

Block-graft copolymers as compatibilizers in polymer blends

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Block copolymers can be good compatibilizers in polymer blends, if tailored carefully. However, they are produced by anionic polymerization which is not a versatile technique and, moreover, is expensive. Suitable alternatives are block-graft copolymers, which can be prepared by radical grafting from readily available block copolymers, in particular from *SbB* (S, styrene; B, butadiene). The efficiency of two block-graft copolymers, *SbBgCHMA* and *SbBgMMA* (CHMA, cyclohexylmethacrylate; MMA, methyl methacrylate), as compatibilizers in PS/PVC blends of polystyrene (PS) and poly(vinyl chloride) (PVC) was investigated by electron microscopy. Both copolymers refined the coarse morphologies of the PS/PVC blends excellently, covering the interfaces between the phase domains of PS and PVC with monolayers. This is in accord with the commonly assumed model of the compatibilizer effect of block copolymers. However, the phase structures were, in fact, even finer than predicted by the model: perfectly compatibilized phase domains were torn apart during mixing in the kneader, whereby the morphology was further refined. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Problems with two-phase polymer blends are, to a large extent, due to weak phase boundaries. During mixing in the liquid state, the interface tension hinders an efficient phase dispersion, so that morphologies with a coarseness commonly on the micrometre scale are obtained. In the solid state, the extended surfaces of such coarse phase domains are particularly sensitive to stress. Insufficiently stabilized by entangled chains, they break ('dewet') comparatively easily, thus initiating cracks.

To minimize the inadequacies of the interfaces, block or graft copolymers are added to blends^{1–4}. The copolymers are supposed to 'compatibilize' the blends via the mechanism indicated in *Figure 1* for a blend of two homopolymers P' and P'' and a symmetric diblock copolymer $B'-B''$ ^{5–9}. If the block B' mixes only with P' , and the block B'' only with P'' , then the copolymer can cover the interface in a monolayer, with the blocks B' and B'' reaching out into opposite phases. In 'ideally compatibilized' systems, (i) the interfaces are totally covered by a continuous copolymer monolayer, and (ii) there are no copolymer chains outside the interfaces¹⁰. In this situation, the interfacial tension is lowered drastically and the blend morphology is in equilibrium. A structure with a coarseness of the order of $\lambda = \lambda^*/\phi$ is expected, where λ^* is the coarseness of the lamellar microstructure of the block copolymer itself, and ϕ is its volume fraction in the blend. With λ^* of the order of tens of nanometres, blend morphologies with λ in the

submicrometre range are predicted, even for $P'/P''/B'-B''$ blends with low copolymer contents.

These fine equilibrium morphologies should be stable. While the unstable phase structures of P'/P'' homopolymer blends grow indefinitely, during annealing in the liquid state, the equilibrium structures of $P'/P''/B'-B''$ blends should remain unchanged, just as the microstructure of the pure $B'-B''$ copolymers do themselves.

This model of the compatibilizer effect of block copolymers has raised high hopes. Meanwhile, however, it has turned out that the compatibilizer effect is subject to very restrictive conditions: If P' and B' , as well as P'' and B'' , are chemically equal pairwise, the copolymer blocks must be longer than the homopolymer chains which are usually already quite long^{9,11–14}. If B' and B'' are different from P' and P'' , the $P'-B'$ and $P''-B''$ pairs must have attractive interactions, which are rare among polymers. Consequently, the copolymers must be adjusted carefully to each blend that they are expected to compatibilize^{1–9,11–14}.

Well-defined block copolymers with long blocks can be made by anionic polymerization. However, the technique works only with a limited number of monomers and is expensive, in particular if a new block copolymer is needed for every new blend. In this present paper, another class of blocky copolymer is discussed, i.e. 'block-graft' copolymers which are prepared by grafting from a diblock copolymer. A particularly advantageous feature of block-graft copolymers is that a whole family of these materials can be made, radically, from only one anionically produced block copolymer.

