

On the Mechanism of Compatibilization of Polyolefin/Liquid Crystalline Polymer Blends with Graft Copolymers

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ABSTRACT: The compatibilization mechanism of some compatibilizers for blends of polyolefins with a liquid crystalline polymer (LCP) was studied. Polyethylene (PE) and polypropylene (PP) were blended with a semirigid LCP (SBH) in a batch mixer, either with and without compatibilizers. The latter were two commercially available samples of functionalized polyolefins, that is, a PE-*g*-MA (HDM) and a PP-*g*-AA (Polybond 1001) copolymer and some purposely synthesized PE-*g*-LCP and PP-*g*-LCP copolymers. Microtomed films of the binary and the ternary blends were annealed at 240°C on the hot stage of a polarizing microscope and the changes undergone by their morphology were recorded as a function of time. The results indicate that the compatibilizers lower the interfacial tension, thereby providing an improvement of the minor phase dispersion. In addition to this, the rate of the coalescence caused by the high-temperature treatment is appreciably reduced in the systems compatibilized with the PE-SBH and PP-SBH graft copolymers. Among the commercial compatibilizers, only Polybond 1001 displayed an effect comparable to that of the above copolymers. HDM improved the morphology of the as-prepared PE blends, but failed to grant sufficient morphological stabilization against annealing-induced coarsening. The results are discussed with reference to the chemical structure of the different compatibilizers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3027–3034, 2000

Key words: polyolefin/liquid crystalline polymer blends; compatibilization; morphology; coalescence

INTRODUCTION

The average size and the size distribution of the minor-phase droplets of polymer blends depend

on a number of factors including the chemical structure of the components and the thermal and mechanical histories. It is generally agreed that, during blend preparation, a dynamic equilibrium is reached whereby droplet breakup, caused by the stress field, is balanced by droplet coalescence driven by interfacial tension.^{1–6} Thus, the resulting steady-state droplet size is expected to be lower in the high-shear regions of the mixing bowl, or extruder, and higher where flow-induced coalescence prevails. It has also been shown that the elasticity of molten polymers has a role in

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drop deformation and failure and that larger droplets are formed in blends of polymers with a stronger elastic character.^{7,8} Blends are generally prepared by the use of extruders, where the equilibrium morphology of the melt can normally be approached within a few minutes mixing. This morphology is thereafter frozen in, during the subsequent quenching and pelletizing operations. Thus, a study of the morphology of blend pellets provides reliable information on the equilibrium situation prevailing at the melt-mixing stage.

In the absence of a stress field, the only active driving force is interfacial tension and the morphology corresponding to thermodynamic equilibrium is that involving a minimum interfacial area. Thus, macroscopic segregation should be expected, under these conditions, from a thermodynamic point of view. Also, in fact, when the blends are used for shaping the final objects, considerable coarsening can take place, especially if relatively long processing cycles with low stress are employed, such as those involved in compression molding. In other cases, coalescence may be severely hindered, kinetically, and almost no coarsening can be observed within relatively long time intervals, especially if the temperature is low, the components viscosity is high, and there is no flow in the system.

An efficient compatibilizer should lower the interfacial tension of a blend, thus reducing the equilibrium droplets' dimensions at the mixing stage and should also lower the coalescence rate, thus limiting the danger of morphology coarsening when new conditions favoring coalescence prevail. The need of a compatibilizer is particularly pressing when blends of polyolefins (POs) with liquid crystalline polymers (LCPs) are to be produced. These blends are potentially interesting because of the strong PO reinforcement that can be achieved by the addition of small amounts of LCPs. The chemical structure of the two polymer types, however, is such as to display very poor interfacial adhesion if no compatibilizer is added into the blend. Recently, different commercially available functionalized polymers have been employed as compatibilizing agents for PO/LCP blends. For example, polypropylene (PP) samples functionalized with maleic anhydride (PP-g-MA) or with acrylic acid (PP-g-AA) have been used for compatibilizing PP/LCP blends,⁹⁻¹⁶ while polyethylene (PE) modified with maleic anhydride (PE-g-MA) or copolymerized with acrylic acid (PE-co-AA) has been tested for the compatibilization of PE/LCP blends.^{17,18} The observed,

slight improvement of the mechanical properties and the concomitant increase of melt viscosity were attributed to polar interactions between either phase and the compatibilizer, but in no case did the results indicate the formation of chemical bonds between the blend components as a result of interphase reactions.

