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Microwave Absorbing Coatings Based on a Blend of Nitrile Rubber, EPDM Rubber and Polyaniline

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Summary

The mechanical and microwave radiation absorbing properties of conductive ternary blends based on nitrile rubber, EPDM rubber and polyaniline, doped with dodecylbenzene sulfonic acid, have been investigated with special interest in the concentrations of nitrile rubber and conductive polymer in the blend. The ternary blends were prepared by melt blending using an internal mixer. Mechanical properties and soluble fraction analyses show that crosslinking occurs during blending, and that the crosslinking degree depends on the concentrations of doped polyaniline and nitrile rubber in the blend. The crosslinking reaction involves the doping acid (dodecylbenzene sulfonic acid) of polyaniline and the -C≡N group in the nitrile rubber. The ternary blends can be used for microwave absorption in the frequency range of 8 - 12 GHz. This property depends on the concentration of the conductive polymer and film thickness.

Introduction

The development of blends based on intrinsically conducting polymers (ICP) such as polyaniline, polypyrrole and polythiophene, and conventional polymers, thermoplastic or rubber materials, has attracted considerable attention during recent years due to their use in the production of radar-absorbing materials (RAM), specifically in stealth defense systems. [1] RAM are obtained by dispersion of conductive additives such as W-hexaferrite [2, 3] and conducting carbon black [4] in dielectric compounds, such as polymers or sintered ceramics. However, the use of magnetic or dielectric fillers has drawbacks, such as: high density, particle aggregation and the necessity of a precise control of the addition rate during processing. These can be avoided by using conducting polymers. The use of resins or rubbery materials is more favorable than using sintered materials, due to their flexibility and processability. In addition, conducting polymers are not susceptible to corrosion, like metallic coatings. [5]

Several blends with RAM characteristics have been reported combining polyaniline (PAni), doped with *p*-toluene sulfonic acid (TSA) or dodecylbenzene sulfonic acid (DBSA), with ethylene-propylene-diene rubber (EPDM) [6], natural rubber (NR), poly(octadecyl acrylate) (PODA) [7], high-density polyethylene (HDPE), low-density polyethylene (LDPE) or polystyrene (PS). [8]

Conducting blends of PAni with EPDM, nitrile rubber (NBR) and polychloroprene have been extensively investigated due to the unique mechanical properties of the rubber. However, the authors observed that the conductivity of these blends is low due to the vulcanization process, which is important to obtain good mechanical properties. These blends have many potential applications, such as pressure sensors, antistatic agents [9, 10], electromagnetic interference (EMI) shielding [9, 10] and stealth technology [6, 11].

The vulcanization process involves crosslinking agents, curing ingredients and high temperature, which may lead to degradation of PAni. Thus, several authors are studying the possibility of using other elastomeric materials that present good mechanical properties without needing a vulcanization process. For example, Ruckenstein et al. [12] have studied the *in situ* chemical polymerization of PAni, doped with different organic acids, such as methanesulfonic acid and benzenesulfonic acid, in the presence of styrene-butadiene block copolymer (SBS), to prepare conducting polyaniline-SBS blends. They used melt mixing and solution processing, obtaining blends with good conductivity and mechanical properties. Also, conducting interpenetrating polymer networks (IPN), made with PAni and polyvinyl alcohol [13], polyurethane [14] or methylcellulose carboxy [15], can be cited as resources to achieve the desired set of physical properties.

In addition, there are some types of blends that crosslink during molding, even in the absence of any crosslinking agents, which have been called “self-crosslinkable polymer blends”. These self-crosslinkable polymer blend systems are based on polymers containing reactive functional groups. Among the different types we can cite blends of poly(vinylchloride) (PVC) and epoxidized natural rubber [16], PVC and carboxylated nitrile rubber [17], polyacrylic acid and polychloroprene [18], and EPDM and epoxidized natural rubber [19].

The present paper deals with reflectivity and mechanical properties of conductive blends based on NBR, EPDM and PAni-DBSA complexes. The effect of NBR on the (EPDM/PAni-DBSA) blend has also been evaluated, aiming to understand the mechanism of a self-crosslinkable polymer blend. In addition, we also studied the influences of the concentration of PAni-DBSA in the ternary blend and of the sample thickness on the microwave absorption properties of the blend.

