Reactive Compatibilization of Maleated Polypropylene and Maleated Poly(styrene-*b*-butadiene-*b*-styrene) Blends

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ABSTRACT: Blends of maleated polypropylene with maleic anhydride (PP–MAH) and maleated styrene–butadiene–styrene triblock copolymer with maleic anhydride (SBS–MAH) were compatibilized with 4,4′-diaminediphenylmethane, at various concentrations, as the coupling agent for the functionalized polymers. Their properties were compared with those of the corresponding blends of PP–MAH and styrene–butadiene–styrene triblock copolymer. The blends containing 15 and 50 wt % elastomers were prepared in a mixer at 190°C and 55 rpm. Torque measurements and solubility tests suggested a graft copolymerization during the melt blending of PP–MAH and SBS–MAH. Infrared spectroscopy was used to characterize the graft copolymer formed during the melt blending of the maleated polymers. The blends presented a morphology of a disperse elastomer phase in a continuous PP–MAH matrix. The size of the elastomeric domains decreased as the diamine and anhydride molar ratio increased. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 366–371, 2002

Key words: blends; elastomers; poly(propylene) (PP); reactive processing

INTRODUCTION

Polypropylene (PP) is one of the most commercially important polymers because of its useful properties, wide applicability, and low cost. However, its applications as an engineering polymer are limited by its lack of impact resistance. For improved impact resistance of the PP matrix, rubbers such as ethylene–propylene copolymer,[1–7] ethylene–propylene–diene terpolymer,[8–13] and styrene–butadiene block copolymer[14–18] have been used as impact modifiers. In general, the PP/rubber blends are immiscible and present poor interfacial adhesion due primarily to the nonpolar nature of PP. One way to improve the interfacial adhesion with other polymers is the chemical modification of PP. The functionalization of PP with a polar monomer such as maleic anhydride (MAH) to form grafted PP (PP–MAH) is an effective way to increase the polarity of PP and, therefore, its affinity with other polar materials.[19–26] PP–MAH has been used as an adhesion promoter, especially in composites,[27–29] in which the interfacial adhesion between the PP matrix and the filler occurs through polar interactions.

The best improvement in interfacial adhesion or blend compatibility can be achieved by the addition of a block or graft copolymer containing segments of chains capable of specific interactions or chemical reactions with the blend components. The compatibilizer can also be generated during the mechanical mixing by graft copolymerization that occurs through the reaction between the components of the blends.[30–32] In this case, the graft copolymer is generated close to the interface; this results in an improvement in the adhesion between the phases and a decrease in the interfacial tension.[33–37] The presence of the compatibilizer at the surface of the particles of the blends may also reduce phase coalescence by the steric stabilization mechanism. Examples of PP/rubber compatibilized in situ include the reaction of PP containing glycidyl methacrylate groups with the carboxylic terminal groups of poly(butylene terephthalate),[38,39] PP containing oxazoline groups with acrylonitrile-*co*-butadiene-*co*-acrylic acid rubber (NBR),[40] maleated PP and phenolic-modified PP with NBR,[41] and maleated modified PP and maleated poly(ethylene–propylene–diene) with a poly(ether amine) as a coupling agent between the functionalized polymers.[42]

The purpose of this study was to examine the reactive compatibilization of maleated PP (PP–MAH) and maleated styrene–butadiene–styrene triblock copolymer (SBS) (SBS–MAH) with 4,4′-diaminediphenylmethane as a coupling agent. The formation of the graft copolymer was investigated by torque rheometry and infrared spectroscopy. Moreover, its effect on the morphology was analyzed with scanning electron microscopy (SEM).

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TABLE I
Selected Properties of the Polymers Used in This Study

	Butadiene (%)[a]	M_w[b] (g/mol)	MAH[c] (%)	Source
SBS	66	105,000	—	Coperbo
SBS–MAH	66	133,000	0.30	Ref. 43
PP–MAH	—	—	0.56	Uniroyal

[a] Determined by ^{13}CNMR.
[b] Determined by gel permeation chromatography.
[c] Determined by titration.

EXPERIMENTAL

The materials used, as well as some of their properties, are summarized in Table I.