It is generally agreed that block or graft copolymers containing polymer sequences identical to those of the blend components should display an optimum compatibilizing ability, provided that the relative lengths of the homopolymer segments are appropriate. In previous articles,¹⁹⁻²³ we showed that PO-g-LCP copolymers synthesized by polymerizing the LCP monomers in the presence of either PP-g-AA²³ or a low molar mass oxidized PE sample,^{20,22} or, alternatively, by blending the functionalized Pos with the LCP in the presence of a transesterification catalyst,²¹ do enhance the interfacial adhesion of the PO/LCP blends both in the solid state and in the melt¹⁹ and improve the dispersion of the LCP minor phase.

In this work, the effect of these compatibilizers on the annealing-induced morphology coarsening was studied on blend films contained between two microscope slides and held on the microscope hot stage for appropriate times, and the results were compared with those found by the use of commercially available PE-g-MA and PP-g-AA compatibilizers. It is possible that the droplet coalescence observed under these conditions is influenced by the geometry of the system, as well as by the presence of the glass surfaces confining the film, and provides, therefore, only a rough picture of the situation prevailing in the bulk material. However, it can be safely assumed that the results may be meaningful as long as the data obtained from the blend films with and without a compatibilizer, as well as with different compatibilizers, are compared.

EXPERIMENTAL

Materials

The POs used in this work, high-density PE and isotactic PP, are commercial materials: A1100, supplied by Solvay, is a relatively low molar mass, injection-molding PE sample having a melt-flow index (MFI) of about 11 dg · min⁻¹, whereas PP was an injection-molding sample,

Table I Source and Properties of the Polymeric Materials

Polymer	Supplier	M_w (g/mol)	M_n (g/mol)	η_{inh} (dL/g)	T_m (°C)	MFI (dg/min)	η_0 at 240°C (Pas)
A	Solvay	—	—	—	136	11.0	950
PP	Montell	270.000	39.000	—	164	12.0	1200 ^a
HDM (PE- <i>g</i> -MA)	Polimeri Europa	—	—	—	—	6	—
Polybond 1001 (PP- <i>g</i> -AA)	Uniroyal	—	—	—	160	40.0	50
SBH	Eniricerche	—	—	0.87 ^b	219	—	^c
COPR	Ref. 20	—	—	—	—	—	^c
COPM	Ref. 21	—	—	—	—	—	^c
COPP50	Ref. 23	—	—	—	—	—	^c

^a Virgin.^b Inherent viscosity measured in pentafluorophenol ($c = 0.1$ g/dL) at 60°C.^c Does not present η_0 in the frequency range investigated.

X30G by Montell, with an MFI ≈ 12 dg min⁻¹ (Table I).

The LCP was a laboratory sample of a copolyester synthesized by Eniricerche S.p.A. (Milan, Italy) having the composition shown in the scheme. The LCP, indicated here as SBH, contains the flexible units (S) of sebacic acid and the rigid ones (B, H) derived from 4,4'-dihydroxybiphenyl and 4-hydroxybenzoic acid, respectively, in a 1:1:2 mol ratio. The characterization of SBH was already described in previous articles.^{24–28}

Commercially available functionalized POs were used as reference compatibilizers: a sample of PE-*g*-MA with $\sim 1\%$ w/w MA grafts (HDM, by Polimeri Europa) and one of PP-*g*-AA with $\sim 6\%$ AA (Polybond 1001, by Uniroyal). Their main properties are shown in Table I.

