Influence of Processing Time and Composition in the Microwave Absorption of EPDM/PAni Blends

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ABSTRACT: Blends of ethylene–propylene–diene monomer (EPDM) and polyaniline (PAni) doped with dodecylbenzene sulfonic acid were prepared by mechanical mixing in an internal mixer at various compositions and times. Reflectivity characteristics of the blends in the 8–12-GHz range were investigated with the Naval Research Laboratory arch method. The microwave absorption behavior was affected by the processing time and blend composition. The correlation of reflectivity measurements with morphology observations made with scanning electron microscopy suggested that the distribution and concentration of the PAni phase within the EPDM matrix altered the wave–matter interactions. The radar-absorbing materials prepared in this work showed broadband behavior with microwave radiation absorption of up to 90%. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1568–1575, 2002

Key words: stealth technology; polyaniline; conductive elastomers; radar-absorbing materials; conductive polymer; scanning electron microscopy

INTRODUCTION

The two most important features related to stealth technology are essentially the shape of the target and the nature of the radar-absorbing materials (RAMs).[1] RAMs are made with compounds having a high loss energy, which enables them to absorb the incident radiation in synchronized frequencies and dissipate it as heat. The manufacture of RAMs basically involves the use of compounds capable of generating dielectric and/or magnetic losses when impinged by an electromagnetic wave.[2]

Intrinsically conducting polymers (ICPs) are a class of RAMs that show a number of advantages over traditional granular materials, presenting high conductivity combined with light weight. However, they often present the disadvantage of poor mechanical properties. Because of their high conductivity (1–50 S cm^{-1}), it is necessary to dilute the conductive phase to obtain an appropriate surface electrical resistance. A common method used to overcome the problems associated with the poor mechanical properties and high conductivity is blending the ICP with an insulating polymer. There are several methods for preparing conductive polymer blends or composites with conventional polymers, such as electrochemical methods,[3,4] mechanical mixing,[5–7] the casting of a solution containing the components to be blended,[8,9] and the polymerization of one polymer into another.[10] These various methods lead to a