The architecture of the two block-graft copolymers studied here, namely '*SbBgCHMA*' and '*SbBgMMA*', is

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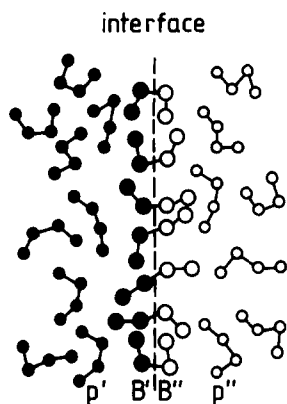


Figure 1 Compatibilizer effect: monolayer of a block copolymer B'-B'' in the interface between the phases of two homopolymers P' and P''

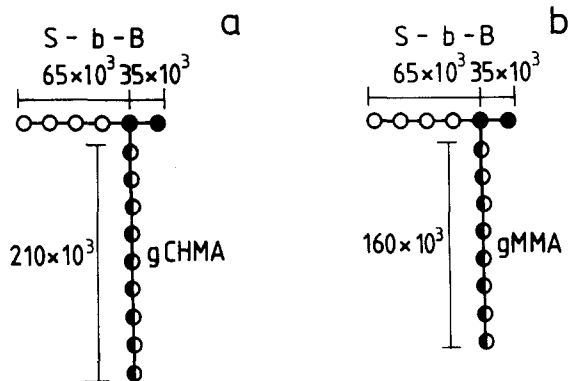


Figure 2 Architecture and weight-average molecular weights of the block-graft copolymers S**b**BgCHMA and S**b**BgMMA

indicated in Figure 2. A diblock S**b**B backbone with a longer styrene (S) and a shorter butadiene (B) block carries, on the B block, on average one cyclohexyl (CHMA) or methyl (MMA) methacrylate graft. As the B block is short, these copolymers are related to the diblock copolymers S**b**CHMA and S**b**MMA. As is demonstrated below, they are good compatibilizers in PS/PVC homopolymer blends of polystyrene and poly(vinyl chloride).

EXPERIMENTAL

The homopolymers used in this study were the poly(vinyl chloride) Vestolit 6554 (Hüls AG, $M_w = 115 \times 10^3$, polydispersity $M_w/M_n = 2.1$) and the polystyrene 168N (BASF AG, $M_w = 329 \times 10^3$, $M_w/M_n = 2.1$). The diblock copolymer S**b**B was provided by BASF AG, explicitly for this study. It has a narrow size distribution, with the molecular weights M_w indicated in Figure 2. The preparation of the block-graft copolymers S**b**BgCHMA and S**b**BgMMA by radical polymerization in solution is described in ref. 15. Unlike S**b**B, the grafts have a normal length and number distribution. The 'average' architecture is indicated in Figure 2. Both copolymers contain 20–30 wt % of ungrafted S**b**B. All blends were prepared by melt mixing in a kneader (Brabender Plastograph, chamber volume 30 ml, 50 r.p.m., 8 min) at 195°C. Transmission electron microscopy was performed on ultrathin sections cut at room temperature. Butadiene phases were stained with

OsO₄¹⁶. The contrast between the PS and PVC phases arises from selective degradation of the PVC by the electron beam¹⁷.

RESULTS

With PS and PVC being strongly incompatible^{18,19}, mechanically mixed PS/PVC blends exhibit coarse morphologies as shown in Figure 3, with domains of the order of a few micrometres across. There was a considerable scatter in the structure coarseness throughout the samples. The 1 : 1 and 3 : 1 (weight ratio PS : PVC) blends in Figure 3 seem to be quite different but the former blend also had coarser spots, while the latter blend had finer spots.

The block-graft copolymers shown in Figure 2, S**b**BgCHMA and S**b**BgMMA, were chosen because the S block can mix with PS and the CHMA or MMA graft with PVC²⁰. The short B block in the centre of the copolymers plays two roles: it is the anchor for the graft, and it makes the copolymers visible in the electron micrographs, since it can be stained black.

The S**b**BgCHMA copolymer compatibilized the PS/PVC blend excellently. As shown in Figure 4, the morphologies of the compatibilized blend are barely resolved (on the scale of Figure 3).