The PO-*g*-SBH copolymers were synthesized in our laboratories as described before.^{20–23} In particular, the PE-*g*-SBH copolymer indicated here as COPR and the PP-*g*-SBH copolymer (COPP50) were synthesized by melt polycondensation of the SBH monomers in the presence of either a low molar mass PE sample containing free carboxyl groups (PEox)²⁰ or, respectively, of Polybond 1001,²³ whereas the other PE-*g*-SBH copolymer indicated here as COPM was produced by reactive blending of SBH with Peox.²¹

Blends Preparation

The PO/SBH blends (80/20 w/w) were prepared in a batch mixer (Brabender Plasticorder, Model PLE330) equipped with a 50-mL mixing bowl. The mixing temperature was 240°C and the speed 30 rpm. To avoid hydrolytic chain scissions, the

LCP sample was dried under a vacuum for about 24 h at 110°C before processing. The compatibilizers were also dried under a vacuum before use for at least 2 days at a lower temperature (60°C) to avoid degradation phenomena. Master batches (50/50 w/w) of the compatibilizers with SBH were first prepared and then blended with the appropriate amounts of the components so as to obtain a weight ratio of PO to SBH equal to 80/20. The mixing speed was 3 rpm at the moment of the charge and was then increased gradually to the final value of 30 rpm after closing the blending chamber. The operation was continued until constant torque was monitored (5–6 min).

Characterization Techniques

The morphological characterization was carried out with a scanning electron microscope (SEM) (Philips Model 501). Compression-molded sheet specimens were fractured in liquid nitrogen and the fracture surface was coated with gold with an SPI sputter coater. Observations were also made with an optical microscope (Leitz Laborlux 12), equipped with a camera, on microtomed films 20–30- μ m thick. The films were placed between two microscope slides on the hot stage of a polarizing microscope previously brought to the required annealing temperature (240°C). Micrographs were taken at intervals and were then analyzed with the proper software (NIH Image 1.6[®]) to measure the average dimension and the size distribution of the dispersed-phase particles as a function of time.

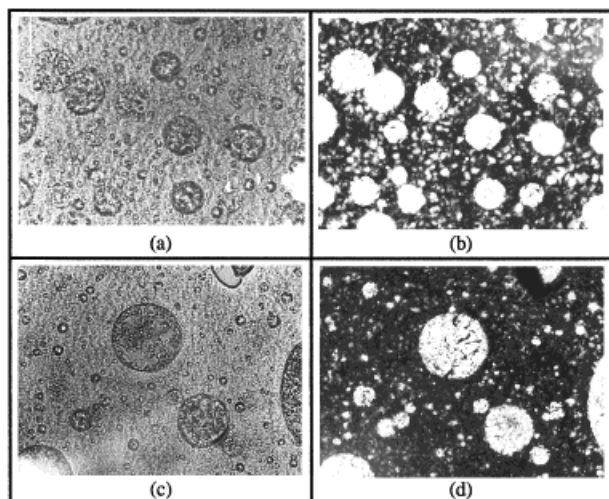


Figure 1 Optical micrographs (40 \times) of a PE/SBH blend film annealed at 240 $^{\circ}$ C for (a,b) 5 min and (c,d) 10 min. Micrographs (a) and (c) were taken with parallel polarizers and (b) and (d) with crossed polarizers.

RESULTS AND DISCUSSION

PE/SBH Blends

The effect of the compatibilizers on the morphology of as-prepared PE/SBH blends was already discussed in a previous article.¹⁹ The observation of the SEM micrographs taken on the fracture surface of samples of 80/20 PE/SBH blends showed clearly that, in addition to increasing the interfacial adhesion, all the employed compatibilizers, that is, COPR, COPM, and HDM, did reduce the average size of the SBH droplets, COPR being the most effective in this respect, and COPM, the least. The observation of microtomed films of the same blends made by the use of a polarizing optical microscope, either with parallel and with crossed polarizers, confirms the conclusion.

The uncompatibilized PE/SBH blend gives rise, upon standing at 240 $^{\circ}$ C, to considerable morphology coarsening, as is shown in Figure 1, where the optical micrographs taken after 5 and 10 min annealing, with parallel [Fig. 1(a,c)] and crossed [Fig. 1(b,d)] polarizers, are shown. It may be clearly observed that the growth of the average size of the SBH particles is due mainly to coalescence of the medium and large droplets. A very large number of microdroplets remains even after considerably long times, but they contribute very little to the average dimensions as calculated with a computer technique.

The behavior of the compatibilized blends is illustrated qualitatively by the micrographs in Figure 2, taken after 1 and 10 min, on a film of the PE/COPR/SBH blend. Here, no macrosegregation occurs, and the average size growth can only be evidenced by the computerized analysis.

