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Reactively and Physically Compatibilized Immiscible Polymer Blends: Stability of the Copolymer at the Interface

Charef Harrats,[1] Kristof Dedecker,[1] Gabriel Groeninckx,[1] Robert Jérôme[2]*

[1] Katholieke Universiteit Leuven, Laboratory of Macromolecular Structural Chemistry, Dept. of Chemistry, Celestijnenlaan 200 F, 3001 Heverlee-Leuven, Belgium
[2] Center for Education and Research on Macromolecules, Institute of Chemistry (B6), University of Liège, Sart-Tilman, 4000 Liège, Belgium

Summary: This paper reports on the interfacial behaviour of block and graft copolymers used as compatibilizers in immiscible polymer blends. A limited residence time of the copolymer at the interface has been shown in both reactive blending and blend compatibilization by preformed copolymers. Polystyrene (PS)/polyamide6 (PA6), polyphenylene oxide (PPO)/ PA6 and polymethylmethacrylate (PMMA)/PA6 blends have been reactively compatibilized by a styrene-maleic anhydride copolymer SMA. The extent of miscibility of SMA with PS, PPO and PMMA is a key criterion for the stability of the graft copolymer at the interface. For the first 10 to 15 minutes of mixing, the in situ formed copolymer is able to decrease the particle size of the dispersed phase and to prevent it from coalescencing. However, upon increasing mixing time, the copolymer leaves the interface which results in phase coalescence.

In PS/LDPE blends compatibilized by preformed PS / hydrogenated polybutadiene (hPB) block copolymers, a tapered diblock stabilizes efficiently a co-continuous two-phase morphology, in contrast to a triblock copolymer that was unable to prevent phase coarsening during annealing at 180°C for 150 minutes.

Keywords: compatibilization, graft and diblock copolymer, interfacial stability, reactive processing

Introduction

The location of the compatibilizer at the interface between the individual phases of a blend is a prime and necessary requirement for an efficient compatibilization and phase morphology stabilization upon further re-processing or thermal annealing. Indeed, a copolymer might be able to locate at the interface during the first minutes of the compounding process reducing

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efficiently the size of the dispersed phase particles and preventing their coalescence. However, is the copolymer able to stay at the interface during long melt-mixing or melt-annealing operations? It is demonstrated in this work that either in reactively or physically compatibilized blends the compatibilizer can easily be rejected from the interface because of its energetically unbalanced design. The composition, molecular weight, and miscibility of the compatibilizer with the individual blend phases, its functionality when it is in-situ generated and its molecular architecture when it is physically added to the blend are the key parameters which affect its stable location at the interface.[1] A huge amount of literature clearly evidences the beneficial effect of various copolymers having various molecular characteristics on the compatibilization of immiscible polymer blends.

The stability of the copolymer at the interface between the blend phases has not been really focused on in literature. Few papers have reported on the stability of the phase morphology during annealing and ascribed the observed effect to the stability of the copolymer at the interface.[2, 3] The ability of the compatibilizer to stabilize a developed phase morphology can be used as an additional criterion for the evaluation of the compatibilization efficiency. E.g. a co-continuous phase morphology exhibits an intrinsic instability when subjected to further processing or thermal annealing.[4-7] We have previously reported that after only 3 minutes of annealing at 200 °C a 20LDPE/80PS blend having a fully co-continuous two-phase morphology exhibited a complete change to a droplet-in-matrix morphology.[2] Veenstra et al. have recently studied the extent of instability of a co-continuous phase morphology of a 50 / 50 polyether-ester / polystyrene blend as a function of temperature and annealing time.[8] In this case the phase morphology preserved its co-continuous character, but a pronouced phase coarsening was observed. Mekhilef et al. reported that the co-continuous phase morphology of 30/70 PS / PE blend also evolved to a droplet--in–matrix type morphology when annealed in the absence of shear.[9] After compatibilization using a SEBS triblock copolymer the stability of the co-continuous phase morphology was significantly improved. Nevertheless, the SEBS copolymer was not able to totally prevent the phase morphology from coarsening when the blend was annealed at 200 °C during 16 minutes.