SBS–MAH was obtained as described in ref. 43. SBS rubber was mixed with an appropriate molar ratio of MAH, benzoyl peroxide, and 4,4′-diaminediphenylmethane in a Haake Rheomixer (Karlsruhe, Germany) at 150°C and 55 rpm for 20 min. SBS–MAH was used without further purification; therefore, it had to contain free residual MAH and diamine.

Binary, nonreactive blends (PP–MAH/SBS) in 85/15 and 50/50 compositions were prepared by melt mixing at 190°C for 10 min and at 55 rpm in a Haake Rheomixer 600. Binary, reactive blends were obtained in the same proportions and under the same conditions used for the binary, nonreactive blends but with SBS–MAH. Two groups of binary, reactive blends were prepared. The first group was obtained by the mixing of PP–MAH and SBS–MAH (reactive I blends); the second was obtained with the addition of 2 wt % diamine to PP–MAH/SBS–MAH blends 5 min after the beginning of mixing (reactive II blends).

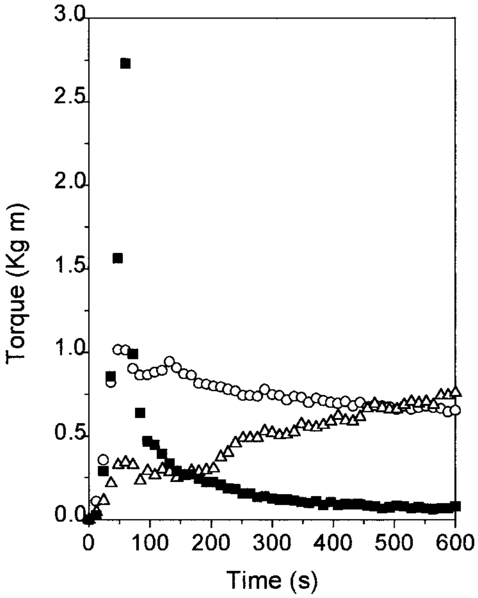

Figure 1 Torque–time curves at 190°C and 55 rpm: (■) PP–MAH, (○) SBS, and (△) SBS–MAH.

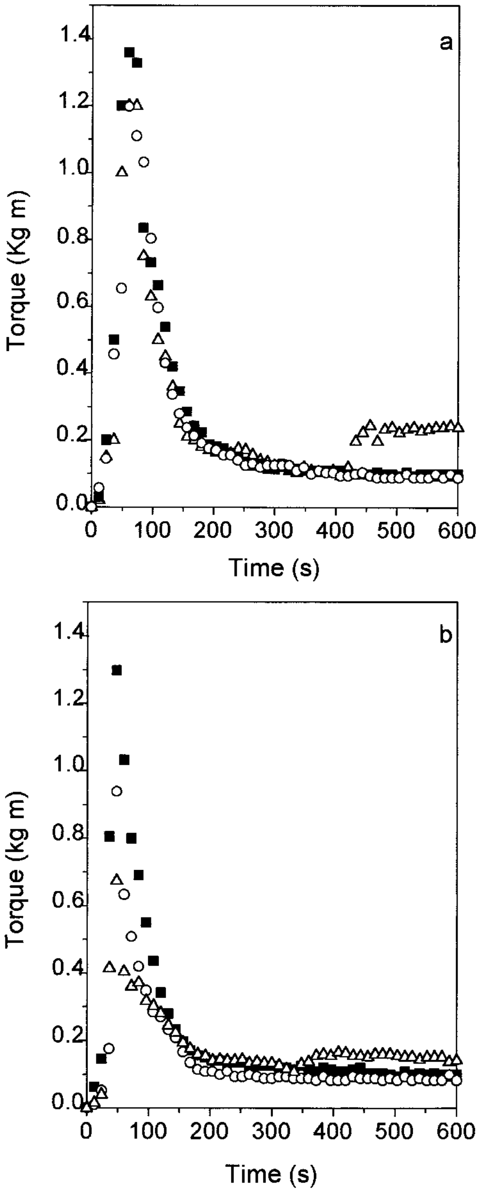

Figure 2 Torque–time curves at 190°C and 55 rpm for (a) 85/15 and (b) 50/50 blends: (■) nonreactive, (○) reactive I, and (△) reactive II blends.

During the melt mixing, 0.3 wt % of the stabilizer Irganox 1010 (Ciba Geigy, São Paulo, Brazil) was added to the blends.

