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Microwave absorption properties of a conductive thermoplastic blend based on polyaniline

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Summary

Conductive thermoplastic blends of polystyrene and polyaniline doped with dodecylbenzene sulfonic acid, DBSA and polystyrene sulfonic acid were prepared in an internal mixer. We used a block copolymer of styrene and butadiene as compatibilizer. Different formulations were tested according to a statistical response surface method. The electrical conductivity and the microwave radiation absorbing properties of the blends were evaluated. The concentration of the compatibilizer and polyaniline and the blend film thickness affect the attenuation properties of the materials.

Introduction

Conductive polymers have created a great interest due to their wide variety of properties and technological applications. In particular, variation of their conductivity with the frequency of an incident radiation suggests their use for microwave absorption applications [1]. Radar absorbing materials (RAM) are generally prepared by adding ferrite, carbon black or other magnetic or dielectric fillers to a matrix. However, these fillers present the disadvantage of having a high specific mass [1]. Intrinsically conducting polymers (ICP) can also be used as RAM with the advantage of having a lower density. However, for this application the ICP must be processed in the form of films. Although it is possible to prepare films of different ICP by solvent evaporation or by electrochemical deposition, to prepare films on large scale it is necessary to use the techniques applied to the production thermoplastic polymer films. To do this it is necessary to prepare blends of the ICP and a thermoplastic, combining processing properties of common thermoplastic polymers with the electronic conductivity of the ICP. Nowadays, there are many reports employing melt processing as a doping method to prepare blends with thermoplastic polymers, also denoted reactive processing [2-5]. Here, doping can be carried during processing, eliminating several steps.

Faez et al. have studied the microwave absorption properties of polyaniline (PAni) doped with sulfonic acids and its blends with elastomers, e.g., poly(ethylene-co-propylene-co-ethylidenenorbornene), EPDM, and poly(butadiene-co-acrylonitrile), NBR [6,7]. These authors showed that the processing parameters exert strong influence on the microwave attenuation characteristics of these materials.
In this work, we have evaluated a conducting polymer-based microwave absorbing material. To solve problems related to mechanical properties and processing by methods currently used by the thermoplastic industries (internal mixer, extrusion or injection molding), it is necessary to blend the conducting polymer with a thermoplastic. Thus, we used blends of polystyrene with polyaniline doped with poly(styrenesulfonate) to manufacture these absorbing materials by extrusion. We evaluated the microwave absorption properties as a function of PAni concentration in the blends and the thickness of the test films.

Experimental

Polymer synthesis and doping

Polyaniline was prepared on a pilot-plant scale by chemical oxidation of aniline (Bann Química, p.a.) using $(NH_4)_2S_2O_8$ (Synth, 98 %) in a HCl (Solvay, p.a., 1 mol L^{-1}) solution [8]. PAni(HCl) was dedoped in an 1 mol L^{-1} NH_4OH (Synth, p.a.) aqueous solution under stirring for 24 h, producing the PAni emeraldine base (PAni EB).
PAni EB was doped using dodecylbenzene sulfonic acid, DBSA, (Chemco, commercial) and poly (styrene sulfonic acid), PSS, (prepared according to our patented procedure, [9]). A plasticizer, zinc stearate, ZnEs, (Quimesp, commercial) was used to improve the interactions of polystyrene, PS, and doped PAni [8]. The doping process occurred by reactive processing simultaneously with blend preparation in an internal mixer and was done by mixing PAni EB with DBSA and PSS (1:2:0.25 mass ratios) [10,11].

Blends preparation

Binary polymer blends containing a thermoplastic polymer (polystyrene, atactic PS with $\overline{M_n}$ = 33.000 and $\overline{M_w}/\overline{M_n}$ = 4.9, Piramidal Termoplásticos) and the complex PAni-DBSA-PSS were prepared in a double screw counter rotating internal mixer coupled to a torque rheometer (Haake, model Rheocord 90), at 180 °C and 50 rpm for 8 min. We used poly(styrene-co-butadiene-co-styrene), SBS, (30 % (m/m) of styrene, Coperflex TR-1061, Petroflex) as compatibilizer [11]. Flat plaques, 65 x 65 x 2 mm, were prepared by compression molding at 140 °C and 4.5 MPa of pressure during 20 min in a hot press. Narrow strips (20 x 7 mm) were cut from flat plaques for reflectivity measurements.

Conductivity and reflectivity measurements

Electrical conductivities of the blends were measured using a Cascade Microtech C4s-64 four-probe system coupled to a Keithley 617 electrometer and an ET-2500 Minipa multimeter [12]. Blend reflectivity measurements over a frequency range of 8 to 12 GHz were done at room temperature using a wave-guide coupled to an Agilant Synthesized Sweeper 8375A and a Hewlett-Packard spectrum analyzer 7000 [13].

Results and discussion

The mixer was simultaneously loaded with PS, PAni EB, PSS, DBSA and SBS, followed by closure of the mixing chamber, mixing and recording of the torque as a function of time until reaching a constant value. The acids DBSA and PSS are the dopants for polyaniline. The composition of the blends was adjusted using a factorial design involving three variables: PS, SBS and doped PAni concentrations (Table 1) [14].

