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Random and Block Copolymers as Compatibilizers, Directly Compared

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Summary: Most blends are two-phase systems that exhibit coarse morphologies with weak interfaces between the phases. It is well known that these blends can be compatibilized by suitably adapted block copolymers is known. Less known is that random copolymers can compatibilize blends as well, forming interphases. In this study, block and random copolymers of styrene and methylmethacrylate were tested in direct comparison, in a blend of polystyrene and polyvinylchloride. The random copolymers are inferior, as regards the phase morphologies, but competitive, as far as the tensile strength is concerned.

Introduction

Since most polymers are immiscible, two-phase blends A/B are the rule. These blends exhibit coarse two-phase morphologies, in which the weak spots are the interfaces between the phase domains. In the interfaces, the interactions between chain segments are reduced and the chain entanglement network is impaired. *Block copolymers* are suited to remedy these problems[1-4]. If appropriately adjusted, the copolymer chains $\alpha b\beta$ concentrate in the interfaces as indicated in Figure 1a, each block extending into one phase, whereby the two blend phases A and B are physically tied together. For this compatibilizer effect, the interactions A-α and B-β must be attractive and the other interactions (A-B, A-β, α-B, α-β) repulsive. Truly attractive interactions are rare among polymers, but the neutral interactions in blends A/B/$\alpha b\beta$ with chemically pairwise equal blocks and chains (A=α, B=β) suffice frequently.

While blends with block copolymers $\alpha b\beta$ have been analyzed extensively[1-4], blends with *random copolymers* have not attracted equal attention. But random copolymers $\alpha co\beta$ are interface active as well, if properly adjusted[5,6]. This is particularly obvious in simple systems where A=α and B=β: copolymers $\alpha co\beta$ will be less incompatible with A and B than these with each other. Therefore, they will concentrate in blends A/B/$\alpha co\beta$ between A and B phases as indicated in Figure 1b, thus compatibilizing the blend.

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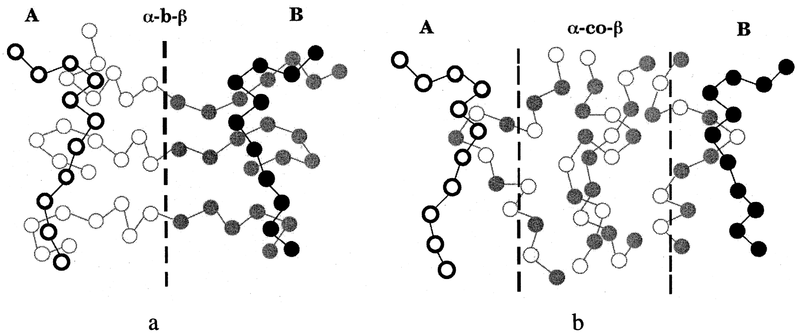


Figure 1. Copolymers between phases A and B of a blend: (a) monolayer of a block copolymer αbβ, (b) interphase of a random copolymer αcoβ

The mechanisms of compatibilization with αbβ and αcoβ are quite different. While αbβ is a "black-and-white" copolymer where α and β are separated into blocks, αcoβ is a "gray" copolymer where the α and β units are intimately mixed. Consequently, αbβ can form a monolayer in the interface (Figure 1a), while αcoβ can only form a true interphase which is thicker than a monolayer (Figure 1b). In other terms: in blends A/B, αbβ acts as a shoe lace while αcoβ has the effect of a glue.

In this report, the effects of block and random copolymers S-MMA consisting of styrene and methylmethacrylate on the morphology and the tensile behavior of blends PS/PVC of polystyrene and polyvinylchloride will be compared. The copolymer system S-MMA was chosen because PMMA and PVC are miscible.

