

In Situ Compatibilization of Polystyrene and Polyurethane Blends by Using Poly(styrene-*co*-maleic anhydride) as Reactive Compatibilizer

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Received 18 September 2000; accepted 26 January 2001

ABSTRACT: Blends of polystyrene (PS) and polyurethane (PU) elastomer were obtained by melt mixing, using poly(styrene-*co*-maleic anhydride) (SMA) containing 7 wt % of maleic anhydride groups as a reactive compatibilizer. Polyurethanes containing polyester flexible segments, PU-es, and polyether flexible segments, PU-et, were used. These polyurethanes were crosslinked with dicumyl peroxide or sulfur to improve their mechanical properties. The anhydride groups of SMA can react with the PU groups and form an *in situ* graft copolymer at the interface of the blends during their preparation. The rheological behavior was accompanied by torque versus time curves and an increase in the torque during the melt mixing was observed for all the reactive blends, indicating the occurrence of a reaction. Solubility tests, gel permeation chromatography, and scanning electronic microscopy confirmed the formation of a graft copolymer generated *in situ* during the melt blending. These results also indicate that this graft copolymer contains C—C bond between SMA and PU chains. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2514–2524, 2001

Key words: reactive compatibilization; *in situ* graft copolymer; PS/SMA/PU blends

INTRODUCTION

Most polymer pairs are thermodynamically immiscible as a result of the small entropy and the endothermic enthalpy of mixing. In some cases, this immiscibility is responsible for phase segregation in polymer blends and for the poor physical properties presented by these materials. To improve the physical properties of the immiscible blends, a reduction of the interfacial energy and an increase of the adhesion between the blend phases can be attained by the addition of a compatibilizer. Just as a surfactant can stabilize oil-

water mixtures, the compatibilizer should be able to enhance the stabilization of the morphology in immiscible polymer blends. The compatibilization can be achieved in different ways, for example, when a graft or a block copolymer is added to an immiscible blend. Different segments of these compatibilizers, when added, can penetrate both phases of an immiscible blend, thus causing more uniformly dispersed domains because of a reduction of the interfacial energy. In addition, the interfacial adhesion is improved because the compatibilizer segments, which reside in separate phases, are covalently linked.¹

Another way to achieve the compatibilization of the system is to generate an *in situ* graft copolymer through covalent or ionic bonding of suitably functionalized polymers during the melt blending. In this kind of reactive compatibiliza-

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Journal of Applied Polymer Science, Vol. 82, 2514–2524 (2001)
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Table I Characteristics of the Started Polymer

Polymer	\bar{M}_w (g/mol)	\bar{M}_w/\bar{M}_n	Flexible Segment	Source
PS	293,000	1.90	—	CBE ^a
SMA	283,000	1.96	—	Aldrich
PU-es	107,000	1.91	Polyester adipate based	Uniroyal Chemical ^b
PU-et	201,000	1.90	Poly(tetramethylene oxide)	Uniroyal Chemical ^b

^a Companhia Brasileira de Estireno, São José dos Campos, São Paulo, Brazil.

^b Uniroyal Chemical Company, Rio Claro, São Paulo, Brazil.

tion, in general, one phase contains reactive groups inherent in the polymer chain, whereas the other has no inherent functionality. Reactive groups can be incorporated into the second phase through the addition of a functionalized polymer miscible with it. In some cases, both phases may be functionalized. The *in situ*-formed copolymer compatibilizer is located preferentially at the interface, thus reducing the size of the dispersed phase and improving the interfacial adhesion between the different phases as well as the physical properties of the blend.²

One of the most commonly used functional groups in reactive blending is maleic anhydride. In some investigations reported in the literature^{3–5} maleic anhydride was incorporated in nonreactive polymers as polyolefins and polystyrene. Poly(styrene-*co*-maleic anhydride) (SMA) has gained attention because it is commercially available, and SMA copolymer has been used in blends of polyamide because of the well-established reaction between anhydride units with amine end groups of the polyamides. Blends of polyamide-6 (PA-6) with ABS or SAN⁶ and PA-6 with poly(phenylene oxide) (PPO)⁷ were compatibilized by SMA. Dedecker and Groeninckx⁸ used SMA to compatibilize the PA-6 and poly(methyl methacrylate) (PMMA) immiscible blends. The thickness of the interface of the PA-12/PS/SMA blends was determined by ellipsometry as a function of SMA content.⁹ SMA has also been used as a reactive compatibilizer in blends of amorphous polyamide (a-PA) and styrene-acrylonitrile (SAN) copolymer.¹⁰

In the present work blends of polystyrene and polyurethane elastomer were prepared by melt blending, using poly(styrene-*co*-maleic anhydride) as a reactive compatibilizer. Polyurethanes containing polyester or polyether flexible segments were used for preparation of the blends. The blends were analyzed by torque rheometry, solubility test, gel permeation chromatography

(GPC), and scanning electronic microscopy (SEM).