Figure 1(a) shows the torque x time curves for PS and for the preparation of formulations PS/doped PAni/SBS blends. The initial peak observed corresponds to feeding and is not considered for analysis. The curves indicate that the conducting polymer and the presence of compatibilizer influence the rheological behavior of PS thermoplastic. The reactive processing corresponds to the doping process, which occurs by mixing, homogenization and reaction among the components during processing. This result is confirmed by figure 1(b), which shows the increase of torque during this mixing. We explain this increase with the dispersion of the doped PAni in the PS matrix [15] .

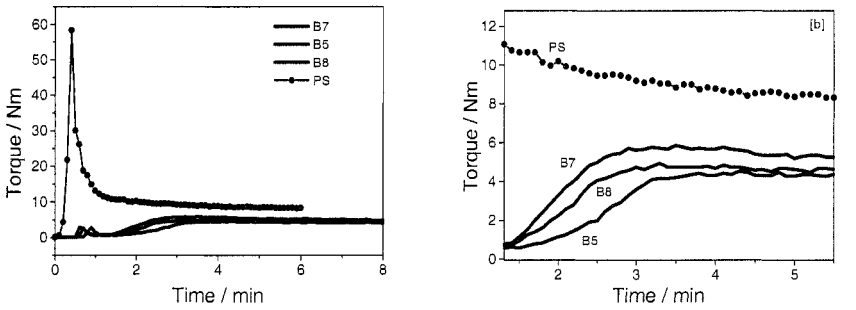

Figure 1 – (a) Torque curves as a function of processing time for PS and PS/doped PAni/SBS blends and (b) expanded torque x time curves.

Figure 2 shows the temperature x time curves for these blends indicating the melt temperature during processing. It was also observed that these blends show endothermic processes, as compared with blends without compatibilizer (exothermic process [11]), indicating, therefore, the compatibilization effect.

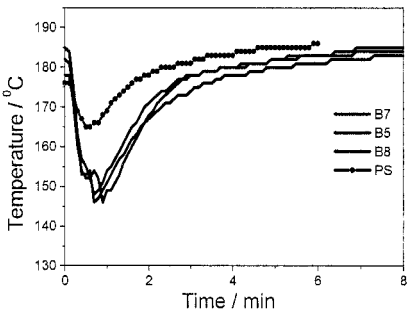

Figure 2- Temperature curves as a function of processing time for PS and PS/doped PAni/SBS blends.

In Table 1 we report the effect of SBS concentration on the electrical conductivity of the PS/doped PAni/SBS blends. Conductivity values of blends containing 6 wt % of SBS increase one order of magnitude with a 10 % increase in PAni concentration, because SBS promotes a better interaction between the blend components. Without SBS and using the same concentrations (70/30 PS/PAni-DBSA-PSS blends) the conductivity was 10^{-6} S cm^{-1} [11]. Furthermore, it is observed that a lower doped PAni concentration (40 % m/m) also shows good conductivity, and it can be used to produce a good interaction in PS/SBS blends. Morphological studies were done by SEM analysis and revealed that the PS thermoplastic matrix has a better miscibility with SBS, indicating a good dispersability and structuring of the PAni-DBSA-PSS particles within PS, producing more compatible blends [11]. These products present good adhesion, which was verified also during the production of homogeneous flat plaques by compression molding.

Conducting thermoplastics based on PS/doped PAni/SBS blends were also examined as microwave absorbing materials. Measurements of absorbed energy in the frequency range of 8 to 12 GHz were performed using the wave-guide method [13]. Figure 3 shows the attenuation of the blends with 30, 40 and 50 % (m/m) of PAni-DBSA-PSS as a function of frequency for different strip thickness. The radiation attenuation is calculated from the difference between the attenuation curves of the blend and an aluminum plate (reference). For PS/doped PAni/SBS blends with 2 mm thickness, Fig.3 (1), we observe low radiation attenuation values, independent of the PAni-DBSA-PSS concentration, in the frequency range of 11 to 12 GHz. However, if the strip thickness is increased to 4 mm a great modification in the attenuation curves is observed Fig.3 (2). A strong attenuation is measured for the blend containing 50 % of doped PAni. In addition to higher attenuation, mainly for 40 and 50 % (m/m) of PAni-DBSA-PS, the frequency range for maximum attenuation also changed, showing a resonant behavior at 8.7 GHz. Thicker strips (6 mm) exhibit a different attenuation behavior, showing a narrow band in the 8 - 11.5 GHz frequency range (Fig.3 (3)). These differences in attenuation as a function of thickness are explained based on the dielectric characteristics of polyaniline known as $\lambda/4$ (λ is wavelength of the radiation). At an approximate thickness of $\lambda/4$, a matching layer occurs [16]. This behavior has also been reported in previous works [1, 17].

Table 1. Statistical factorial design and electrical conductivity values for PS / doped PAni / SBS blends.