After processing, the blends were milled in a Marconi MA 580 Croton-type mill (São Paulo, Brazil). Sheets 1.10 mm thick were prepared by compression molding in a Marconi MA 098/A laboratory press at 190°C and 2 MPa with an appropriate steel mold.

The elastomer phase of the blends was extracted in toluene at room temperature for 9 days, and the soluble and insoluble fractions were analyzed by infrared spectroscopy. Transmittance spectra of the compression-molded films were recorded in a wave-number range of 400–4000 cm^{-1} for 20 scans at a 2-cm^{-1}

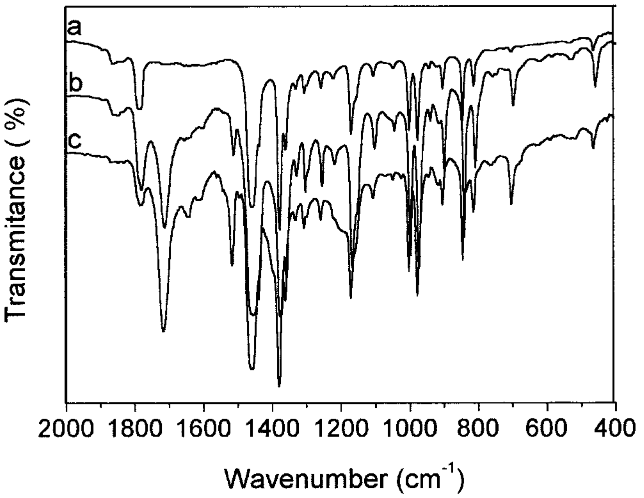

Figure 3 FTIR spectra of insoluble fractions in toluene for 50/50 blends: (a) nonreactive, (b) reactive I, and (c) reactive II blends.

resolution with Bomem, Hartman & Braun–Michelson MB series equipment (Quebec, Canada).

The morphology of the molded blends was examined in a scanning electron microscope (JEOL T-300, Middleton, WI). The specimens were cryomicrotomed at −110°C with a Leica ultramicrotome (Nussloch, Germany) so that a flat surface was obtained. Phase contrast between PP–MAH and the elastomer was achieved by the staining of the elastomeric phase with osmium tetroxide (OsO_4) vapor for a period of 20 h. SEM with a backscattering electron signal was used analyze the surface. The domain size was determined from the photomicrographs with Image Pro Plus software from Media Cybernetics (Silver Spring, MD). Several micrographs were taken for each blend, and about 200 domains were analyzed.

RESULTS AND DISCUSSION

The formation of a graft copolymer between PP–MAH and SBS–MAH through the coupling agent 4,4′-diaminediphenylmethane was initially investigated with torque rheometry.

The torque–time curves for the pure components recorded during the processing are shown in Figure 1. PP–MAH presented the lowest torque and, therefore, the lowest viscosity, probably because of the low molecular weight. The torque of SBS–MAH increased as the processing time increased, probably because of the reaction between the anhydride groups and residual diamine, which resulted in a crosslinked elastomer. SBS presented similar torque values after 400 s of processing at 190°C and 55 rpm, indicating similar viscosities under these conditions.

Figure 2 shows the torque–time curves for the nonreactive, reactive I, and reactive II blends. The reactive II blends presented a considerable increase in the torque after the addition of diamine in approximately 400 s of mixing in comparison with the other blends [Fig. 2(a)]. This increase in the viscosity must reflect a modification of the polymer chains as an increase in the molecular weight caused by the graft copolymer formation or by the crosslinking between SBS–MAH and PP–MAH chains. Solubility tests in hot *o*-xylene indicated that the increase in the torque was due, predominantly, to the formation of a graft copolymer because the blends were completely soluble. The reactive I blends presented viscosities similar to those of the nonreactive blends. This behavior was attributed to the low concentration of the graft copolymer in the former case caused by the low concentration of free diamine in SBS–MAH.[43]

The effect of the diamine addition was more pronounced for the reactive II blend containing 85 wt % PP–MAH [Fig. 2(a)]; this indicated that the graft reaction occurred to a larger extent in this blend in comparison with the 50/50 blend [Fig. 2(b)]. This result agrees with the observations of Phan et al.[42] that smaller chains have a higher probability to diffuse and, therefore, to react.