Polymers

Polystyrene 168N (BASF, $M_w=329\times10^3$) and polyvinylchloride Vestolit 6554 (HÜLS, $M_w=115\times10^3$) were used. The two were always blended 1:1 by weight. The copolymers SbMMA, prepared anionically, and ScoMMA, prepared radically, are characterized in Figure 2. The block copolymers are longer-chained than the random copolymers since short blocks endanger the monolayer formation (Figure 1a). Of the copolymers in Figure 2, only those two will be described that conformed best with Figure 1: the symmetric block copolymer $S_{51}bMMA_{49}$ and the asymmetric random copolymer $S_{31}coMMA_{69}$. From now on, these two will be denoted SbMMA and ScoMMA.

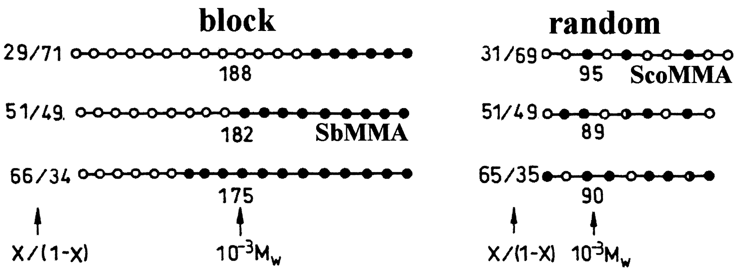


Figure 2. Block and random copolymers of styrene and MMA, molecular weight M_w and S/MMA weight composition x (SbMMA and ScoMMA are discussed in the text)

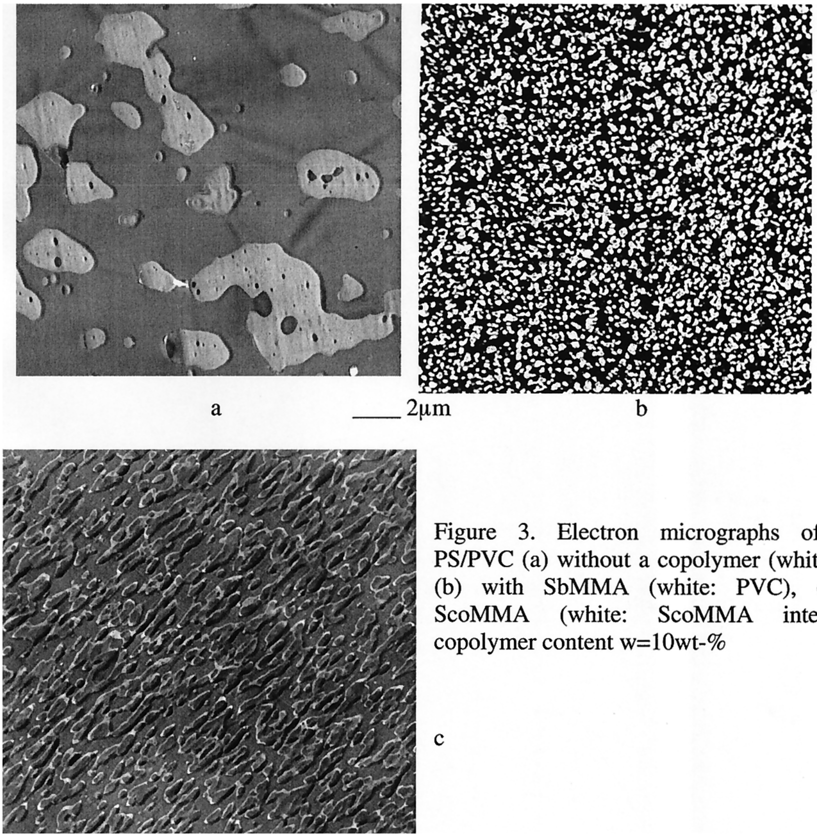
Morphologies

The phase morphology of the blend PS/PVC (always 1:1 by weight) as obtained after 8min blending in a kneader at 190°C is shown in Figure 3a. It is coarse, with PVC domains on the micrometer scale. Any copolymer deserving the rank of a compatibilizer must refine this morphology since both mechanisms shown in Figure 1 lower the interface tension.