Several films of the blends were studied with this technique and the results of the droplets' average size calculation carried out on each of the micrographs taken at different time intervals are plotted in Figure 3. It can be observed that the average size of the particles increases dramatically for the uncompatibilized blend, passing from about 12 μ m to over 35 μ m in 10 min, following an almost linear trend. The blend compatibilized with HDM displays a much finer dispersion of the SBH phase, just after preparation. However, upon annealing, the average size of the droplets increases with a rate which is not far from that characterizing the blend with no compatibilizer. It is only after about 5 min annealing that the coarsening rate starts decreasing progressively. At any rate, the droplet dimensions of this blend grew from 3–4 μ m to over 20 μ m in 10 min, which corresponds to an increase exceeding 500%, which is even stronger than that (about 300%) of the uncompatibilized blend.

The behavior of the blends containing the PE-g-SBH copolymers as compatibilizers is completely different. In fact, the reduction of the average particle size achieved at the mixing stage,

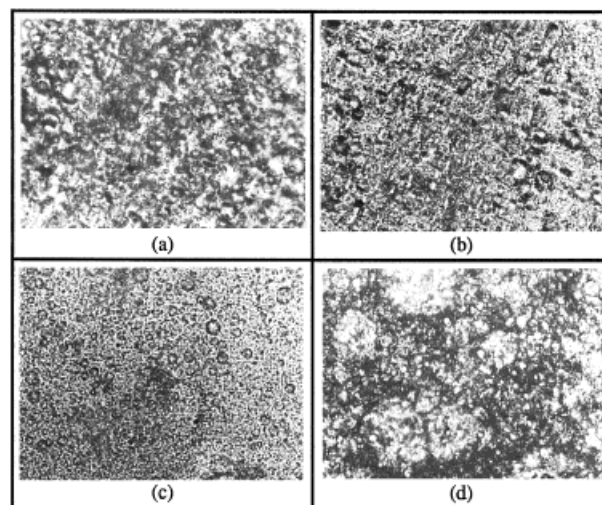


Figure 2 Optical micrographs (40 \times) of a PE/COPR/SBH blend film annealed at 240 $^{\circ}$ C for (a,b) 35 s and (c,d) 9 min. Micrographs (a) and (c) were taken with parallel polarizers and (b) and (d) with crossed polarizers.

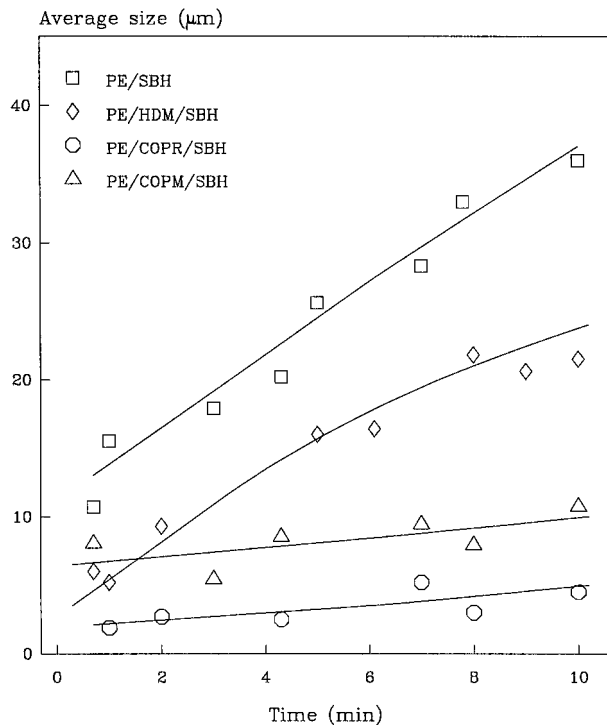


Figure 3 Average dimensions of the SBH particles versus time of annealing at 240°C for the PE/SBH blends without and with compatibilizers.

which is stronger for COPR, as already pointed out,¹⁹ is accompanied by a much lower coarsening rate. Indeed, for both the PE/COPR/SBH and PE/COPM/SBH blends, the droplet growth is almost negligible during the annealing time investigated. It should be pointed out that the three compatibilized blends display very similar viscosity at 240°C,¹⁹ and, therefore, the different coarsening rate can only be attributed to differences in the nature of the interphase.

