

Dynamic Mechanical Properties and Morphological Structure of PS/EPDM Blends Prepared by *In Situ*-Polymerization of Styrene

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ABSTRACT: PS/EPDM blends prepared by *in situ*-polymerization of styrene in the presence of EPDM are immiscible and show two phases. Furthermore, the dynamic mechanical behavior of injected specimens is quite different from that of noninjected blends. This is attributed to the differences in morphology before and after injection molding. The morphology of the noninjected blends consists of PS spherical domains covered by a thin layer of EPDM, whereas the injected blends show elastomeric dispersed phase morphology in a rigid matrix. SEM analysis was important to elucidate the changes in the dynamic

mechanical behavior of PS/EPDM blends, but TEM analysis is more precise for morphological characterization and yielded the real average diameter of EPDM particles. Comparing the average diameters for the PS/EPDM blends obtained from SEM and TEM analyses, the diameters obtained from the SEM analysis are wider than those of TEM which is due to the solvent extraction effect on the blend morphology. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2280–2289, 2009

Key words: TEM; blends; polystyrene

INTRODUCTION

Polymer blending is an efficient method for designing and controlling the performance of polymeric materials using available polymers.¹ The incorporation of dispersed elastomeric particles into a rigid matrix has attracted considerable attention because of its industrial importance among other types of polymer blends.^{2–4} The essential characteristic of rubber toughening is that impact resistance of the rigid polymer is increased substantially in return for a limited reduction in stiffness.^{5–7} A great deal of rubber toughening is used to improve interfacial adhesion, rubber particle dispersion and stress transfer between the phases to provide a good balance of properties.

High impact polystyrene (HIPS) is one of the commercially most important toughened polymer.^{8,9} HIPS is produced by polymerization of styrene in the presence of polybutadiene (PB) and is widely applied in the automotive industry and in home appliances.¹⁰ Aging is a great problem in HIPS and other rubber-toughened plastics, especially those

based on polybutadiene. The major contribution to photodegradation is usually attributed to the polybutadiene phase, which is constituted by different isomers that present different stabilities to degradation.¹⁰ Exposure to sunlight causes a drastic drop in impact resistance attributed to photooxidation of the rubber phase induced by UV radiation, limiting the lifetime in outdoor applications.^{8,11,12} To overcome this problem, polybutadiene is often replaced in blend compositions by a saturated rubber, such as poly(ethylene-*co*-vinyl acetate) (EVA), poly(butyl acrylate) or ethylene-propylene-diene terpolymer (EPDM).^{5,8} EPDM is widely used in outdoor applications, because it is more stable than other conventional elastomers, such as butadiene and isoprene rubbers. In EPDM, ethylene and propylene monomers provide a saturated backbone interrupted by the incorporation of nonconjugated diene monomers such as 2-ethylidene-5-norbornene (ENB), which provide a low and controlled concentration of unsaturated groups that can be easily cross-linked.¹³

In an earlier work, PS/EPDM blends were prepared by *in situ*-polymerization of styrene.^{14,15} These blends are immiscible and show two phases. Furthermore, the dynamic mechanical behavior of the injected specimens is quite different from that of the noninjected blends. Thus, the aim of this work is to investigate the relation between dynamic mechanical properties and morphology of these blends before and after injection molding by means of dynamic

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TABLE I
PS/EPDM Blends Prepared in this Work

Name	wt% EPDM in styrene solution ^a	wt% EPDM in the blends ^b	\bar{M}_w of PS ($\times 10^3$ g mol ⁻¹)	\bar{M}_n of PS ($\times 10^3$ g mol ⁻¹)	\bar{M}_w/\bar{M}_n	Reaction temp (°C)
5E60	5.0	5.2	575	239	2.4	60
11E60	11.0	11.1	591	282	2.1	60
17E60	17.0	17.2	565	270	2.1	60
5E80	5.0	5.1	111	67	1.7	80
			1511	1256	1.2	
11E80	11.0	11.4	337	137	1.5	80
17E80	17.0	17.5	352	137	2.5	
PS60	–	–	367	140	2.6	60
PS80	–	–	419	193	2.2	80
EPDM	–	–	252	133	1.9	–

^a EPDM content in styrene solution before polymerization.

^b EPDM content in the blends.

mechanical analysis (DMA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

EXPERIMENTAL

Materials

Rhodia Brazil (Paulínia, Brazil) supplied styrene. DSM Elastomers. (Triunfo, Brazil) supplied EPDM (Keltan[®] 5508) with 2-ethylidene-5-norbornene (ENB) as diene. EPDM contains 69.0 wt % of ethylene, 26.2 wt % of propylene and 4.8 wt % of ENB.

Styrene monomer purification

Styrene monomer was submitted to extraction of polymerization inhibitors with a 5% NaOH solution. After this, the organic layer was washed with distilled water. The water residue was extracted with dry Na₂SO₄ and the styrene was then distilled at 50°C under vacuum.

In situ-polymerization of PS/EPDM blend

EPDM was dissolved in styrene monomer under agitation, then benzoyl peroxide (0.1 wt %) was added to the viscous and homogeneous solution and the bulk polymerization were performed at 60 or 80°C in a cylindrical reactor. Each polymerization reaction produced approximately 600 g of material. After this, the styrene monomer residue (~ 5 wt %) was extracted at 50°C in a vacuum oven for 48 h. Polystyrene homopolymer was also prepared at 60 and 80°C. Table I shows the composition of the EPDM solution in styrene and the composition of the PS/EPDM blends expressed in terms of “wt % EPDM in the blends.” The nomenclature used to describe the blends is based on the EPDM content and on the temperature of polymerization. For example, the

blend containing 5 wt % of EPDM polymerized at 60°C is named 5E60, where E represents EPDM.