Figure 3 PS/PVC blends with weight ratios of (a) 1 : 1, and (b) 3 : 1; PS grey, PVC white

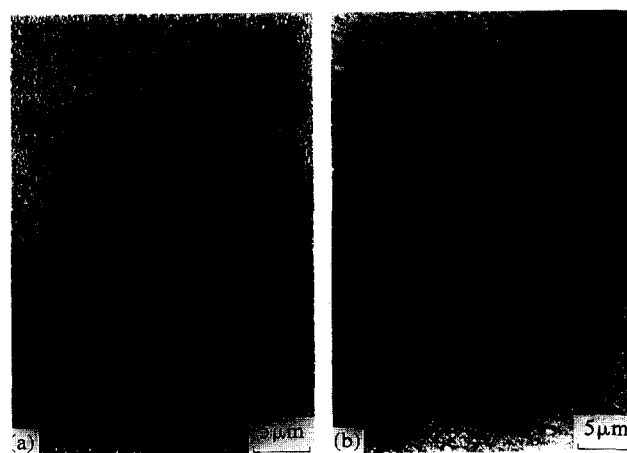


Figure 4 PS/PVC blends of Figure 3, compatibilized with 20 wt % of S**b**BgCHMA

The original *SbB* diblock copolymer is not a compatibilizer. It enters exclusively the PS phase, forming micelles, and the phases of PS and PVC remain coarse (Figure 5). Scanning electron micrographs of cryofracture planes of a PS/PVC blend with *SbBgCHMA* or *SbB* are shown in Figure 6. While the surface of the former blend (Figure 6a) is smooth, that of the latter (Figure 6b) is rough and reveals that the fracture was initiated by dewetting of the interfaces. Accordingly, the blend with *SbBgCHMA* broke in tension at $\epsilon > 5\%$, beyond a yield point, while the blend with *SbB* was extremely brittle,



Figure 5 PS/PVC (1:1) blend with 20 wt % of *SbB*; the small dots inside the PS matrix are micelles of the copolymer *SbB*



Figure 6 Scanning electron micrographs of a cryofracture plane of the PS/PVC (1:1) blend with 20 wt % of (a) *SbBgCHMA*, and (b) *SbB*

breaking at $\epsilon < 1\%$, in the same way as the original PS/PVC blend itself.

Simple *BgCHMA* graft copolymers are as ineffective as *SbB*, although the CHMA grafts are miscible both with PS and PVC²¹.

To summarize, the block-graft copolymer owes its efficiency, as expected, to the combination of the S block and the CHMA graft. This efficiency is demonstrated again in Figure 7 which shows a magnification of Figure 4. However, despite the quality of the morphologies, Figure 7 leaves some doubts as to whether this is really the finest dispersion that it is possible to achieve. According to Figure 1, an ideal compatibilizer would cover the interface in a continuous lamellar monolayer. However, Figure 7 appears very differently: (i) the *SbBgCHMA* copolymer forms spherical micelles, (ii) only a part of these micelles covers the interfaces, with the other part being dispersed in the PS phase, and (iii), most irritatingly, the interfaces are partly 'free', i.e. not covered by micelles. The compatibilization thus seems incomplete.

This can be changed, quite easily, by annealing. Figure 8 shows the blend of (PS/PVC) (1:1) with *SbBgCHMA* (20 wt %) after 1 h annealing at 200°C. All of the micelles have travelled into the interfaces, which are now covered completely. This structure deviates from the model shown in Figure 1 only in as much as the micelles in the interfaces still do not merge into continuous lamellae, but instead remain spherical.

Since the annealed structure shown in Figure 8 is more perfectly compatibilized than the original one shown in Figure 7, it should be finer. However, it is coarser. As shown in Figure 9b (lowest curve), annealing makes the structure coarsen until a stable morphology, corresponding to the equilibrium predicted by Figure 1, is reached.

