

Controlling the Phase Stability of Polymer Blends Through the Introduction of Impenetrable Interfaces

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Received 4 March 2002; accepted 29 May 2002

ABSTRACT: In this work, the effect of the introduction of modified solid surfaces into polymer blends on the phase-separation process was investigated. Glass fibers with surfaces having different chemistries were introduced into polystyrene–poly(methyl methacrylate) blends. The glass fibers used either had fully hydrated surfaces or had surfaces covered with a random copolymer, poly(styrene-co-methyl methacrylate). The copolymer was synthesized by free-radical polymerization of styrene and methyl methacrylate in the presence of previously vinyl silane-treated glass fibers. The copolymerization and grafting procedures were investigated by FTIR and thermal analysis. Blends containing the fibers were studied using FTIR microscopy and optical mi-

croscopy. FTIR microscopy results showed that the composition of the phases in the blends was shifted by using fibers with different surface chemistries. Fibers with grafted copolymers were capable of narrowing the immiscibility region in the phase diagram, while fully hydrated fibers were able to expand the gap. It was proposed that interfacial interactions regulated by a hydrophilic–hydrophobic type of forces were responsible for guiding the described phase-separation process. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1619–1627, 2003

Key words: blends; compatibilization; fibers

INTRODUCTION

Until the beginning of the 1980s, the blending or compounding polymers was a rare procedure on plastic production lines. Nevertheless, in the end of the same decade, the number of products based on blends reached very large values. In 1989, for every pound of pure resin sold, another pound was sold as a blend in the United States.¹ This growth was a result of the recognition that blending is a very useful technological approach to reduce cost and to produce products with optimized properties.

Blends are also potentially useful in favoring the recycle of plastics. In this case, instead of sorting out different types of polymers to recycle each one individually, it could be more cost-effective to just process the mixture of polymers as a blend.

When different polymers are mixed, they seldom produce homogeneous solutions. More often, free energy is reduced by keeping the components separated in distinct phases. Phase-separated systems can have enhanced properties usually if the phases are fully

integrated by interfacial interactions. Compatibilization of immiscible blends is therefore normally required to achieve a desirable and useful set of properties.

Many strategies have been described as being capable of or, at least, having the potential of leading to the compatibilization of blends²: (a) incorporation of grafted or block copolymers³; (b) addition of reactive polymers⁴; (c) reaction between phases; (d) partial degradation of polymers induced by themomechanical treatments⁵; (e) chemical modification of polymers to introduce specific sites for interactions; (f) crosslinking between the different polymers in the mixture to form an interpenetrating network; (g) addition of ionomers; and (h) addition of a third polymer, miscible in the phases.

The introduction of solid surfaces in the form of fillers has also been suggested as a potential approach for modifying the phase stability in polymer blends.^{6–8} This approach has the potential advantage of reducing the cost in blending operations, since it may avoid the need for using, sometimes, more expensive block copolymers or other types of compatibilizers.

It was demonstrated that the boundaries of the upper critical solution domain in polystyrene–polybutadiene blends could be shifted vertically by the addition of untreated silica particles.⁶ On the other hand, modifying silica particles with either silane coupling

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Contract grant sponsor: CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) of the Brazilian Government.

agents or polystyrene chains could reduce the cloud-point temperatures, showing, clearly, that the surface energy of fillers can alter the phase stability of blends. It has been also reported that the thermodynamic interaction parameter between two polymers (χ_{12}) can be reduced by introducing kaolin into poly(butyl methacrylate)–poly(methyl methacrylate) blends.² The formation of diffuse interfaces near the surfaces of the fillers was used to explain the enhanced compatibilization. This trend was also observed in studies that calculated the thermodynamic parameter from the glass transition data of phase-separated poly(vinyl acetate)–poly(methyl methacrylate) blends.⁷ For this system, it was also shown that the filler could improve the solubility of one component in another. Specific interactions and surface segregation of one polymer at the surface of the filler were used to explain the observed phenomena.

However, for blends of chlorinated polyethylene and an ethylene–vinyl acetate copolymer, it was shown that the temperature of phase separation could either increase or decrease depending on the amount of filler (silica) added to the mixture.⁸ It was proposed that both selective adsorption and redistribution of molecular weight components within the polymer system and at the surface could be responsible for the observed effect.

In this work, the phase stability of polystyrene–poly(methyl methacrylate) (PS–PMMA) blends was modified by the incorporation of glass fibers having different surface chemistries. FTIR microscopy was used to determine the shifts in composition of the phases upon the incorporation of chemically designed solid surfaces.