EXPERIMENTAL

Materials

The characteristics of the materials used to prepare the blends are summarized in Table I. Two different polyurethanes were used: a polyurethane containing polyester flexible segments (PU-es) and a polyurethane containing polyether flexible segments (PU-et) because these flexible segments present different reactivities. Both PU-es and PU-et contain toluene diisocyanate (TDI) as hard segment, which is 80% 2,4 isomer and 20% 2,6 isomer. The TDI concentration used in PU-es and PU-et was approximately 4 wt %. PU-es and PU-et also present unsaturated groups at low concentration.¹¹

The SMA used contained 7 wt % of maleic anhydride.

Melt Blending

Initially, PS/PU and SMA/PU binary blends were prepared. The PS/PU blends were used as a control material because they are not reactive blends. To study the effect of the compatibilizer content, ternary blends PS/SMA/PU were prepared with

Table II Anhydride Content in the Blends

Anhydride (wt %)	PS (wt %)	SMA (wt %)
0	100	—
0.5	93	7
1.0	86	14
3.0	56	44
5.0	28	72
7.0	0	100

varying content of maleic anhydride from 0.5 to 7 wt %. This variation in maleic anhydride concentration was achieved by the addition of different amounts of SMA to the blends (Table II). Blends containing 10 and 20 wt % of the PU were prepared by melt mixing in an internal mixer (Haake Rheometer 600, Karlsruhe, Germany) at 30 rpm and 190°C for 12 min, while the torque was recorded. After 2 min of mixing dicumyl peroxide was added to the blends (0.4 and 1.2 wt % to PU-es and to PU-et, respectively, as recommended by the supplier¹¹). Blends containing 2 wt % of sulfur were also prepared. Both dicumyl peroxide and sulfur were added to the blends to promote the PU crosslinking, thereby improving their mechanical properties. The blends were compression molded into 1.35-mm-thick plates using a hot press, at 200°C under 4.4 MPa for 3 min.

Solubility Test¹²

The solubility characteristics of the PS/PU (90/10) and SMA/PU (90/10) blends prepared by melt mixing were analyzed after being stirred for 1 h in different solvents: xylene, tetrahydrofuran (THF), chloroform, and dioxane. Films of the SMA/PU blends were obtained by evaporation of the solvent. SMA/PU (90/10) blends were also prepared by casting from polymer solutions in the same solvents used in the solubility test. The films obtained by casting were compared with the films of the corresponding blends prepared by melt mixing. The “visual” characteristics of the films were analyzed.

Molecular Weight

GPC analyses were carried out for the PS/PU and SMA/PU blends containing 20 wt % of the PU obtained by casting from polymer solution in THF and by melt blending. GPC-Waters (Waters Instruments, Rochester, MN), equipped with polystyrene gel columns (Ultrastayragel), was used to determine M_n , M_w , M_z , M_{z+1} , and M_w/M_n . The detector was a refractive index type (Waters-410) and the carrier solvent was THF. PS standards were used for calibration.

Morphology

The morphology of the blends obtained by melt mixing was studied by scanning electronic microscopy. PU-es blends were cryogenically fractured, after which the samples were refluxed in

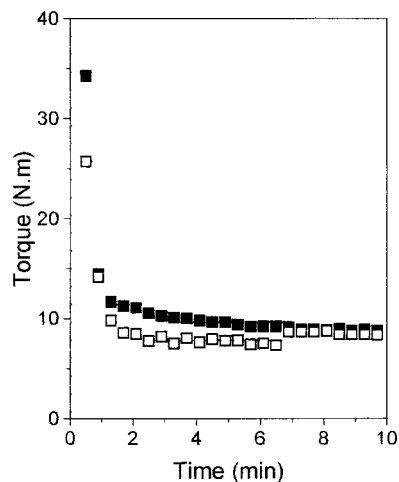
KOH ethanol solution (0.5 mol/L) for 3 h to remove the PU-es phase, given that polyester is quickly hydrolyzed in alkaline solution. Fractured samples of the PU-et blends were refluxed for 24 h in a 5 vol % phosphoric acid aqueous solution. The extracted surface was coated with a gold layer and the morphology of the blends containing up to 1 wt % of anhydride was analyzed by a JEOL JSTM-300 microscope (JEOL, Middleton, WI). All other blends were examined with an FE-SEM JSM-6340F microscope (Tokyo, Japan).