The graft copolymer was characterized by Fourier transform infrared (FTIR). The 50/50 blends were sub-

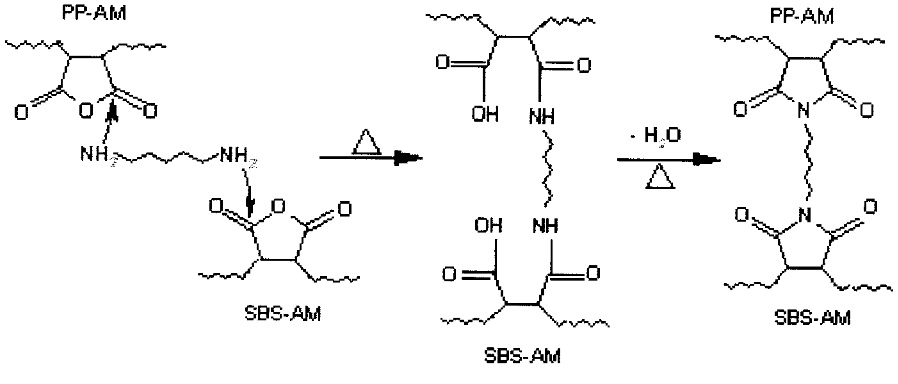

Figure 4 Scheme illustrating the graft copolymerization.

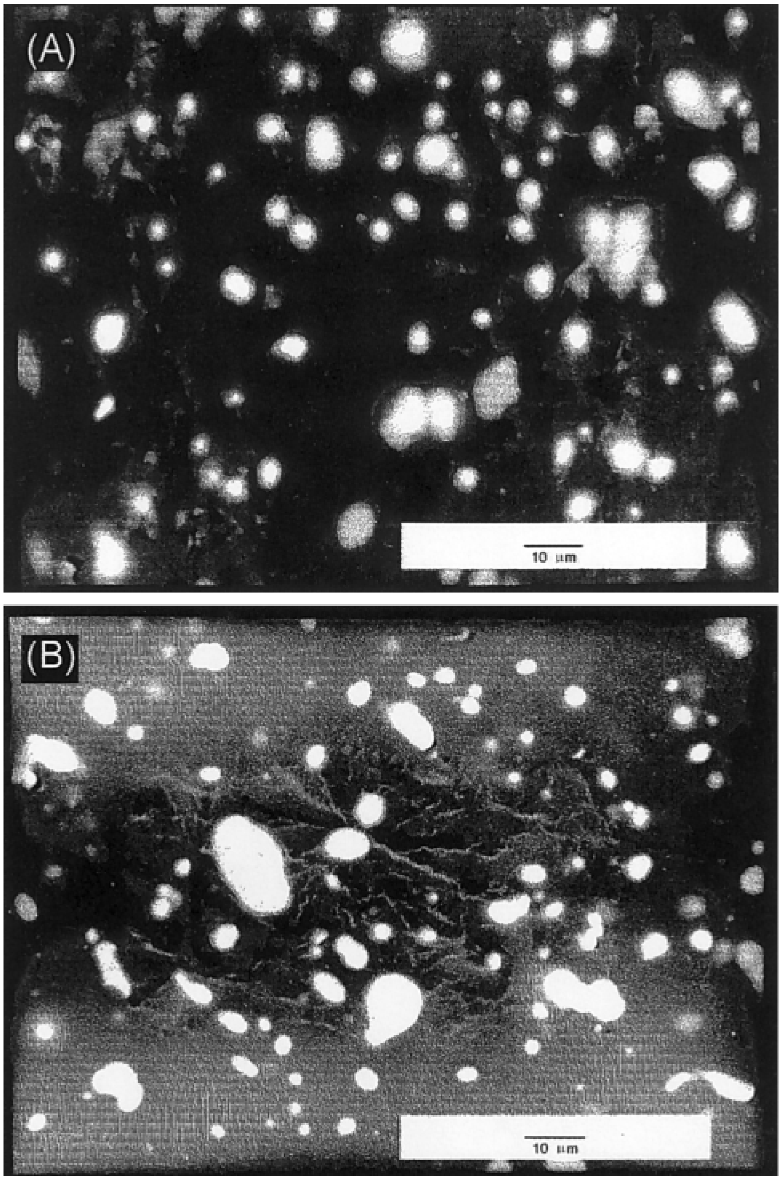

Figure 5 SEM photomicrographs of 85/15 blends: (A) nonreactive, (B) reactive I, and (C) reactive II blends.

mitted to extraction with toluene at room temperature to obtain the elastomer soluble fraction. The resulting polymer solution in toluene for the nonreactive blend was limpid and cloudy for the reactive blend, suggesting the extraction of the graft copolymer PP-*g*-SBS. Similar results were observed for polyamide-6/polyepichloridrin reactive blends[44] and polyurethane/poly(styrene-*co*-maleic anhydride) reactive blends.[45] The insoluble fractions were 50, 52, and 61 wt % for the nonreactive, reactive I, and reactive II blends, respectively.