EXPERIMENTAL

Materials

Styrene and methyl methacrylate monomers (Polyscience) were purified using a column packed with alumina particles. Toluene and benzoyl peroxide were used as received. PS (20,000 g/mol) and PMMA (25,000 g/mol) were obtained, respectively, from BASF and Metacril. Hollow glass spheres and milled E-glass fibers were purchased, respectively, from Aldrich and Corning. They were heat-treated at 500°C to eliminate any possible residual organics and then introduced into an aqueous solution (pH 2.0, adjusted using HCl) at 80°C for 3 h to force the rehydration of the glass surfaces.

Copolymerization and grafting

A poly(styrene-*co*-methyl methacrylate) random copolymer, having 50 weight % of styrene and 50 weight

% of methyl methacrylate, was grafted onto glass surfaces by copolymerizing styrene and methyl methacrylate in the presence of glass surfaces previously treated with vinyl triethoxysilane. Vinyl triethoxysilane can be incorporated during free-radical polymerization of vinyl monomers, thus producing a strong linkage between the substrate and the copolymer.⁹ According to the literature,¹⁰ the reactivity ratios, respectively, for methyl methacrylate (r_{MMA}) and styrene (r_{Sty}) are 0.46 and 0.52, respectively. The silane treatment consisted of allowing the reaction of glass spheres or fibers with the vinyl silane in a dry toluene solution (1% vol of silane) for 1 h at room temperature. The glass substrates were then collected through filtration. Free-radical copolymerization of styrene, methyl methacrylate, and vinyl triethoxysilane (grafted onto glass surfaces) was allowed to run in toluene for 10 h at 80°C (benzoyl peroxide was used as the initiator). The glass substrates were again collected by filtration and then rinsed with toluene to leach out nongrafted species. The remaining solution containing the nongrafted copolymer was solvent-cast to produce free-standing poly(styrene-*co*-methyl methacrylate) films.

Preparation of blends

PS–PMMA blends were prepared by dissolving the polymers in toluene (10% wt/vol). The solution was then solvent-cast onto glass slides to produce a 55% vol PS–45% vol PMMA blend. Blends containing glass fibers were prepared by introducing them into the polymer solution prior to being solvent-cast.

Characterization techniques

The grafting procedure was studied using hollow glass spheres with a composition similar to glass fibers as a substrate for graftization. The low density of hollow glass spheres expands the capability of thermogravimetric methods in detecting polymeric species grafted onto inorganic surfaces. Hollow glass spheres containing the grafts were submitted to thermogravimetric analysis (Shimadzu TG-50, heating rate of 20°/min, nitrogen atmosphere).

Polymer blends and copolymers were analyzed by dynamic scanning calorimetry (DSC, Shimadzu DSC-50, heating rate of 10°/min, nitrogen atmosphere) and FTIR. Two different FTIR techniques were used to study the blends and blends containing fibers: FTIR microscopy and direct transmission FTIR. In direct transmission FTIR, the IR beam, measuring typically 1–2 mm in width, was used to cross the thickness of the polymer thin films. By using this technique, the FTIR results of blends having micrometer-separated phases provided a general view of the chemical as-