A pure and a tapered diblock hPB-b-PS copolymers have shown substantial differences in their ability to stabilize a co-continuous two-phase morphology when PS rich (ca. 80 wt %) binary

LDPE / PS blends were annealed at 180 °C in the absence of shear.[2] Even at a 10 wt % concentration the pure diblock had a less efficient stabilizing activity than the tapered version. For instance, after only 3 minutes of quiescent annealing at 180 °C, the phase co-continuity was altered by the LDPE phase break-up and subsequent coarsening even in the presence of the pure diblock copolymer. When the tapered diblock was used, no phase morphology evolution was observed and, depending on the concentration, the co-continuous character was better preserved. This clear difference has prompted us to compare the emulsification activity of a triblock SEBS with a tapered diblock using the very unstable co-continuous phase morphology developed in a LDPE / PS 20 / 80 blend system. In this case and because the differences were expected to be very subtle, the blends were subjected to longer annealing times of 150 minutes.

Experimental

Table 1. Characteristics of the homopolymers and copolymers used.

PA6	3 samples from DSM: Mw_1: 18 000; Mw_2: 24000; Mw_3 : 44 000
PPO	Mw : 54000
PMMA	DIAKON MG 102 from Rhom & Haas, Mw: 69 000
PS1	Denka Styrol GP-1 Mw : 180 000
PS2	Polystyrol 158K BASF Mw: 100 000
SMAx	samples having different MA contents were used; x denotes the wt % of maleic anhydride reactive groups
LDPE	Shell 33 , Mw: 40 000
Triblock S-*b*-hB-*b*-S	Mw for the three sequences : 7500-35000-7500
Tapered diblock S-*b*-P(E-co-B)-*b*-hB	Mw can be given as : 23000-19000-28000

The blends were prepared using a conical twin screw mini-extruder (4 gr total mixing capacity) designed by DSM-Research.[10, 11] The mixing temperature was kept constant at 240 °C for the blend systems PA6 /(PMMA/SMA) and PA6 /(PS/SMA) and 270 °C for the blend systems PA6 /(PPO/SMA). When not specified, the screw speed was kept at 100 rpm. The miscible preblends (PS/SMA, PMMA/SMA and PPO/SMA) were also prepared using the mini-extruder. The preblends were cut into small pieces, and subsequently used in the final extrusion step with polyamide6. The polystyrene / LDPE blend system compatibilized using the triblock and the tapered S/hB copolymers was melt-mixed using a roll mill at 200 °C for 5 minutes at a roll speed of 30 rpm. The copolymer was first mixed with the minor phase; subsequently the major phase was progressively added to the mixture.

Discussions

In the reactive blends systems based on polyamide 6 and PMMA, PPO or PS, the SMA-g-PA6 compatibilizer is formed in-situ during mixing as a result of the reaction between the anhydride groups of SMA and the amino end groups of PA6. The imidation reaction involved is well documented and frequently employed in reactively designed blends based on polyamides.[10; 12-18]

Optimum Functionality of the SMA Compatibilizer

SMA compatibilizers having 14, 17, 20, 25, 28 and 33 weight % of maleic anhydride have been used in PA6 / PMMA blends. With respect to their compatibilizing efficiency, it is very important to take into account the miscibility behaviour between SMA and PMMA. PMMA/ SMA blends always show an LCST behaviour. At the extrusion temperature of 240 °C, SMA is miscible with PMMA for MA contents between 10 and 35 wt %. As the cloud point of the PMMA / SMA blends depends on the molecular weight of PMMA and SMA and on the blend composition, the miscibility behaviour was checked for the components used.

The compatibilized blends PA6 / (PMMA/SMA) under consideration have the composition 75/ (20/5). The miscibility behaviour was thus analyzed for the PMMA / SMA blends in a weight ratio of 80 / 20 ; they were prepared at 240 °C in a mini-extruder. The transparency of the blends was considered as a first indication of miscibility. The blends of PMMA with SMA14, SMA17, SMA20, SMA25 and SMA28 were transparent after 3 minutes of extrusion. The blend PMMA / SMA33 (80 / 20) was opaque at short extrusion times but became transparent after longer extrusion times (10 min). The blend PMMA/SMA8 remained opaque, even after longer extrusion times (10 min) indicating that this blend is not miscible at 240 °C. The miscibility of PMMA / SMA was evaluated using d.s.c. on blend samples quenched in liquid nitrogen. The results of the d.s.c. measurements are given in Figure 1 which clearly shows that SMA is more miscible with PMMA at the mid-concentration of about 20 wt % maleic anhydride. The more one deviates from this concentration in either directions, low or high MA content, the less the system is miscible.