The infrared spectra of the soluble fractions in toluene of the blends were similar to the spectrum of pure SBS–MAH. The spectrum of the insoluble fraction for the nonreactive blend was similar to the spectrum of pure PP–MAH; this indicated that no reactions took place in this blend (Fig. 3). However, the insoluble fractions for the reactive I and II blends presented, besides the characteristic bands of anhydride carbonyl at 1780 ^{1} and 1856 cm^{-1} grafted in PP–MAH, a new carbonyl band at 1717 cm^{-1} that was characteristic of imides[46,47] formed by the reaction between anhydride and amine groups and bands at 1641 and 1602 cm^{-1} attributed to the C=C deforma-

TABLE II
Number-Average Domain Size ($\bar{d}_n$), Weight-Average Domain Size ($\bar{d}_w$), and Polydispersity ($\bar{d}_w/\bar{d}_n$) for Nonreactive and Reactive I and II Blends at 85/15

	Nonreactive	Reactive I	Reactive II
d_w (μm)	5.3	4.8	3.7
d_n (μm)	4.2	3.2	2.3
d_w/d_n	1.2	1.4	1.6

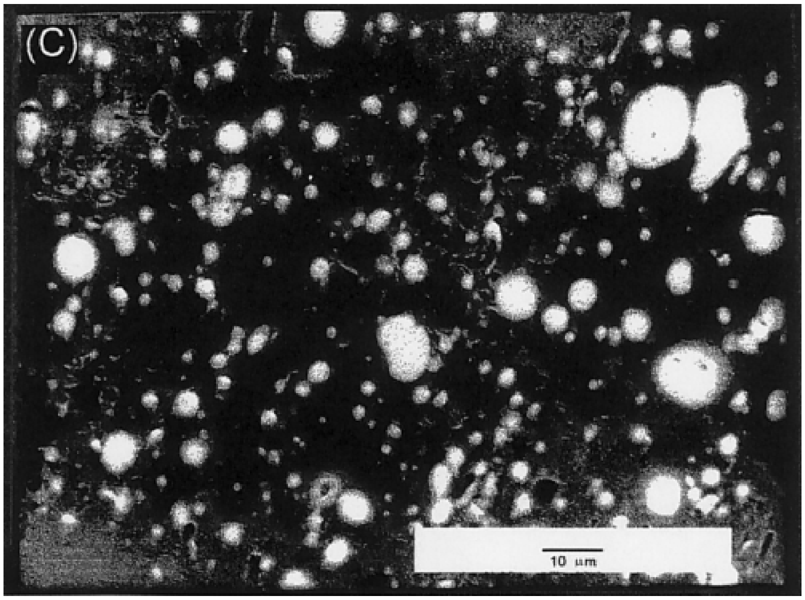

Figure 5 (*Continued from the previous page*)

tion of the SBS–MAH copolymer, among others. These bands indicate the formation of a graft copolymer between PP–MAH and SBS–MAH or crosslinking between SBS–MAH and PP–MAH chains. The last hypothesis was refuted because the insoluble fraction in toluene at room temperature was soluble in hot *o*-xylene. The intensity of the bands at 1780 and 1850 cm^{-1} decreased for the reactive II blend, whereas the intensity at 1717 cm^{-1} increased; this indicated that more imides groups were formed in the reactive II blend.

Even though the reactive I blend did not present an increase in torque in comparison with the nonreactive blend [Fig. 2(a)], the results obtained by extraction and infrared spectroscopy showed that graft copolymerization also took place for this blend. This shows that when the reaction occurred to a small extent in the reactive blends, it might not have been detected by torque rheometry, necessitating the use of a more sensitive complementary technique such as infrared spectroscopy, for example.