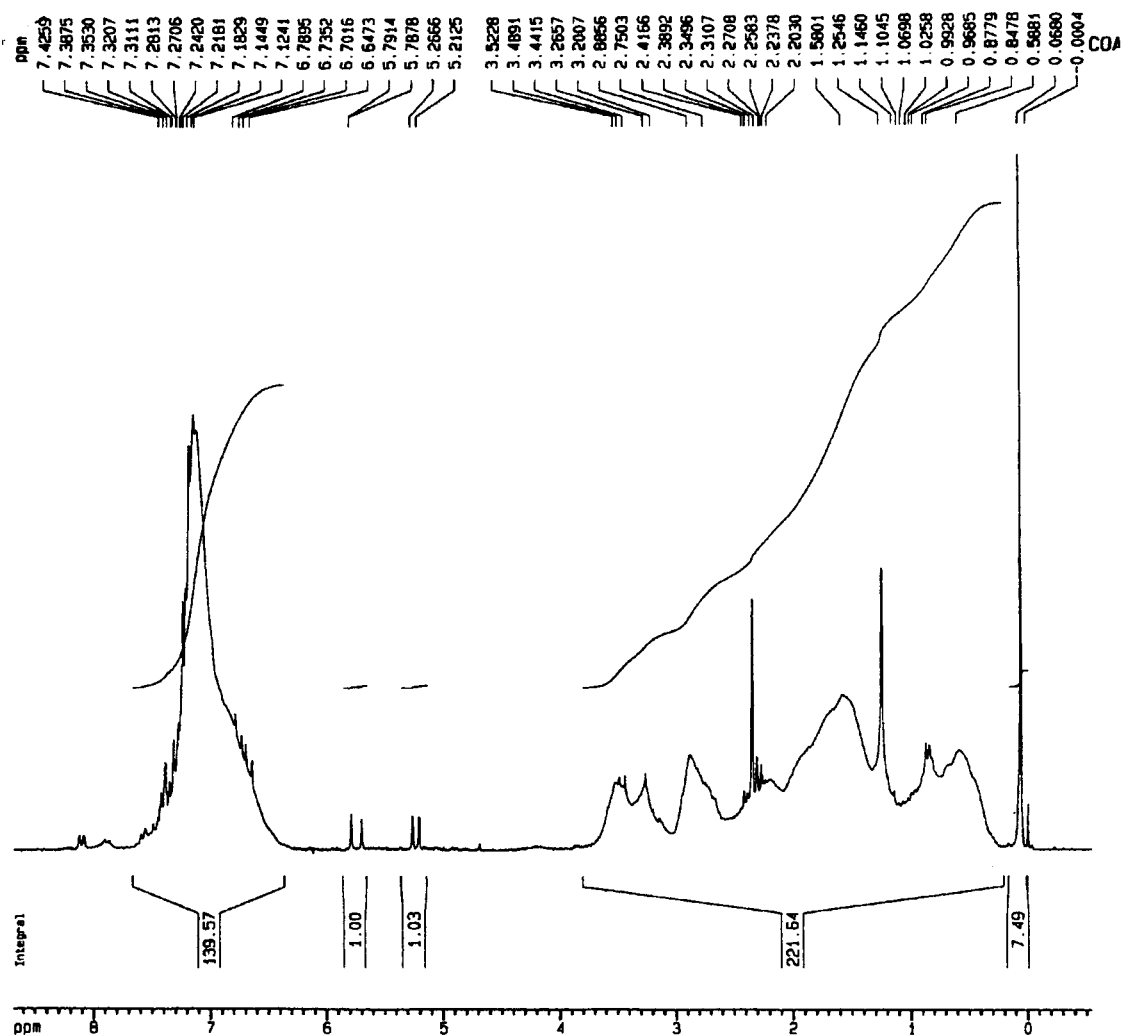


Figure 1 $^1\text{H-NMR}$ of the poly(styrene-*co*-methyl methacrylate) copolymer.

pects of the material. On the other hand, FTIR microscopy allows the analysis of each micrometer phase individually. FTIR analyses were conducted in a Perkin-Elmer Paragon 1000.

RESULTS AND DISCUSSION

The results from the proton NMR ($^1\text{H-NMR}$) indicated that the chemical procedure adopted was successful in producing the poly(styrene-*co*-methyl methacrylate) random copolymer. The $^1\text{H-NMR}$ spectrum of the copolymer in Figure 1 shows frequencies due to the CH_3 group from the methyl methacrylate repeat unit (2.5–3.0 ppm) and frequencies due to the benzene ring of the styrene repeat unit (6.0–7.0 ppm).

The DSC results (Fig. 2) also showed that free-standing and transparent copolymer films have a single T_g (glass transition temperature) that is located in between the T_g 's of the pure components (T_g of PS

= 95°C , T_g of PMMA = 112°C). The Fox equation¹¹ can predict the T_g of copolymers based on the T_g of the homopolymers and the weight fraction of each repeat unit (M):

$$\frac{1}{T_g} = \frac{M_1}{T_{g1}} + \frac{M_2}{T_{g2}} \quad (1)$$

By inserting the T_g 's of the homopolymers into eq. (1), the predicted T_g of the copolymer with a 50% weight fraction of each repeat unit would be 102°C . The measured T_g of the copolymer was 100°C . Since the error of the DSC analysis was detected to be $\pm 2^\circ\text{C}$, the T_g of the copolymer is close to the one that can be estimated by the Fox equation. On the other hand, two T_g 's were detected in the PS/PMMA blends. The presence of two T_g 's is usually associated with phase separation.

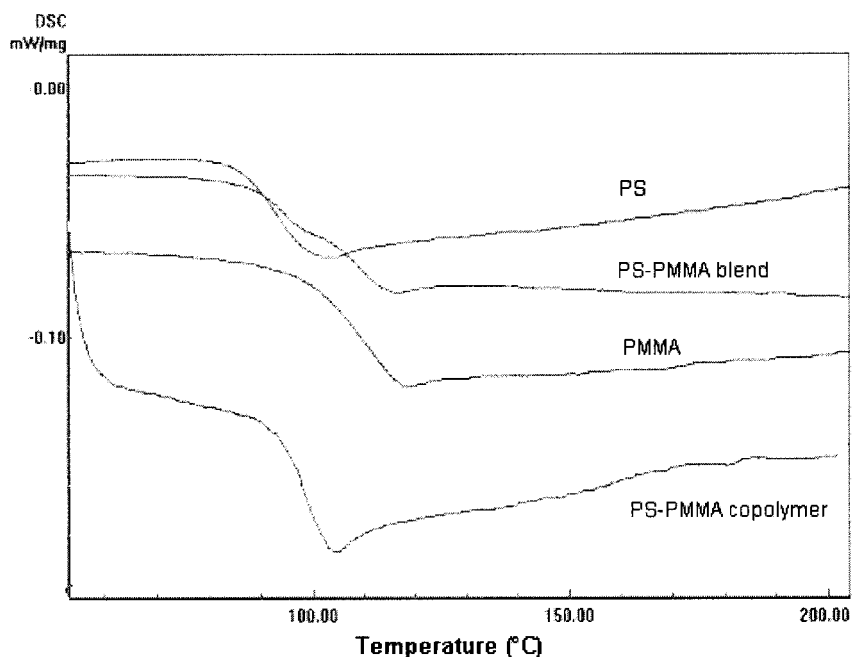


Figure 2 DSC results of PMMA-PS copolymer and blends.