Injection molding

The prepared materials were crushed, dried in a vacuum oven for 48 h at 50°C and injection molded into Izod bars (ASTM D256) and dog-bone shaped tensile specimens (ASTM D638) using an Arburg Allrounder molding machine model 221M 250-55 (Lossburg, Germany). The following temperature was kept along the barrel zones: 200, 210, 220, 230, and 240°C. The mold temperature was kept at 40°C.

Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) of the non-injected and injected blends was performed in a Rheometric Scientific DMTA V Analyzer (Piscataway, NJ). The specimens (9.0 × 6.0 × 1.0 mm³) were subjected to a sinusoidal deformation at frequency of 1.0 Hz, amplitude of 0.01% in the temperature range from –100 to 180°C. The samples of the noninjected blends were extracted from the center of the cylindrical body of the blend.

Scanning electron microscopy

The morphology of the PS/EPDM blends was analyzed using a JEOL JSM-6360 LV scanning electron microscope (SEM) (Middleton, WI). Two groups of samples were prepared: (1) blends that were cryogenically fractured with the resulting surfaces subjected to EPDM extraction with hexane and (2) blends that were subjected to impact resistance tests with the resulting surface submitted to EPDM phase extraction. The fracture surfaces of both groups of samples were covered by a thin gold layer and observed using an acceleration voltage of 20 kV.

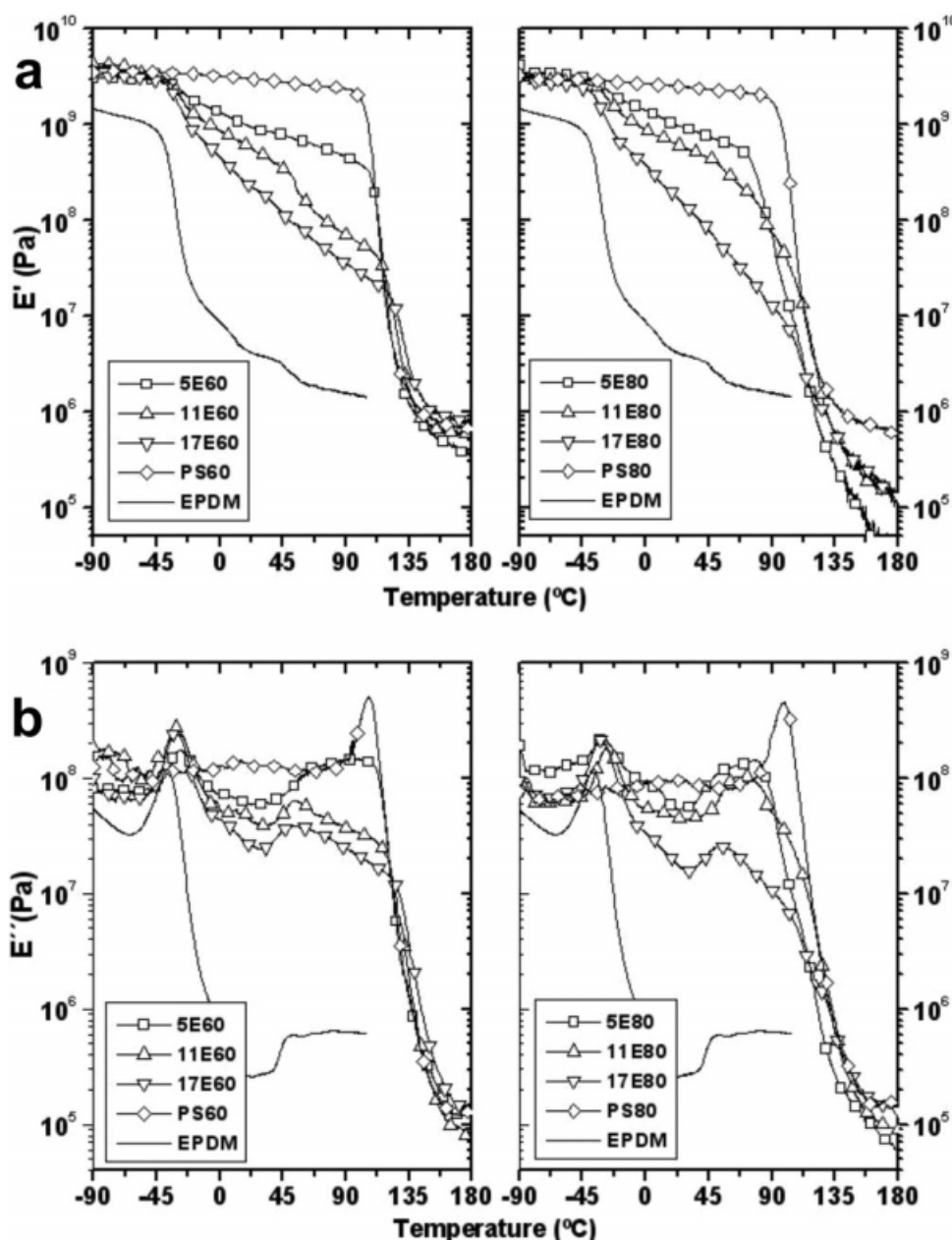


Figure 1 Dynamic mechanical behavior of noninjected PS60, PS80, EPDM, and PS/EPDM blends: (a) Storage modulus (E') and (b) loss modulus (E'').