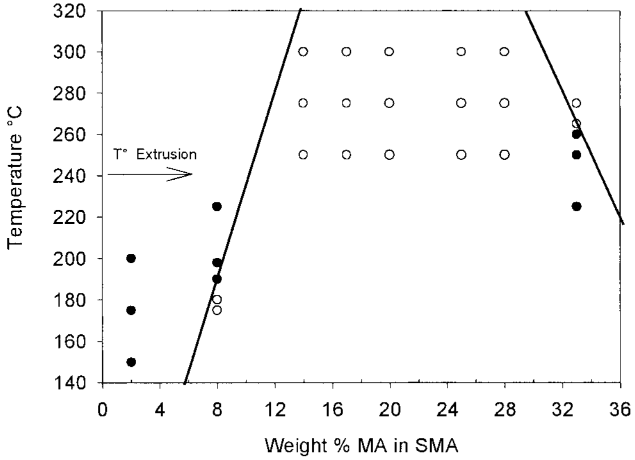

Fig. 1. Miscibility of PMMA / SMA 80/20 blends as a function of the MA content in SMA, (O) miscible; (•) immiscible.

The weight average particle diameter of PMMA dispersed phase in SMA compatibilized PA6 / PMMA blends is plotted in Figure 2 as a function of the extrusion time when SMA 20, SMA28 and SMA33 were used. Compared to the case of SMA20, a completely different behaviour is observed with SMA28 and SMA33 as compatibilizers. The dispersed phase particle size can still decrease after 3 minutes of extrusion for the blends containing SMA28 or SMA33, while this is not the case for SMA20. This behaviour can be directly correlated with the extent of miscibility of SMA and the minor phase PMMA. Indeed, in the beginning of the melt-extrusion process, SMA-g-PA6 graft copolymer is formed at the interface causing a significant particle size decrease. As the compounding process continues further, the SMA copolymer reacts more quantitatively so that an unbalanced graft copolymer, richer in PA6, is built-up. It has a strong tendency to be driven out from the interface into the PA6 phase where it is expected to be the most stable. This is made easier when the extent of miscibility of the SMA (28 and 33 wt % MA) with PMMA does not 'counter-balance' the unfavorable compositional effect (a graft copolymer richer in PA6 exhibits more interaction with the PA6 matrix). This correlation is also illustrated in Figure 3 with SMA copolymers covering a broader range of MA concentration. The weight average particle size of PMMA / PA6 blends is plotted as a function of the weight % of maleic anhydride of SMA copolymer after 20 minutes of extrusion time. The Figure clearly reveals that for the compatibilizers closer to the boundaries of the miscibility region of PMMA and SMA (refer to Fig. 1), a larger PMMA particle size is obtained.

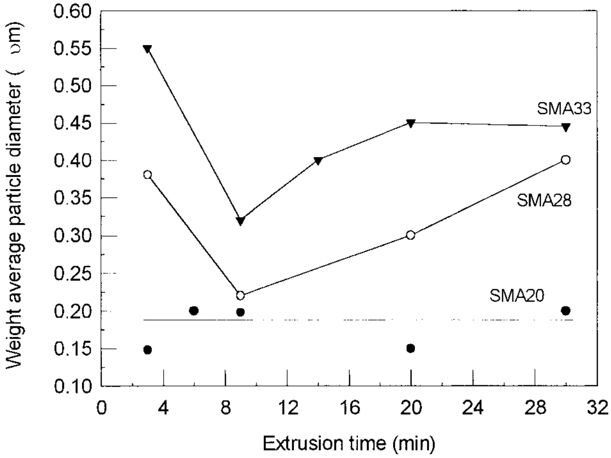

Fig. 2. Weight average particle diameter as a function of the extrusion time for the blend PA6 / (PMMA / SMA) 75 / (20 / 5) with different MA contents for SMA.