RESULTS AND DISCUSSION

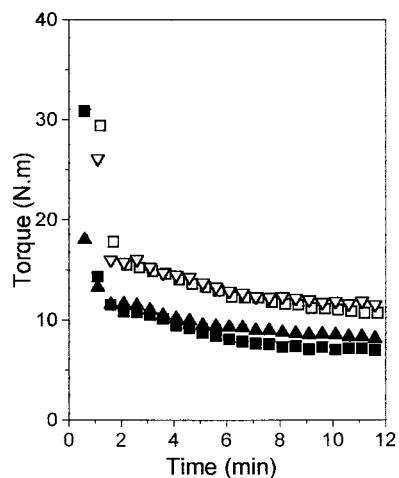
Torque Behavior

The dependency of torque on time during the processing of the blends can be directly related to the viscosity of the system, and it can be used to a certain extent to judge whether a reaction is occurring in a functionalized system.^{6,13,14} Reactions between the polymers are expected to lead to an increase in viscosity as a consequence of the increase in molecular weight, as a function of processing time, depending on the rate of reaction.⁶ Additionally, an increase in viscosity can also be related to crosslinking. A torque decrease can be ascribed to the polymer chain scission.^{13,14}

PS and SMA were processed under the same conditions used to process the blends. The torque versus time curves are shown in Figure 1(a). Torque as a function of the time curve for PS is very close to that for SMA, indicating that these polymers have a similar viscosity, thereby permitting the use of torque data for evaluation of possible reactions in SMA/PU blends compared to those of nonreactive PS/PU blends. The dependence of torque on time for nonreactive blends (PS/PU) and reactive blends (SMA/PU) containing 10 wt % of the PU-es and PU-et and dicumyl peroxide as crosslinker agents is shown in Figure 1(b). SMA/PU blends show higher torque values compared to those of the corresponding PS/PU blends over the course of the entire processing time. This result is attributed to an increase of molecular weight because of a graft copolymer formed *in situ* in the blends containing SMA as the matrix. Triacca et al.⁶ observed a similar torque behavior for blends of nylon 6 and styrene-acrylonitrile (SAN) using SMA containing 25 wt % of anhydride as a compatibilizer. They prepared nylon 6/SAN/SMA blends containing 50 wt % of nylon and SAN/anhydride 40/10 and 45/5,



(a)



(b)

Figure 1 Torque versus time curves: (a) PS (■) and SMA (□); (b) blends containing 10 wt % of the PU crosslinked with dicumyl peroxide: PS/PU-es (■), PS/PU-et (▲), SMA/PU-es (□), and SMA/PU-et (▽).

which gave a concentration of 1.25 and 2.5 wt % of anhydride, respectively. These investigators attributed this torque behavior to a very fast reaction occurring between anhydride units and amine groups of nylon 6, forming a graft copolymer. They also observed a decrease in torque with time that probably reflected mastication of the graft copolymer. In this work a decrease in torque with an increase of processing time was observed for all the blends.

An immediate increase in torque after the initial melting of the polymers was also observed by Teselios et al.,¹⁵ who investigated the structure of poly(ethylene-co-vinyl alcohol) (EVAL) and poly-

(styrene-co-maleic anhydride) (SMA) blends obtained by melt mixing. This torque behavior was attributed to the reaction between the hydroxyl group of EVAL and maleic anhydride groups of SMA, thus leading to the formation of branched and crosslinked molecules, which have higher melt viscosity.

In the present work, the reaction of graft copolymer formation during the melt blending of the SMA and PU must also be very fast, causing the shifting of the torque versus time curves to higher values since the beginning of the blending process. Blends obtained with no crosslinker agents or with sulfur showed the same torque behavior. To complement the information obtained from the torque curves, solubility tests were carried out for the blends.

Solubility Testing

PU-es Blends

Solubility tests were introduced in 1965 by Molau,¹² who set out to evaluate the efficiency of a compatibilizer when it is added to an immiscible polymeric blend. To carry out this test, a modification of Molau's original test was used, and our choice was a solvent, which was an appropriate solvent for one phase and a nonsolvent for the other. In this way, when the chosen solvent is added to an immiscible blend containing an ineffective compatibilizer two phases are produced: a soluble phase that gives a clear solution and an insoluble phase that remains in the bottom of the test tube as a precipitate [Fig. 2(a)]. On the other hand, if the immiscible blend contains an effective compatibilizer, a fine and homogeneous dispersion should be obtained when it is added to the solvent [Fig. 2(b)]. The solubility test was applied to confirm the formation of a graft copolymer dur-

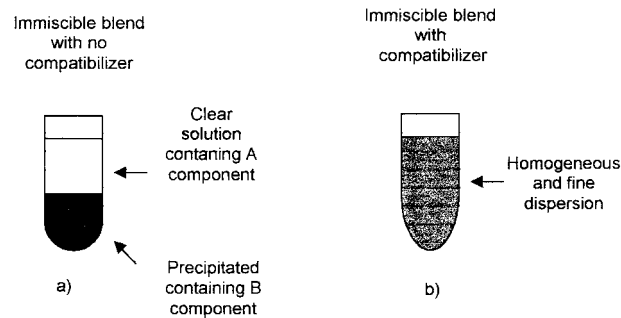


Figure 2 Schematic representation of the results that can be obtained in polymer blends solubility tests.