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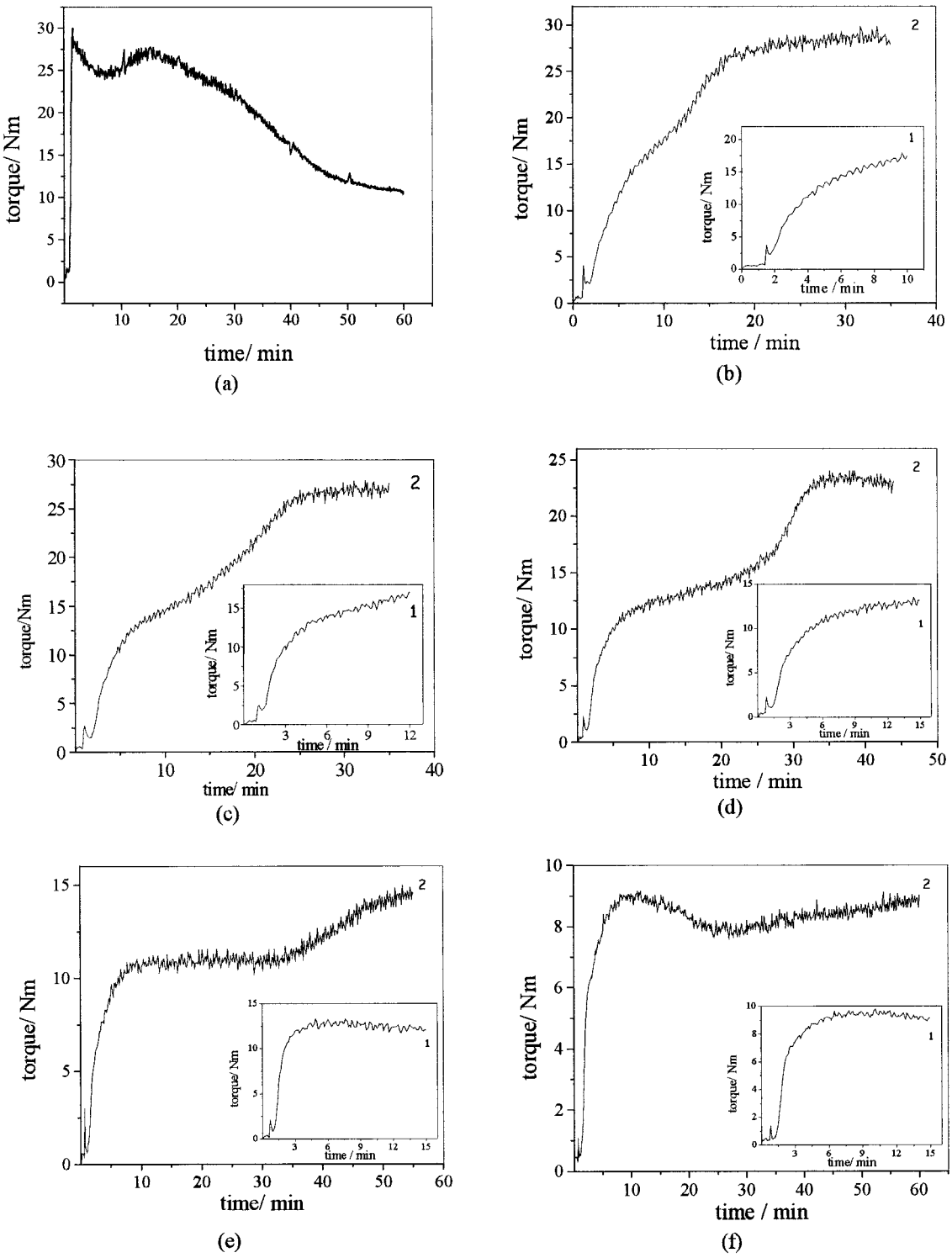

Figure 1 Torque–time curves for (a) EPDM and (b–f) EPDM/PAni–$(DBSA)_3$ blends with the following compositions (w/w): (b) 70/30, (c) 60/40, (d) 50/50, (e) 40/60, and (f) 30/70. Inserts correspond to the initial mixing times.

wide range of absorbing material properties. Mechanical mixing is the usual method for large-scale processing.

Polyaniline (PAni) is a particularly interesting ICP because of the presence of the chemically flexible —NH— groups in the polymer backbone,

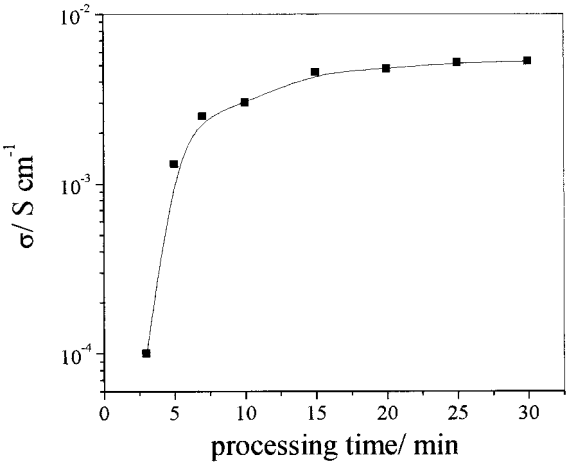

Figure 2 Variation of the electrical conductivity of an EPDM/PAni–$(DBSA)_3$ blend (60/40 w/w) at different processing times.

which not only take part in the protonation/deprotonation mechanism but also contribute to the π-band formation.[11] The latest advance concerning the preparation of PAni and its blends[12–14] has involved the use of industrial techniques such as extrusion, injection molding, calendering, and mechanical mixing. Little has been reported on the electromagnetic response of these materials,[15–20] but many attempts have been made to understand their charge-transport properties.[21–24]

This work deals with the reflectivity measurements of PAni–$(DBSA)_3$ (where DBSA is dodecylbenzene sulfonic acid) blended with ethylene–propylene–diene monomer (EPDM) rubber by mechanical mixing and the correlation of these results with the morphology of the RAM prepared.