From the results of infrared spectroscopy, the mechanism shown in Figure 4 was proposed for the graft copolymerization between PP–MAH and SBS–MAH in presence of diamine.

Figure 5 shows photomicrographs for the 85/15 blends stained with OsO_4. The blends presented a morphology of two phases with elastomer domains (clear areas) dispersed in a continuous PP–MAH matrix. The size of the elastomer domains decreased from nonreactive blends to reactive I and II blends, probably as a result of the increase in the graft copolymerization, whereas the polydispersity of the domain sizes increased (Table II).

Figure 6(a) illustrates the dependence of the size of the elastomer domains on the torque and on the diamine and anhydride molar ratio in the reactive blends. The nonreactive and reactive I blends presented similar torque values during the processing, even though they had different domain sizes, as can be observed in Figure 6(a), points 1 and 2. This was attributed to the presence of the graft copolymer in the reactive I blend, which minimized the interfacial energy, reduced the size of the domains, and stabilized the morphology. The reactive II blend presented the smallest domain size and the highest torque [point 3 in Fig. 6(a)]; this indicated that the grafting reaction occurred to a larger extent. In Figure 6(b), it can be observed that the larger the NH_2/MAH ratio was in the mixtures— 0.3/1 and 2.3/1 for reactive blends I and II, respectively—the smaller the domains were of the elastomeric phase. These data show that the graft copolymer affected the morphology of the blends and that the increase in its concentration resulted in the decrease in the size of the domains of the dispersed phase. The effect of the graft copolymer formation on the size of the dispersed particles for the 50/50 blends was not evaluated because they presented a morphology of cocontinuous phases.

CONCLUSIONS

A graft copolymer was obtained from a melt mixture of PP–MAH and SBS–MAH in the presence of diamine. The grafting extension depended on the amine and anhydride molar ratio and influenced the morphology of the blends. The blends presented a morphology of a disperse SBS–MAH phase in a PP–MAH matrix. The SBS–MAH domain size decreased as the diamine and anhydride molar ratio increased. The smallest particles size was obtained at a diamine/anhydride molar ratio equal to 2.3.

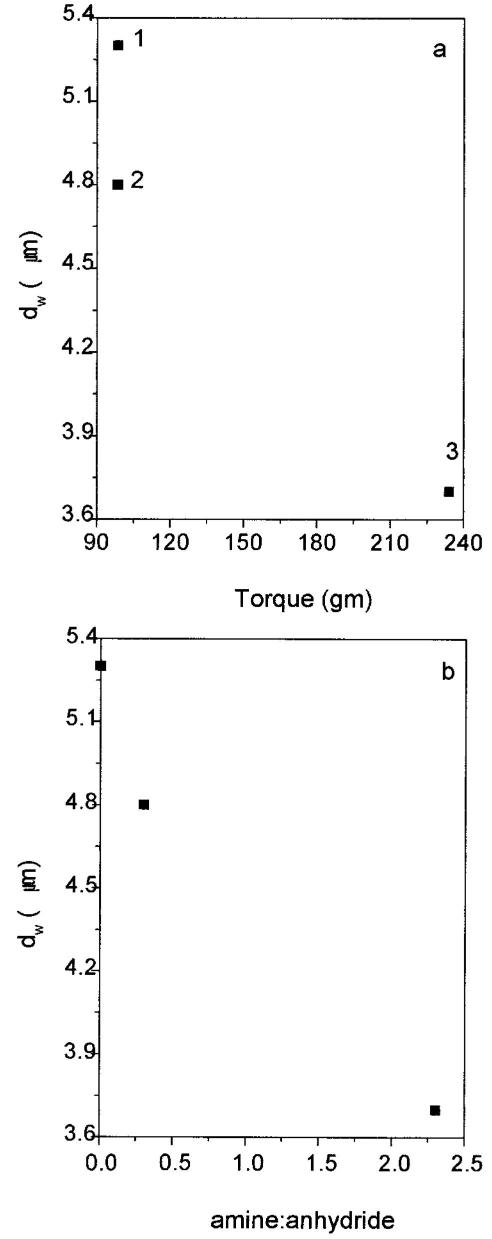

Figure 6 Effects of (a) the torque and (b) the amine/anhydride ratio on the average domain size of the dispersed phase for the nonreactive, reactive I, and reactive II blends (85/15).

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