Experimental

Materials

Polyaniline was chemically synthesized with ammonium peroxydisulphate in aqueous 1.0 mol L^{-1} HCl at 0 °C in a 10 L reactor, according to Gazotti and De Paoli [20]. Neutralization was performed with 1.0 mol L^{-1} ammonium hydroxide for 24 h at room temperature to yield the polymer in the emeraldine base form. Aniline (technical grade, Merck), ammonium peroxydisulphate ($(NH_4)_2S_2O_8$, analytical grade, Merck), and hydrochloric acid (HCl, analytical grade, Merck) were used without further purification. The dodecylbenzenesulfonic acid (DBSA) used in the PAni doping reaction was supplied by Hoechst do Brasil (São Paulo – Brazil) and was also used without further purification.

EPDM (67, 28 and 5 wt. % of ethylene, propylene and ethylidene-norbonene, respectively) was supplied by the DSM Americas Brazilian plant and acrylonitrile-co-butadiene rubber or nitrile rubber (NBR) having 33 % of acrylonitrile (NP2021) was supplied by Nitriflex. For this study the polymers were used as received.

Blend preparation

EPDM/PAni-DBSA blend

The binary blend based on EPDM and PAni-DBSA (50/50) was prepared in an internal mixer chamber coupled to a torque rheometer (Haake, model Rheocord 90) at 150 °C and 50 rpm for 15 min. The blend was prepared by the simultaneous addition of EPDM, PAni emeraldine base and DBSA (molar ratio PAni:DBSA = 1:3). The doping reaction of PAni with mechanically mixed DBSA is a time-dependent process, and accelerated by heating, and without gas elimination. According to Faez et al. [21] and Titelman et al. [22] the thermal doping process includes the following main stages: heating the blend, exothermic PAni-DBSA doping reaction accompanied by a paste-to-solid-like transition, and plasticization of the resulting PAni-DBSA complex by excess of DBSA. In addition, according to Faez et al, an excess of DBSA is necessary to preclude cross-linking of PAni and to improve its dispersion in the polymer matrix.[6, 11] The unloading of the mixing chamber was followed by lamination in an open roll mill at 70 °C. After that, flat 2 mm thick sheets with 15 x 15 cm dimensions were prepared by compression molding at 150 °C, 2 MPa for 10 min.

NBR/(EPDM/PAni-DBSA) blend

An initial mixing trial was done to determine the processing conditions and limiting time, which correspond to the torque stabilization. In this trial, processing was interrupted at regular time intervals and samples were taken for analysis, Figure 1. The ternary blends based on NBR and (EPDM/PAni-DBSA) blend were prepared in an internal mixer at 80 °C, 30 and 60 rpm, with processing times of 12 or 3 min, respectively. The NBR and (EPDM/PAni-DBSA) blend ratios (wt. %) were: 95:5, 80:20, 70:30, 60:40, 50:50, 40:60 and 20:80. In addition, ternary blends containing different loadings of PAni-DBSA complex using the same equipment at 80 °C and 30 rpm for 3 min were also prepared. The compound formulations are given in Table 1.

Table 1. Formulations of the NBR/EPDM/PAni-DBSA blends.

	Composition ratios (wt. %)		
Compound code	NBR	EPDM	PAni-DBSA
NEP I	50	25	25
NEP II	60	16	24
NEP III	50	20	30
NEP IV	40	30	30