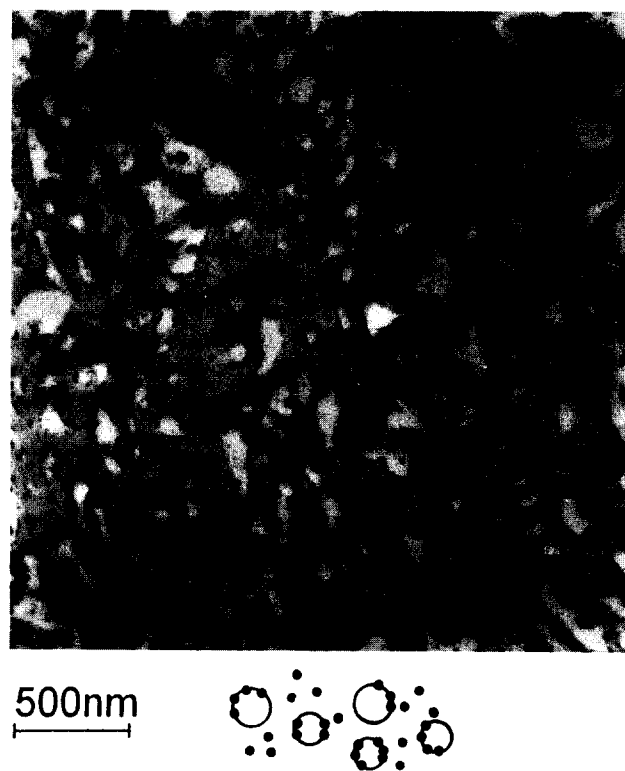
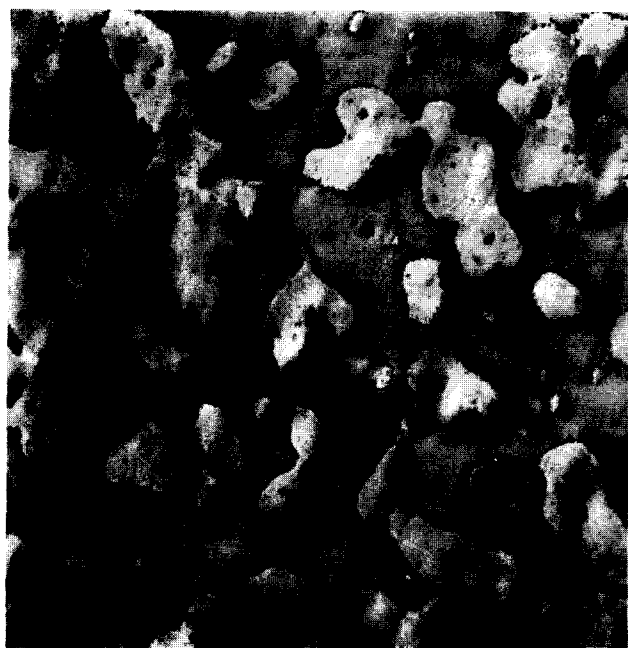


Figure 7 Magnified region of Figure 4a: PS/PVC blend with weight ratio 1:1 compatibilized with 20 wt % of *SbBgCHMA*; the small black dots are micelles of the copolymer *SbBgCHMA*



500nm



Figure 8 (PS/PVC) (1:1) blend with *SbBgCHMA* (20 wt %), as in *Figures 4a* and *7*, but annealed for 1 h at 200°C. The interfaces are covered by strings of micelles

Now, this equilibrium structure, which according to the model should be the finest possible, is more than twice as coarse as the original structure in *Figure 7*.

Figure 10 confirms these results. The blend of (PS/PVC) (3:1) with *SbBgCHMA* (20 wt %) is shown, after 1 h annealing at 200°C. The interface layers of the copolymer appear quite lamellar, but, in the magnifications in *Figure 11*, the same strings of spherical micelles are seen as in *Figure 8*. (Similar interfacial layers were reported for cast films of blends with ternary triblock copolymers²².)

In *Figures 8* and *11*, practically all of the micelles are in the interfaces. Since the *SbBgCHMA* copolymer contains ungrafted *SbB*, this is a bit surprising. The *SbB* is apparently pulled along by the *SbBgCHMA* into the interfaces.

So far, blends with 20 wt % of the copolymer *SbBgCHMA* have been considered, because their morphologies are particularly uniform. However, the compatibilizer effect sets in at a much lower copolymer content. As shown in *Figure 9a*, the blend with 2 wt % of the copolymer already has a morphology which is three times finer than the PS/PVC (1:1) homopolymer blend. It is very obvious from *Figure 9a* that the morphologies obtained immediately after mixing in the kneader are much finer than the 'ideally compatibilized' equilibrium structures that are obtained after annealing. *Figure 9b* shows the kinetics of the structure coarsening during annealing: while the unstable phase structure of the PS/PVC blend grows indefinitely, all of the blends containing *SbBgCHMA* approach an equilibrium coarseness.