Pötschke and coworkers^{29–31} studied the effect of the viscosity ratio and of the compatibilizer addition on the morphology and coalescence in blends of thermoplastic polyurethanes (TPU) with POs. The effect played by different types of compatibilizers in kinetically hindering the coalescence of the PO droplets in TPU matrices was discussed by these authors in terms of their capability to form more or less stable interphase films. Coalescence of two drops, once they have approached each other, can, in fact, take place only as a result of failure of the matrix film between them, and this step is generally considered as the rate-determining one.³ The results found in this work indicate very clearly that HDM is capable only of lowering the interfacial tension of PE/

SBH blends, but practically fails to cause serious kinetic hindrance against coalescence. On the contrary, both COPR and COPM also display very good efficiency in this respect.

It may be speculated that the microstructure of the two kinds of compatibilizers is responsible for their different behavior. HDM is a PE sample containing a very small amount (about 1% w/w) of MA grafts and it seems reasonable to assume that, whereas during mixing it migrates to the interface and lowers the interfacial tension, it probably remains well anchored on the surface of the PE cavities and simply makes it sufficiently polar to give rise to a weak physical attraction for the SBH droplets. Also, in fact, no experimental evidence in favor of chemical reactions taking place between the MA functionalities and the end groups, or the internal ester bonds, of SBH has ever been found.^{17,1} The two other compatibilizers (COPR and COPM), on the contrary, consist of intricate mixtures of unreacted PEOx, pure SBH, and PE-g-SBH copolymer molecules containing different amounts of PE and SBH sequences with different relative lengths. These materials also migrate to the interface, during mixing, and bring about a reduction of interfacial tension. Here, however, the different types of molecules, depending on their composition and microstructure, either dissolve in the alike phases or remain strongly anchored to the surface of one (or both) of them, thus giving rise to a fairly stable interphase. As a result, these compatibilizers not only improve the interphase interactions with consequent reduction of the steady-state particle size, but also provide a strong hindrance against coalescence, thus practically eliminating the risk of thermally induced morphology coarsening.

PP/SBH Blends

A study of the blends with a PP matrix fully confirmed the results described in the previous section. Indeed, also for these blends, the compatibilizing effect of the ad-hoc synthesized PP-g-SBH copolymers was clearly demonstrated not only by the much finer blend morphology, but also by its appreciable stabilization with respect to annealing-induced coarsening. In this case, however, the behavior of a commercial PP-g-AA compatibilizer (Polybond) was found to be comparable to that of the copolymer containing SBH branches.

It was already demonstrated²³ that the uncompatibilized PP/SBH blend with 20% w/w SBH is a

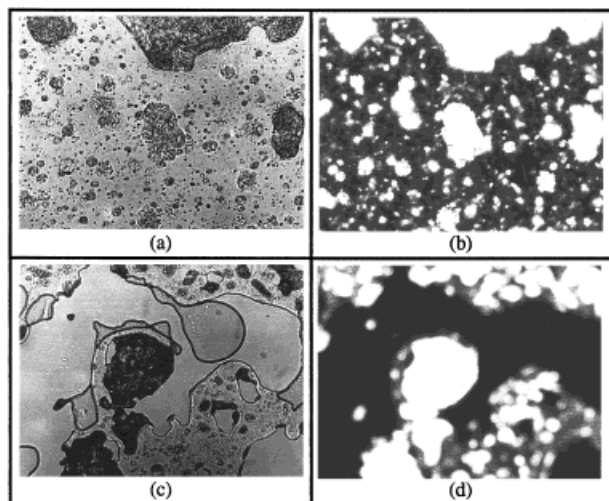


Figure 4 Optical micrographs (40 \times) of a PP/SBH blend film annealed at 240 $^{\circ}$ C for (a,b) 3 min and (c,d) 10 min. Micrographs (a) and (c) were taken with parallel polarizers and (b) and (d) with crossed polarizers.