Transmission electron microscopy

Blend morphologies were examined using a Carl Zeiss CEM 902 transmission electron microscope (Thornwood, NY). The films were microtomed under cryogenic conditions (-140°C) to obtain ultra-thin sections (40 nm). Phase contrast between the blend components was achieved by exposing the samples to vapors of OsO_4 for a period of 4 h. Photomicrographs of selected blends were employed for particle size analysis by a digital analysis technique based on Image Pro Plus[®] software. The particle size distribution and the weight average particle diameters, d_{wv} , were determined from these results.

RESULTS AND DISCUSSION

The aim of this work was to evaluate the influence of injection molding in the dynamic mechanical and morphological behavior of PS/EPDM blends prepared by *in situ*-polymerization of styrene.

Dynamic mechanical analysis

Figure 1 shows the dynamic mechanical behavior of noninjected PS60, PS80, EPDM and PS/EPDM blends. The storage modulus (E') curve of EPDM [Fig. 1(a)] shows a drop of two decades at around -40°C corresponding to the EPDM glass transition

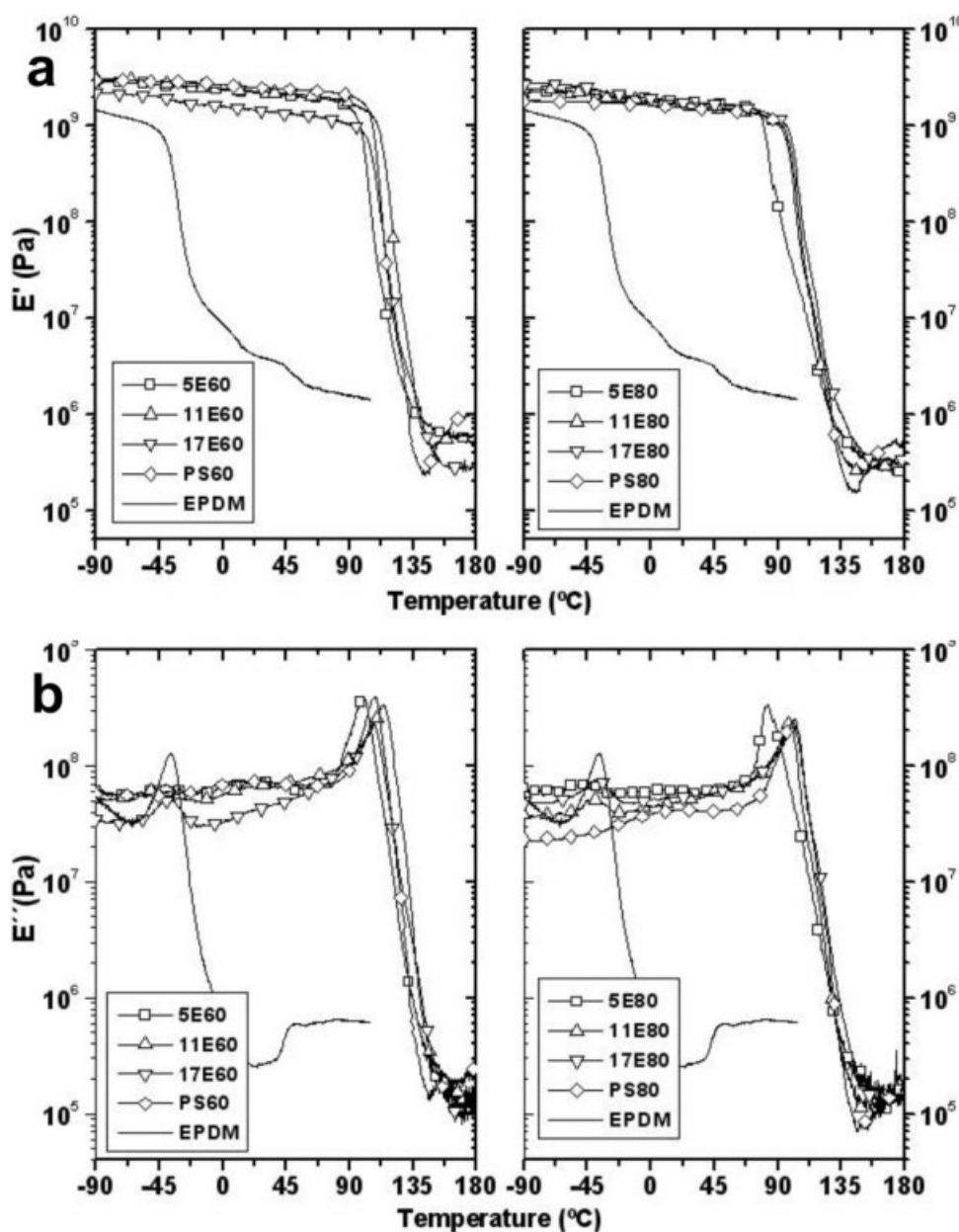


Figure 2 Dynamic mechanical behavior of injected PS60, PS80, EPDM and PS/EPDM blends: (a) Storage modulus (E') and (b) Loss modulus (E'').

phase. The storage modulus curves of the noninjected PS/EPDM blends show a small drop in the region of the EPDM glass transition ($\sim -40^{\circ}\text{C}$), a progressive drop proportional to the EPDM content in the temperature range between PS and EPDM glass transitions, and a drop of two decades in the region of PS phase glass transition. The loss modulus (E'') curve of EPDM [Fig. 1(b)] shows a peak at -40°C corresponding to the EPDM glass transition phase and a broad peak around 50°C corresponding to a EPDM secondary transition.^{16,17} The loss modulus curves of the noninjected PS/EPDM blends show a peak around -30°C corresponding to the glass transition of EPDM phase, a broad peak between 50 and 120°C , and a

drop of two decades at around 120°C corresponding to the glass transition of PS phase.