The *SbBgMMA* copolymers are different from the *SbBgCHMA* copolymers only in as much as the CHMA grafts are miscible both with PS and PVC, but the MMA grafts are miscible only with PVC. Since CHMA also prefers PVC, this difference is relatively unimportant.

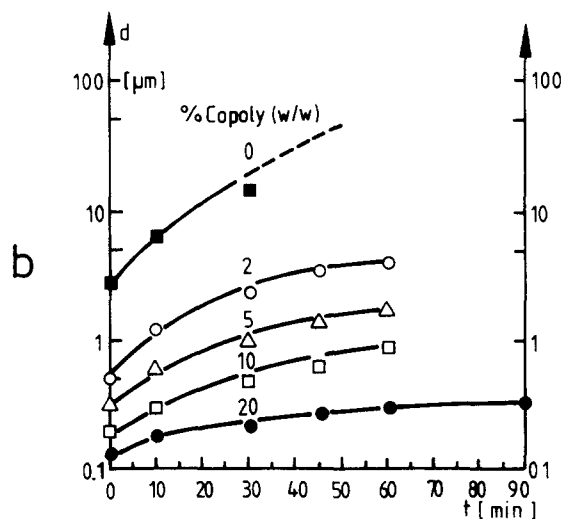
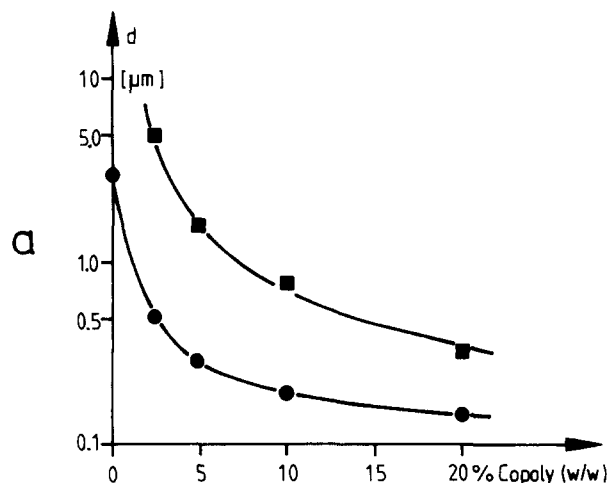


Figure 9 (a) Coarseness of PS/PVC (1:1) blends, compatibilized with different amounts (wt %) of the *SbBgCHMA* copolymer: (●) immediately after mixing in the kneader; (■) after 90 min annealing at 200°C ('ideally compatibilized' morphology). (b) Kinetics of structure coarsening during annealing

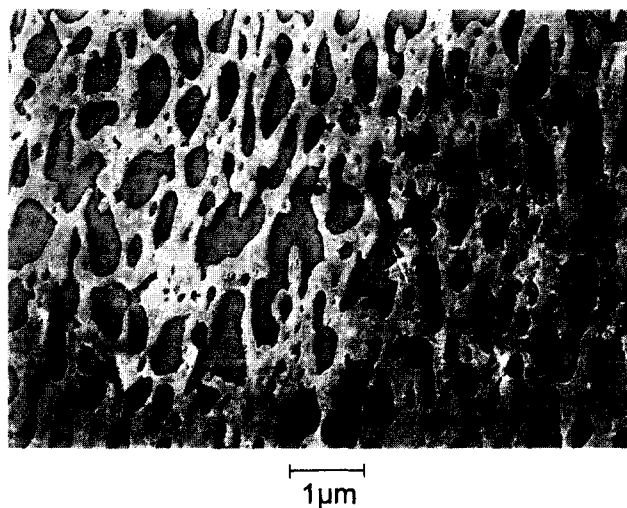


Figure 10 (PS/PVC) (3:1) blend with *SbBgCHMA* (20 wt %) annealed for 1 h at 200°C