Table III Solubility Parameters (δ) and Its Components for Different Solvents

Solvent	δ^a (J/m ³) ^{1/2}	δ_d^b (J/m ³) ^{1/2}	δ_p^c (J/m ³) ^{1/2}	δ_h^d (J/m ³) ^{1/2}	H-Bonding Group
Xylene	18.0	17.7	1.0	3.1	Poor
Chloroform	19.0	17.6	3.1	5.7	Poor
THF	18.6	16.8	5.7	8.0	Moderate
Dioxane	20.5	19.0	1.8	7.3	Moderate

^a Total solubility parameter.

^b Component due to dispersion forces.

^c Component due to polar forces.

^d Component due to hydrogen bonding.

Brandup, J.; Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed.; John Wiley: New York, 1975; IV-337.

ing the melt mixing. When the solvent is added to the blends, the dispersed PU elastomer phase, which is crosslinked, is not soluble, although the matrix must dissolve because the chains are not crosslinked. In the absence of a graft copolymer, which acts as a compatibilizer, a system containing two phases is formed, consisting of a thermoplastic solution and a precipitate of the crosslinked PU particles. In the presence of a compatibilizer a homogeneous dispersion of fine PU particles, with no precipitate, is obtained.

In the present work xylene was used because it is a solvent to PS and SMA and a nonsolvent to PU-es. When PS/PU-es blends are added to xylene, two phases were observed, as schematized in Figure 2(a). This result was also obtained for the blends containing PU-es crosslinked with dicumyl peroxide or sulfur as well as to those prepared with PU-es without a crosslinker agent. However, when SMA/PU-es blends were added to xylene a homogeneous dispersion was obtained, as shown in Figure 2(b), independent of the crosslinker agent. According to Molau's theory, this result indicates that a compatibilizer should be present in the interface of the SMA/PU-es blends, causing the stabilization of the dispersion. However, a second hypothesis must be recognized: the morphology of the SMA/PU-es blends could be stabilized by strong interactions as hydrogen bonding, which could occur among carbamate, ester, or hydroxyl groups of PU-es and anhydride groups of SMA.

In the literature¹⁶⁻²² there are several works in which the miscibility or the compatibility of blends of thermoplastic polyurethane with different polymers is attributed to the hydrogen bonding. These interactions by hydrogen bonding must not be affected by the presence of xylene solvent. To verify these hypotheses, the SMA/PU-es (90/10) blends obtained by melt mixing were dis-

solved in different solvents: THF, chloroform, and dioxane. These solvents were chosen according to solubility parameters. Therefore, each solvent presents different hydrogen-bonding strengths, as shown in Table III. These solvents can compete with the supposed hydrogen bonding between the blend components and, consequently, the solvent may cause a phase segregation if the dispersion is stabilized only by hydrogen bonding. After the dissolution of the SMA/PU-es (90/10) blends in the different solvents, opaque films were obtained by casting and no macroscopic phase segregation was observed. This result is a strong indication of the presence of a graft copolymer formed *in situ* during the blend preparation and it is in accordance with torque data. A final test was made with SMA/PU-es blends to confirm that hydrogen bondings were not solely responsible for the macroscopically homogeneous films. SMA/PU-es (90/10) blends were prepared by dissolving both polymers in THF, chloroform, or dioxane, which are mutual solvents to SMA and to PU-es. The films obtained by casting from solutions showed macroscopic phase segregation independently of the solvents used, which indicates that hydrogen bonding alone cannot stabilize the dispersion of PU-es domains in the SMA matrix when the solvent is removed. Therefore, the result of the solubility test observed for the SMA/PU-es (90/10) blend obtained by the melt mixture confirms the existence of a graft copolymer in the interface of this blend, which was generated *in situ* during the blend processing.

PU-et Blends

Solubility tests for the PU-et blends were performed using a mutual solvent for the different phases. Films of the SMA/PU-et blends prepared by melt mixing obtained by casting from the xy-