The success of the grafting procedure, that is, the incorporation of copolymer chains onto glass substrates through the use of vinyl triethoxysilane, was demonstrated using hollow glass spheres. The presence of the grafted chains was clearly confirmed by thermogravimetric analysis (TGA; Fig. 3). The TGA results showed that spheres with grafts had a 6% weight loss during heating up to 600°C, while no

weight loss was observed for spheres with no polymer grafts.

The FTIR results in Figure 4 showed that the spectrum of the PS-PMMA blend is basically a combination of the spectra of the pure components (PS and PMMA). Table I reports the most important FTIR peaks of the PMMA and PS.¹² The relationship between the absorbance of the peaks related to PMMA

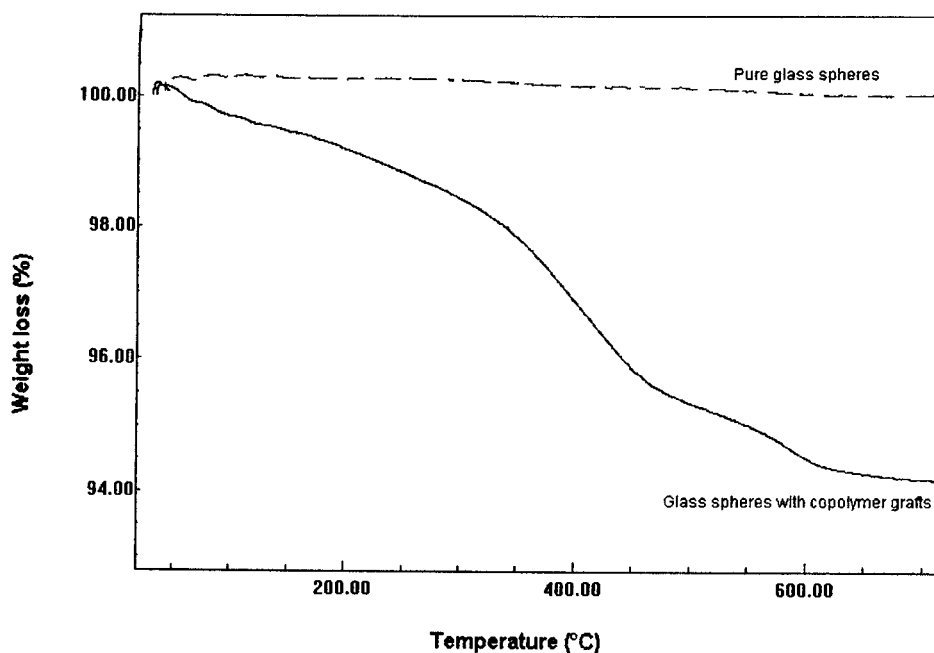


Figure 3 Thermogravimetric analysis on hollow glass spheres with polymer grafts.