The unstability of the graft copolymer formed at the interface is also illustrated for melt-blended and SMA compatibilized PA6 /PPO blend system where the particle size of the PPO dispersed phase is plotted as a function of the extrusion time (Fig. 4). In this case SMA8 is less miscible with PPO than SMA2.[19] As can be seen, the particle size of SMA8 modified blend is smaller than that of SMA2 modified blend at short extrusion times. The kinetics of interfacial reaction is faster with SMA8 containing four times more MA reactive groups than SMA2. Beyond 15 minutes of extrusion time, the in-situ formed SMA-g-PA6 copolymer becomes reacher in PA6 grafts causing an unbalanced structural design which drives the copolymer out off the interface into the PA6 matrix, forming micelles. The moderate miscibility of SMA8 with PPO could no more 'counter-balance' the strong interactions the copolymer develops with the PA6 matrix. As a result of this 'decompatibilization' process, the PPO dispersed phase coarsens via a coalescence process.

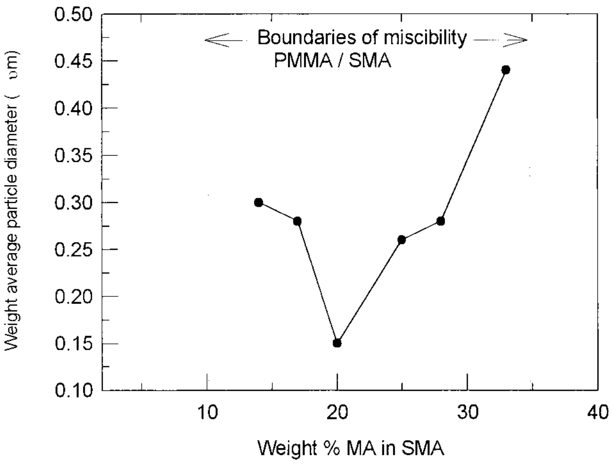

Fig. 3. Weight average particle diameter of the blend PA6 /(PMMA/SMA) 75 / (20 / 5) as a function of the MA content in SMA. All the blends contain 5 wt % of SMA and were compounded at 240 °C for 20 min.

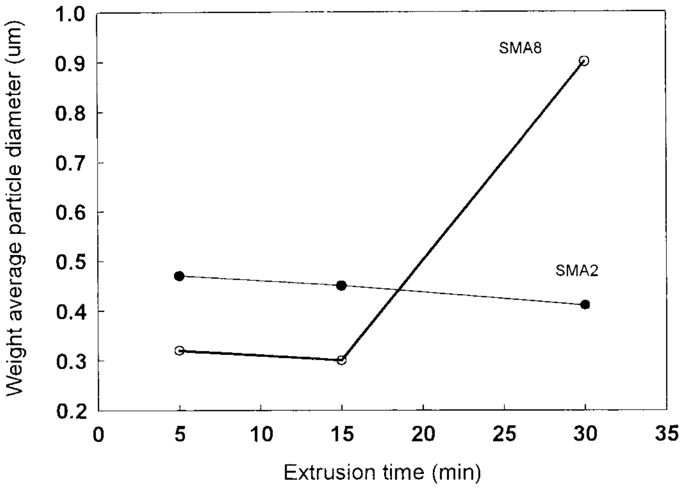

Fig. 4. Weight average particle diameter of PA6 / (PPO / SMA) blends in a weight ratio 75 / (20/5) as a function of the extrusion time. (●) SMA2 ; (O) SMA8.

A third example of copolymer expelling or pull-out from the interface between the individual phases of the blend is illustrated for the SMA reactively compatibilized PA6 / PS blend system. In this system the same SMA2 which is at the limit of miscibility with polystyrene homopolymer[20] results in the in-situ formation of SMA-g-PA 6 compatibilizer which is moderately stable at the interface. Indeed, we could show by doubling the PA6 matrix molecular weight and therefore its melt-viscosity that the formed SMA-g-PA6 copolymer was really driven out of the interface by the larger shearing forces exerted on it. The shearing forces developed by the PA6 matrix of which the molecular weight is 44000 were superior to the interactions the SMA has with the polystyrene minor phase. Contrary to the blend where the PA6 matrix has a molecular weight of 18000, the blend where the molecular weight of PA6 is 44000 exhibited a considerable particle coalescence process as a result of compatibilizer inefficiency. The graft copolymer is expelled from the interface forming micelles in the PA6 matrix, as can be seen from Figure 5a.[21] One would expect a dispersed phase size reduction (drop break-up process) when the matrix viscosity is higher (large MW) compared to a blend where the matrix viscosity is low, as is the case in Figure 5b. The opposite effect is observed which clearly demonstrated the 'just stable' location of the reactively formed SMA-g-PA6 copolymer at the interface. A larger PA6 matrix viscosity completely alleviated the compatibilization efficiency and caused the opposite effect.

