Stabilized Polymer Blends

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INTRODUCTION

Today, producers of plastics are expected to tailor very different properties on request, without much financial and technical effort. But since the costs and the risks of newly developed polymers are high, the interest of industries has turned to combinations of polymers that are already available: 1) In blends [1, 2], different polymers are simply mixed; 2) in copolymers [3], different polymer segments or blocks are chemically tied together. Both principles are combined in blends with copolymer components.

For a controlled design, one-phase blends and copolymers are particularly suited because their properties result quite linearly from those of the components. But it is rare that polymer chains or blocks are homogeneously miscible, so that blends and blocky copolymers commonly feature two or more phases. In blends from recycled plastics, there are often as many phases as there are polymer components. This report deals with two-phase and "multiphase" (a term which usually means "more than two") blends, mostly with copolymer components.

The pivotal properties of demixed blends, i.e., their mechanical and the optical properties, are difficult to predict. The dependence on composition can be linear, but also synergistic, antergistic, or matrix-dominated. There are only two general rules concerning demixed blends: 1) They are practically never perfectly transparent, and 2) the internal interfaces between the domains of different phases are usually mechanically weak. The latter effect is of the utmost importance.

The weakness of blend interfaces is not necessarily detrimental. In thermoplastic elastomers [3] it does not interfere, and in rubber ("impact") modified thermoplastics [4] it even leads to improved toughness. But in blends of thermoplastics and

in recycling blends, the mechanics are unfavorably modified by interfaces, some-times disastrously so. Some thermoplastic blends are barely coherent.

The phase morphology is crucial. The phase structures of blends are discussed in what follows, and ways to stabilize morphologies are considered [5, 6]. Further-more, the mechanism of brittle failure in blends is addressed.

SIMPLE BLENDS

Two-phase blends of common components, i.e., of homopolymers or random copolymers, yield phase morphologies of the types shown in Fig. 1 [7, 8]. Either one component is dispersed in the matrix of the other (M_A, M_B), or both compo-nents form a cocontinuous phase network (CC).

But structures as well-ordered as in Fig. 1 are obtained only after annealing. Mixing in extruders or kneaders leads, due to mechanical stresses, to morphologies that are more or less perturbed, depending on the composition, the interface tension and, even more, on the viscosities of the components. For a blend of polymethyl methacrylate (PMMA) and polystyrene (PS), Fig. 2(a) shows that the minor com-ponent PS (black) is spread out in the extruder and forms the matrix because it is less viscous. The more viscous major component PMMA (white) takes over the matrix only after annealing (Figs. 2b and 2c). This matrix inversion proceeds on a scale of minutes in Fig. 2, but it can also be complete on a scale of seconds at higher temperatures.

Figure 3 shows, in a universal phase diagram, at which blend compositions (φ) of cocontinuous morphologies are observed. The diagram was recorded with blends of PMMA and random copolymers $P(S_xMMA_{1-x})$ of styrene and MMA. The inter-face tension grows with the degree of incompatibility χ/χ_c, where χ is the interaction parameter and χ_c is its critical limit [7].

As seen in Fig. 3, the CC morphologies formed by extrusion are located in a sector of the phase diagram on the side of the more viscous component, the PMMA. The less viscous component is always more inclined to form the matrix [9]. Only after additional annealing, the CC sector moves to the center of the phase diagram where cocontinuous structures might have been expected from the start. Generally, the range of CC morphologies is more narrow for strongly incompatible blends (high χ/χ_c). Figures 2 and 3 emphasize how enormously phase morphologies of blends can change in annealing periods during processing and reprocessing.

The second characteristic parameter of blend structures, in addition to the type of morphology, is the coarseness of the phase domains which depends on the same system parameters. Strongly incompatible blends and blends with a very fluid matrix are often difficult to disperse, while moderately incompatible blends of components with similar viscosities can yield morphologies in the submicrometer range. All morphologies "ripen," i.e., coarsen via coalescence of domains and thick-ening of cocontinuous networks. The CC networks coarsen particularly rapidly [7].