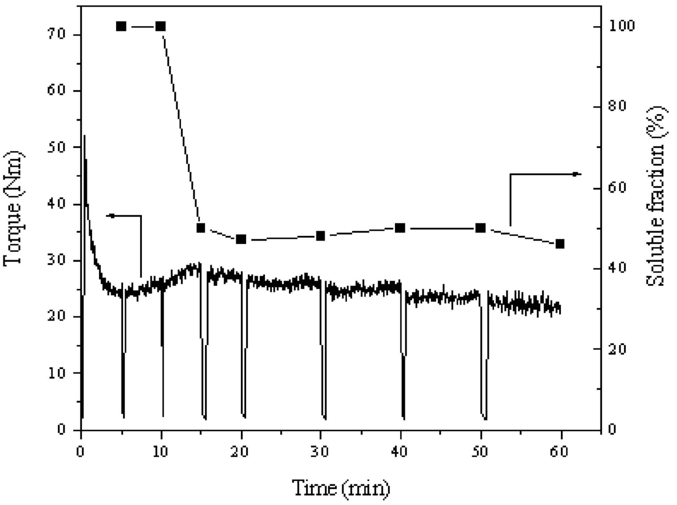

Figure 1: Torque and soluble fraction curves as a function of processing time for a 50:50 NBR:(EPDM/PAni-DBSA) blend. Negative torque peaks correspond to sampling for soluble fraction determination.

Characterization

Soluble fraction (SF) measurements of the blends were done by the swelling test at room temperature in chloroform during 8 days. SF was calculated from the weight ratio of the dried sample before and after extraction, according to the ASTM D471-93 standard.

Stress-Strain tests were done using a EMIC DL 2000 equipment, according to the DIN 53504 standard. The crosshead speed used was of 200 mm min^{-1}.

Blend reflectivity measurements, over the frequency range of 8 to 12 GHz, were done using a waveguide coupled to an Agilent Synthesized Sweeper model, 8375A, and a HP 7000 spectrum analyzer. The radiation attenuation was calculated from the difference between the attenuation curves of the blend and an aluminum plate used as reference.

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

Results and discussion

Processing characteristics

The variations on mixing torque and SF with time, during the NBR:(EPDM/PAni-DBSA) (50:50) blend processing, are shown in Figure 1. In this trial, processing was interrupted at regular time intervals and samples were taken for SF analysis. A torque increase is observed in the curve between 10 and 20 min of mixing after loading the mixing chamber. After that, there is a stabilization of the torque with the processing time, considering that the amount of material in the chamber is reduced each time when a sample is taken for SF determination. In this experiment we also observed gas evolution during the first 10 min of processing, as evidenced by a very strong smell. This phenomenon can be attributed to the scission of the C≡N bond of the nitrile rubber caused by the excess of the doping acid of PAni. Hence, in this case the excess of DBSA reacts with the nitrile group, hydrolyzing it to the respective amides and acids. Then the new functional groups in the nitrile rubber react with EPDM, leading to crosslinking. This behavior is similar to that observed by Manoj et al. [23] for the NBR/PVC blend, where the crosslinking between NBR and poly(vinyl chloride) (PVC) occurs through the allylic chlorine sites in PVC and the -C≡N groups in NBR. In our study, we suggest that the new functional groups in the nitrile rubber react with EPDM, leading to crosslinking. This behavior was confirmed by the soluble fraction (SF) values obtained, Figure 1. For samples taken after 5 and 10 min of processing the SF is negligible in comparison to samples taken after 15 min. The chemical products of SF correspond to NBR, according the infrared spectrum. Hence, curing or cross-linking occurs after 15 min of processing. For this reason we choose to process the samples for 12 minutes.

For commercial applications of the NBR:(EPDM/PAni-DBSA) blend it is necessary to further reduce the processing time. This can be achieved by increasing the rotor rotational speed to 60 rpm, reducing the processing time by a factor of 4. In Figure 2 we compare the stress-strain curves for blends prepared at 30 and 60 rpm and different processing times. We observe a decrease in strain and an increase in stress for shorter processing times and higher rotational speed (higher shearing), which leads to a higher degree of crosslinking, and hence more rigid materials. Thus, it is possible to modulate the mechanical properties of the blend according to the processing conditions.

