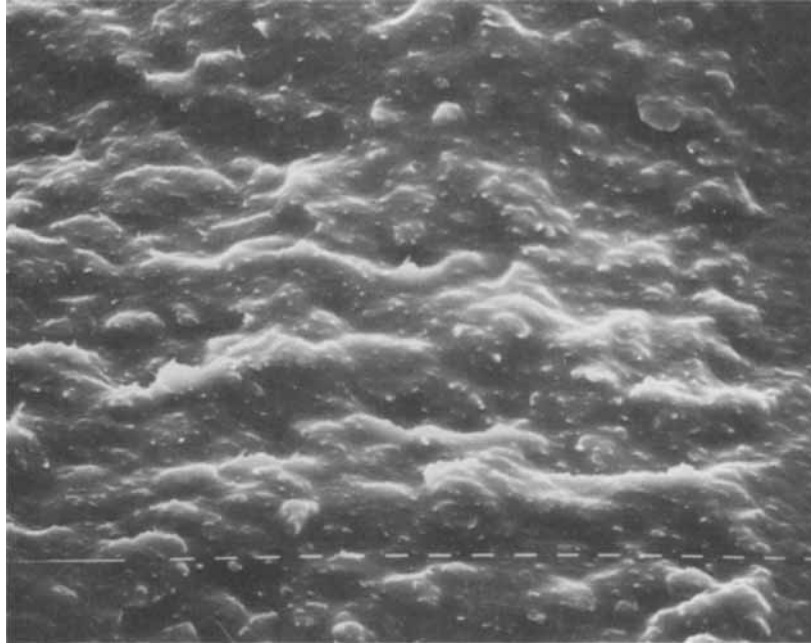


Figure 12 SEM micrograph of fracture surface at room temperature of HMW20 blend (320 \times).

particles of Figures 11 and 12 to the glassy PMMA particles subincluded in the rubbery domains, these last domains being highly deformed during the fracture. This indicates that a large amount of energy is dissipated, probably in the form of crazes, during the impact process. The above considerations account

for the very high impact toughness observed in such materials.

The influence of the VA content of EVA copolymers on the impact properties of blends can be explained as follows: For low MW EVA, where, as we have previously reported, the phase inversion pro-

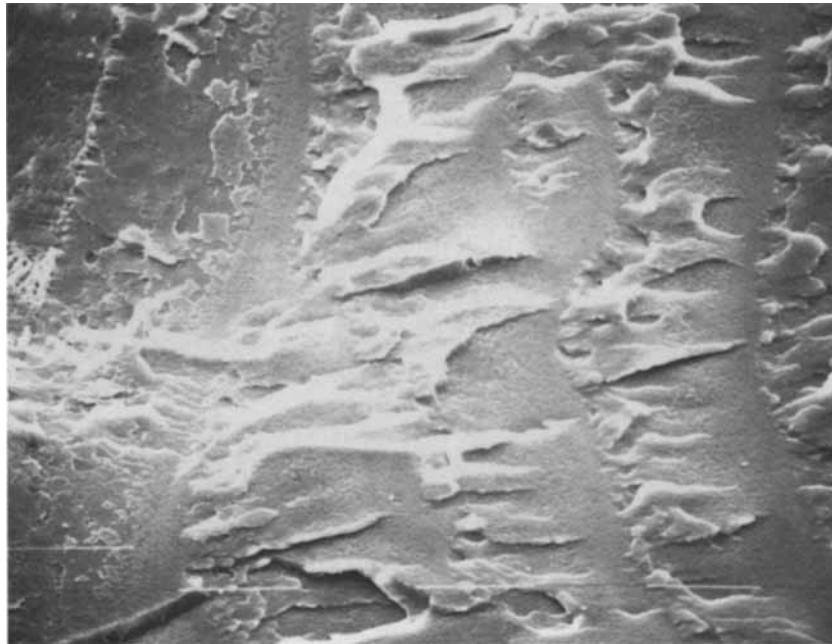


Figure 13 SEM micrograph of fracture surface at room temperature of PMMA/PVAc blend (160 \times).

cess does not occur during the stage of polymerization under stirring, an increase in the VA content should, in principle, lead to increased miscibility of EVA with growing PMMA chains and in liquid MMA; this will, in turn, cause a further delay in the phase-separation process with a consequent decrease of mechanical properties of the final cured material at higher VA content. For high MW EVA, the phase-separation and phase-inversion processes do occur during the first stage under stirring and the effect of an increase in the VA content is to improve the polarity of EVA copolymers and to create a stronger interfacial adhesion between EVA and PMMA with a consequent improvement in the impact properties.

For MMW blends, such effects are less evident. No large differences are observed in the impact properties as function of VA content of EVA rubbers, at least at room temperature.

Graft Copolymers Formation

The high-impact properties of HIPS are at least partially interpreted as a result of the formation of graft copolymer species between polybutadiene and the growing chains of polystyrene.^{1,2} In our case, we used radical polymerization to grow PMMA, and EVA copolymers are constituted by long polyethylene sequences that are known to be reactive toward radical copolymerization. To get indirect proof that grafted EVA-*g*-PMMA species are formed in our system, we prepared and characterized a blend using poly(vinyl acetate) as a second phase. The G_c values at different temperatures reported in Figure 8 and the value of G_c at room temperature reported in Table I show that this blend has very poor impact properties, comparable with those of plain PMMA. Also, the fracture surface (see Fig. 13) resembles that of unmodified PMMA. The surface is covered with brittle fracture bands originated from a cyclic process of formation and breakdown of crazes. We believe that this result indicates that, in the absence of a graft copolymerization reaction between PMMA and the dispersed phase, an effective toughening process cannot occur, although the dispersion of the minor phase is very intimate. This could also explain why the impact properties of HMW blends seem to go through a maximum as a function of VA content (HMW20 > HMW36). In fact, we can suppose that a balance occurs between the increase in interfacial compatibility between EVA and PMMA by increasing the VA content (better impact properties) and the decreased ability to form graft copolymer species, due to the diminution of the length of polyethylenic sequences on EVA chains at higher VA content.

CONCLUSIONS

We have demonstrated that, by a suitable choice of EVA copolymer, new types of rubber-toughened PMMA can be obtained during the radical polymerization of MMA. A very low content of rubber is sufficient in order to get strong improvement of mechanical properties.

Different EVA copolymers have been tested and the obtained results demonstrate that the VA content and MW of EVA can strongly affect the morphology and the impact properties of the blends. We have observed that, for the occurrence of the phase inversion, an efficient stirring is necessary, as well as a sufficient viscosity of the rubbery component. In particular, we have found that the best matching of properties is obtained for a VA content of about 20% and an η_{inh} of 1.0 or more. The results have been interpreted on the basis of a phase-inversion process similar to that occurring in HIPS and on the basis of a graft-copolymerization between PMMA and EVA.

Work is in progress to study in detail and to control the phase-inversion process and to understand the detailed mechanism accompanying the fracture process of such a new class of high-impact PMMA.

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