Multiphase blends of thermoplastics with a submicroscopic morphology often respond mechanically like one-phase blends. The mechanical performance deterio-rates as the phase structures coarsen. Therefore, all attempts to stabilize the mor-phologies of thermoplastic blends aim at phase structures as fine as possible.
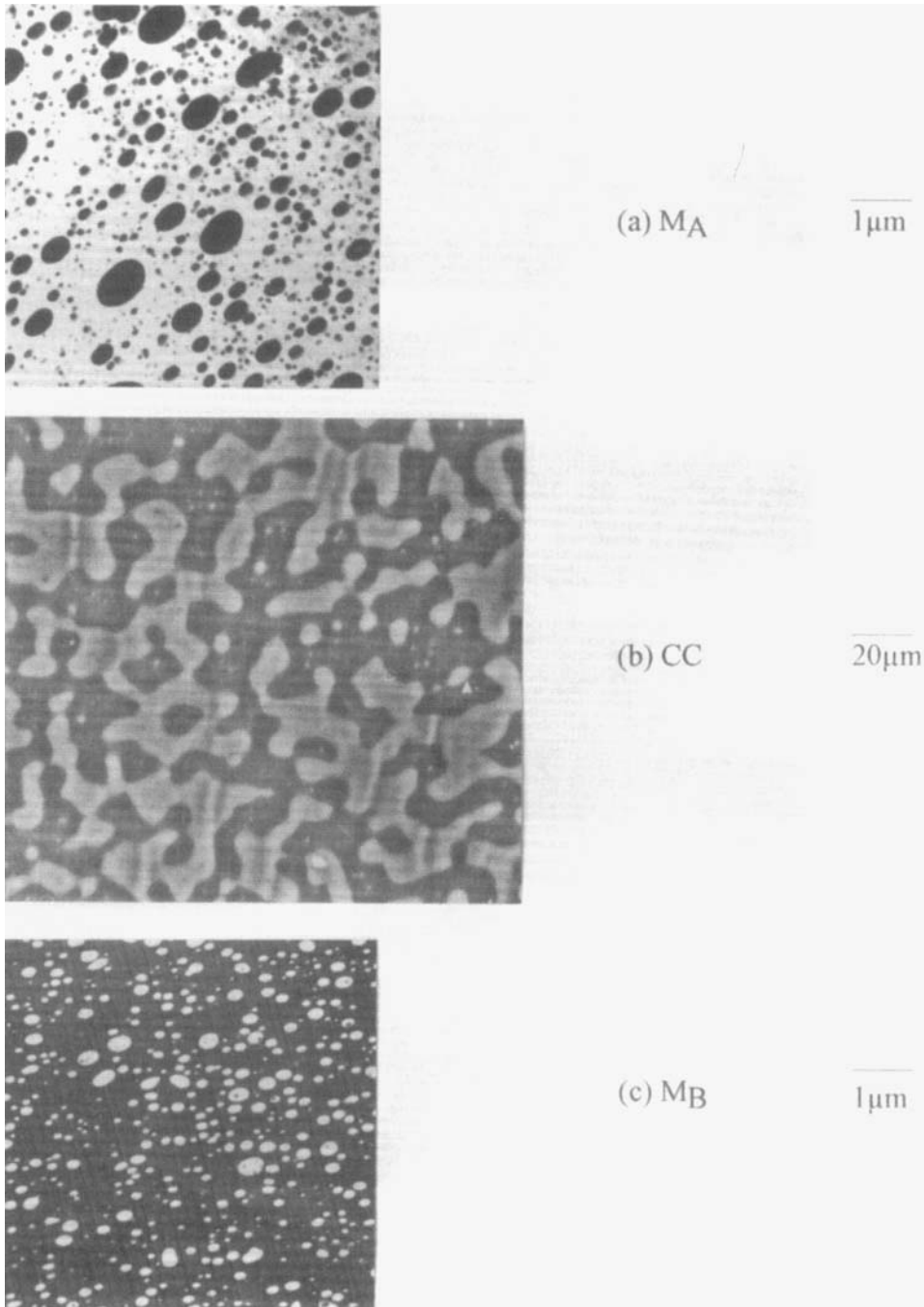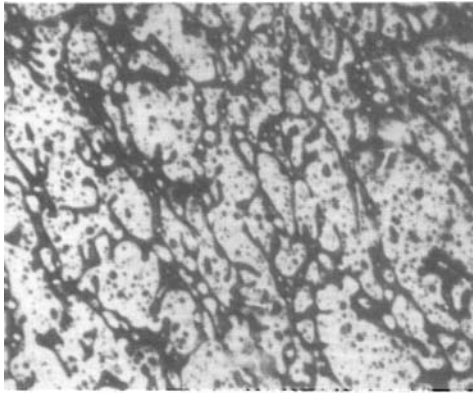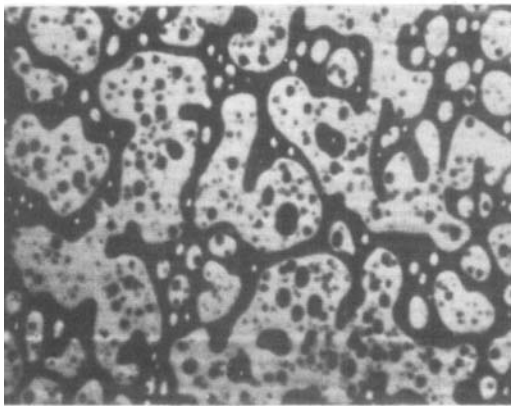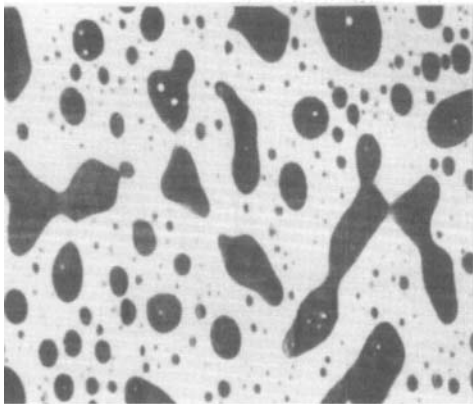
FIG. 1.   Phase morphologies of blends PMMA/PS with the compositions (ratios of weight fractions) (a) 3/1 (M_A: matrix PMMA), (b) 1/1 (CC: cocontinuous network), (c) 1/3 (M_B: matrix PS). PMMA white, PS black.