Formulation of the blends / %m/m				Electrical conductivity / x 10^5 S cm^{-1}
Blends	PS	PAni-DBSA-PSS	SBS	
B5	64	30	6	0.11
B8	55	40	5	1.67
B7	44	50	6	1.39

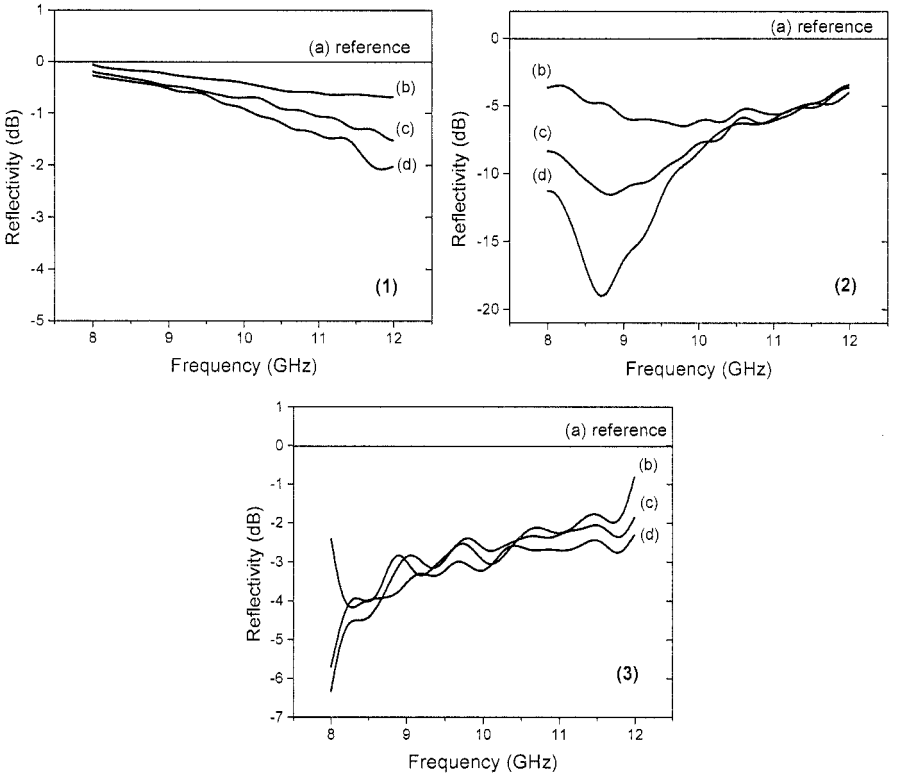

Figure 3. Attenuation of PS blends with: (b) 30, (c) 40 and (d) 50 % (w/w) of PAni/DBSA/PSS. Thickness of plates: (1) 2, (2) 4 and (3) 6 mm. The solid line corresponds to the curve for Al plate used as reference (a).

Conclusions

A conducting thermoplastic blend of polyaniline and polystyrene was prepared by thermal reactive processing with the use of the elastomer SBS as compatibilizer. Our results clearly demonstrate that PS/PAni/SBS blends are very promising for applications such as electromagnetic radiation absorption for radar absorbing materials (RAM). The doped PAni concentration and the thickness of the blend films affected the reflectivity results.

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References

1. Olmedo L, Hourquebie P and Jousse F (1997). In: Handbook of Organic Conductive Molecules and Polymers. Nalwa HS (ed.). John Wiley New York (vol 3)
2. Freitas PS and De Paoli M-A, (1999) Synth Met 102:1012
3. Zilberman M, Titelman GI, Siegmann A, Haba Y, Narkis M and Alperstein D, (1997) J Appl Polym Sci 66:243
4. Davies SJ, Ryan TG, Wilde CJ and Beyer G, (2002) Synth Met 69: 209
5. Mitzakoff S and De Paoli M-A, (1999) Eur Polym J 35:1791
6. Faez R, Martin IM, De Paoli M-A and Rezende MC, (2001) Synth Met 119:435
7. Faez R, Martin IM, De Paoli M-A and Rezende MC, (2002) J Appl Polym Sci 83:1568
8. Freitas PS, (2000) "Preparação da Polianilina em Escala Piloto e seu Processamento", PhD Thesis, Unicamp, Campinas
9. Martins CR and De Paoli M-A, (2001) Brazilian Patent PI 101700-4
10. Martins CR, Freitas PS and De Paoli M-A, (2003) Polym Bull 49:379
11. Martins CR and De Paoli M-A, (2002), Proc. 18th Annual Meeting of Polymer Processing Society, Guimarães, Portugal, 53
12. Girotto EM and Santo IA, (2002) Quim Nova 25: 639
13. Franchitto M, (2001) "Caracterização eletromagnética de materiais absorvedores de microondas", MSc Thesis, Instituto Tecnológico de Aeronáutica, São José dos Campos
14. Barros BN, Scarminio IS and Bruns RE (1995). Planejamento e Otimização de Experimentos. Unicamp, Campinas
15. Titelman GI, Zilberman M, Siegmann A, Haba Y, Narkis M, (1997) J Appl Polym Sci 66:2199
16. Chatterton PA and Houlden MA (1992). EMC – Electromagnetic theory to practical design. John Wiley , West Sussex
17. Hourquebie P and Olmedo L, (1994) Synth Met 65:19