

STABILITY OF CO-CONTINUOUS PHASE MORPHOLOGIES IN EMULSIFIED POLYETHYLENE-POLYSTYRENE BLENDS

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Introduction

The interfacial activity of block copolymers in incompatible polymer blends is generally and primarily evaluated in terms of decrease of the particle size, enhancement of interfacial adhesion and improvement of mechanical properties. All these features are indirect evidences of the preferential location of the block copolymer at the blend interface. As another consequence of it, the copolymer is also able to prevent the coalescence of the emulsified microphases. By investigating the extent of that protective effect when the emulsified blends are annealed at temperatures well above the T_g or T_m of the components, additional informations should be gained on the interfacial activity of the copolymer emulsifier: in particular, its location, and temperature-induced rearrangements at the blend interfaces. In addition, these morphological analysis might be a convenient and simple method for comparing the efficiency of various emulsifiers and designing their optimal molecular characteristics.

In that prospect, polyethylene - polystyrene blends (PE / PS) containing small amounts of PE (20 wt %) constitute very suitable models since they display a co-continuous phase morphology which is very unstable in the absence of an emulsifier.^{1,2} Therefore, the kinetics of coalescence (disruption of the PE network) at high temperature is expected to be very sensitive to slight differences in the interfacial activity of various emulsifiers and further, to even minute differences in their structure. This approach is illustrated here by investigating the morphology as a function of annealing time at 180°C, of low density PE / PS (20 / 80) blends added with 10% of a pure or a tapered hydrogenated polybutadiene-b-polystyrene (HPB-b-PS) block copolymer respectively. We had indeed reported earlier that the latter is more efficient than the former for controlling the morphology and tensile properties of LDPE / PS blends.³ It was therefore expected that the superiority of the tapered emulsifier would also be evidenced by a better stability of the co-continuous blend morphology at high temperature.

In order to characterize and quantify the morphological evolution of these blends, classical mathematical treatments of microscopic images as well as multiscaling analysis were used.

Experimental

A low density polyethylene Alkathene XDG 33 from ICI and a general purpose polystyrene Polystyrol 158 K from BASF were used throughout this study. The anionic synthesis of the pure and tapered PB-b-PS copolymers and further hydrogenation of the PB blocks were performed by already reported classical techniques.³ Both copolymers have the same total molecular weight ($M_n = 70,000$) and same styrene content (50 wt %). In other words, M_n of each block for the pure diblock is 35,000 whereas the tapered sample can be schematically described by sequences of molecular weights 23,000 - 19,000 - 28,000 for PS - P(S-co-B) - PB, 20 parts of LDPE and 80 parts of PS were melt-blended with 10 parts of the pure or the tapered copolymer on a laboratory two-roll mill at 200°C for 5 min. The mixtures were thereafter compression molded (under 2500 psi at 200°C for 3 min) into sheets which were further annealed at 180°C. At various time intervals (i.e. 5, 10, 20, 30 and 90 min) a sample was withdrawn for morphological analysis. Thin sections (1 μm thick) were prepared by cryo-ultramicrotomy and were observed by transmission optical microscopy. The images were further digitized and binarized using the Noesis software on a Microvax II. Details of that procedure are reported elsewhere.⁴

Results and discussion

As already reminded, a co-continuous structure is formed when 20 % LDPE is melt-blended with 80 % PS on a laboratory two-roll mill.¹⁻³ This particular morphology is however quite unstable. Upon compression molding the mixture at 200°C for 3 min only, the PE network is completely disrupted and coalescence leads to a coarse dispersion of more or less spherical PE particules in a PS matrix. When the same thermal treatment is applied to the blend added with a pure or a tapered HPB-b-PS block copolymer (actually 10 % added), finely interlocked PE and PS phases are observed (figures 1a,2a). These block copolymers act therefore as efficient emulsifiers by preventing the coalescence of the continuous PE phase. Figures 1 and 2 show how this

morphology evolves when these emulsified blends are annealed at 180°C for additional times ranging from 5 to 90 min (times recorded after 3 min compression molding at 200°C). It clearly appears that the morphology of the blend containing the tapered copolymer is not significantly affected by this thermal treatment, even after 90 min. On the other hand, some coalescence of the phases with disruption of the co-continuous structure is evidenced in the blend containing the pure block copolymer, this phenomenon being already apparent after 10 min annealing.