(a)

(b)

$\overline{1\,\mu m}$

(c)

FIG. 2. Morphology of the blend PMMA/PS (2/1) (a) after extrusion and after (b)
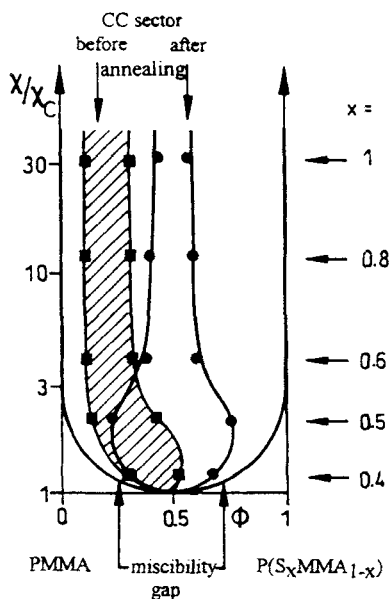. 4 minutes and (c) 7 minutes additional annealing at 190°C.

FIG. 3. Universal phase diagram for two-phase blends as a function of the degree of incompatibility χ/χ_c, recorded using the morphologies of blends PMMA/P(S$_x$MMA$_{1-x}$). The miscibility gap is shown and, inside of the gap, the sector CC of cocontinuous structures, immediately after extrusion ("before") and after additional annealing ("after").

STABILIZED BLENDS

The structure of multiphase blends can be refined with polymeric "compatibilizers." A compatibilizer is supposed to lower the interface tension by concentrating in the interfaces of the blend morphology. Therefore, the compatibilizer must be less incompatible with the main components of the blend than these are with each other, but it must not mix with those components. An ideal compatibilizer 1) leads to refined phase structures that 2) coarsen less rapidly upon annealing, and 3) ties the phases together so efficiently that the interfaces of the phase morphology are no longer weak under tension or impact. This ideal case is difficult to realize [1, 3].

Diblock copolymers with blocks that are chemically equal to the chains of the main blend components, or that are attracted by these chains, seem to be the compatibilizers of choice. As indicated in Fig. 4, the block copolymer chains can, sitting in the interfaces, enter with their blocks both neighboring phases and tie them together. Diblock as well as triblock, graft, and block-graft copolymers were tested in this respect in blends, more or less successfully [3, 10, 11].