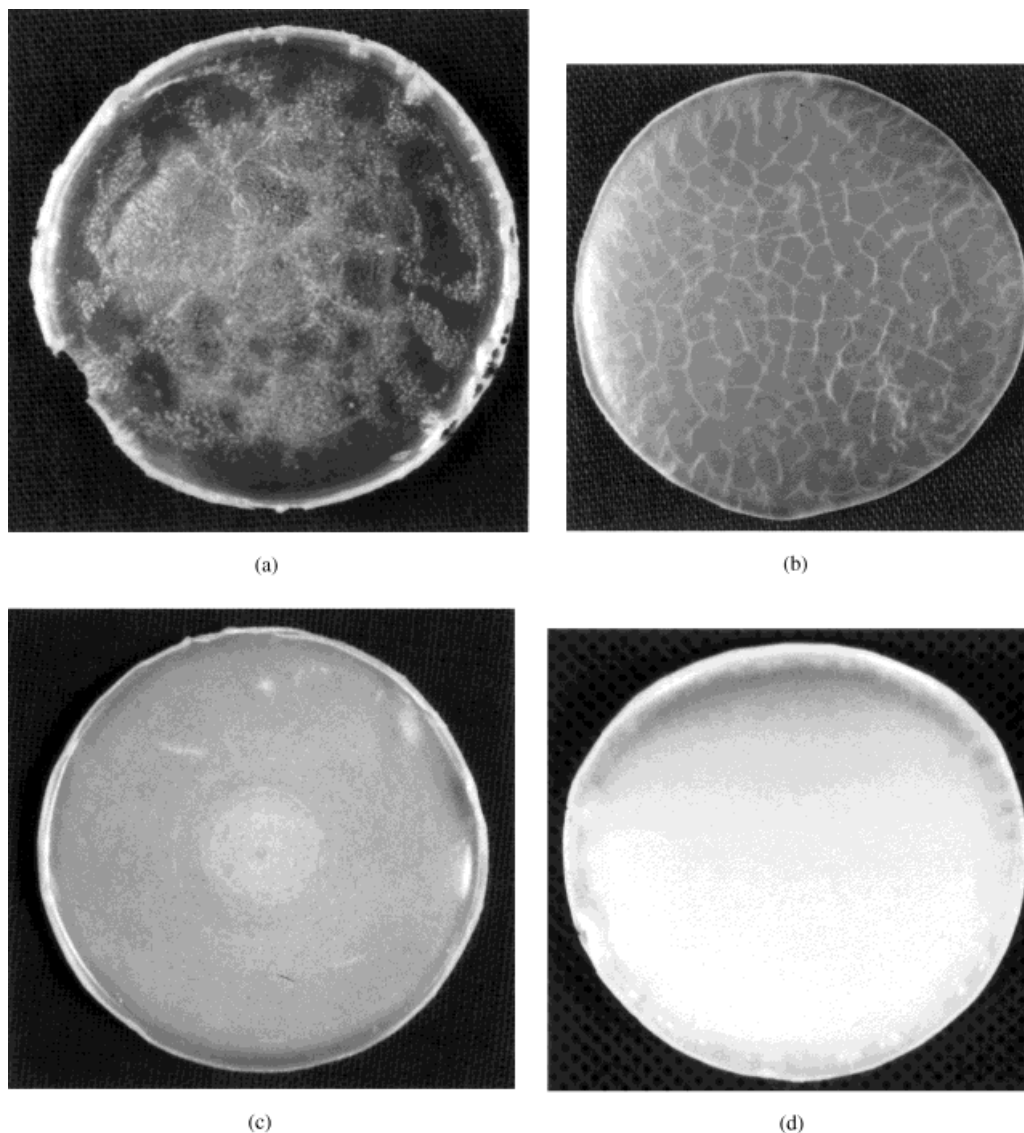


Figure 3 Films obtained from casting of xylene of the SMA/TPU-et (90/10) blends: (a) blend prepared by polymer solution, (b) blend prepared by melt mixture with no crosslinker agents, (c) blend prepared by melt mixture with dicumyl peroxide, and (d) blend prepared by melt mixture with sulfur.

lene solution were compared to those obtained by casting from the polymers dissolved in xylene (Fig. 3). The latter showed a clear macroscopic phase segregation where the PU-et phase appears in the middle of the film [Fig. 3(a)]. The former films prepared with no crosslinker agent showed some phase segregation, although to a lesser extent than was observed in the first case [Fig. 3(b)]. The addition of crosslinker agents, dicumyl peroxide, or sulfur, to the SMA/PU-et blends during the melt mixing resulted in films macroscopically homogeneous after being cast from the xylene

solution [Fig. 3(c), (d)]. These results indicate that the crosslinker agents aid the SMA-g-PU-et formation during the melt blending. The crosslinker agents should also affect the graft copolymerization in blends containing PU-es, although it is more difficult to observe as a result of the higher reactivity of ester groups compared to that of ether groups. This higher PU-es reactivity should be responsible for the macroscopically homogeneous films obtained, in spite of the absence of the crosslinker agent in SMA/PU-es blends.

Table IV Molecular Weights of SMA/TPU (80/20) Blends

Blends ^a	$\overline{M}_w \times 10^3$ (g/mol)	$\overline{M}_z \times 10^3$ (g/mol)	$\overline{M}_{z+1} \times 10^3$ (g/mol)	$\overline{M}_w/\overline{M}_n$
SMA/PU-es (80/20) ^(s)	233	404	567	2.64
SMA/PU-es (80/20) ^(m)	255	575	1059	2.92
SMA/PU-et (80/20) ^(s)	262	428	613	2.47
SMA/PU-et (80/20) ^(m)	246	432	638	2.03

^a Superscript (s): THF polymer solution; superscript (m): blends obtained by melt mixture.

The degree of grafting could not be determined because it was not possible to isolate the graft copolymer from the fine and stable dispersion.