Figure 2 shows the dynamic mechanical behavior of injected PS60, PS80 and PS/EPDM blends. The dynamic mechanical behavior of injection molded PS60 and PS80 does not differ from those of the corresponding noninjected polystyrenes. On the other hand, the dynamic mechanical curves of the molded blends differ significantly from the curves of the noninjected blends.

The curves of loss modulus of injected blends no longer show the broad peak between 50 and 120°C , but they do show a narrower peak around 100°C corresponding to the glass transition of the PS

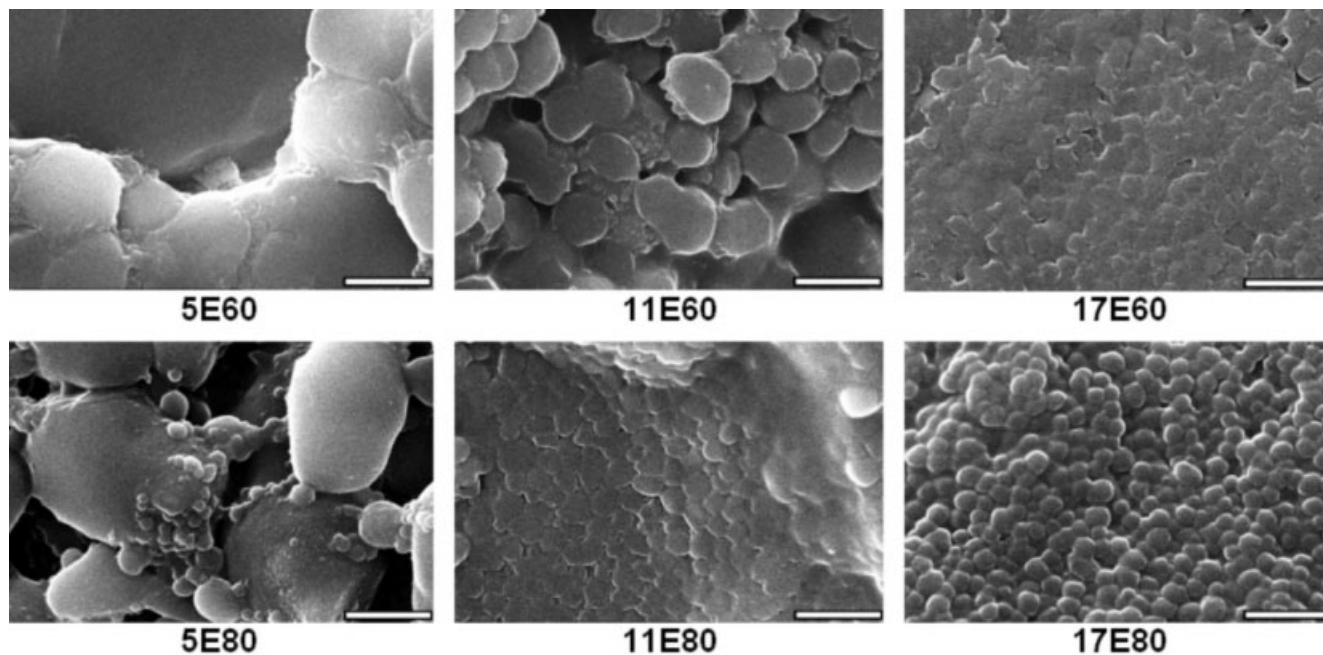


Figure 3 SEM micrographs of the cryogenic fracture surfaces of noninjected PS/EPDM blends after EPDM phase extraction. Scale bars correspond to 5 μm .

matrix. Moreover, the peaks corresponding to the EPDM glass transition are not detectable for the blend with low EPDM content.

The EPDM phase of all blends presents a glass transition temperature at lower temperature than neat EPDM. This behavior was also observed in earlier work of our research group with PMMA/AES

blends,¹⁸ PHB/AES blends¹⁹ and *in situ* polymerized PS/AES blends.¹⁴ A decrease in the glass transition temperature of the elastomer phase has been observed for impact modified polymers and for the blends of both amorphous²⁰ and crystalline components.²¹ According to Booij,²⁰ the smaller the elastomer content the higher is the shift of the elastomer