Figure 6 demonstrates for the blend PVC/PS (polyvinyl chloride and polystyrene), which is part of the recycling blends coming from domestic waste, that the block-graft copolymer indicated in Fig. 5 is an excellent compatibilizer for this system. In Fig. 6(b) the coarse morphology in Fig. 6(a) is refined to a degree that is barely resolved. The toughening effect of the copolymer is gratifying, too. The blend behaves mechanically almost as if it were homogeneous. Figure 7 proves that this is due to a compatibilizer effect, exactly as predicted by Fig. 4. The copolymer chains cover the interfaces between the phase domains of PVC and PS in a micellar
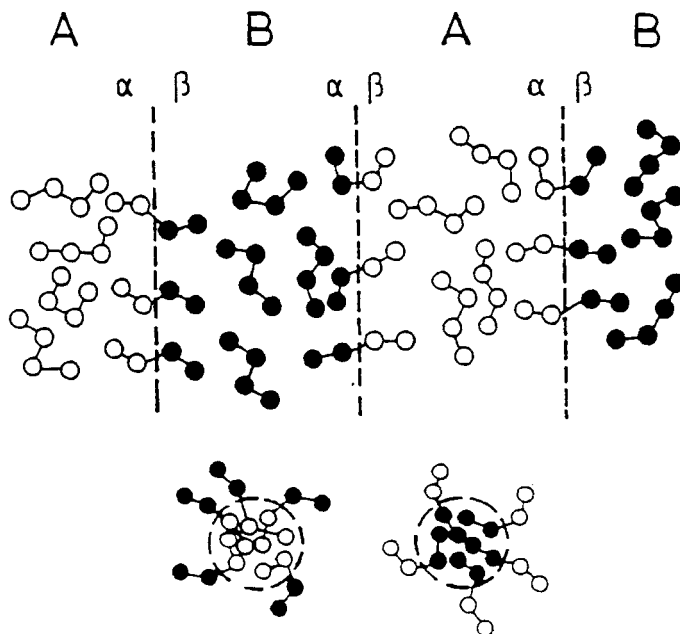
FIG. 4.   Compatibilizer effect of a diblock copolymer $\alpha\beta$ in a blend of two homopoly-
mers, A and B. The copolymer covers the interfaces in a monomolecular layer (top). A
competing mechanism is micelle formation inside the phases of A and B (bottom).
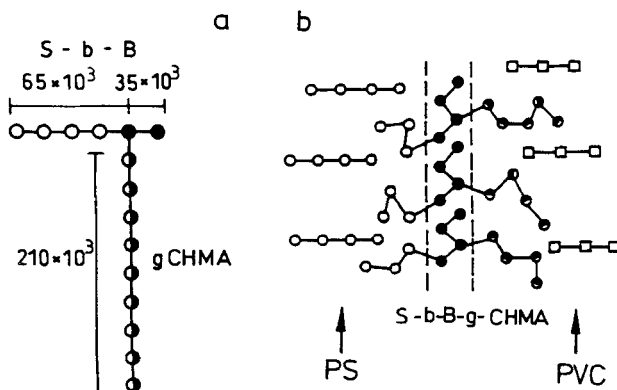

FIG. 5.   (a) Block-graft copolymer P(S-*block*-(B-*graft*-CHMA)) (B: butadiene,
CHMA: cyclohexyl methacrylate) with weight-average molecular weights, (b) compatibilizer
effect in the blend PVC/PS. PVC and the CHMA grafts are miscible.
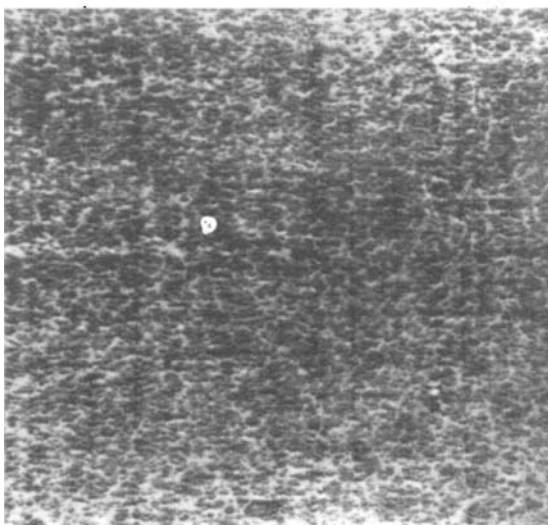
5μm