GPC

GPC is an excellent technique to evaluate molecular weight modification in polymer systems. This technique was applied by Stutz et al.²³ to investigate the possibility of occurrence of a reaction between the maleic anhydride of the SMA and the PU. They prepared blends by melt mixing of SMA containing 14 wt % of anhydride, and PU containing polyether flexible segments, varying the mixture times: 10, 20, and 30 min. The GPC analysis of the blend processed for 30 min showed a change of the curve profile at the region of higher molecular weight, where an increase of \overline{M}_z was observed compared to that of blends processed for 10 or 20 min, whereas \overline{M}_n and \overline{M}_w were not modified. Given that all the molecules present in the blend have an equal chance to react, the shape of the distribution curve would remain unaffected and only a shift to higher molecular weights would be caused by the reaction, although this was not observed. Therefore, Stutz et al.²³ concluded that the preferential formation of large molecules is consistent only with multiple additions at the same molecule. This means that the surface of the dispersed particles remains essentially unchanged during blending and a molecule once reacted remains at the interface for thermodynamic reasons, thus having an enhanced chance for further reactions. Similar results were reported by Guégan et al.²⁴ for blends of polystyrene containing carboxylic acid end groups and PMMA containing epoxy end groups. These blends were prepared by melt mixture and a graft copolymer was generated *in situ* during the mixture.

To verify the change in the molecular weight, GPC analyses were carried out for the mixtures of the polymer and for the blends obtained by the

melt mixture (Table IV). As observed by Stutz et al.,²³ the weight-average molecular weight \overline{M}_w , obtained for both SMA/PU-es and SMA/PU-et blends, is practically constant, independent of the blend preparation method. However, higher values of molecular weight can be observed for the SMA/PU-es blends prepared by melt mixture in higher regions of molecular weight, \overline{M}_z and \overline{M}_{z+1} . The \overline{M}_z value increased by a factor of 1.4 and \overline{M}_{z+1} increased by a factor of 1.9 for the blends obtained by melt mixing. In the SMA/PU-et blends this effect is abated, and there is a small increase in \overline{M}_{z+1} for the blends obtained by the melt mixture. This result is attributed to the lower reactivity of the ether group compared to that of the ester group.

SEM

Morphological modification is another important parameter to confirm the efficiency or the presence of a compatibilizer in an immiscible system, because a suitable compatibilizer should promote a fine and homogeneous phase dispersion. Figure 4 shows SEM micrographs of the blends with 20 wt % of the PU-es containing different concentrations of anhydride and dicumyl peroxide as the crosslinker agent for the PU-es phase. In a general way, the PU domains are spherical and uniformly distributed in the matrix. It can be observed that the size of the PU-es domains decreases drastically with the increase of anhydride content. These same features were observed for both the blends containing 10 and 20 wt % of the PU-es crosslinked with sulfur and the blends containing 10 and 20 wt % of the PU-et crosslinked with dicumyl peroxide or sulfur. In the blends with up to 3 wt % of anhydride content some agglomeration can be seen [Fig. 4(d)–(f)], which must be ascribed to the PU phase not extracted by hydrolysis. It suggests that there is a fraction of the PU that should be chemically bonded to the matrix through a graft copolymer.