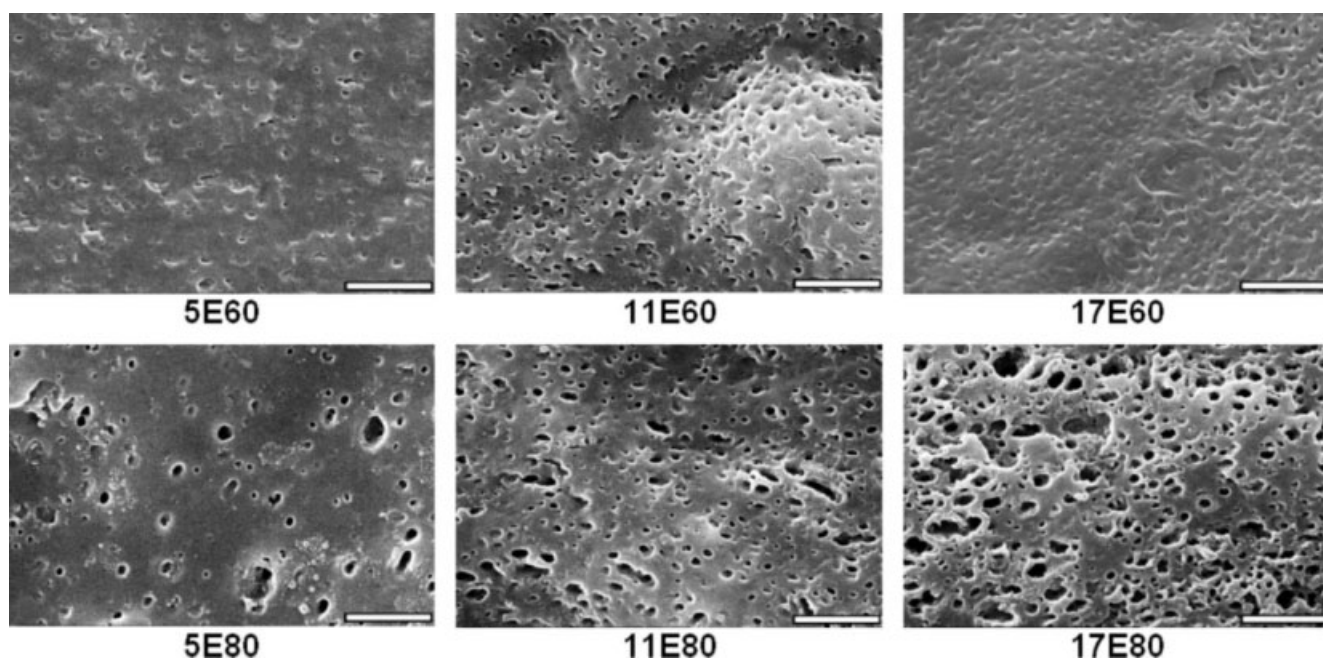


Figure 4 SEM micrographs of the fracture surfaces obtained from impact resistance tests after EPDM phase extraction. Scale bars correspond to 5 μm .

TABLE II
The Average Diameter of Rubber Particles in PS/EPDM
Calculated From SEM and TEM Micrographs

Material	Average diameter (nm)	
	From TEM micrographs	From SEM micrographs
5E60	102 ± 2	181 ± 6
11E60	nd	210 ± 3
17E60	130 ± 2	238 ± 9
5E80	189 ± 9	303 ± 14
11E80	nd	236 ± 8
17E80	231 ± 6	263 ± 7

phase transition towards lower temperatures. This shift to lower temperatures is attributed to hydrostatic dilatational thermal stresses generated within the rubber particles due to the differences in thermal expansion coefficients of the rubber and the glassy matrix.^{20–23} This dilatational stress promotes an increase in the rubbery phase free volume, which allows reduction of the relaxation time of the rub-

bery chains and therefore reduces the glass transition temperature of the corresponding phase.¹² The T_g decrease can also be attributed to the good adhesion between the components.²²

Scanning electron microscopy

Figure 3 show the SEM micrographs of cryogenic fractures of noninjected PS/EPDM blends after extraction of the EPDM phase and Figure 4 shows the SEM micrographs of the fracture surface obtained from impact resistance tests of injection-molded PS/EPDM, after extraction of the EPDM phase.

Figure 3 shows spherical domains that correspond to the PS phase of PS/EPDM blends. In the Figure 4, the voids correspond to the EPDM phase extracted from the PS matrix. The great difference between the morphology of noninjected and injected PS/EPDM blends can be observed. The SEM micrographs suggest that the morphology of noninjected PS/EPDM blends consists of PS spherical domains covered by