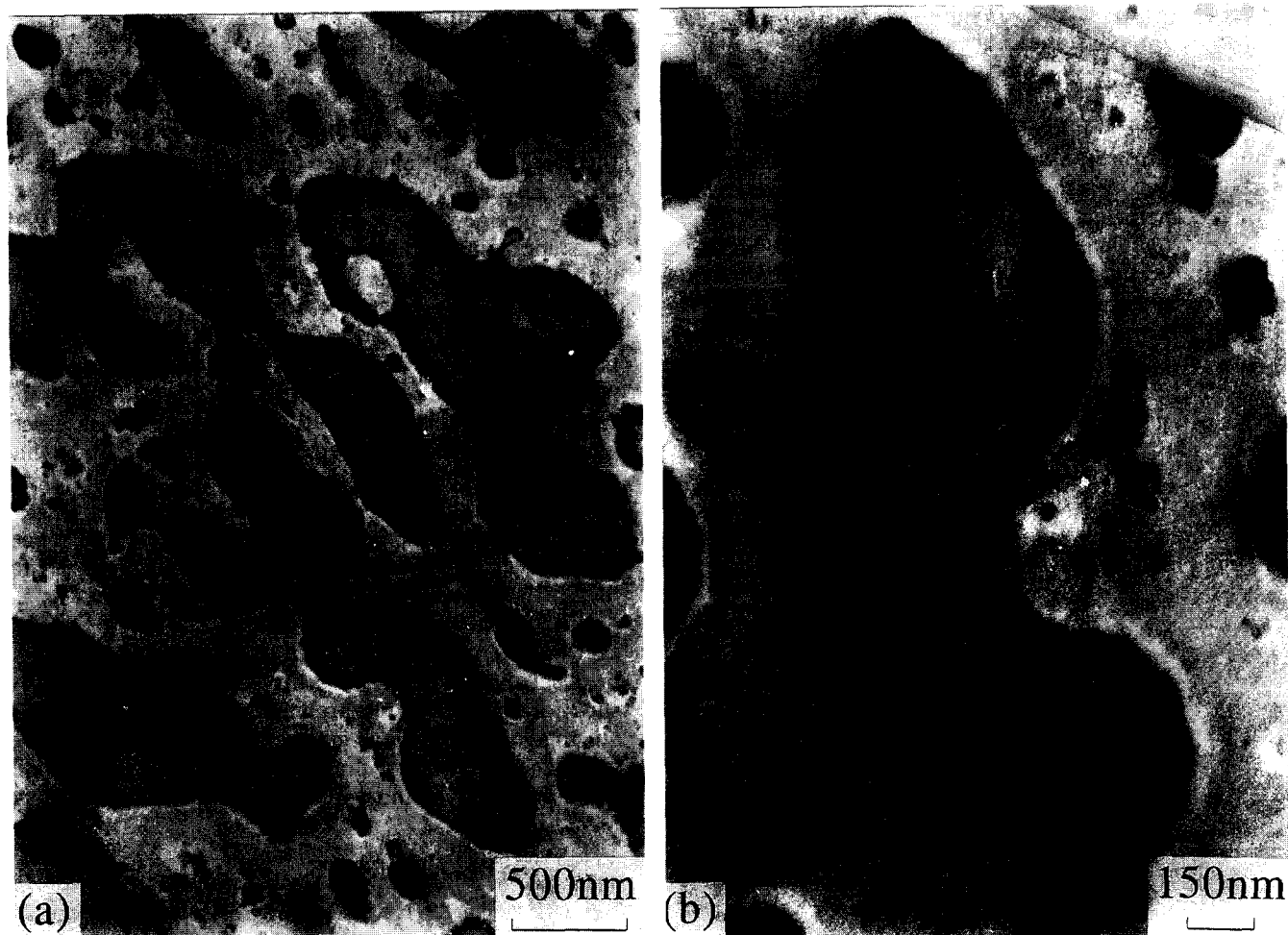


Figure 11 Magnifications of the micrograph shown in Figure 10; the interfaces are covered by strings of micelles

Therefore, the *SbbgMMA* copolymer was not expected to introduce any new effects. Indeed, it behaved quite similarly, as demonstrated, for the blend of (PS/PVC) (1:1) with *SbbgMMA* (20 wt %), in Figure 12.