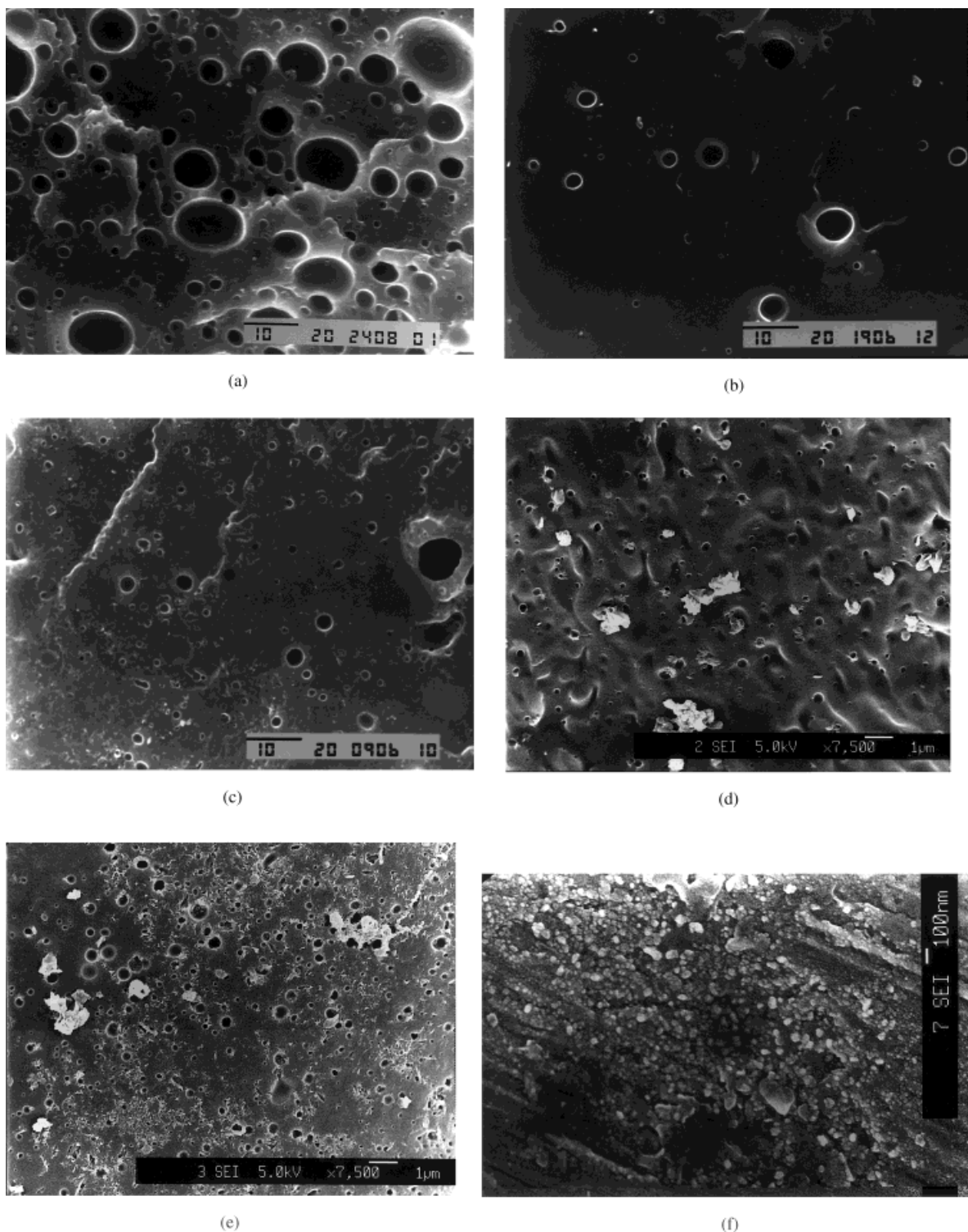
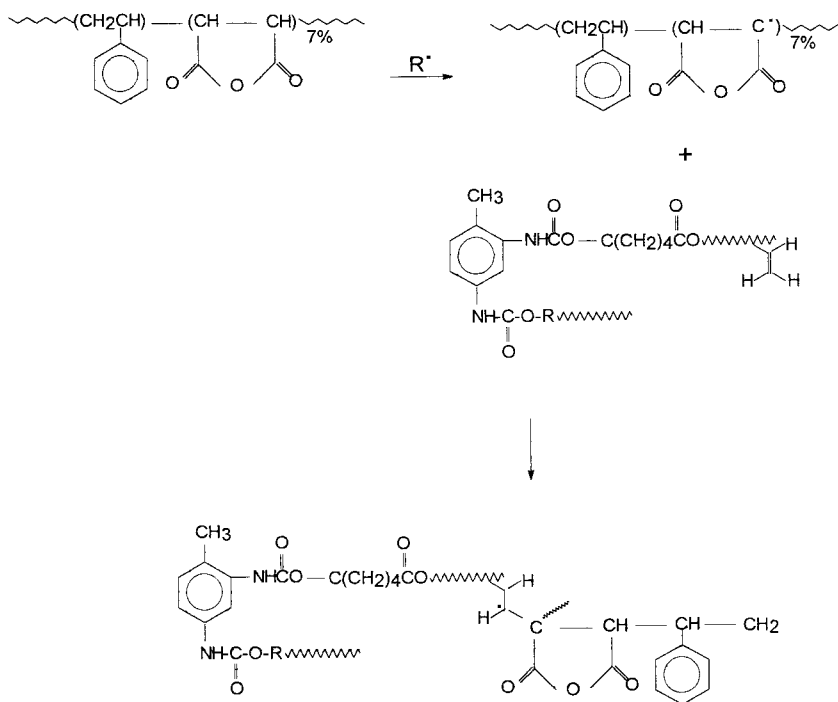


Figure 4 SEM micrographs of the blends containing 10 wt % of the PU-es crosslinked with dicumyl peroxide. Anhydride content: (a) 0 wt % ($\times 1500$), (b) 0.5 wt % ($\times 1500$), (c) 1.0 wt % ($\times 1500$), (d) 3.0 wt % ($\times 7500$), (e) 5.0 wt % ($\times 7500$), and (f) 7.0 wt % ($\times 30,000$).