FIG. 6. Morphology of the blend PVC/PS (1/1) (a) without and (b) with the block-graft copolymer P(S-*block*-(B-*graft*-CHMA)) as a compatibilizer, immediately after the extrusion.
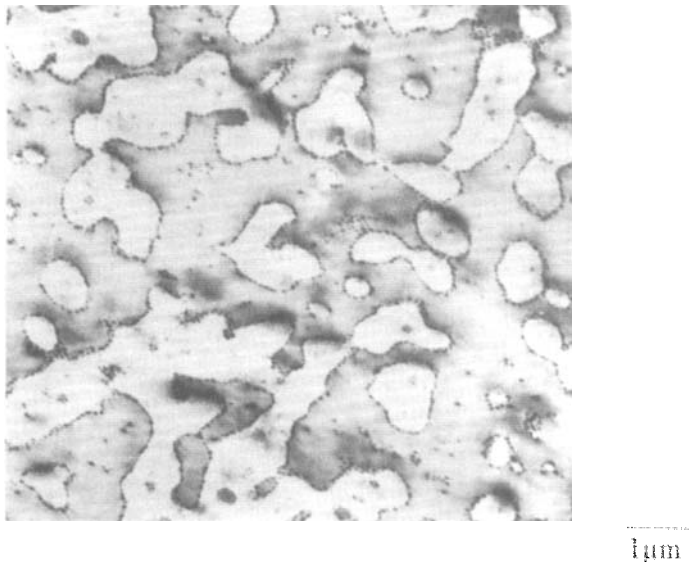
1 μm

FIG. 7. Structure of the blend PVC/PS/P(S-*block*-(B-*graft*-CHMA)) after anneal-
ing; PVC white, PS grey. The block-graft copolymer P(S-*block*-(B-*graft*-CHMA)) (Fig. 5a)
covers the interfaces in strings of micelles. Visible (small black spheres) are only the butadiene
blocks.

monolayer. It should be mentioned that only the short butadiene center block (Fig.
5) of the copolymer is seen (black spheres). The outer blocks of styrene extend
invisibly into the PS phase, and the CHMA grafts also extend invisibly into the
PVC phase, as indicated in Fig. 5(b).

A problem is that the compatibilizer effect must be paid for. The copolymer
shown here (Figs. 5–7) and all other blocky copolymers are expensive. Not all of
these copolymers are efficient. The blocks of the block or graft copolymer must be
long, not shorter than the chains of the main blend components unless there are
special attractive interactions [10–13]. This is a restrictive condition. Moreover,
refined morphologies improve the toughness only if the blocks are long enough to
entangle in the interfaces with both adjacent phases. In summary, the copolymers
must be adjusted very carefully to every blend.

Consider random copolymers, especially those that are made of monomers of
the main blend components. Random copolymers do not have long blocks, of
course. Instead, the comonomers alternate in short sequences, so that monomolecu-
lar interface layers as in Fig. 4 are impossible. Nonetheless, random copolymers can
spread in the interfaces of a blend morphology and form thin interphases that lower
the interface tension. Figure 8 shows that a random copolymer ($P(S_xMMA_{1-x})$ does
indeed refine the phase structures of a homopolymer blend PMMA/PS consider-
ably.

Figure 9 proves that the random copolymer covers the interfaces with thin
interphases. This copolymer has a special composition, $P(S_{65}MMA_{35})$ (weight frac-
tions), that makes it equally incompatible with both main components, PMMA and
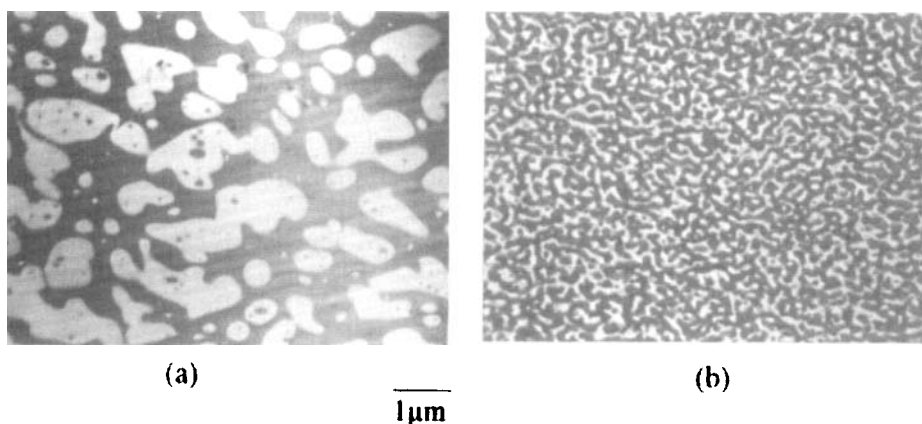
(a) (b)