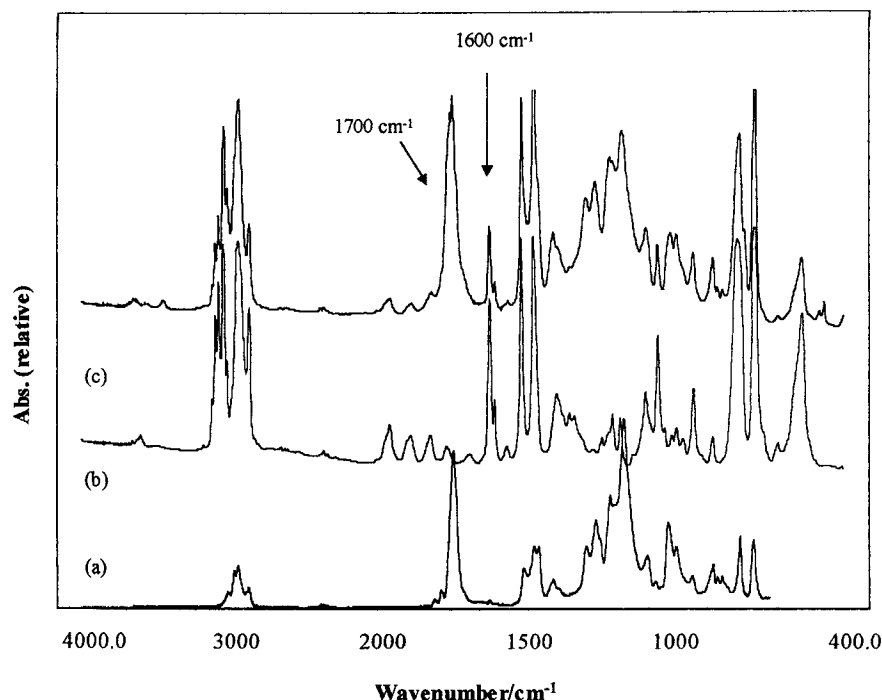


Figure 4 FTIR spectra: (a) PMMA; (b) PS; (c) PS-PMMA blend.

carbonyl groups (1740 cm^{-1}) and PS aromatic C double bonds (1600 cm^{-1}) was used in this work to estimate the relative amount of the components in the blend.

The microstructure of the blends was evaluated by optical microscopy coupled with FTIR microscopy. The results were useful to provide information regarding the effect of the surface treatment of the fibers on the phase stability of the systems. Figure 5(A) shows the microstructure of the PS-PMMA blend with no fibers. Spectra of the distinct phases, obtained by FTIR microscopy, are revealed in Figure 5(B). The results showed clearly that the dispersed phase is rich in PMMA, while the matrix is rich in PS. The ratio between the height of the 1740 cm^{-1} (PMMA carbonyl) peak and the 1600 cm^{-1} (PS aromatic C=C) peak is exhibited in Figure 6. The peak ratios were converted to the composition using the value of the peak ratio obtained from the spectrum of the overall PS-PMMA blend (Fig. 4).

TABLE I
FTIR Frequencies of PS and PMMA

Polymers	FTIR peaks (cm^{-1})	Peak assignment
PS	3050	C—H stretch
	1600, 1450	C=C ring stretch
	780, 700	C—H out-of-plane bending
PMMA	2900–2800	C—H stretch
	1740	C=O stretch
	1150	C—O stretch

When hydrated fibers were introduced into the blends, optical micrographs showed [Fig. 7(A)] that they would rather stay within the dispersed phases instead of the matrix. FTIR spectra of the phases are exhibited in Figure 7(B). The obtained peak ratio was also included in Figure 6 to allow comparison with the other types of blends. The results showed clearly that the dispersed phase containing hydrated glass fibers is richer in PMMA than is the dispersed phase of the blend with no fibers.

For blends with fibers having surfaces modified with copolymer grafts, optical microscopy showed that these modified fibers tend to stay either at the interface of the polymer phases or crossing it [Fig. 8(A)]. The FTIR microscopy results in Figure 8(B) demonstrate that the dispersed phases of the blends having surface-treated fibers have a lower concentration in PMMA than has the blend with no fibers (Fig. 6).

The overall result (Table II) shows that the use of hydrated fiber in the blends tended to expand the immiscibility region of the PS-PMMA phase diagram. On the other hand, surface-treated fibers led to immiscibility regions narrower than those of the original blend with no fibers. These results demonstrate that the fibers and their surface chemistry can be used to manipulate the stability of polymer phases in a blend.

The Flory-Huggins theory, developed for polymer solutions, can also be used to study the phase compatibility in polymer blends.^{7,13,14} Based upon the data