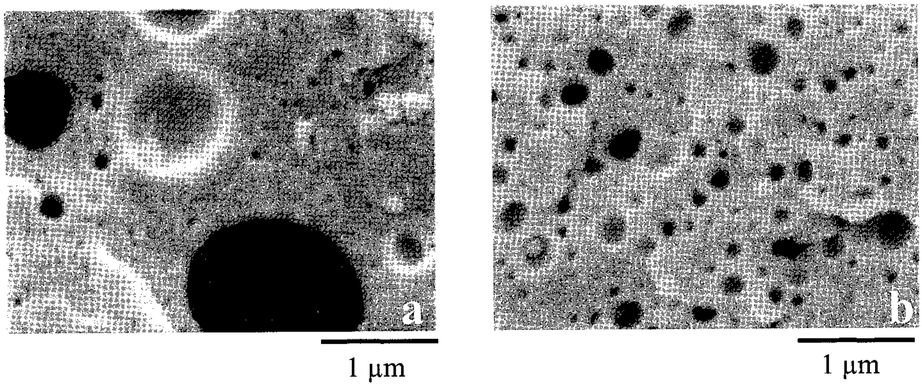

Fig. 5. SEM of cryo-smoothed and THF etched PA6 / (PS /SMA2) blend : 80 / (16 / 4); a) MW of PA6 = 44 000, b) MW of PA6 = 18 000.

The fourth example of this report illustrates a comparison between a tapered diblock copolymer S-*b*-P(E-co-B)-*b*-hB and a triblock S-*b*-hB-*b*-S used as physical compatibilizing agents in low density polyethylene / polystyrene blends. The two copolymers exhibit an excellent compatibilization activity in 80 LDPE/20PS blends where PS forms the dispersed phase. As illustrated in Figure 6, the unmodified blend exhibits, as expected, a coarse phase size (3 μm) as well as catastrophic mechanical properties (elongation at break : 30 %, tensile strength at break : 8.5 MPa). The addition to the blend of 10 wt % of the tapered diblock or the triblock copolymer results in a PS particle size reduction by a factor of 8. The copolymers were not only able to reduce the particle size of the PS phase, but efficiently improved the interfacial adhesion imparting to the modified blends a higher tensile strength and elongation at break (see table 2).