1 µm

FIG. 8. Structure of the blend PMMA/PS (1/1) (a) without and (b) with the random copolymer P(S$_{65}$MMA$_{35}$) as a compatibilizer.

PS. The copolymer improves the brittleness of the blend PMMA/PS, but not to the degree that the blend would behave if it were homogeneous.

Random copolymers are usually cheaper than block and graft copolymers, and the chain length ratios are not nearly as crucial for the compatibilizer effect. There is hope that the random copolymers will prove themselves generally as compatibilizers. In many cases, and certainly in blends from recycled plastics, one will have to dismiss block or graft copolymers, superior as they may be, because of the economics.
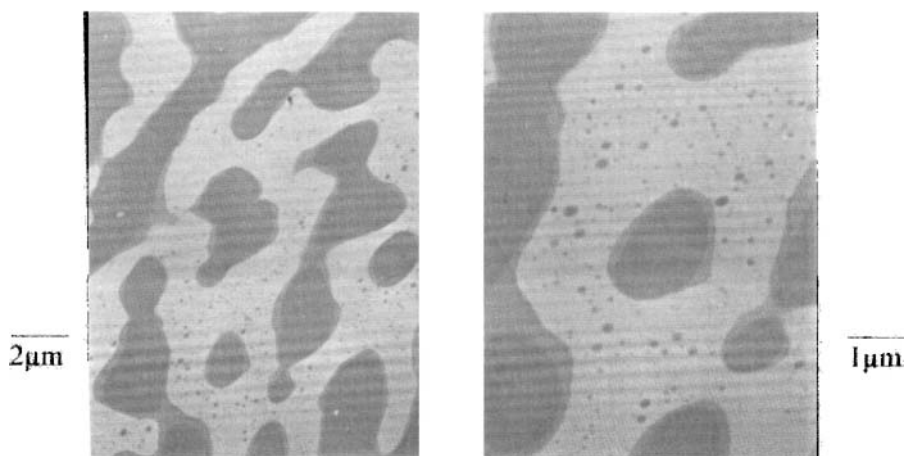

2µm 1µm

FIG. 9. Structure of the blend PMMA/PS/P(S$_{65}$MMA$_{35}$) after annealing; PMMA light, PS dark. The copolymer forms grey interphase layers between the homopolymer phases.

FAILURE IN IMPACT MODIFIED THERMOPLASTICS

Brittle thermoplastics and many of their blends break by developing crazes which turn into cracks [14]. A typical large craze growing in a PMMA/PS blend is shown in Fig. 10. It is distinguished from a crack by fibrils of stretched material that tie the faces together. When this fibrillar substructure is disrupted, a crack is formed.

Compatibilization of thermoplastic blends by copolymers cannot change this pattern of crazing, cracking, and brittle fracture. The compatibilizers can, at most, stabilize the interfaces of the blend morphology so efficiently that the demixed blend behaves as if it were homogeneous. This often amounts to quite an improvement. But blends of two thermoplastics can usually not be tougher than both its components.

However, enhanced toughening is well-known in thermoplastic-elastomeric blends, i.e. "rubber-modified thermoplastics." The elastomer acts as an impact modifier if dispersed in domains, the size and internal structure of which have been varied and optimized in many ways. The elastomeric domains are either generated in situ during the polymerisation of the thermoplastic (high impact PS) [15] or they are prepared separately in emulsion (ABS). In the former case the domains are heavily filled with subdomains of the thermoplastic ("salami" domains); in the latter they are often covered by a layer of the thermoplastic ("core-shell" domains). In both cases the elastomeric phase consists in large part of elastomeric chains that are grafted with thermoplastic branches. The domains are crosslinked and therefore stable. These domains initiate multicrazing [14] in the thermoplastic matrix, as shown in Figs. 11 and 12.