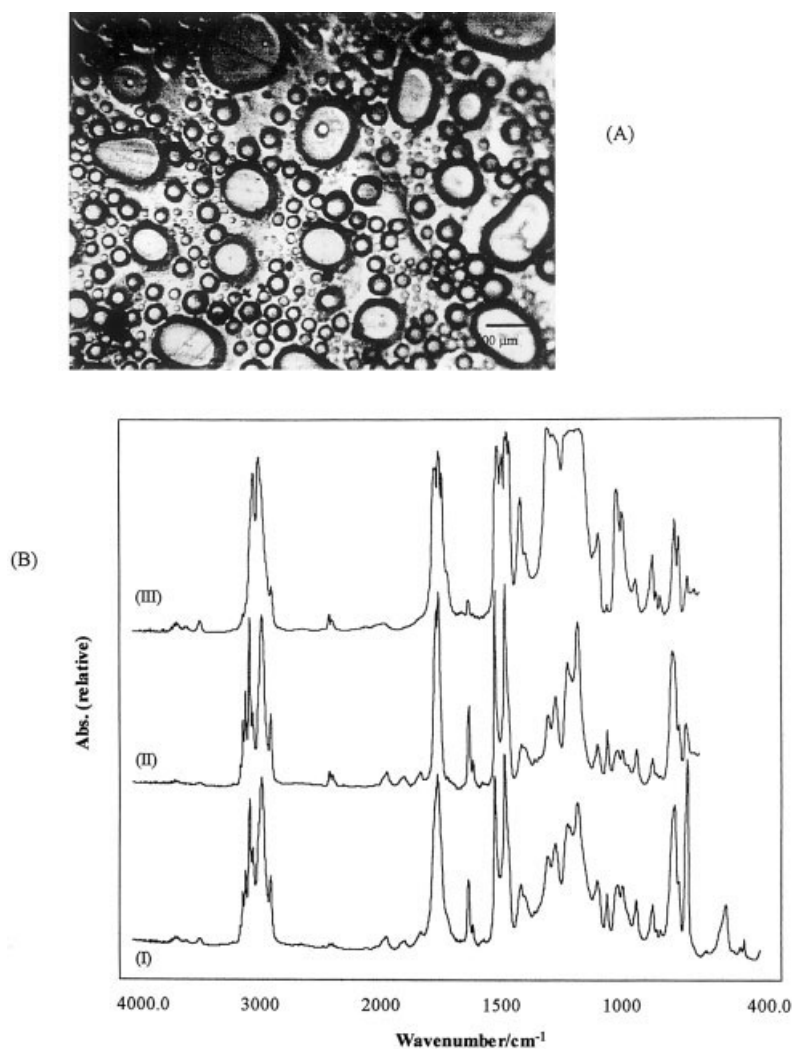


Figure 5 (A) Optical micrograph of PMMA–PS blends with no fibers. (B) PMMA–PS blends with no fibers: (I) FTIR spectrum of the overall blend; (II) FTIR microscopy spectrum of the matrix; (III) FTIR microscopy spectrum of the dispersed phase.

obtained from FTIR microscopy (Table II), it is possible to determine the Flory–Huggins polymer–polymer interaction parameter ($\chi_{1,2}$). Assuming that the equi-

librium condition for the blend systems was met, the following expression (2) can be derived from the free energy of mixing of two polymers:

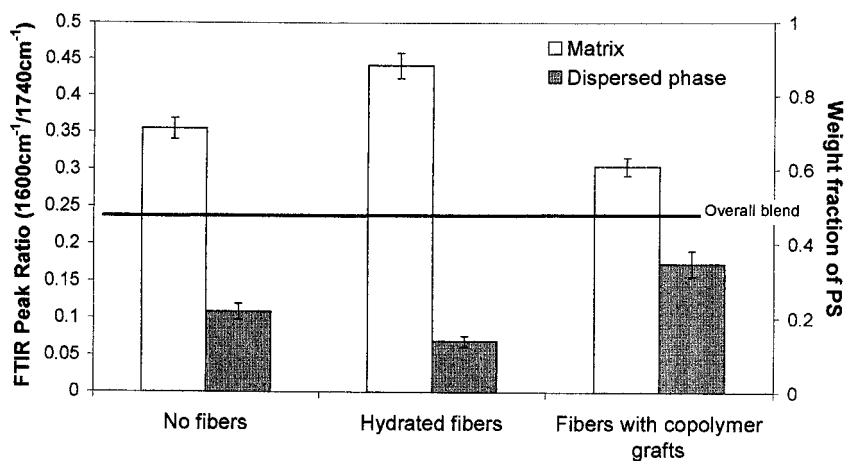


Figure 6 Composition of phases in PS–PMMA blends measured by FTIR microscopy.