EXPERIMENTAL

Polymer Synthesis

PAni was chemically synthesized with ammonium peroxydisulfate as an oxidant in aqueous 1.0*M* HCl at 0°C in a 10-L reactor, as described elsewhere.[25] Deprotonation was performed with 1.0*M* ammonium hydroxide for 24 h at room temperature to yield the polymer in the emeraldine-base form. EPDM (67% ethylene, 28% propylene, and 5% ethylidene–norbonene) was purchased from DSM South America (São Paulo, Brazil) and used as received. DBSA used in the PAni doping reaction was supplied by Hoechst do Brasil (São Paulo, Brazil).

Preparation of the Blends

Several blends of EPDM and PAni–DBSA (70/30, 60/40, 50/50, and 30/70 w/w) were prepared in an internal mixer with counter rotatory cams coupled to a Haake Rheocord 90 to study the processing time–morphology relationship. As the mixing chamber attained the set temperature, EPDM, PAni emeraldine base, and DBSA were charged and allowed to mix. The processing time was changed according to the blend composition.

Characterization

Electrical conductivity was measured by an adaptation of the Coleman method with a Keithley 617 programmable electrometer and a four-probe sensor with gold contacts.[26]

Scanning electron microscopy (SEM) was performed in a Zeiss DSM 950 operated at 25 kV on surface samples without gold coating.

Reflectivity measurements were performed with an NRL arch.[27,28] This is a microwave measurement system that can measure the free space radar reflection coefficient of flat RAMs. The Naval Research Laboratory (NRL), where the first measurement system was built, standardized the NRL arch. This system uses two horn-type antennae in the microwave range. One antenna is connected to a microwave transmitter, and the other is connected to a microwave receiver. The microwave energy launched from the transmitter horn travels and impinges on the target. The electromagnetic wave reflected from the target travels to, and is collected by, the receiver horn. A pyramidal absorber is placed around the target to eliminate microwave energy that travels around the sample. Measurements were carried out at room temperature over a frequency range of 8–12 GHz.

RESULTS AND DISCUSSION

Rheology of the Blends

The rheological behavior of blends influences their morphological structure, so the rheological characteristics of the studied system were analyzed with a Haake Rheocord torque rheometer. Figure 1(a–f) shows the torque–mixing time profiles of the EPDM and the 30/70 to 70/30 EPDM/