In order to characterize and quantify the morphological evolution of the annealed blends, two kinds of digitized images were used: images obtained by the intersection of the minor phase features with the section plane are formed by separate objects which allows one to use the standard granulometry method for studying the size evolution of the PE phase. On the other hand, images obtained by the projection of all thickness features on the section plane give a picture of the degree of co-continuity of the phases (as in figures 1 and 2) and allows one to study these morphologies by the opening size granulometry distribution method and by multiscaling analysis.

Using the standard granulometry, we have determined the mean equivalent radius r , of the minor PE phase as a function of the annealing time (figure 3). These results indicate that r is practically unaffected in blends stabilized by the tapered copolymer whereas it significantly increases during the first 10 minutes of annealing in blends modified by the pure block copolymer.

The opening size granulometry distribution can be used for both semi-continuous and dispersed phases. Figure 4 shows the distributions obtained for some blends of the two series. We can see that the mean size λ remains almost constant during all the annealing process of the blend containing 10% of the tapered copolymer. On the other hand, λ increase abruptly after 10 min of heating for the blend added with the pure diblock. The difference between the size values obtained with the standard and the opening size granulometric methods just tells us that the geometry of a co-continuous feature differs from a circle.

Recently, we have found that the concepts of fractal dimension⁶ and multifractal distribution were relevant to quantify the co-continuous structure of polymer alloys.⁴ Figure 5 shows the $f(\alpha)$ spectra of singularities of the 20PE/80PS blends added with 10% of the pure or tapered block copolymer (before annealing). A narrower distribution and therefore a less multifractal character is observed for the blend containing the tapered copolymer. This alloy exhibits therefore a more uniform co-continuous structure than the one containing the pure diblock. The $f(\alpha)$ spectrum of the former is not significantly modified by annealing even after 90 min. Similar conclusions are drawn by examining the values of general dimensions D_q (in all cases, $2 \geq D_q \geq 1.94$ for $0 \leq q \leq 3$). The difference between D_0 and the other D_q dimensions is a measure of the nonuniformity of the structure. When the morphology of the pure diblock modified blend is similarly investigated the D_q dimensions and the $f(\alpha)$ spectrum are available only for the blends annealed for 5 min. For longer time $D_q=2$ for all q , which means that the co-continuous fractal morphology is breakdown into dispersed particles.

Conclusions

These results clearly and quantitatively demonstrate that a tapered HPB-b-PS block copolymer is definitely more efficient than the corresponding pure diblock for stabilizing the co-continuous structure of LDPE/PS blends rich in PS (80 %) at high temperature (180°C). Even after 90 min at that temperature, co-continuity of phases is not disturbed, whereas apparent phase size is only slightly increased. On the other hand, disruption of co-continuity and phase coalescence appear rapidly (after 5 min) in blends emulsified by the pure block copolymer.

The various image treatments applied for quantifying these morphological features give complementary and coherent results. These analytical approaches therefore appear as very useful tools for comparing quantitatively the efficiency of various polymeric emulsifiers in immiscible polymer blends.

The differential behavior of pure and tapered copolymers was already evaluated in a comparative study of the morphology and mechanical characteristics of modified PE/PS blends.³ The superiority of the tapered sample was assumed to result from its particular miscibility at the interface; in other words, the copolymer could behave as a solubilizing agent for the homopolymers, producing some diffuse interface. The actual results can be similarly explained.

The interfacial area generated by the tapered block copolymer remains stable at high temperature because the copolymer has much less tendency to segregate by forming its own domains; on the other hand the driving force to micelle formation is much more important for the pure diblock. As a result, rearrangement occurs readily at high temperature in that case.

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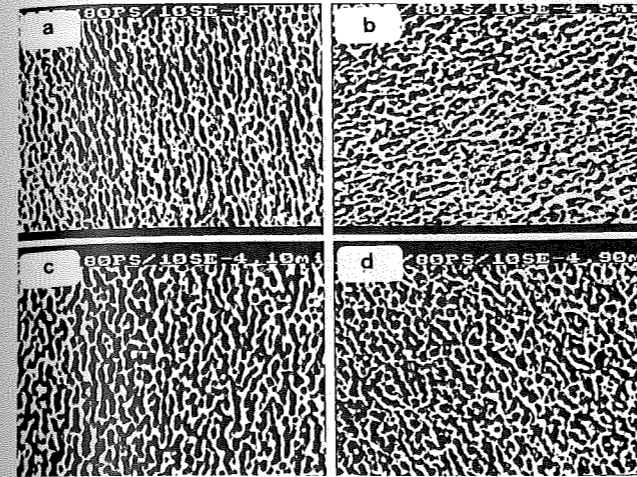


Figure 1: Digitized images of 20PE/80PS+10 Tapered Cop.: (a) initial sample after (b) 5 min, (c) 10 min and (d) 90 min. annealing at 180°C.