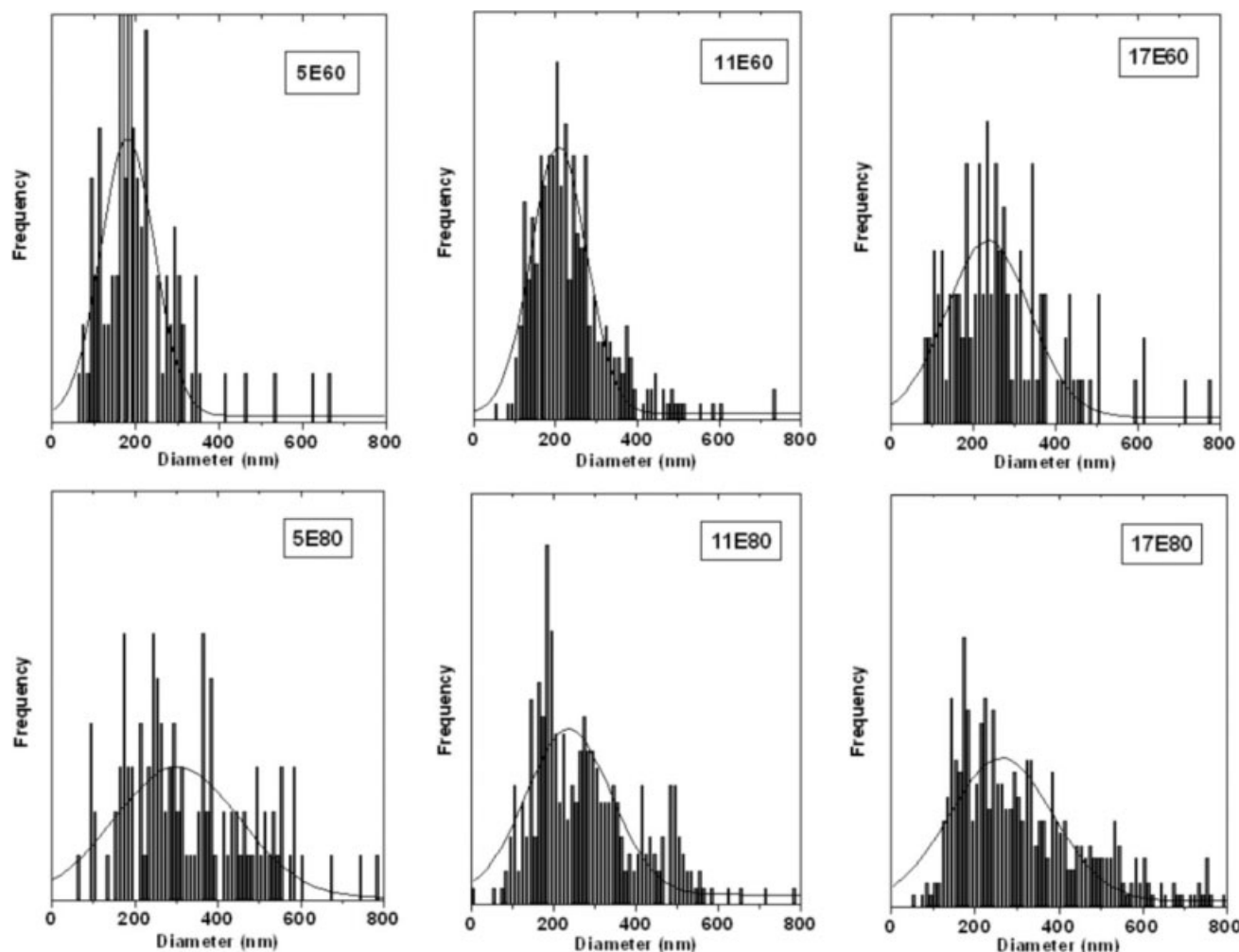


Figure 5 Rubber particle size distribution obtained from SEM micrographs of selected PS/EPDM blends from impact resistance tests.

a thin layer of EPDM, whereas the morphology of injected blends correspond to an elastomeric phase morphology dispersed into the PS matrix.

As seen in Figure 4, the shapes of the voids of extracted rubber particles are very complex making determination of an average diameter difficult; nevertheless a quantitative measure of the micrographs of these blends was performed. The average diameter of rubber particles in each blend composition was calculated by image analysis of SEM micrographs. The results are summarized in Table II. Figure 5 shows the histograms for these analyses for each blend composition. Comparing the histograms it can be observed that an increase in the polymerization temperature and in the EPDM content lead to an increase in the average diameter and the widening in the diameter distribution of the voids. Although the SEM analysis was important to elucidate the changes in the dynamic mechanical behavior of PS/EPDM blends, TEM analysis will be more precise for the morphological characterization.

Transmission electron microscopy

Figure 6 shows the TEM micrographs of noninjected PS/EPDM blends and Figure 7 shows the TEM micrographs of injected PS/EPDM blends. In Figure 6, the thin sections were not stained; the polystyrene is the dark phase. In Figure 7, the sections were stained and the rubber particles become the dark phase. As observed by means of SEM, there is a great difference between the morphologies of noninjected and injected blends. The morphology of noninjected blends consists of spherical domains of PS surrounded by a thin layer of EPDM, whereas the morphology of injected blends shows an elastomeric phase morphology dispersed in the PS matrix, explaining the differences in the dynamic mechanical behavior of the blends.

The morphology of the blends before and after injection molding presented important differences in comparison to the salami morphology of HIPS. The main difference is the absence of PS microocclusions in the EPDM domains that are attributed to a higher