distinctly biphasic material characterized by very poor phase dispersion and practically no interfacial adhesion. The average size of the SBH droplets, as estimated from the SEM micrographs, was found to be 20–70 μm .²³ This means that the particle dimensions of this blend are even larger than the thickness of the microtomed films employed in this study. As a consequence, the average droplet sizes measured for the blend by the optical microscopic analysis were not as reliable as those found for the PE/SBH blends. In addition to this, the tendency of the SBH particles not to take a spherical shape, probably due to preferential interactions with the glass surface, also prevented the accurate estimation of their dimensions. As an example, the micrographs taken on the hot stage of the polarizing microscope on a film of the 80/20 PP/SBH uncompatibilized blend, after 5 and 10 min annealing at 240 $^{\circ}$ C, either with parallel and with crossed polarizers, are shown in Figure 4. Thus, the actual droplets dimension could be estimated only roughly by this technique. Nevertheless, a comparison of the figures drawn from the optical analysis with those obtained from SEM micrographs taken on cryofractured samples annealed in a thermostated oven provided a qualitative, yet satisfactory, indication of the coalescence behavior of this blend.

The optical microscopic technique provided much better results with the two PP/SBH blends compatibilized with the PP-g-SBH copolymer (COPP50) and with the commercial PP-g-AA co-

polymer (Polybond). Examples of the micrographs taken on a film of PP/Polybond/SBH are shown in Figure 5.

The results of the measurements carried out on the three PP-based blends are collected in Figure 6. A comparison of Figures 3 and 6 shows that the dispersion of the SBH droplets within the PP matrix is much coarser than that within PE, either in the absence and in the presence of a compatibilizer. Also, the coalescence rate, measured as the average increase of the droplet dimensions (in $\mu\text{m}/\text{min}$) observed over a period of 10 min annealing, is at least an order of magnitude higher for the blends with a PP matrix (Table II). On the basis of the rheological properties of the POs and of the LCP used in this work, there seems to be no reason for attributing these differences to the different viscosity ratios characterizing the two types of blends. Thus, the comparative results provide an indication that the chemical structure of the matrix is mainly responsible for the different morphology, and morphology stability, of the PO/SBH blends.

The addition of a compatibilizer into the PP/SBH blends causes a fourfold reduction of the average droplet dimensions, as well as a strong decrease of the coalescence rate (Fig. 6). It is noteworthy that, in contrast with the PE-based blends, those containing a PP matrix seem to undergo substantial improvement of the phase dispersion and morphology stabilization even

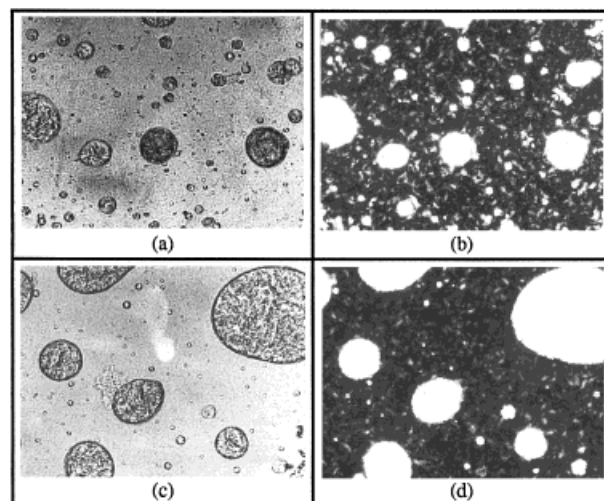


Figure 5 Optical micrographs (40 \times) of a PP/Polybond/SBH blend film annealed at 240 $^{\circ}$ C for (a,b) 4 min and (c,d) 10 min. Micrographs (a) and (c) were taken with parallel polarizers and (b) and (d) with crossed polarizers.

when added with a commercial sample of functionalized PO. It should be emphasized, however, that the content of the AA grafts of Polybond is much higher (6% w/w) than that of the MA groups of HDM (1% w/w). Therefore, although it was shown that no significant ester exchange reactions do probably take place between the functionalities of the PP-*g*-AA compatibilizer and the ester bonds of SBH,¹⁸ it may be assumed that the AA grafts of Polybond are sufficiently polar and bulky to give rise to strong physical interactions with the SBH droplets and to depress the coalescence rate to an extent very similar to that of the PP-*g*-SBH copolymer (COPP50).