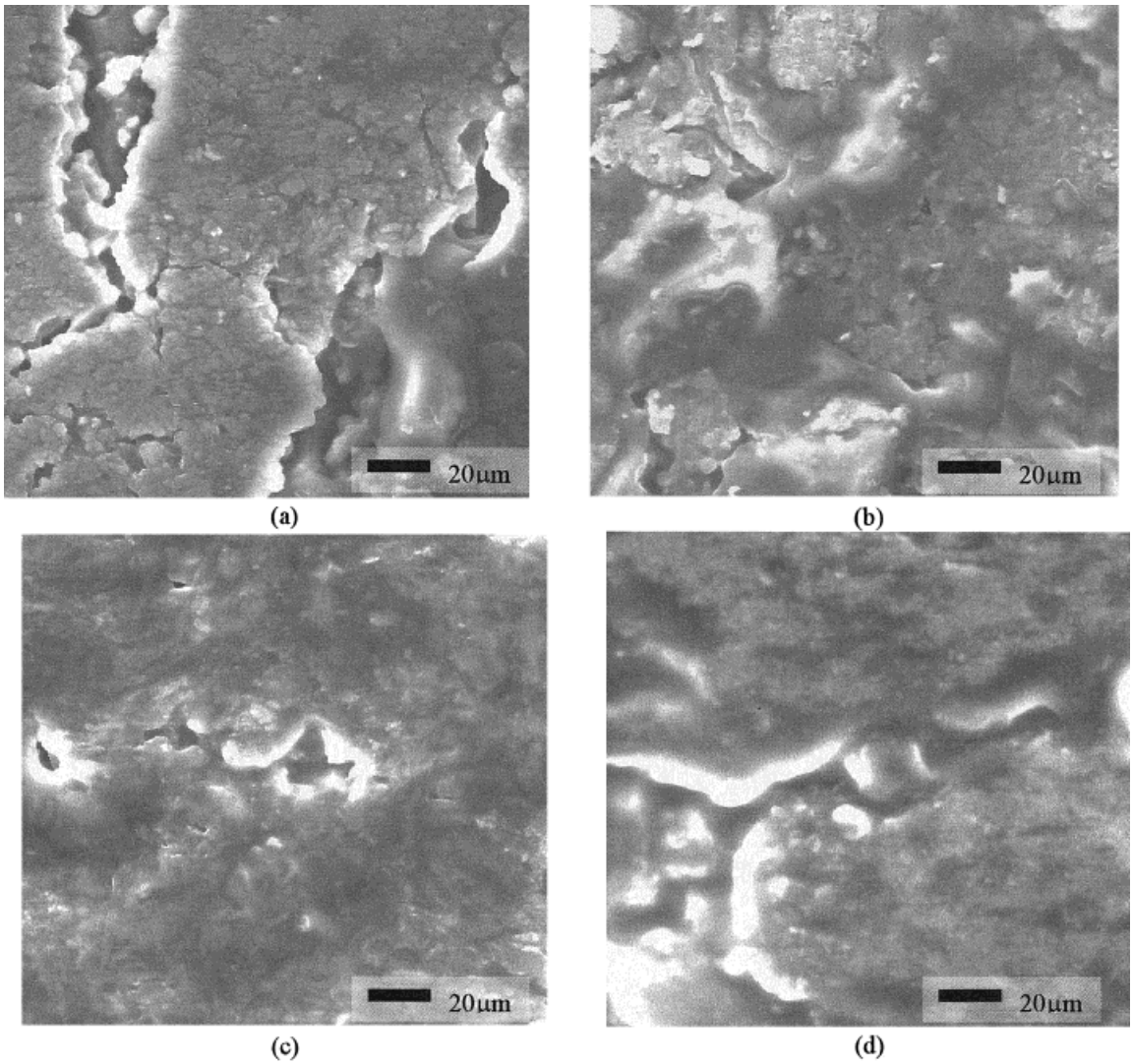

Figure 3 SEM images of an EPDM/PAni–$(DBSA)_3$ blend (60/40 w/w) for processing times of (a) 5, (b) 10, (c) 30, and (d) 40 min.

PAni blends. Of the single polymers, EPDM shows a decrease in torque after 15 min of processing due to thermal degradation. PAni–DBSA shows an increase due to protonation and crosslinking reactions.[5] Torque data for the blends show an increase with mixing time as well. During the mixing process, some reactions occur, such as (1) a PAni doping reaction by DBSA, (2) PAni–DBSA crosslinking, and (3) PAni–DBSA and EPDM interactions. The increase in the torque during the mixing is caused by an increase in viscosity, which is a result of the crosslink density increase. The first torque increase is mainly due to PAni–DBSA protonation. This is based on conductivity measurements of the samples at different stages of the torque curves, showing a plateau after 10 min of processing time, independent of the EPDM concentration. Figure 2 illustrates the electrical conductivity behavior of EPDM with 40% (w/w) PAni–$(DBSA)_3$. The second torque increase is due to the interpenetration and overlapping of the two phases, as revealed by SEM. This phenomenon has been further studied with swelling measurements, as described in another article.[29]