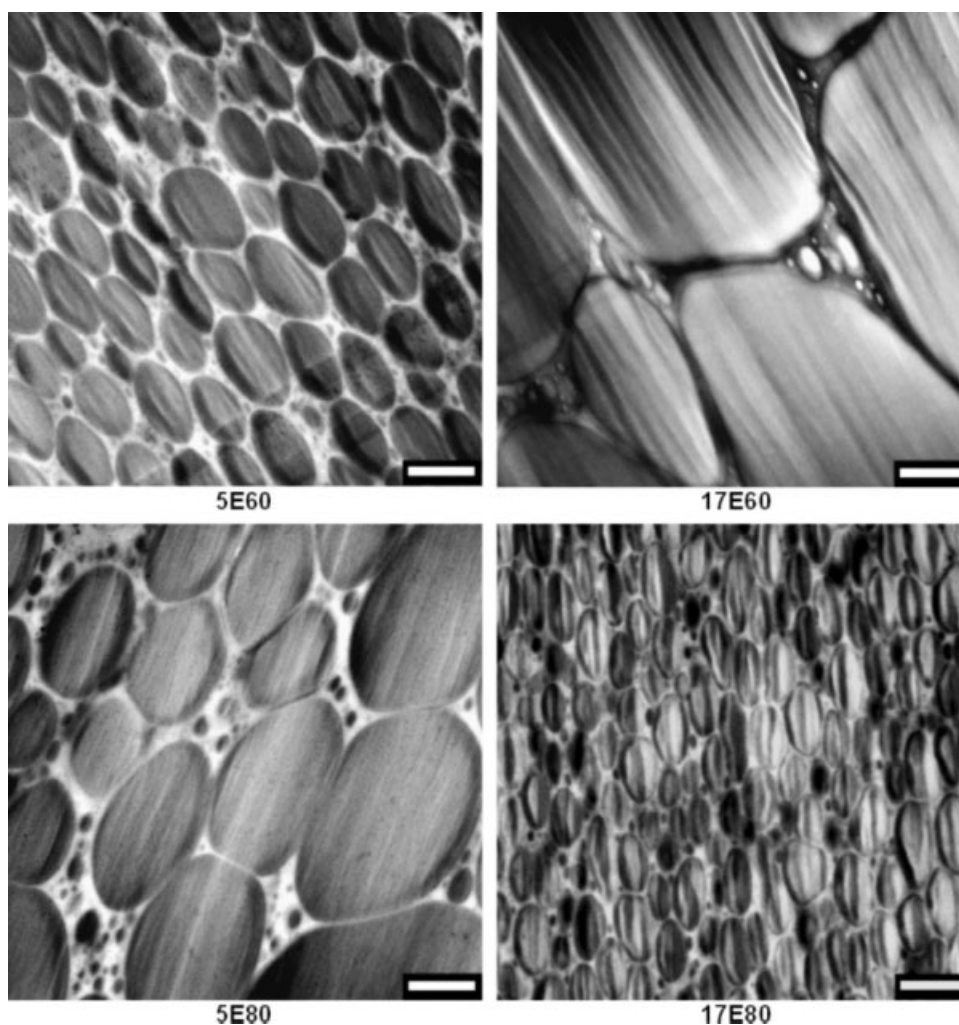


Figure 6 TEM micrographs of noninjected PS/EPDM blends. Scale bars correspond to 1000 nm.

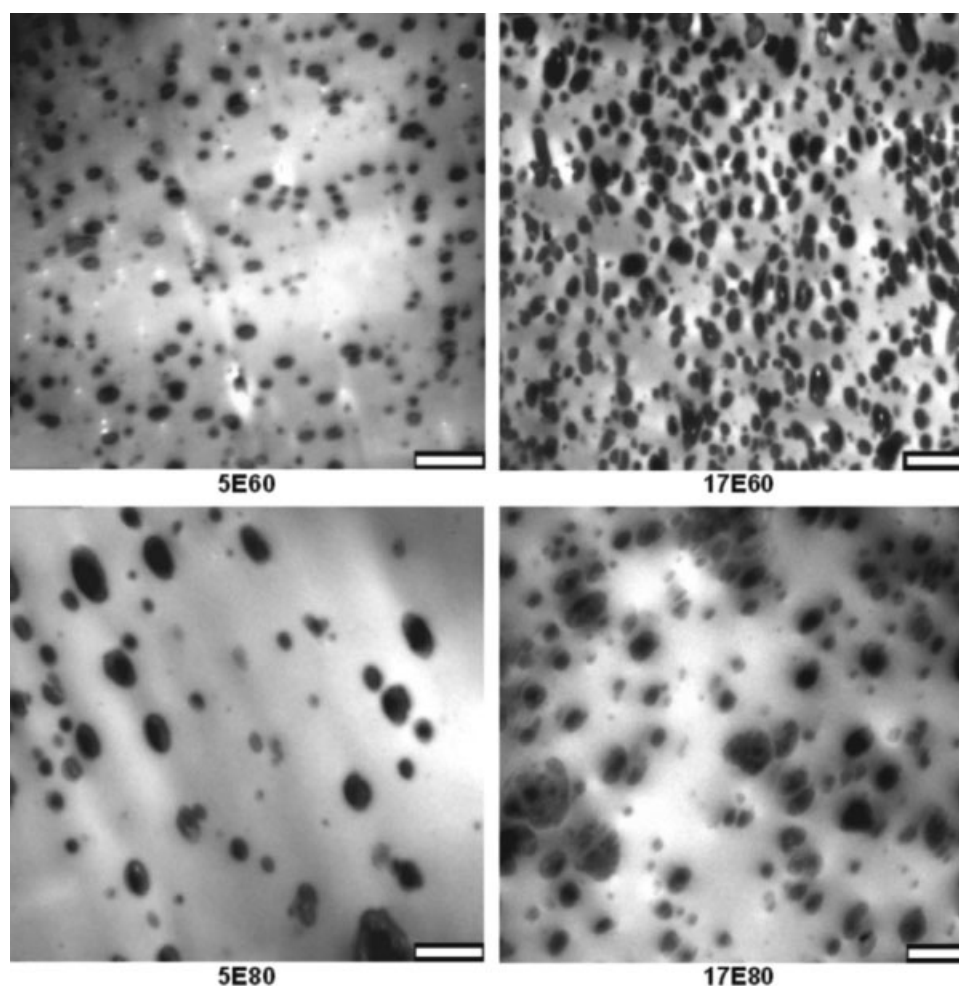


Figure 7 TEM micrographs of injected PS/EPDM blends. Rubber particles are stained dark by OsO_4 . Scale bars correspond to 1000 nm.

tensile stress for the elastomeric phase. Moreover, the diameter of the elastomeric domains of the blends is smaller than the critical size for PS toughening described in the literature (1–2 μm).²⁴ The morphology of noninjected blends is due to the polymerization conditions that were performed using static condition.²⁴

Figure 8 shows the histograms for the analysis of the quantitative distribution of the diameter of the PS/EPDM blends.

The average diameter of rubber particles of each blend composition was also calculated by image analysis of TEM micrographs and the results are summarized in Table II, together with corresponding results obtained from SEM analysis. The increase in the polymerization temperature promotes enhancements in the average diameter of the particles and a widening of the diameter distribution. The increase in the EPDM content leads to an enhancement in the average diameter of the EPDM phase.

