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Study of Conductivity of dEPDM Rubber and PAni Blends

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Summary: Blending is a promising approach, in the conducting polymer field, for taking advantage of the good mechanical properties and processability of conventional polymers and of the electroative properties of such conjugated polymers. The challenge of producing blends with conducting polymers has been studied by many researchers in the last years. Several approaches have been used to prepare these blends such as, eletrochemical deposition, in situ chemical polymerization, powder dispersion, melt blending and solution blending. Among the conducting polymers, blends with polyanilines have obtained the greatest technological importance due to the remarkable properties of such conductive polymer namely, easy of synthesis and doping, environmental stability, solubility and processability. In this work, blends of polyaniline (PAni) doped with dodecylbenzenesulfonic acid (DBSA) and ethylene-propylene-diene-monomer rubber devulcanizated (dEPDM) by microwave were prepared by mechanical process. This EPDM used is a recycled material originating from car spare industry. Flexible, free-standing and stretchable films were obtained, which were characterized by electrical conductivity measurements. As expected, the blend conductivity gets higher with increasing contents of conducting polymer. The onset of the conductivity at low contents of conducting polymer indicates a low percolation threshold for the blends. The rubbery and conductive properties of these blends are great to produce devices like touch pad, weight and pressure measurer, etc.

Keywords: blends; conductive elastomer; dEPDM; polyaniline

Introduction

Intrinsically conducting polymers are a largely researched class of materials due to their interesting properties, as electrical conductivity, electrochromism and electroactivity.[1] The development these polymers has attracted great attention from the scientific community because of the increasing potential for technological applications such as rechargeable batteries, protecting coatings against corrosion, electrochromic and optoelectronic devices, sensors, electrolytic capacitors, electrocatalysis electrodes, artificial muscles, among others.[2] However, their poor mechanical properties, low thermal stability and insolubility in common organic solvents precluded for several years their use by the polymer industry.[1]

In order to improve processability, strategies such as the synthesis of new polymer structures, doping with functional protonics acids or the development of

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composites or blends with conventional polymers have been performed.[2] Incorporation of conductive polymers into a hosting polymer substrate, forming a blend, composite or interprenetrated bulk network has been widely used as an approach to combine electronic conductivity with desirable mechanical strength of polymers.[3] Conducting blends of PANI with poly(methyl methacrilate) (PMMA),[4,5] polystyrene (PS),[6,7] polyethylene (PE)[8,9] and terpolymer ethylene-propylene-diene (EPDM)[10] were obtained and a great number of practical applications proposed.[11–13]

Conductive rubber composites are widely used for different applications such as electrostatic charge dissipation (ESD), touch control switches and electromagnetic interference (EMI) shielding. Various rubbers are being widely used for preparation of such composites, e.g., silicone, nitrilic, butyl, natural and rubber. These rubber compounds are made conductive by addition of conductive carbon black, carbon or metallic fibers, and they are called of extrinsically conducting elastomers.[3]

The aim of this work is to prepare a conductive film with devulcanizated rubber (dEPDM) containing a few of carbon black and polyaniline doped with dodecylbenzenesulfonic acid (PADB) by mechanical process. Flexible, free-standing and stretchable films were obtained and they were characterized by electrical conductivity measurements through four probe method.

Electric Conductivity

The first conducting polymer was obtained in 1977 by exposition of polyacetilene in insulator form (conductivity, $\sigma = 10^{-5}$ S/cm) to doping agents, oxidants or reductors, becoming intrinsic electric conductor ($\sigma = 10^{2}$ S/cm).[14]

An important way to select potentially conducting polymers is the facility that the system can be oxidated or reduced. This leads to the polymer choice with conjugated insaturations, that possess low potential of oxidation.[14]

Since the discovery of the conducting polymers, scientists study aiming at optimization of its conductivity electric, without that it has prejudice of the typical properties of the polymeric materials. The conducting polymers can have conductivity values that go since insulator until conductor, depending on the doping degree.