Processing–Morphology Relationship

In this study, the morphology and structure of blends with different processing times and compositions of EPDM and PAni doped with DBSA were investigated. Figure 3(a–d) shows the sig-

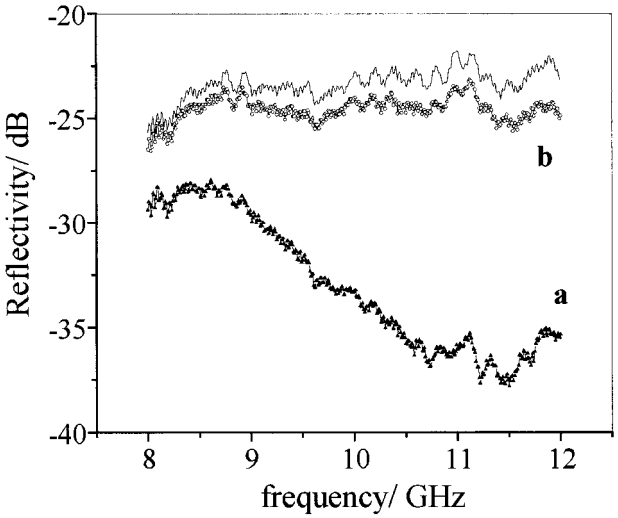

Figure 4 Reflectivity (dB) of an EPDM/PAni–$(DBSA)_3$ blend (70/30 w/w) processed for (a) 10 and (b) 35 min. The solid line corresponds to the curve for the Al plate used as a reference.

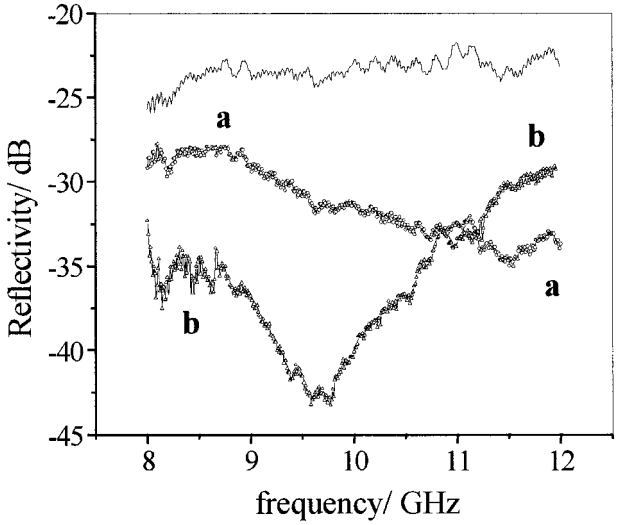

Figure 6 Reflectivity (dB) of an EPDM/PAni–$(DBSA)_3$ blend (60/40 w/w) processed for (a) 12 and (b) 35 min. The solid line corresponds to the curve for the Al plate used as a reference.

nificant morphology changes for the 60/40 EPDM/PAni–DBSA blend mixed for 5, 10, 30, and 40 min, respectively. At 5 min of processing time [Fig. 3(a)], a compact and hard structure is observed, mainly due to the PAni–DBSA phase not being mixed with EPDM. PAni obtained by dispersion processing exhibits spherically shaped particles, which tend to make very compact and hard agglomerates. A compact structure still remains for blends mixed for 10 min [Fig. 3(b)], although two phases can be distinguished: a smooth EPDM phase and a hard PAni–DBSA agglomerate. As the processing time increases to 40 min, the agglomerate size becomes smaller, and a spongelike morphology appears [Fig. 3(c,d)]. According to the torque curves, this sponge structure is formed after the second rise in the torque curves, which confirms the interaction of the two polymers. This supposition can also be proven with torque–time curves for blends prepared with