Now, comparing the average diameter values for the PS/EPDM blends obtained from SEM and TEM

analyses, the values obtained from the SEM analysis are larger than those of TEM. These results can be due to the different sample preparation conditions used for both microscopic techniques. For SEM analysis, the samples were submitted to solvent extraction to selectively remove the EPDM phase whereas for TEM analysis, the samples were prepared by cryo-ultramicrotomy followed by staining of the EPDM phase with OsO_4 . The observed differences on the EPDM phase average diameters can be caused by the solvent effect on the morphology of the samples prepared by solvent extraction. Solvent extraction experiments require one of the phases to be selectively removed from the sample. Often one phase is significantly more solvent resistant than the other phase; however it is impossible to selectively extract one phase without affecting the other phase. Based on this, the increased average diameter values obtained from SEM analysis can be explained by morphological artifacts which resulted from the swelling or even the partial extraction of the polymer matrix during sample preparation.

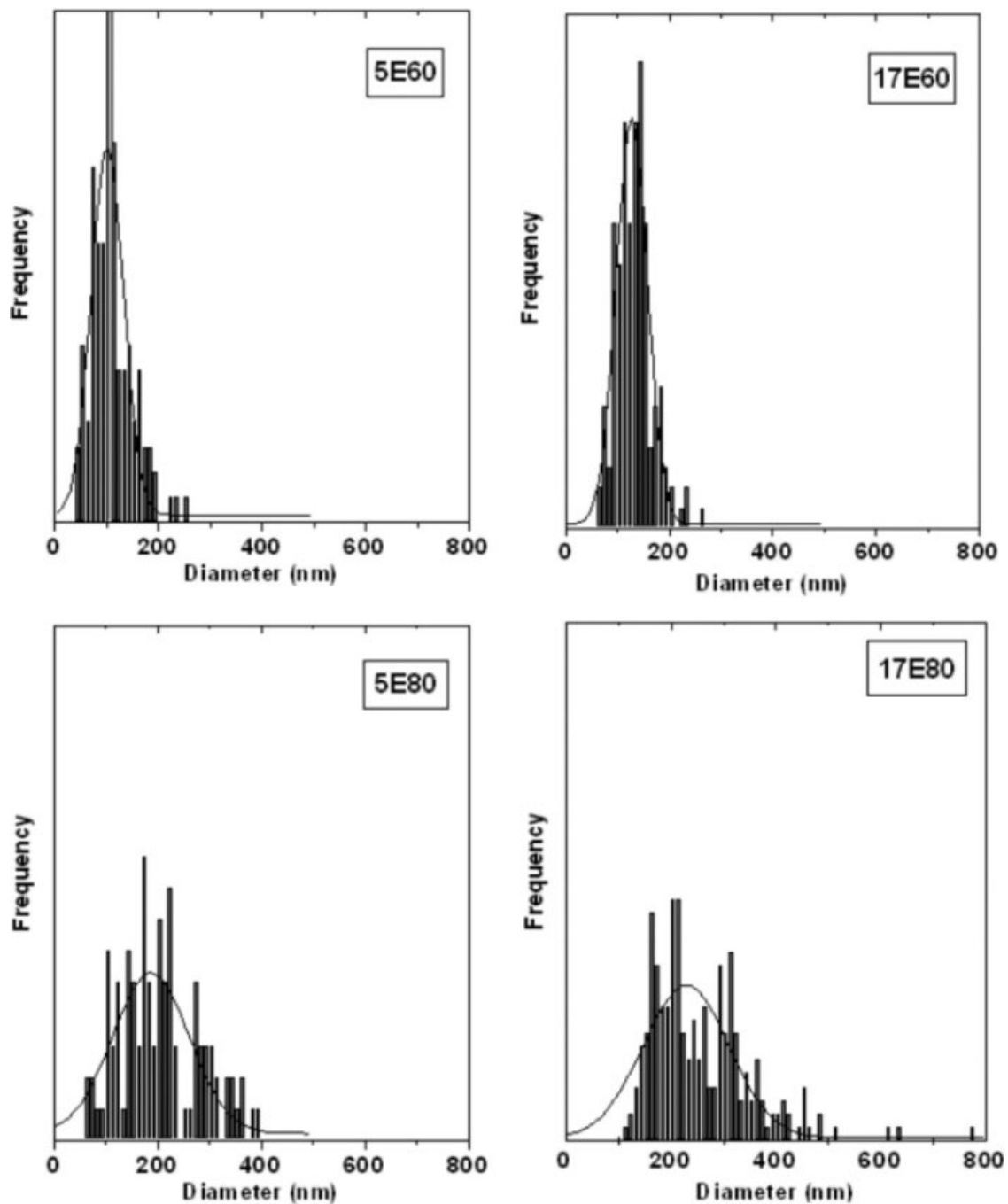


Figure 8 Rubber particle size distribution obtained from TEM micrographs of selected PS/EPDM blends.

CONCLUSIONS

The dynamic mechanical behavior of the injected specimens is quite different from that of the noninjected blends. This is attributed to the differences in morphology before and after injection molding. The SEM and TEM micrographs showed that the morphologies of noninjected PS/EPDM blends consist of PS spherical domains covered by a thin layer of EPDM, whereas the morphologies of injected blends show an elastomeric dispersed phase morphology. The weight average diameter values, obtained from

SEM and TEM analyses of the EPDM domains of PS/EPDM blends from injection molding samples, are not in agreement. The higher average diameter values obtained for SEM samples are caused by the effect of solvent extraction treatment on the phase morphology of PS/EPDM blends.

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