PAni forms a new conducting polymer class because it can be doped by protonation, that is, without occur alteration in the electron number associates to the polymeric chain.[14] Unlikely other aromatic conjugated polymers, PAni attains its highest conductivity when it is not completely oxidized.[15] According to literature,[14] studies suggest that the polyaniline protonation is not homogeneous, but that completely protronated regions are formed, that originate metallic islands embedded into not protonated insulator regions. In this sense the bulk conduction depends on the resistance between each of those islands and the carriers need "to jump" from one island to another in order to the polymer to achieve a measurable conductivity.[16,17]

Experimental

EPDM Rubber Desvulcanization Process

EPDM rubber was devulcanizated by microwave oven (home mode) at 700 W about 300 s. The EPDM was triturated, placed into an ovenproof and led to microwave oven. This equipment has one spatula linked on an electric engine in order to keep the mixture in constant movement. Thus the EPDM rubber receives the microwaves in uniform way. The power of this microwave oven is fixed at 700 W therefore the process was controlled by time. The aim of this process is to remove the sulphur particles to obtain EPDM rubber without crosslink. EPDM devulcanization was carried out by microwave because this process is simpler than chemical process, which is more expensive and it leaves residues in the blends.

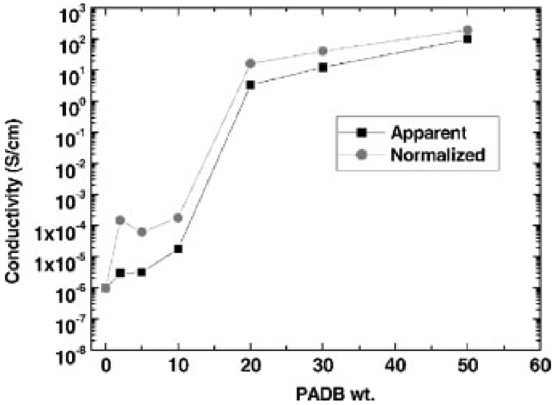

Figure 2.
Electrical conductivity of PADB/dEPDM films *vs.* PADB weight content.

Blend Preparation

Blends of dEPDM the PADB, in form of powder, were prepared in the mangle equipment resulting in PADB/dEPDM blends, in form of films, in the following proportions: 0/100; 2/98; 5/95; 10/90; 20/80; 30/70; 50/50. However, the PADB/dEPDM blends of 70/30 and 90/10 proportions were not possible to be transformed in films due to the large amount of PADB because this polymer is breakable and therefore were not analyzed.

Characterization

The IR-spectra of all samples were obtained from a Nicolet 380 FTIR. Electrical conductivity was measured at room temperature using a LCR Meter HP4284A by four-probe method.

Results and Discussion

The obtained dEPDM and PADB/dEPDM blends characterized by FTIR are shown in Figure 1. The characteristic peaks are listed as following: (a) **dEPDM** –2920 cm^{-1} (belonging to the main chain C–H); 1460 cm^{-1} (C–H lateral groups $-CH_3$); 1735 cm^{-1} (carbonyls groups present in carbon black); 3700–3200 cm^{-1} (groups –OH present in carbon black); (b) **PADB**

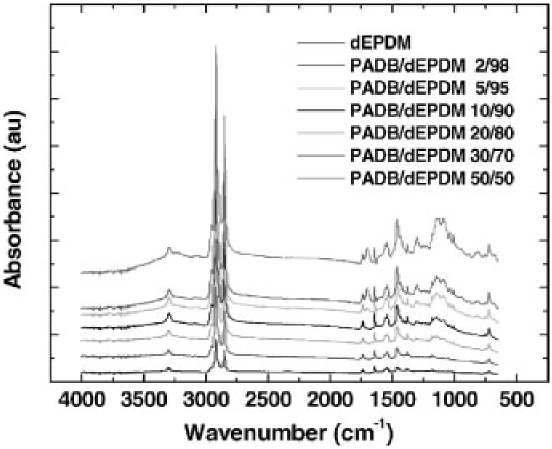

Figure 1.
IR-spectra of dEPDM alone and PADB/dEPDM at different compositions.