Both SbMMA and ScoMMA did well (Figure 3b,c). SbMMA was particularly efficient. The blend PS/PVC/SbMMA in Figure 3b, at a copolymer content of w=10wt-%, exhibits an extremely fine microstructure on the same scale as structures of neat SbMMA. As shown in Figure 4a, the domain size d drops steadily with increasing copolymer content w, according to $d=d_{\alpha\beta}/w$ where $d_\alpha=11nm$ describes the structure of neat SbMMA.

ScoMMA, too, made the morphology of the blend PS/PVC finer, as shown in Figure 3c. The white envelopes about the PVC domains in the figure are ScoMMA interphases (to emphasize these interphases, no contrast was used for the electron micrograph in Figure 3c, while RuO_4 was used for Figure 3b). While these ScoMMA interphases are visibly thick, SbMMA monolayers are invisibly thin.

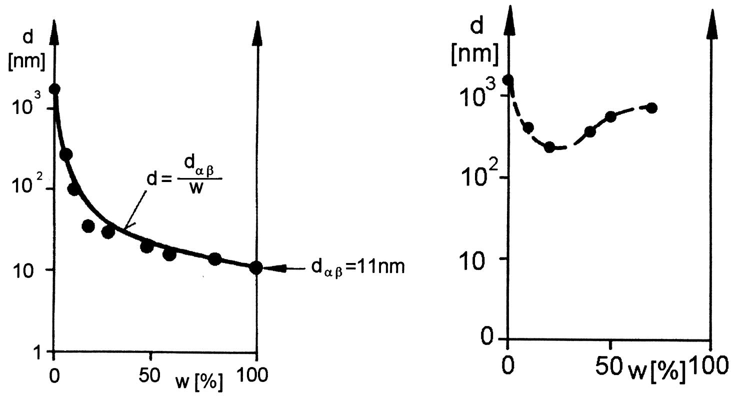
The different effects of SbMMA monolayers and ScoMMA interphases are documented in Figure 4. Addition of SbMMA leads to an increase the interface area in the blend PS/PVC steadily, which results in a monotonous drop of the morphology coarseness in Figure 4a. But Figure 4b shows a minimum of coarseness. Evidently, the ScoMMA interphases result in an increase of the interface area at low copolymer contents, too. However at higher contents, additional ScoMMA simply makes these interphases thicker, with the effect that the morphology coarseness remains constant or increases again.



a ____ 2μm b

c

Figure 3. Electron micrographs of blends PS/PVC (a) without a copolymer (white: PVC), (b) with SbMMA (white: PVC), (c) with ScoMMA (white: ScoMMA interphases), copolymer content w=10wt-%



a b

Figure 4. Structure coarseness d of compatibilized blends PS/PVC as function of the copolymer weight content w, (a) with SbMMA, (b) with ScoMMA