CONCLUSIONS

In this work, a semirigid LC polymer was added to two PO matrices together with appropriate amounts of different types of compatibilizers, including some ad-hoc synthesized PO-*g*-SBH copolymers, in order to obtain information on the mechanism of compatibilization through a study of the dispersion of the minor phase and of the annealing-induced morphology coarsening. The

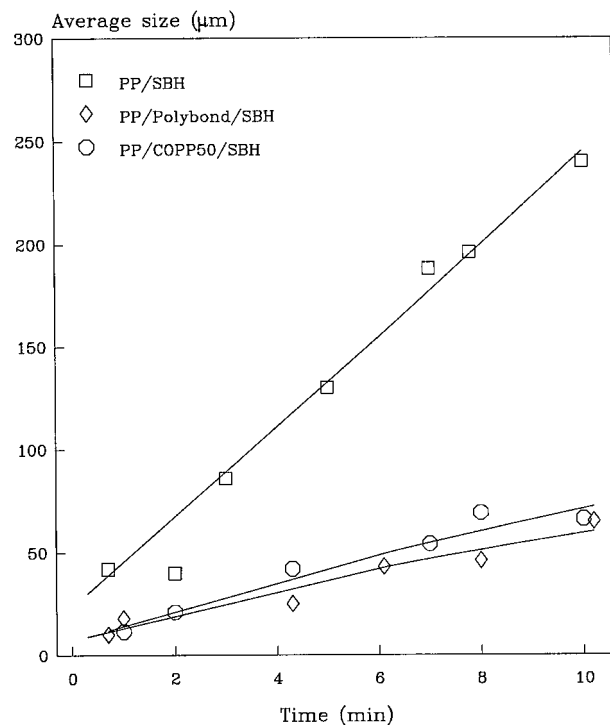


Figure 6 Average dimensions of the SBH particles versus time of annealing at 240°C for the PP/SBH blends without and with compatibilizers.

Table II Average Coalescence Rate Measured for the PO/SBH Blends over a 10-min Annealing Period at 240°C

Blend	Coalescence Rate (μm/min)
PE/SBH	2.59
PE/HDM/SBH	2.08
PE/COPR/SBH	0.31
PE/COPM/SBH	0.35
PP/SBH	22.12
PP/Polybond/SBH	5.26
PP/COPP50/SBH	6.17

results indicate that the PO-*g*-SBH copolymers do, in fact, produce a strong reduction of both the average size of the SBH particles and the coalescence rate. Among the conventional, commercially available compatibilizers, HDM (a PE sample with 1% w/w MA functional groups) causes a reduction of interfacial tension and, thereby, an improvement of the steady-state phase dispersion of the as-prepared PE/SBH blends, but is unable to lower the rate of morphology coarsening caused by prolonged (5–10 min) annealing at 240°C, whereas the PP-*g*-AA copolymer with 6% w/w AA branches (Polybond 1001) is very effective in both respects. The results demonstrate that the chemical structure of the compatibilizers is very important not only for the effect on the morphology that can be induced in a given blend by melt mixing, but, even more, also for the extent to which that morphology proves stable when the blend is subjected to thermal treatments.

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REFERENCES

1. Tokita, N. *Rubb Chem Technol* 1977, 50, 292.
2. Roland, C. M.; Böhm, G. C. A. *J Polym Sci Polym Phys Ed* 1984, 22, 79.
3. Elmendorp, J. J.; Van der Vegt, A. K. *Polym Eng Sci* 1986, 26, 1332.