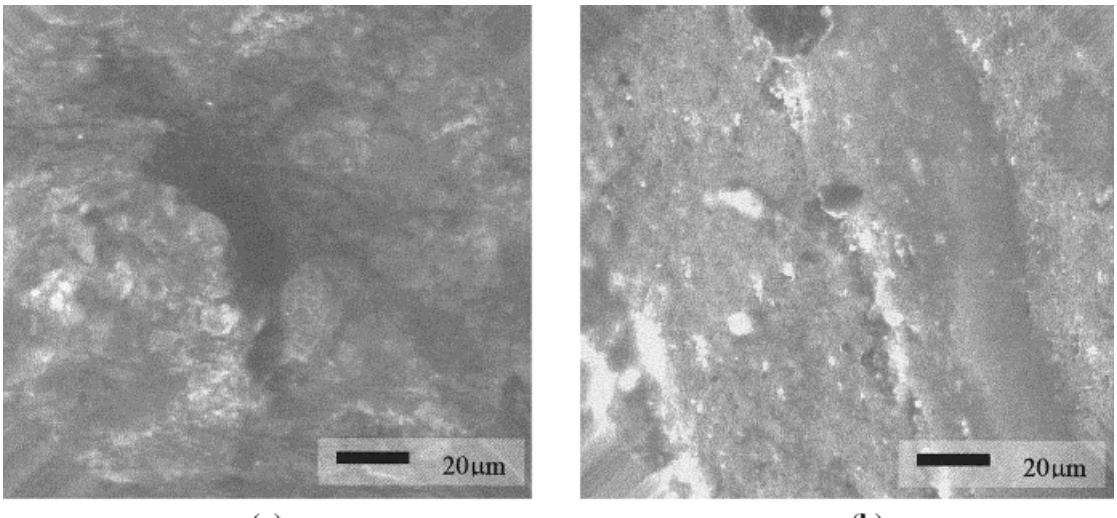

Figure 5 SEM images of an EPDM/PAni–$(DBSA)_3$ blend (70/30 w/w) processed for (a) 10 and (b) 35 min.

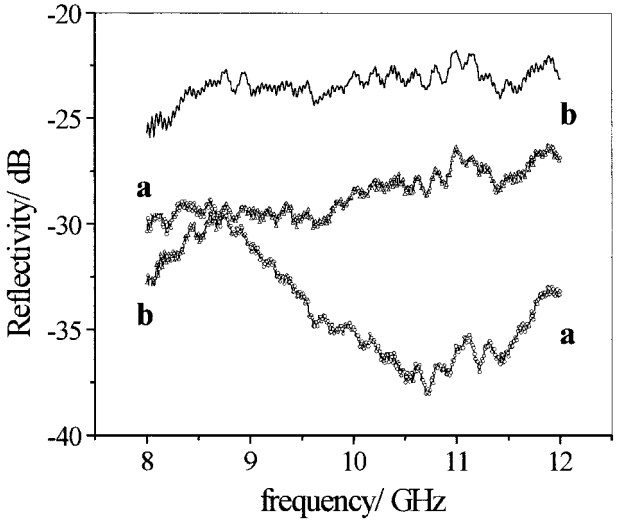

Figure 7 Reflectivity (dB) of an EPDM/PAni–$(DBSA)_3$ blend (50/50 w/w) processed for (a) 15 and (b) 44 min. The solid line corresponds to the curve for the Al plate used as a reference.

70% (w/w) PAni–DBSA, for which the second increase in torque is not observed. This phenomenon can be explained in terms of the composition of the blends in which a low EPDM content does not allow the interaction between the polymers.