In purely thermoplastic blends, this effect of enhanced crazing is avoided, if possible, with the help of compatibilizers, because the crazes grow in length and
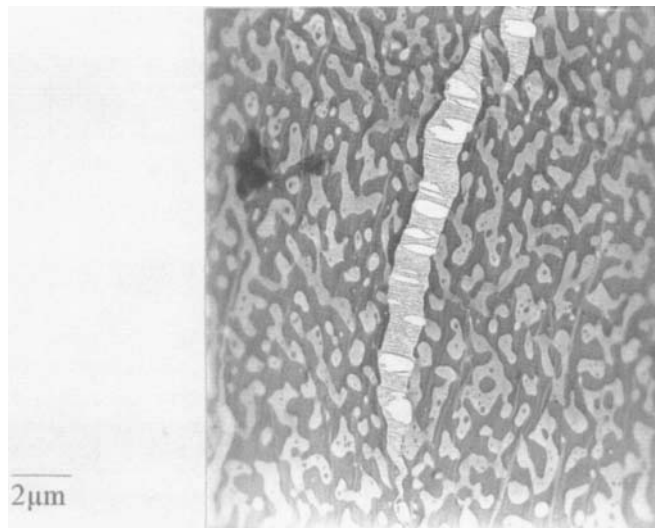

FIG. 10.   Craze with a pronounced fibrillar structure in a blend PMMA/PS (1/1 w/w) with a cocontinuous structure.
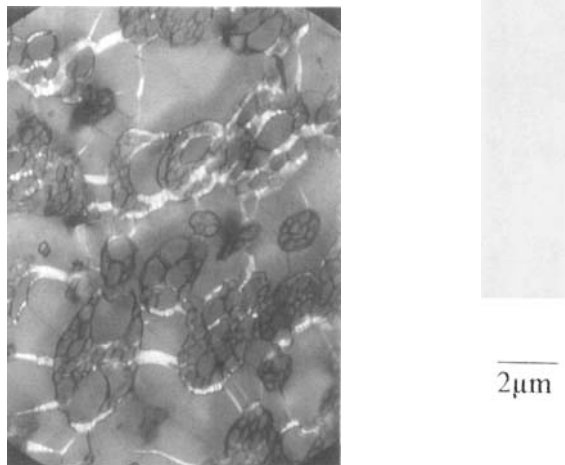
FIG. 11. Crazes in impact modified PS (HIPS), forming a network between the rubbery salami domains.

width and turn into disastrous cracks. But crazing is welcome in thermoplastic-elastomeric blends since elastomeric domains produce so many crazes that none of them acquires an overcritical length [4, 14]. The impact-modified versions of brittle thermoplastics can be deformed considerably before they break because of the mechanism of induced multicrazing that is observed as stress whitening.

The graft copolymer chains ensure that the interfaces between the elastomeric domains and the thermoplastic matrix do not break when the crazes are initiated.
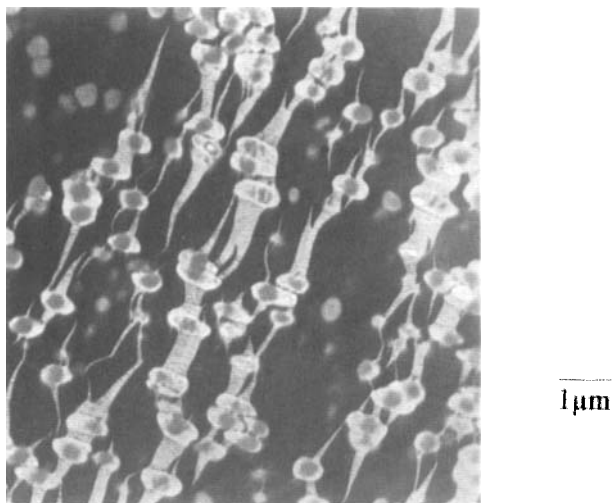

FIG. 12. Crazes in a rubber-modified thermoplastic, grown under tensile stress normal to the crazes: PS matrix and core-shell particles (core: polybutylacrylate and PMMA, shell: PMMA).

These copolymer chains are, in fact, the actual impact modifiers in rubber-modified thermoplastics.

ACKNOWLEDGMENT

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