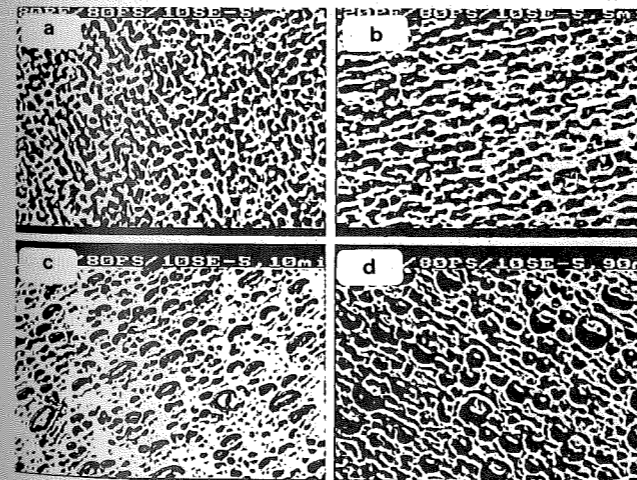


Figure 2: Digitized images of 20PE/80PS+10 Pure Cop.: (a) initial sample after (b) 5 min, (c) 10 min and (d) 90 min. annealing at 180°C.

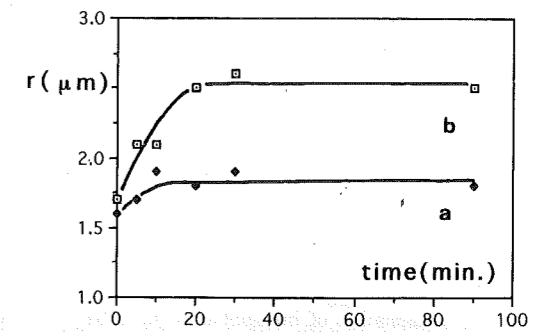


Figure 3: Variation of the apparent particle size (r), of 20PE/80PS as a function of annealing time at 180°C: (a) +10 Tapered Cop. and (b) +10 Pure Cop.

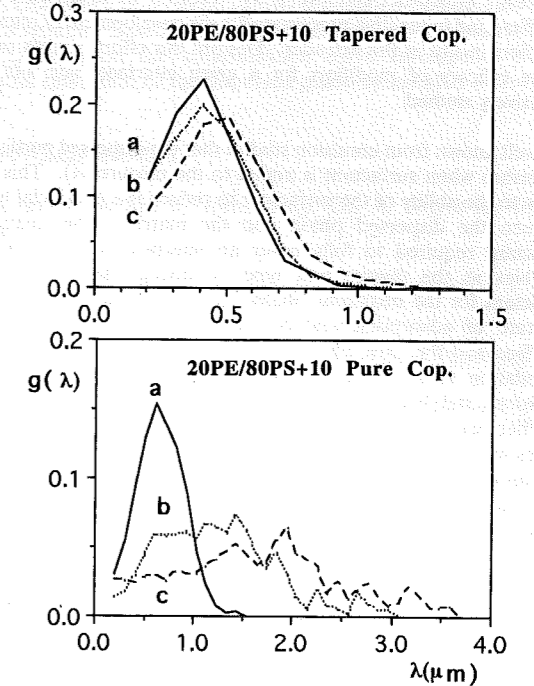


Figure 4: Opening size distribution as a function of the size λ for various annealing time at 180°C (a) initial sample, (b) 10 min. and (c) 90 min.

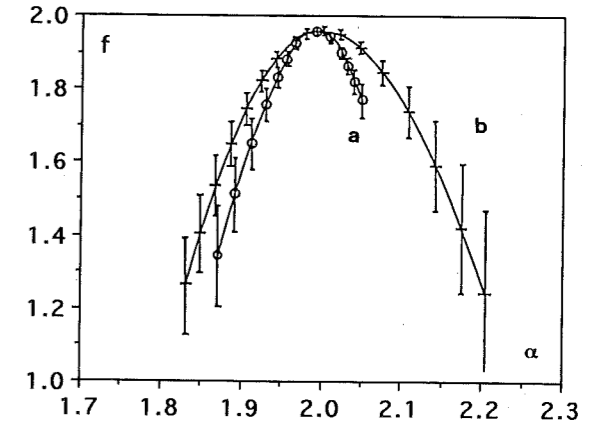


Figure 5: Spectra of singularities $f(\alpha)$ before annealing for: (a) 20PE/80PS+10 Tapered Cop. and (b) 20PE/80PS+10 Pure Cop.