Effects of Composition and Processing Time on the Reflectivity Properties of the Blends

The results of reflectivity R (dB) presented as a function of frequency (GHz) for several compositions and processing times are presented in Figures 4, 6, 7, and 9 (shown later). The processing time controls the microstructure and the nature of the wave–matter interaction. First for blends with 30% (w/w) PAni–DBSA processed for 10 min [Fig. 4(a)], a resonant absorption is observed near 11.5 GHz, giving 90% attenuation (−10 dB), whereas almost no attenuation is observed for the sample processed for 35 min [Fig. 4(b)]. Morphology changes can explain this behavior, as shown in Figure 5. For blends prepared with 10 min of mixing [Fig. 5(a)], the presence of PAni–DBSA agglomerates between the EPDM phase acts on the wave–matter interaction. The smooth surface of the blend prepared with 35 min of mixing [Fig. 5(b)] precludes the wave–matter interaction because PAni–DBSA agglomerates are more dispersed within the EPDM phase; moreover, EPDM is highly transparent to microwave frequencies.[30]

With the PAni–DBSA concentration of the blend increased to 40% (w/w), the reflectivity parameters are different (Fig. 6). For the sample processed for 12 min, a resonant absorption in the frequency range 10.5–11.5 GHz is observed, attenuating −10 dB, whereas for the blend processed for 35 min, an attenuation of −15 dB in the frequency of 9.5 GHz is observed. Comparing the surface morphology of the blends [Fig. 3(b,d)], we observe a spongelike morphology, instead of a smooth morphology, due to an increase in the PAni–DBSA concentration in the blend. After a PAni–DBSA dispersion is mixed with a matrix

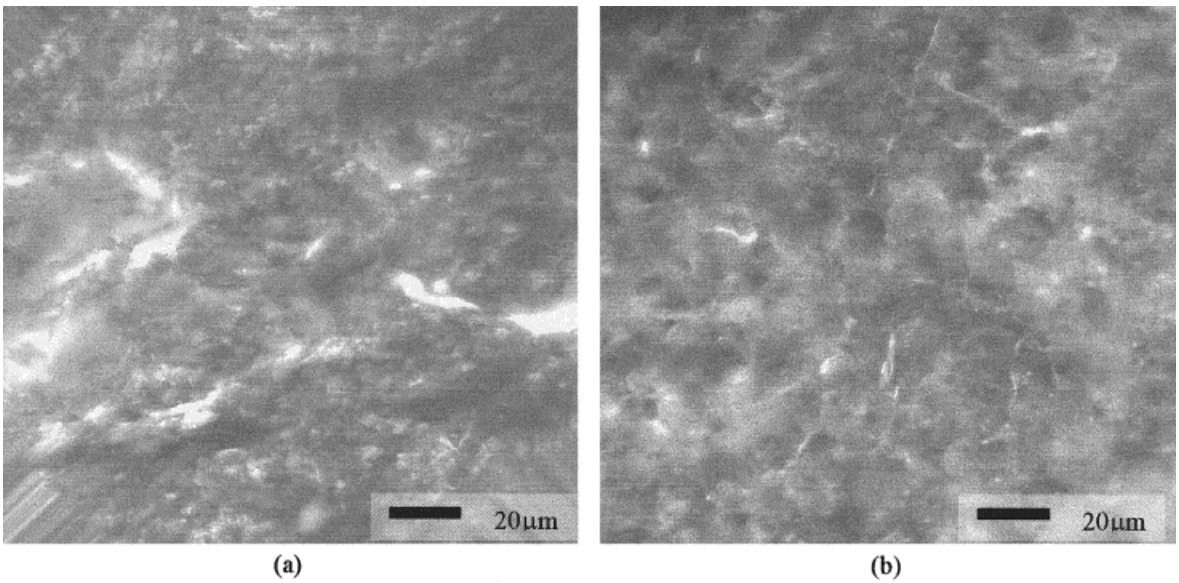

Figure 8 SEM images of an EPDM/PAni–$(DBSA)_3$ blend (50/50 w/w) processed for (a) 15 and (b) 44 min.