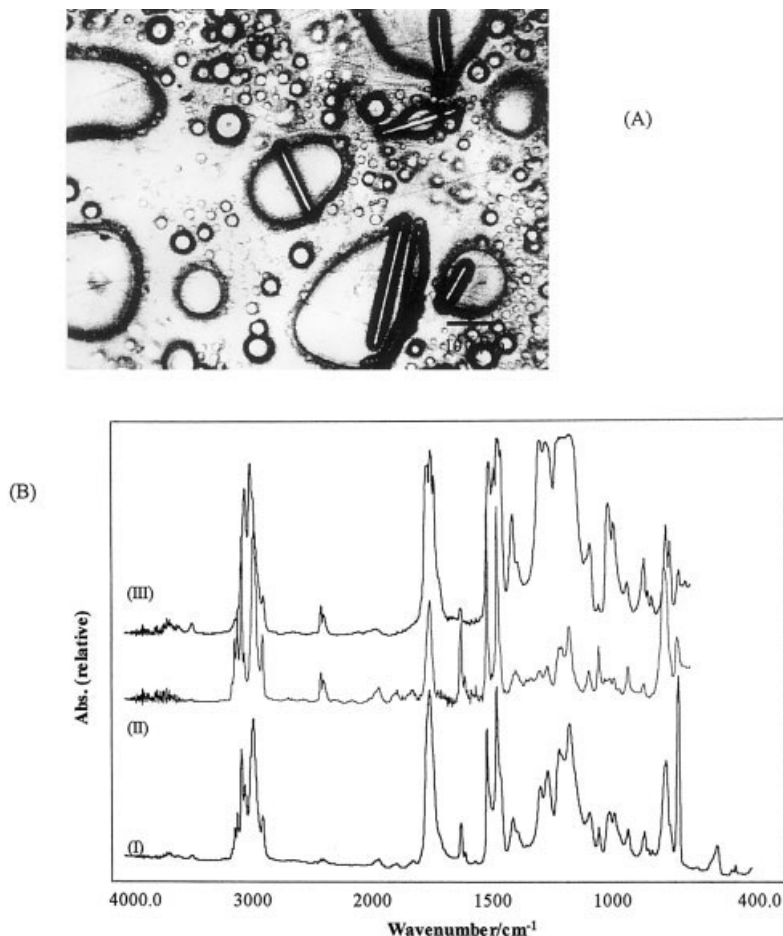


Figure 7 (A) Optical micrograph of PMMA-PS blends with hydrated fibers. (B) PMMA-PS blends with hydrated fibers: (I) FTIR spectrum of the overall blend; (II) FTIR microscopy spectrum of the matrix; (III) FTIR microscopy spectrum of the dispersed phase.

$$\chi_{1,2} = \frac{(\phi_{11}^2 - \phi_{12}^2) \left[m_2 \ln \left(\frac{\phi_{12}}{\phi_{11}} \right) + (m_1 - m_2)(\phi_{21} - \phi_{22}) \right]}{2m_1m_2(\phi_{11}^2 - \phi_{12}^2)(\phi_{21}^2 - \phi_{22}^2)} + \frac{(\phi_{21}^2 - \phi_{22}^2) \left[m_1 \ln \left(\frac{\phi_{22}}{\phi_{21}} \right) + (m_2 - m_1)(\phi_{11} - \phi_{12}) \right]}{2m_1m_2(\phi_{11}^2 - \phi_{12}^2)(\phi_{21}^2 - \phi_{22}^2)} \quad (2)$$

where ϕ_{11} and ϕ_{21} are, respectively, the volume fraction of polymer 1 in phase 1 and polymer 2 in phase 1. In the same way, ϕ_{12} and ϕ_{22} are, respectively, the volume fraction of polymer 1 in phase 2 and polymer 2 in phase 2. The values of m_1 and m_2 can be considered equal to the degree of polymerization of polymers 1 and 2. Expression (2) can then be used to calculate the Flory-Huggins ($\chi_{1,2}$) for blends.

The Flory-Huggins theory also accomplishes the task of determining the critical condition for stability. The critical Flory-Huggins parameter ($\chi_{1,2}$)_c can be calculated as follows and defines the set of conditions in which dissolution or phase separation will occur:

$$(\chi_{1,2})_c = \frac{1}{2}((m_1)^{-0.5} + (m_2)^{-0.5})^2 \quad (3)$$

Table II reports the χ_{12} parameter for the studied systems [values obtained by applying eq. (2) to the FTIR microscopy data]. The volume fraction of the phases in each system was calculated using the data shown in Figure 6. The weight fraction was converted to a volume fraction using the density of the pure polymers (density PS = 1.04 g/cm³ and density of PMMA = 1.18 g/cm³). The results showed that the interaction parameter χ_{12} increases when hydrated fibers are inserted into the blends and decreases for blends with treated fibers. The critical value of χ_{12} can also be determined by using eq. (3). For the PS-PMMA blends in this work, it was found that this critical value is equal to 0.0095. The fact that the values of χ_{12} for the blends are larger than (χ_{12})_c is an indication that the PS-PMMA blend is immiscible for the studied composition. The introduction of fibers containing polymer grafts shifted the χ_{12} to values closer to the