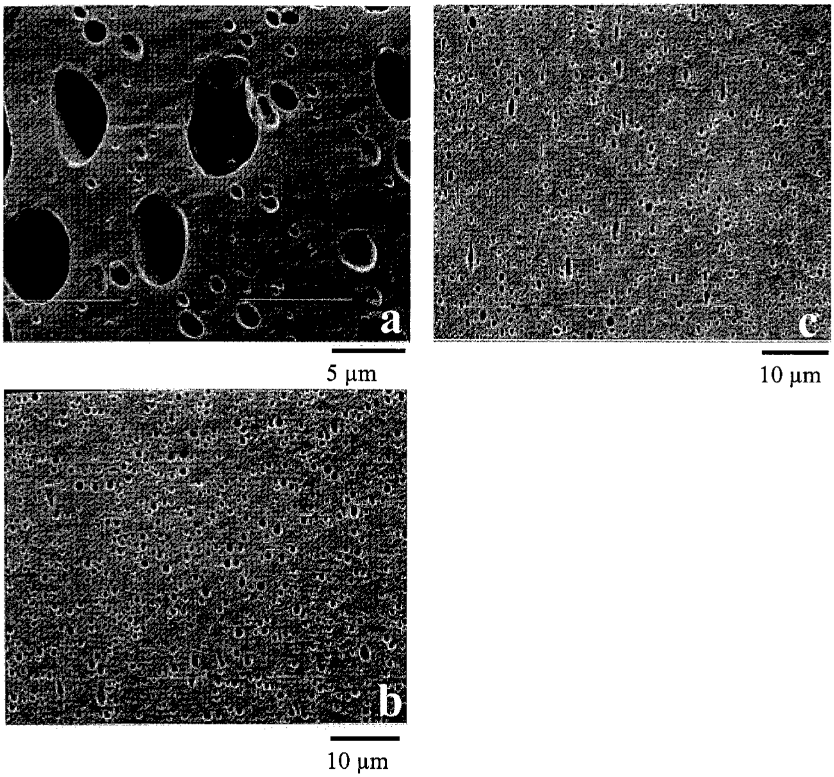

Fig. 6. SEM of cryo-smoothed and THF etched 80 LDPE/20 PS blends:
a) unmodified blend,
b) 10 wt % tapered diblock copolymer modified blend and
c) 10 wt % triblock copolymer modified blend.

In the symmetrically opposite composition of 20 LDPE / 80 PS where the phase morphology developed is co-continuous and not stable upon annealing, the two copolymers behaved differently. As shown in Figure 7 of the unmodified blend, the co-continuous phase morphology evolves to a dispersed phase morphology after as short as 3 minutes of quiescent thermal annealing at 180 °C. For the compatibilized blends a much longer annealing time is required to depict a phase morphology evolution. As shown in Figure 8 the triblock copolymer was not able to prevent phase coarsening to occur. The solvent extraction of PS phase using THF revealed that about 20 % of the phase continuity has been transformed into dispersion.

The blend modified with the tapered diblock copolymer was not only able to prevent the phase coarsening to occur but efficiently preserves the co-continuous character of the phase morphology (Fig. 9). The solvent extraction test carried out on this blend did not show any alteration of phase continuity.

Table 2. Tensile properties and PS phase particle size of unmodified and copolymer compatibilized 80 LDPE / 20 PS blends.

Blend	σ_b (MPa)	E_b (%)	PS Particle size (μm)
Unmodified blend	8.5	30	3
+ 10 wt % tapered copl.	17	350	0.4
+ 10 wt % triblock copl.	16	380	0.4

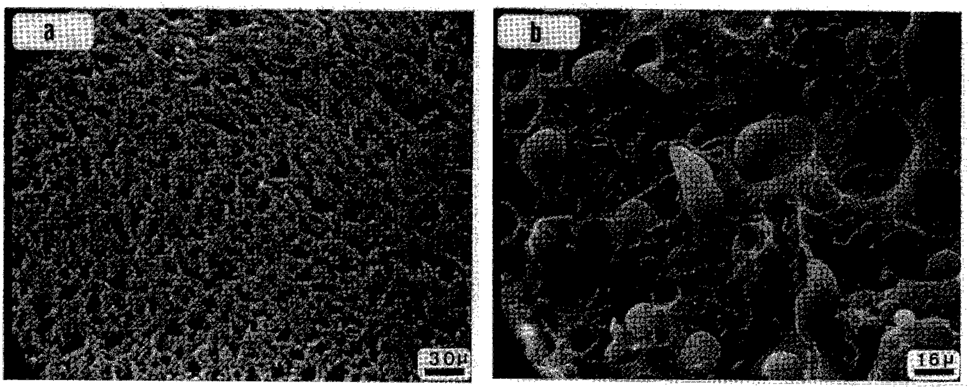

Fig. 7. SEM of unmodified 20LDPE /80PS blend (a) cryofracture and THF etched, non annealed sample, b) cryo-fracture, annealed for 3 minutes at 180 °C.

The clear superiority of a tapered diblock copolymer most likely results from the particular intermediate (tapered) sequence which consists of a mixture of styrene (A) and hydrogenated butadiene B monomeric units as : *-AAABBABABABAABBB-*. A similar sequence is expected to be neither miscible with polystyrene nor with polyethylene phases but has a strong tendency to locate at their interface forming an interphase. It can be considered as the driving sequence that forces the tapered diblock copolymer to locate efficiently and in a more stable manner at the

LDPE / PS interface than the triblock copolymer which is susceptible to partly distribute as own microdomain in either of the two phases, more preferably in the LDPE phase beause of its own phase morphology (PS domains in HPB matrix).