–2958 cm^{-1} (–CH_3); 2924 cm^{-1} –CH_2-); 1561 cm^{-1} (doped –C=N– of quinoid); 1467 cm^{-1} (–C=C– of benzoid); 1030 cm^{-1} (–S=O of –SO_3H); 1005 cm^{-1} (–S=O of –SO_3H); 801 cm^{-1} (C–H *para* substituted aromatic out of plain bending). The prepared polymer films were flexible solids with rough surface under visual inspections. According to this data it was noted that there is a great incorporation of the PADB into the dEPDM matrix. Figure 2 shows the electrical conductivity as a function of the blend composition for PADB/EPDM films prepared by mechanical process. As expected, the conductivity increased with PADB concentration in the blends and a low percolation threshold is observed with the onset of conductivity occurring at lower concentrations of the conductive materials (<20%) than is the case of metallic fillers, as shown in Figure 2. For blends of compositions above 50 wt% it wasn't possible to obtain flexible films due to hardness of the conductive polymer. The reported normalized conductivity is the apparent conductivity divided by PADB weight percentage that should be expected to be constant and equal to that of neat PADB, provided the blends behave according to the simple rule of mixtures.

Conclusion

In this work, conducting PADB/dEPDM blends were prepared by mechanical process. In this type of conducting polyblend, the conductivity is controlled by composition of PADB, and these blends became conductive with small amount of conducting polymer, that is, they present a low percolation composition. It can be assumed that electrical conduction these blends one behaves as conducting metallic islands embedded into an insulator matrix. As expected, the electrical conductivity was higher with the increase of PADB content in the blends from 20 to 50 wt% (by weight). Conducting PADB/dEPDM blends were successfully obtained and these blends present the great advantage of having either an extremely low or no percolation threshold. The films are chemically stable, easy to handle and to cutout. And, due to its flexibility and elasticity properties, they serve as transductor, since their conductivity can vary according to the mechanical tension. So they can be used as pressure sensor and similar things.

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[1] S. C. Domenech, J. H. Bortoluzzi, V. Soldi, C. V. Franco, W. Gronski, H. J. Radusch, *J. Polym. Sci: Part B: Polym. Phys.*, **2004**, *42*, 1767.
[2] V. Schmidt, S. C. Domenech, M. S. Soldi, E. A. Pinheiro, V. Soldi, *Polym. Degrad. and Stabil.*, **2004**, *83*, 519.
[3] R. Faez, M. A. De Paoli, *Eur. Polym. J.*, **2001**, *37*, 1139.
[4] Y. Cao, P. Smith, A. G. MacDiarmid, *Synth. Met.*, **1992**, *48*, 91.
[5] C. Y. Yang, Y. Cao, P. Smith, A. J. Heeger, *Synth. Met.*, **1993**, *53*, 293.
[6] V. Jousseaume, M. Morsli, A. Bonnet, O. Tesson, S. Lefrant, *J. Appl. Polym. Sci*, **1998**, *67*, 1205.
[7] Y. Roichman, G. I. Titelman, M. S. Silverstein, A. Siegman, M. Markis, *Synth. Met.*, **1999**, *98*, 201.
[8] G. R. Valenciano, A. E. Job, L. H. C. Mattoso, *Polymer*, **2000**, *41*, 4757.
[9] C. Y. Yang, A. J. Heeger, Y. Cao, *Polymer*, **2000**, *41*, 4113.
[10] R. Faez, W. A. Gazzoti, M. A. De Paoli, *Polymer*, **1999**, *40*, 5497.
[11] B. Wessling, *Synth. Met.*, **1998**, *93*, 143.
[12] J. Anand, S. Palaniappan, D. N. Sathyanarayma, *Prog. Polym. Sci.*, **1998**, *23*, 993.
[13] S. Roth, W. Graupner, *Synth. Met.*, **1993**, *57*, 3623.
[14] L. H. C. Mattoso, *Química Nova*, **1996**, *19*, 388.
[15] J. C. Chiang, A. G. MacDiarmid, *Synth. Met.*, **1986**, *13*, 193.
[16] M. Gosh, A. Barman, A. K. Meikap, S. K. De, S. Chatterjee, *Phys. Lett. A*, **1999**, *260*, 138.
[17] R. F. Bianchi, R. M. Faria, G. F. Leal, M. C. Ferreira, *J. Chem. Phys.*, **1999**, *110*, 4602.