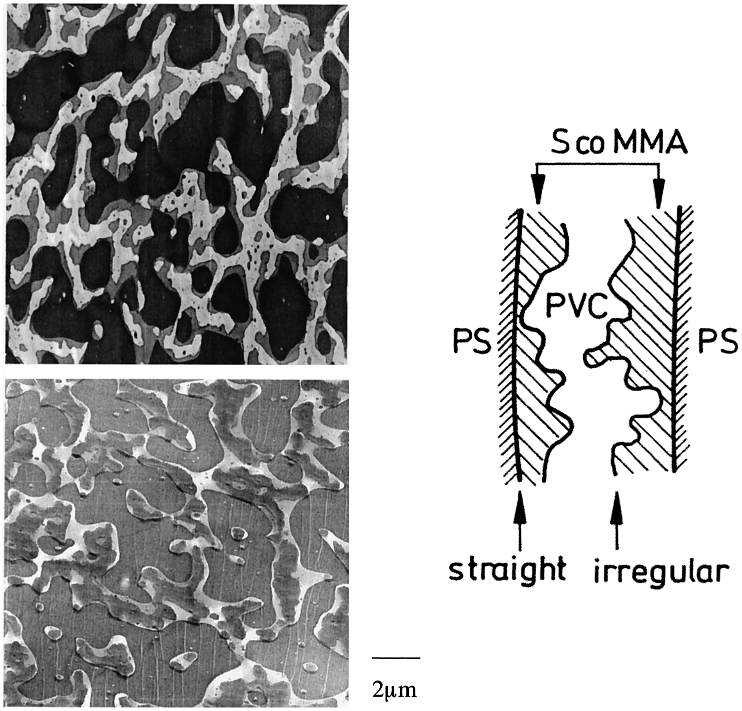


Figure 5. Blend PS/PVC/ScoMMA (w=20wt-%), unstained (below, copolymer white) and stained with RuO_4 (above, PVC white, copolymer gray, PS black)

ScoMMA was chosen, for this report, from the three random copolymers in Figure 2 because only ScoMMA formed interphases in the blend PS/PVC while the other two copolymers, containing more styrene, concentrated their phases inside the PS phase. Evidently, ScoMMA forms interphases because it interacts with both polymers similarly.

It was of interest to know whether ScoMMA interacts, in fact, equally with PS and PVC or only similarly. Electron microscopy yielded an answer. The blend PS/PVC/ScoMMA with w=20wt-% copolymer in Figure 5 had been annealed to allow the morphology to coarsen spontaneously under thermodynamic control. In the resulting structure, the ScoMMA phase has two differently shaped interfaces: the one with the PS phase is as straight as possible, but the one with the PVC phase is irregularly curved and bent. The PVC-copolymer interface is thus much larger than the PS-copolymer interface, indicating better interactions PVC-ScoMMA than PS-ScoMMA. This detail would certainly not have been detected by any other method.

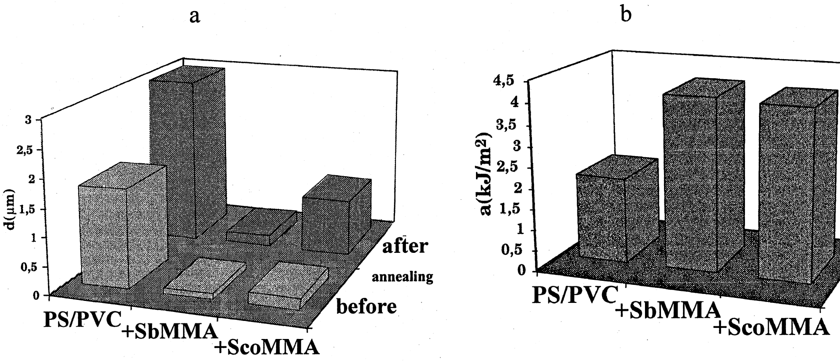


Figure 6. Behavior of the blend PS/PVC without copolymer and with SbMMA or ScoMMA (w=10wt-%): (a) structure coarseness d before and after annealing in the melt, (b) impact resistance a

Since both SbMMA and ScoMMA can refine the PS/PVC morphology, the question arises whether the fine phase structures are thermodynamically stable or not. According to the models indicated in Figure 1, the blend structures with SbMMA should be stable, due to the inherent tendency of SbMMA to form monolayers, while the blend PS/PVC/ScoMMA, as any other ternary blend of homopolymer or random copolymer components, should form unstable structures. Indeed, as shown in Figure 6a, annealing in the melt (30min, 190°C) left the structure coarseness d of the blend with SbMMA practically unaltered, while the blend structure with ScoMMA was coarsened almost to the same degree as the blend PS/PVC itself.

Mechanics

The morphologies seemed to indicate that the block copolymer SbMMA is the better compatibilizer. However, the random copolymer ScoMMA yielded mechanically competitive products. Figure 6b proves that both SbMMA and ScoMMA doubled the impact resistance.

The failure mechanisms are illustrated by Figure 7. In the blend PS/PVC, an unstable crack runs in the interfaces (Figure 7a). The copolymers change this. In the blend with w=10wt-% of SbMMA (or ScoMMA, the pictures are equal) in Figure 7b, a long craze runs not in the interfaces but through the PS and PVC phases. The impact resistance is improved because both phases are being deformed and thus absorb energy, the PS phase by fibrillar crazes and the PVC phase by homogeneous elongation.