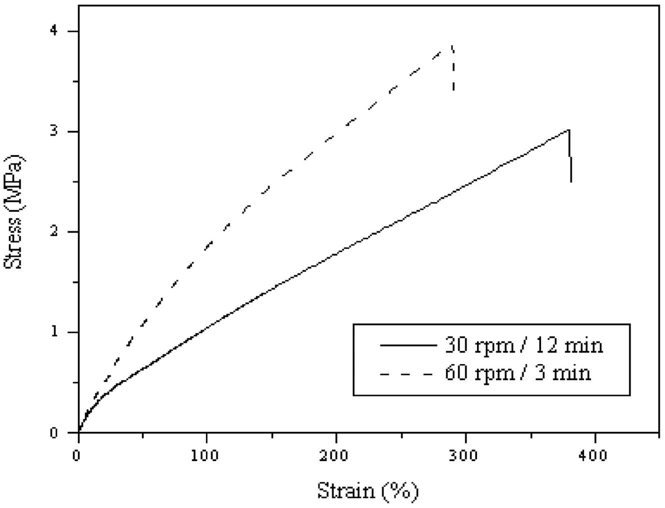

Figure 2: Stress-strain curves for 50:50 NBR:(EPDM/PAni-DBSA) blends prepared using different processing conditions.

Effect of the blend composition

The variation of the mechanical properties and SF of the blend as a function of the weight percentage of (EPDM/PAni-DBSA) in the ternary blend is shown in Figure 3. Upon increasing the (EPDM/PAni-DBSA) content, there is a decrease of SF as well as of the elongation at break. This is due to higher crosslinking, caused by the increase in

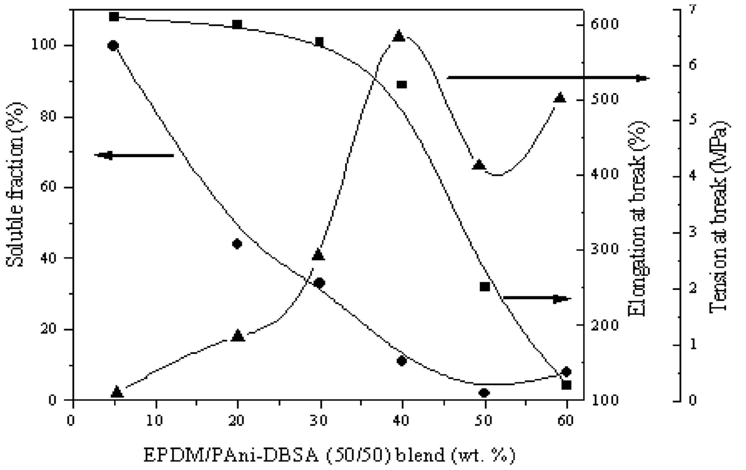

Figure 3: Soluble fraction, elongation and tension at break curves for ternary NBR:(EPDM/ PAni-DBSA) blends at different concentrations of EPDM/PAni-DBSA (50/50).

the number of new groups derived from C≡N scission. This is also observed in the tension at break values, which reach a maximum at 40 wt. % of (EPDM/PAni-DBSA) in the ternary blend.

In addition, in Figure 3 we observe that, at 50 wt. % of (EPDM/PAni-DBSA) in the ternary blend, complete crosslinking is achieved, since only negligible amounts of soluble materials were removed by solvent extraction.

Effect of NBR and EPDM content in the ternary blend on mechanical properties

To verify the effect of EPDM content on the soluble fraction of the ternary blends, samples were prepared with 50:50 and 60:40 NBR:(EPDM/PAni-DBSA) ratios, where EPDM/PAni-DBSA ratios were 25/25 (NEP I) and 16/24 (NEP II), respectively, Table 1. In the figure 4 we observed a decrease in the elongation at break for the

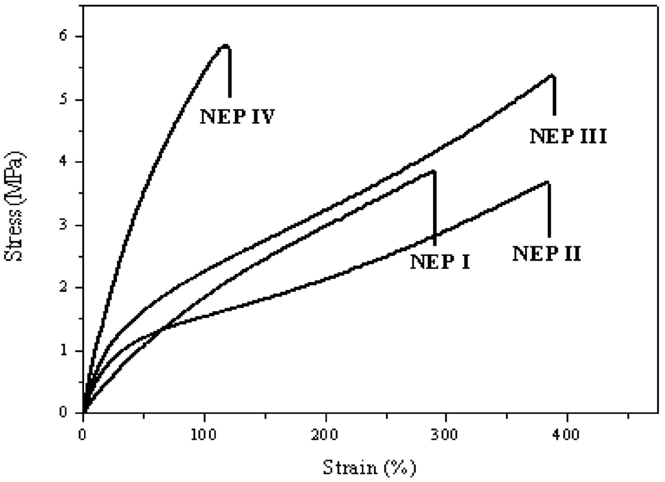

Figure 4: Stress–strain curves of the ternary blends.