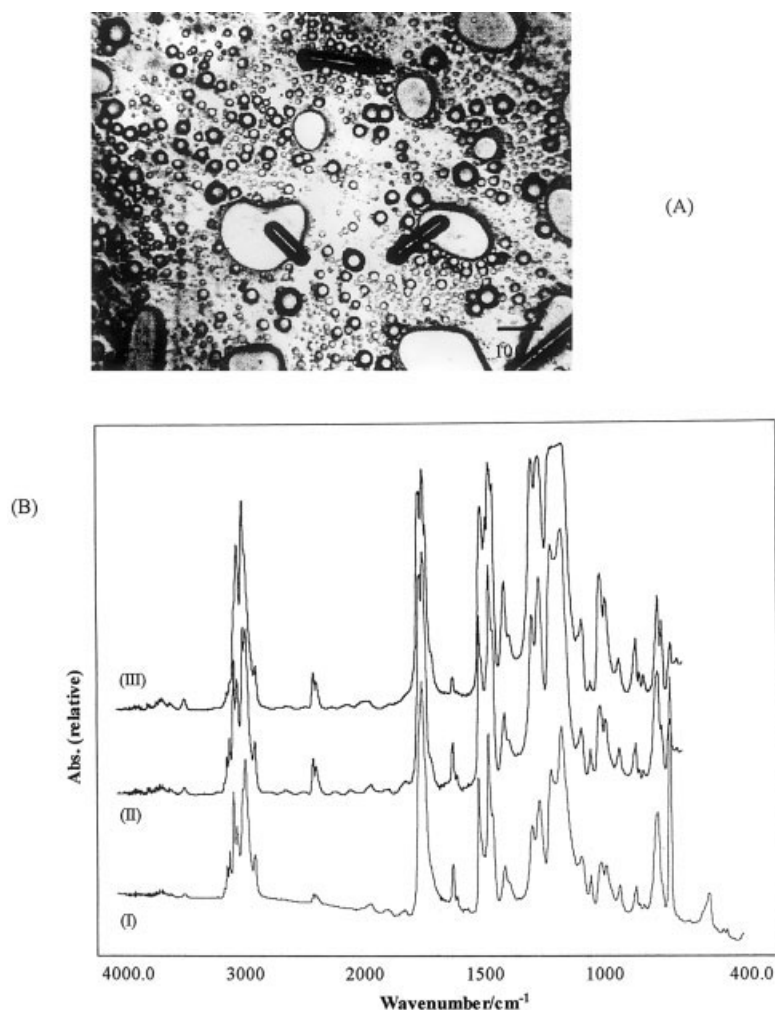


Figure 8 (A) Optical micrograph of PMMA–PS blends with copolymer-treated fibers. (B) PMMA–PS blends with copolymer-treated fibers: (I) FTIR spectrum of the overall blend; (II) FTIR microscopy spectrum of the matrix; (III) FTIR microscopy spectrum of the dispersed phase.

critical one, meaning that a much more compatible system was achieved.

Thermodynamics clearly shows that entropy and enthalpy are both important in defining the phase stability of polymer blends. The introduction of impenetrable surfaces naturally imposes new features to these components of the free energy. Since impenetrable surfaces divide the space in two halves, polymer

chains are then limited in conformation and only half of the possible conformation modes are allowed for chains near this type of surface. Fewer modes of conformation can mean both higher viscosities and reduction in entropy, which leads, consequently, to less ability to mix. Selective adsorption is also a very likely main event that can play an important role. The presence of specific chemical functionalities on surfaces can induce a type of molecular recognition process where a variety of forces, such as hydrophobic forces, hydrogen bond, and ionic, can act. In this work, it was shown that glass fibers with fully hydrated surfaces expand the immiscibility region of the PS–PMMA phase diagram. Since, PS is more hydrophobic than is PMMA, chemical interactions between, for example, hydrophobic groups located on PS chains and hydrophilic groups on rigid surfaces promote mutual repulsion and PS chains are forced to stay away from the surface. On the other hand, hydrated fibers can readily

TABLE II
Phase Compositions and Interaction Parameters of PMMA–PS Blends Modified with Fibers

PS–PMMA blends	Volume fraction of PS		Interaction parameter
	Dispersed phase	Matrix	
No fibers	0.24	0.74	0.0107
Hydrated fibers	0.17	0.9	0.0124
Fibers with copolymer grafts	0.38	0.63	0.0099

interact with hydrophilic ester groups on PMMA, leading to selective adsorption. Therefore, the combination of selective adsorption and entropically affected chains due to the presence of impenetrable surfaces can be responsible for the reduction in compatibility observed when hydrated fibers were introduced into PS-PMMA blends.

In PS-PMMA blends having fibers with polymer grafts, the presence of a random copolymer containing styrene and methyl methacrylate repeat units at the surface of the fibers allow free interaction between compatible groups present in the components and in the copolymer. Therefore, copolymer-treated fibers can reduce the immiscibility domain of the PS-PMMA phase diagram by promoting intersegmental bonding between both components and the copolymer.

CONCLUSIONS

In this work, the phase stability of PS-PMMA blends was modified by the introduction of glass fibers with different surface chemistries. The phase-separation process was studied by a combination of optical microscopy and FTIR microscopy. The results showed that fully hydrated glass fibers could expand the original immiscibility region of the PS-PMMA phase diagram. The presence of hydrophilic groups on fibers restricts the adsorption of PS chains and leads to larger values of the Flory-Huggins interaction parameter.

On the other hand, by grafting a poly(styrene-co-methyl methacrylate) random copolymer onto glass fibers, it was possible to reduce the width of the im-

miscibility gap of the PS-PMMA phase diagram. This increase in compatibility, also detected by showing that the Flory-Huggins interaction parameter is reduced, was proposed to be due to intersegmental interactions between both PS and PMMA components and the copolymer. Potential applications of the results of this work include the use of inorganic fillers and fibers to enhance compatibilization between different polymers.

The authors would like to acknowledge the financial support from CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) of the Brazilian Government.

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