In the PS/PVC blend without copolymer, on the contrary, neither phase is deformed because the interface fails prematurely.

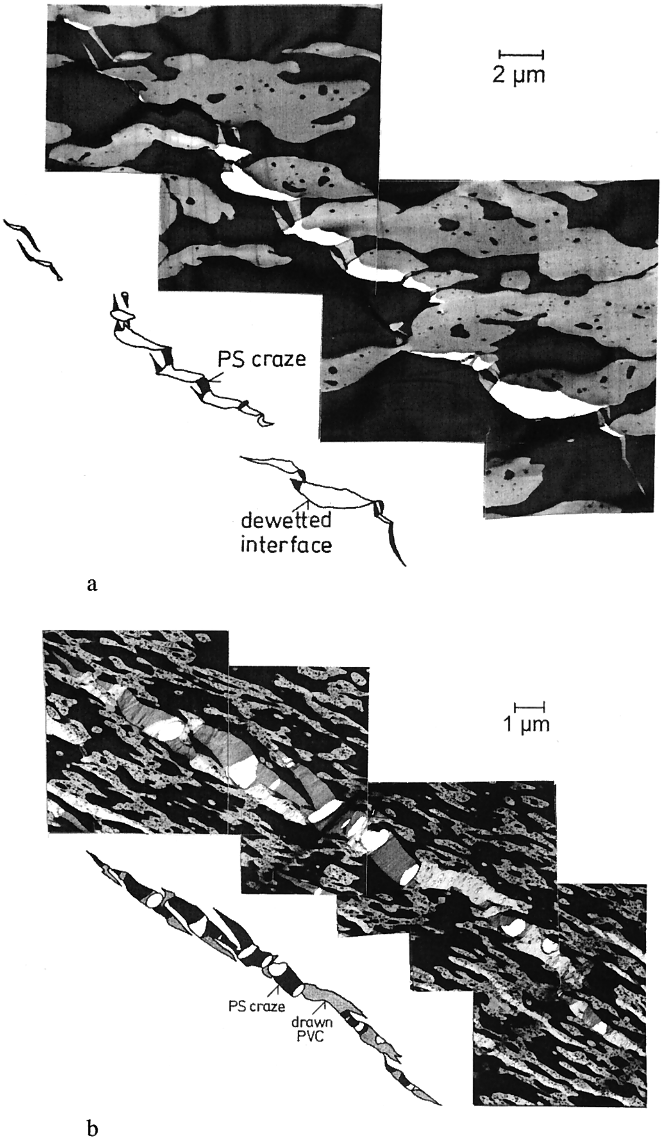


Figure 7. Failure in blends PS/PVC (PS dark, PVC light): (a) interface crack without copolymer, (b) craze with SbMMA (w=10wt-%); in the schemes: cracks (white), fibrillated PS crazes (black) and homogeneously deformed PVC (gray)

Conclusions

In this study, the block copolymer SbMMA behaved in a blend PS/PVC in all respects like a perfect compatibilizer: it formed monolayers between the blend phases, refined the morphology, prevented coarsening of this morphology during annealing in the melt and improved the impact resistance by changing the fracture mechanism from cracks in the interfaces to crazes through the phases.

The random copolymer ScoMMA behaved like an efficient while not perfect compatibilizer: it formed interphases between the blend phases by which the morphology was refined, but less so than with SbMMA monolayers. This morphology coarsened again at annealing. However, the improvement in mechanical properties was similar in blends compatibilized by ScoMMA and SbMMA.

These differences are rooted in the chain structure of the two copolymers. SbMMA can form thermodynamically stable microphases and thus, in a two-phase blend, also stable interface monolayers. Random copolymers such as ScoMMA are not able to form such microphases. ScoMMA cannot, therefore, anchor itself in interfaces in a thermodynamically stable manner. It can just form interphases. Why these, nonetheless, are mechanically quite efficient, is not known yet.

Acknowledgement

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