higher EPDM content in the blend (NEP IV), and that the Young Modulus increases with an increase of EPDM content (NEP II, III and IV). This behavior is due to the higher degree of crosslinking, as confirmed by the lower SF values. Thus, different EPDM concentration can be used to produce blends having the required mechanical properties.

Reflectivity properties of the ternary blends

Figure 5 shows the reflectivity (R) of NBR/(EPDM/PAni-DBSA) blends as a function of the frequency (GHz), from 8 to 12 GHz. We observe that the ternary blend NEP I exhibits low radiation attenuation values in this frequency range and attains a maximum of 5 dB, corresponding to an attenuation of 65 % of the incident radiation energy, at 12 GHz. Also, it was observed that the ternary blends NEP II, III and IV present high radiation attenuation values, from 7 to 20 dB. For the ternary blend NEP IV a 20 dB reflectivity is reached, corresponding to a dissipation of 99 % of the incident radiation energy or to 1% of reflected energy, in the frequency range of 11 to 12 GHz. The reflectivity properties of the blends are due to the conducting polymer (PAni) and, specifically, by the level doping and type of dopant. Permittivity data are not available for these samples, thus, comparison with theoretical reflection curves is not possible.

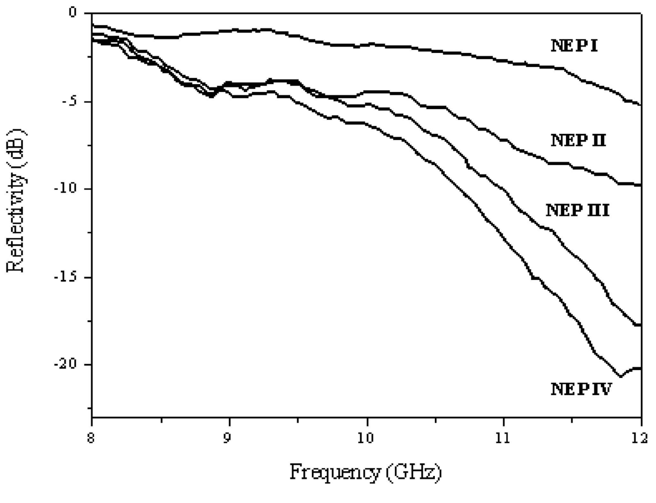

Figure 5: Reflectivity of the ternary blends. Thickness of plate: 2 mm.

Also was observed that the reflectivity of the blends at 12 GHz change from 5 and 8 dB (NEP I and NEP II) to 17 and 20 dB (NEP III and NEP IV) when PAni-DBSA concentration changed from 24-25 to 30 wt.%. This substantial reflectivity change with the increased of 5 wt.% of PAni-DBSA in the blend can be explain by the microstructure attained in the end of the processing. NEP III e IV present PAni-DBSA agglomerates of higher size than NEP I and II, Figure 6. According to Faez et al. [24] the PAni-DBSA agglomerates between elastomeric phase acts on the wave-mater interaction. In addition, was observed that the ternary blends prepared in this work present microwave absorbing properties similar to the binary blend based on EPDM and PAni-DBSA complex [24]. However, the ternary blends present the advantage of no loss of DBSA by exudation as a function of time.