4. Plochocki, A. P.; Dagli, S. S.; Andrews, R. D. *Polym Eng Sci* 1990, 30, 741.
5. Utracki, L. A.; Shi, Z.-H. *Polym Eng Sci* 1992, 32, 1824.
6. Huneault, M. A.; Shi, Z.-H.; Utracki, L. A. *Polym Eng Sci* 1995, 35, 115.
7. Van Oene, H. J. *J Colloid Interf Sci* 1972, 40, 448.
8. Ghodgaonkar, P. G.; Sundararaj, U. *Polym Eng Sci* 1996, 36, 1656.
9. Datta, A.; Chen, H. H.; Baird, D. G. *Polymer* 1993, 34, 759.
10. Datta, A.; Baird, D. G. *Polymer* 1995, 36, 505.
11. O'Donnell, H. J.; Baird, D. G. *Polymer* 1995, 36, 3113.
12. Heino, M. T.; Hietahoja, P. T.; Vainio, T. P.; Sepälä, J. V. *J Appl Polym Sci* 1994, 51, 259.
13. Kozłowski, M.; La Mantia, F. P. *J Appl Polym Sci* 1997, 66, 969.
14. Miller, M. M.; Brydon, D. L.; Cowie, J. M. G.; Mather, R. R. *Macromol Rapid Commun* 1994, 15, 857.
15. Miller, M. M.; Cowie, J. M. G.; Tait, J. G.; Brydon, D. L.; Mather, R. R. *Polymer* 1995, 36, 3107.
16. Qin, Y.; Miller, M. M.; Brydon, D. L.; Cowie, J. M. G.; Mather, R. R.; Wardman, R. H. In *Liquid Crystalline Polymer Systems*; American Chemical Society: Washington, DC, 1996; p 98.
17. La Mantia, F. P.; Scaffaro, R.; Plado, G.; Magagnini, P. L.; Paci, M. *Polym Networks Blends* 1996, 6, 171.
18. Scaffaro, R. PhD Dissertation, University of Palermo, 1998.
19. La Mantia, F. P.; Scaffaro, R.; Magagnini, P. L.; Paci, M.; Chiezzi, C.; Sek, D.; Minkova, L. I.; Miteva, Ts. *Polym Eng Sci* 1997, 37, 1164.
20. Magagnini, P. L.; Paci, M.; Minkova, L. I.; Miteva, Ts.; Sek, D.; Grobelny, J.; Kaczmarczyk, B. *J Appl Polym Sci* 1996, 60, 1655.
21. Minkova, L. I.; Miteva, Ts.; Sek, D.; Kaczmarczyk, B.; Magagnini, P. L.; Paci, M.; La Mantia, F. P.; Scaffaro, R. *J Appl Polym Sci* 1996, 62, 1613.
22. La Mantia, F. P.; Scaffaro, R.; Magagnini, P. L.; Paci, M.; Minkova, L. I.; Miteva, Ts. *J Appl Polym Sci* 1999, 71, 603.
23. Magagnini, P. L.; Pracella, M.; Minkova, L. I.; Miteva, Ts.; Sek, D.; Grobelny, J.; La Mantia, F. P.; Scaffaro, R. *J Appl Polym Sci* 1998, 69, 391.
24. Magagnini, P. L.; Pedretti, U.; Perego, G.; Bresci, B.; Carrozzino, S.; Roggero, A. U.S. Patent 4 833 299, 1989 (to Eniricerche).
25. Magagnini, P. L.; Bresci, B.; Paci, M.; Roggero, A.; Pedretti, U.; La Mantia, F. P. In *Recent Advances in Chemical Engineering*; Saraf, D. N.; Kunzru, D., Eds.; Tata McGraw-Hill: New Delhi, 1990; p 541.
26. La Mantia, F. P.; Magagnini, P. L.; Paci, M.; Pedretti, U.; Roggero, A.; Valenza, A. In *Research Trends in Polymer Science*; Menon, J., Ed.; Research Trends: Trivandrum, India, 1990; Vol 1, p 9.
27. La Mantia, F. P.; Valenza, A.; Paci, M.; Magagnini, P. L.; Pedretti, U.; Roggero, A. *Polym Eng Sci* 1993, 33, 944.
28. Pedretti, U.; Roggero, A.; Città, V.; Montani, E.; La Mantia, F. P.; Magagnini, P. L. In *Processing and Properties of Liquid Crystal Polymers and LCP Based Blends*; Acierno, D.; La Mantia, F. P., Eds.; ChemTec: Toronto, 1993.
29. Pötschke, P.; Wallheinke, K.; Fritsche, H.; Stutz, H. *J Appl Polym Sci* 1997, 64, 749.
30. Wallheinke, K.; Pötschke, P.; Stutz, H. *J Appl Polym Sci* 1997, 65, 2217.
31. Wallheinke, K.; Pötschke, P.; Macosko, C. W.; Stutz, H. In *Proceedings of the Regional Meeting of the Polymer Processing Society, Göteborg, Sweden, August 18–21, 1997*; Vol. 2, p 24.
32. Sundararaj, U.; Macosko, C. W. *Macromolecules* 1995, 28, 2647.