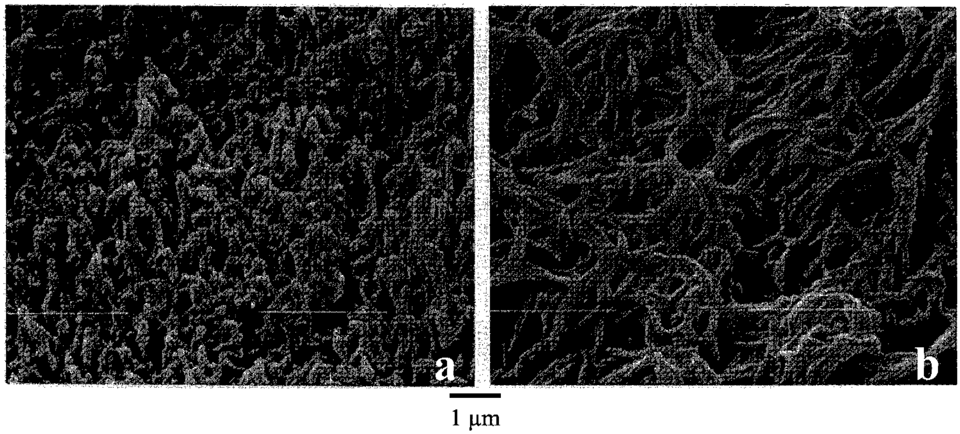

Fig. 8. SEM of room temperature fracture and THF etched 20 LDPE / 80 PS blend added with 10 wt % triblock copolymer : a) non annealed, b) annealed at 180 °C for 150 minutes.

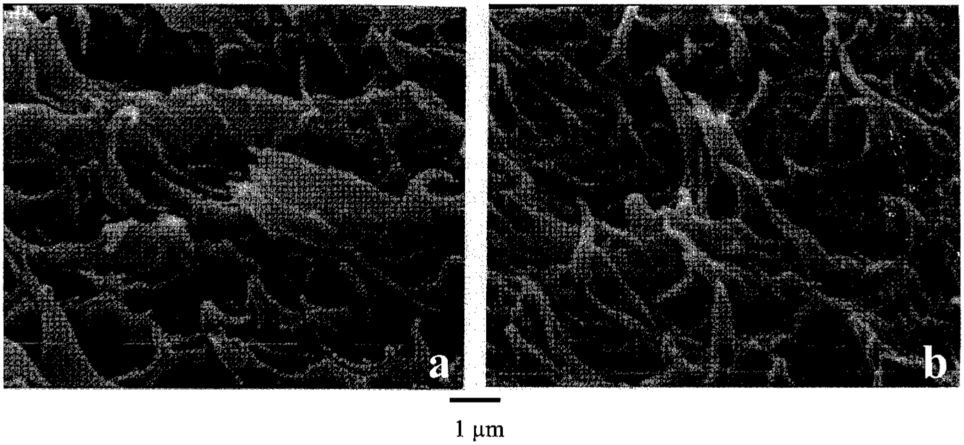

Fig. 9. SEM of room temperature fracture and THF etched 20 LDPE / 80 PS blends added with 10 wt % tapered diblock copolymer : a) non annealed, b) annealed at 180 °C for 150 minutes.

Conclusions

In this paper we reported examples from four different blend systems either reactive blends including PA6/PMMA, PA6/PPO and PA6/PS or physically compatibilized blends LDPE/PS, where the copolymer (graft or diblock) although efficient in developing a fine phase morphology was not able to locate permanently at the interface. A number of factors that cause its delocalization were illustrated. The stability of the copolymer at the interface may be altered because the balance of interaction between its own sequences and the individual phases of the blend is not suitable or the copolymer may organize into micelles in one of the phases. Reactive blending during longer times than usually experienced revealed a state of 'decompatibilization' that resulted in phase coarsening. Thermal annealing can also cause a phase morphology coarsening as a result of copolymer expelling from the interface.

The design of the copolymer compatibilizer must be based on the optimal interaction balance between its own sequences and the respective individual phases of the blend. Depending on the interaction balance, the compatibilizer might easily be rejected from the interface to the phase where it has the best thermodynamic affinity.

Acknowledgements

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