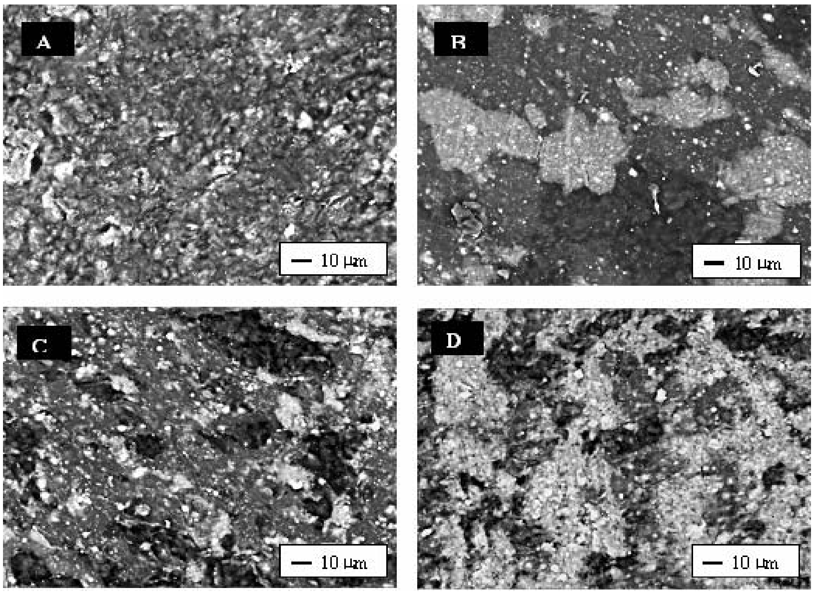

Figure 6: SEM photographs of NBR:(EPDM/PAni-DBSA) blends: (A) NEP I, (B) NEP II, (c) NEP III and (d) NEP IV. (bright phase and dark phase corresponding to PAni and elastomeric phase, respectively).

Figure 7 shows the attenuation curve of the NEP IV blend as a function of the frequency for samples of different thicknesses. An increase in the thickness of the sample leads to a shift of the maximum of the attenuation values to lower frequencies, from 11.8 to 9.7 GHz for samples of 2 and 3 mm thickness, respectively. For a higher thickness (4.5 mm), the blend present a different attenuation behavior: it exhibits lower attenuation values (2.5 to 5 dB) for a frequency range between 8 and 12 GHz, which is due to the dielectrical characteristics of polyaniline, known as λ/4 material

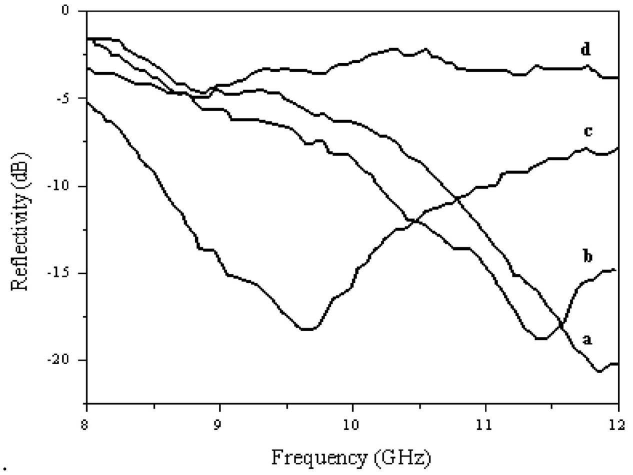

Figure 7: Reflectivity of NEP IV blend plates with different thicknesses: (a) 2.0, (b) 2.5, (c) 3.0 and (d) 4.5 mm.

(λ is wavelength of the radiation). Phenomenon previously observed for other materials such as poly(octyl-3-thiophene) [25], polyoctylthiophene-EVA blend [25], PAni-DBSA/poly(styrene sulfonic acid) blend [26], and poly(p-phenylene-vinylene) derivates [27]. Hence, this shows that the attenuation peak frequency of the ternary blend can be manipulated easily by changing the thickness of the materials.

Conclusions

A new ternary blend, based on NBR, EPDM and PAni-DBSA, was successfully prepared by melt blending. The permeability of the blends in the frequency range of 8 – 12 GHz shows that the blends exhibit good absorption performance between 11 and 12 GHz, and that the absorption peak frequency can be easily shifted to lower frequencies by changing the thickness of the microwave absorber. This blend presented no exudation after prolonged ambient exposure.

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