The fine morphologies of the PS/PVC blends compatibilized with the *SbbgCHMA* or *SbbgMMA* copolymers improved the solid-state mechanics in the expected manner. The extremely low tensile and impact strengths of the PS/PVC blends were practically remedied. As

discussed in ref. 23, the compatibilized blends behaved mechanically almost as if they were homogeneous.

DISCUSSION

This study demonstrates the quality of the *SbbgCHMA* and *SbbgMMA* block-graft copolymers as compatibilizers for the PS/PVC homopolymer blend. Ideally compatibilized morphologies are seen in Figure 8 and Figures 10–12. Two points will be discussed, namely (i) why the copolymers form micelles in the interfaces, instead of lamellae, and (ii) where the morphology shown in Figure 7, which seems to be ‘too fine’, judging from the model in Figure 1, actually comes from.

Point (i) is easy to explain. The micelles seen in the interfaces in Figures 8 and 11 are misleading. The block-graft copolymers do, in fact, form lamellar monolayers in the interfaces. An interface covered by copolymer chains is indicated in Figure 13. The S blocks and the grafts form continuous layers on both sides of the central B blocks. However, the B blocks, being too short, do not really fill the centre layer and are, therefore, forced to form micelles. Since only these micelles are visible, the electron micrographs displayed in Figure 8 and Figures 10–12 convey the impression of very thin, and not continuous, interface layers of the block-graft copolymer. In fact, the monolayers are much thicker and continuous.

Point (ii) is more delicate. The PS/PVC/*SbbgCHMA* blends form, immediately after mixing in the kneader,

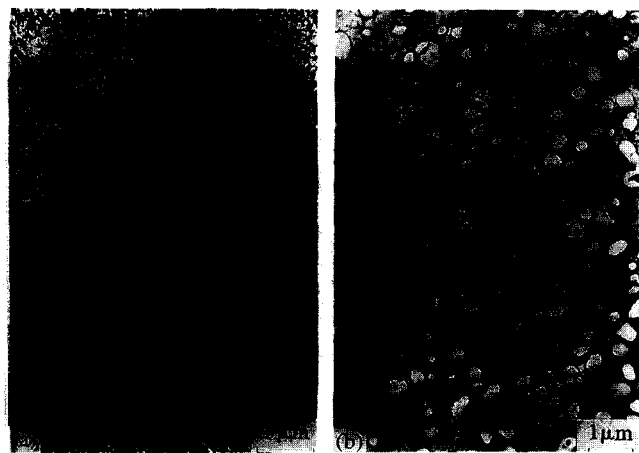


Figure 12 (PS/PVC) (1:1) blend with *SbbgMMA* (20 wt %): (a) immediately after mixing in the kneader; (b) magnification of the same region

the extremely fine but disordered morphologies of Figure 7 although annealing proves later that they are perfectly able to assume the well-ordered 'ideally compatibilized' morphologies of Figure 8. The ill-defined phase structures shown in Figure 7 do not appear to profit much from the compatibilizer effect, i.e. the interfaces are only partly protected by the *SbBgCHMA* chains. Nonetheless, *this 'bad' morphology is finer than the equilibrium morphology* (see Figure 9).

An interpretation of Figure 7 is offered in Figure 14, presented in terms of two stages of the compatibilizer effect. In the first stage, the blends indeed attain the ideally compatibilized structure, with all interfaces covered by copolymer micelles (Figure 14a). For the model (Figure 1), this is the end-point of phase dispersion. However, a second stage can follow which is not controlled by the thermodynamics of the system, but by its special viscoelasticity. The 'ideally compatibilized' phase domains *can be torn apart mechanically*, in the following manner.