These results indicate that the graft copolymer must contain C—C bonds between SMA and PU chains, which occur by the free-radical attack in

two ways: (1) by the PU unsaturated groups and (2) by hydrogen abstraction from CH_2 segments in the PU flexible segments. This morphology also

Reaction 1



Reaction 2

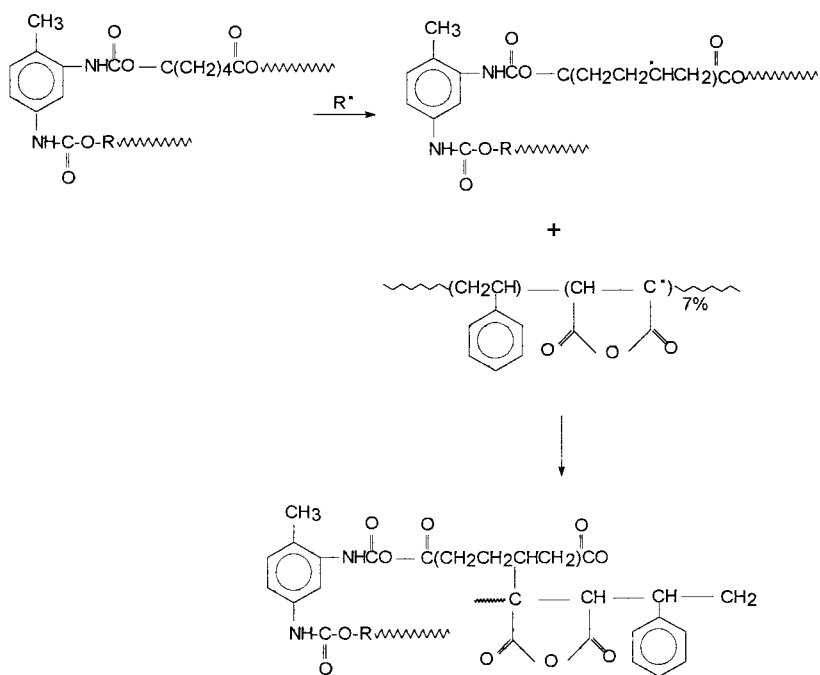


Figure 5 Possible reactions (1 and 2) between the anhydride groups and the PU groups when a free radical is present.

suggests that an increase in the anhydride content causes an increase in the *in situ*-formed graft copolymer concentration, which must be located in the interface. At high anhydride contents the PU domains seem to be completely protected by this graft copolymer, which must contain C—C bonds, stable to hydrolysis extraction. The effect of this stability can be clearly observed in the SMA/PU-es blend [Fig. 4(f)] in which the domains are practically not removed by the hydrolysis extraction. As described in the solubility test, it was not possible to isolate the graft copolymer. However, according to the SEM results, some possible structures for this graft copolymer are proposed as follows.

Graft Copolymer: Possible Structures

Some well-known reactions involving anhydride groups in polymer blends obtained by melt mixture were previously reported in the literature, for example, the reaction between anhydride and amine end groups in nylon^{6,13,14,25} and the reaction occurring with epoxy groups.²⁵

The compatibility or miscibility in some blends containing PU is attributed to hydrogen bonding, which, in general, involves the NH group of polyurethane.^{16–22} The possibility of transesterification in PU-es blends²¹ should also be considered.

In this work, we must consider the presence of the crosslinker agent. This compound was initially used for the crosslinking of the PU. However, the crosslinker agent used, dicumyl peroxide, generates free radicals and it is known that when PS is processed in the presence of free radicals, internal PS· macroradicals are generated as a result of hydrogen abstraction from the backbone of the PS chain by the free radicals or other species generated by rapid decomposition of the peroxide. The internal PS· macroradicals undergo disproportionation to lower molecular weight PS chains with terminal PS· macroradicals and terminal styrenic unsaturation. When anhydride is present, the internal PS· macroradicals react with anhydride to form PS–anhydride· radicals. The extent of degradation resulting from internal PS· macroradical disproportionation is limited by the competitive reaction of PS· macroradicals with anhydride.²⁶ The PS–anhydride· radicals are more reactive than PS· macroradicals, which leads to the preferential reaction between PS–anhydride· radicals and PU unsaturated groups or to abstraction of hydrogen from CH₂ groups of PU flexible segments or of PU chains, as schema-

tized in Figure 5 (Reactions 1 and 2). This mechanism has been proposed to explain the graft copolymerization of anhydride onto the polyolefins in the presence of peroxide.²⁷ When dicumyl peroxide is replaced by sulfur a similar free-radical mechanism should occur. The mechanism of crosslinking caused by sulfur is not completely known; however, it is believed to occur through a free-radical mechanism.²⁸

CONCLUSIONS

A graft copolymer was formed during the melt blending of SMA and polyurethane. The extent of the grafting depends on the nature of the flexible segments: polyester segments are more reactive with anhydride groups than with polyether segments. The crosslinker agents aided in the formation of the graft copolymer. The graft copolymer content is directly dependent on the anhydride content and determines the morphology of the blend. Furthermore, the graft copolymer formed should contain C—C bonding between the SMA units and the PU chains because the copolymer located in the surface of the PU domains precludes their extraction by hydrolysis.

The authors thank FAPESP for financial support (Proc. n° 97/07461 and 97/04339-6), Uniroyal Chemical Company and CBE for supplying the material used in this work.

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