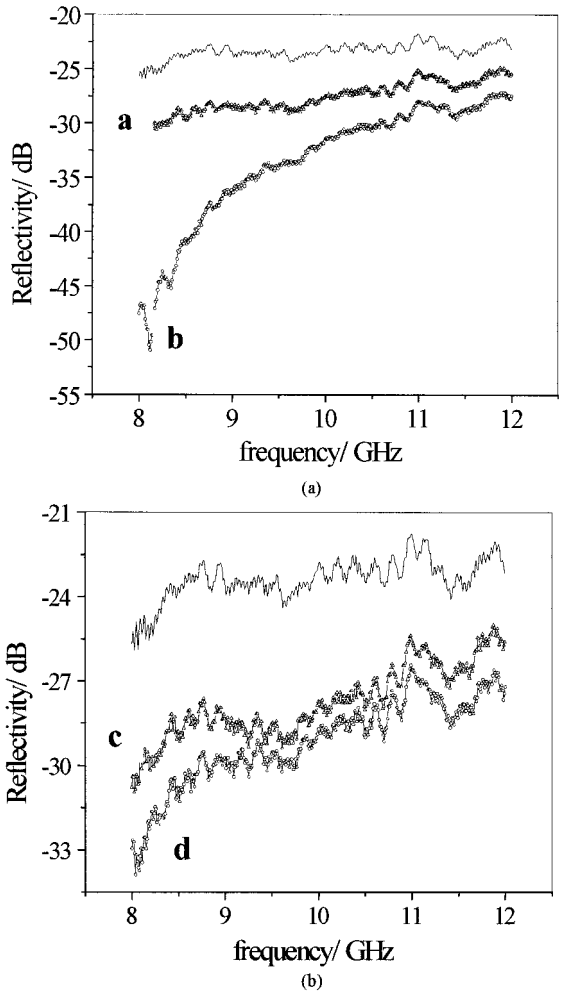

Figure 9 Reflectivity (dB) curves of (a,b) 40/60 and (c,d) 30/70 (w/w) EPDM/PAni–$(DBSA)_3$ blends processed for (a,c) 15 and (b,d) 60 min. The solid line corresponds to the curve for the Al plate used as a reference.

polymer, the PAni–DBSA agglomerates disintegrate, and an apparently homogeneous mixture is obtained.

In Figure 7, we observe higher attenuation values for EPDM/PAni–DBSA (50/50) blends prepared with 44 min of processing time (−10 dB in the frequency range 10–12 GHz) and a broadband characteristic curve (−5 dB) for 15 min of processing time. Figure 8 shows the micrographs for these samples. The surface morphology of blends prepared with 50% (w/w) PAni–DBSA are similar to those with 40% (w/w); however, different reflectivity properties are observed.

For blends prepared with 30 and 40% (w/w) PAni–DBSA, we observe that the reflectivity depends on the frequency of irradiation. This is a typical characteristic for semiconductive materials, in which conduction occurs by a hopping process. With 50, 60, and 70% (w/w) PAni–DBSA [Figs. 7 and 9(a,b)], the frequency dependence decreases to a minimum, and broadband behavior is observed. The extent of EPDM–PAni–DBSA interaction and its influence on reflectivity properties depend on the blend composition and processing time, as observed in the torque×time curves previously discussed.

CONCLUSION

The extent of EPDM–PAni–DBSA interaction and its influence on reflectivity properties depend on the blend composition and the processing time. Higher concentrations of PAni in the blends allow more efficient absorption of the incident radiation (8–12 GHz) by the prepared RAM in a broadband range, with the maximum attenuation varied with the frequency. The blend morphology presents different phases as a function of the processing time. A compact structure for PAni/DBSA and a smooth EPDM phase are observed when the blend is mixed for short periods. When the processing time increases, the PAni agglomerate size becomes smaller, and a spongelike morphology appears. The PAni concentration within the insulating polymeric matrix and the morphology of the processed RAM alter the wave–matter interaction. Very rigid control of the processing conditions of the EPDM/PAni–DBSA blends allows one to obtain RAMs that have end-use performance for an absorber application in a broadband range.

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