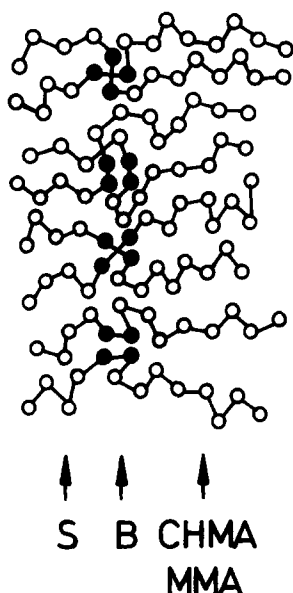


Figure 13 Interface layer of the block-graft copolymers in the interfaces. Note that in all of the electron micrographs displayed in this paper, only the B blocks, which form micelles, are observed

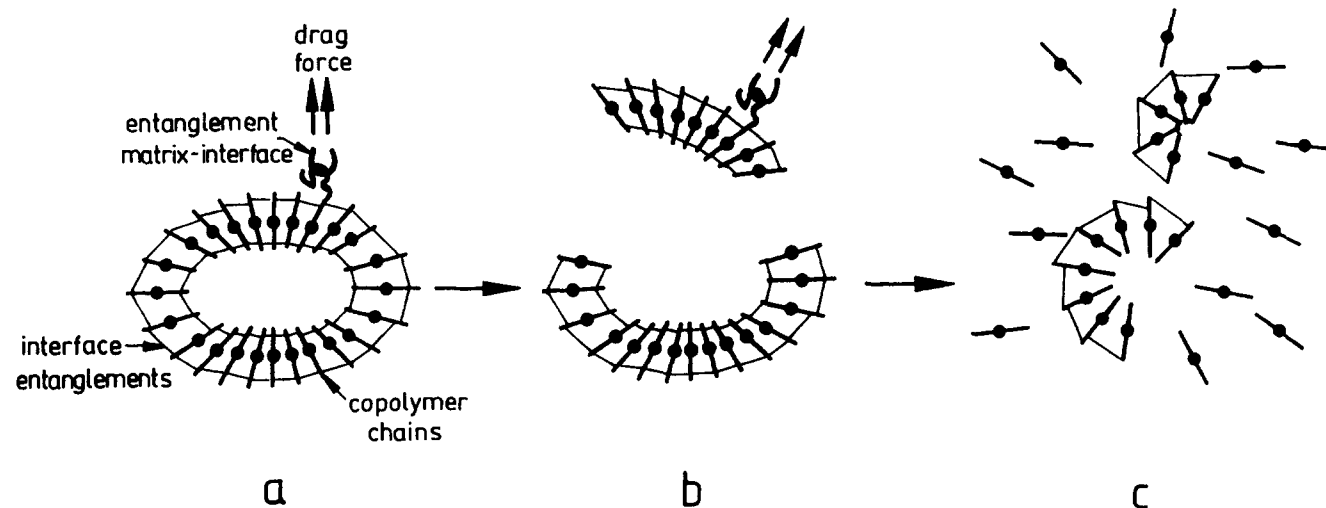


Figure 14 Model of a two-stage compatibilizer effect. (a) A phase domain which is totally covered by copolymer chains (1st stage) is (b) torn apart by drag forces from the matrix which are transmitted by an entanglement. This produces (c) smaller domains, which are not totally covered by copolymer chains, as well as dispersed micelles of the copolymer

The naked interfaces in the uncompatibilized blends are traversed by only a few chains and are, therefore, weakly entangled. In contrast, the copolymer-covered interfaces in the compatibilized blends are traversed by very many chains, albeit the copolymer chains, and are, therefore, strongly entangled (provided that the blocks of the copolymer are long enough). When stress is exerted, during mixing, by the matrix on to the compatibilized phase domain in Figure 14a, it is transmitted efficiently through entanglements between the copolymer chains in the interface. The interface and, therefore the domain, can be torn apart (Figure 14b), which leads to an even finer morphology. The result is shown in Figure 14c which explains directly the 'too fine' morphologies of Figure 7: domains 'smaller than possible' are observed which are not perfectly covered by copolymer, and some copolymer micelles, torn away from the interfaces, float inside the homopolymer phase of the PS.

In conclusion, the compatibilizing efficiency of block and graft copolymers can vary from zero (Figure 5) to 'better than thermodynamically possible' (Figure 7).

Block-graft copolymers therefore proved to be excellent compatibilizers in this study, but it cannot be decided yet if the block-graft architecture is generally superior to the diblock architecture. However, the big advantage of these block-graft copolymers is certainly the versatile preparation technique of radical polymerization which is employed in their production.

ACKNOWLEDGEMENTS

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