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A conductive rubber based on EPDM and polyaniline
I. Doping method effect

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Abstract

In this work a methodology is described to prepare blends of ethylene–propylene-diene (EPDM) rubber and polyaniline (PAni) by mechanical mixture. PAni was synthesized by chemical polymerization in a pilot-plant scale and doped with dodecylbenzene sulfonic acid (PAni–DBSA). Different doping methods were used: solution, grinding in a mortar and reactive processing. PAni–DBSA acts simultaneously as reinforcement and conductive filler for EPDM rubber, independently of the doping method. Swelling measurements for blends showed that EPDM is partially soluble, evidencing partial interaction between the components. We show that a conductive rubber based on EPDM and PAni can be prepared by reactive processing without a crosslinking agent. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyaniline; EPDM rubber; Conductive rubber; Internal mixer

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1. Introduction

Incorporation of conductive polymers into a hosting polymer substrate, forming a blend, composite or interpenetrated bulk network has been widely used as an approach to combine electronic conductivity with desirable mechanical strength of polymers [1–3]. Polyaniline (PAni) has been intensively studied as a practical conducting polymer material because of its good conductivity, stability and easy synthesis [4]. Doping PAni with inorganic acids produces an unstable and insoluble material [5]. However, an organic protonic acid doping method resulting in a thermally stable doped complex has recently achieved great progress towards stability [6]. The use of bulky protonic acids, such as *p*-toluene sulfonic acid, makes PAni soluble in organic solvents in the doped state and its processing properties are greatly improved [7]. Similarly, dodecylbenzene sulfonic acid (DBSA) has been also used as dopant resulting in a conducting complex, which is also soluble in organic solvents [8]. In blends the protonic acid also enhances the compatibility of PAni with conventional polymers [9]. The conventional method for doping PAni is by mixture in a liquid medium [10]. Recently, several researches reported a "thermal doping" process, in which PAni base emeraldine and DBSA are mixed at high temperature and the formation of a PAni–DBSA conductive complex occurs. The presence of unbound, excess DBSA, only physically mixed with PAni, leads to a dispersion of PAni particles in DBSA, a paste that is mainly ionically conducting. Heating causes solidification of the paste, and the PAni–DBSA complex becomes electrically conducting (1–10 S cm^{-1}). If large amounts of excess DBSA are used, a plasticized complex is obtained [11–13].

In the present study a conductive PAni–DBSA complex prepared by solution, grinding in a mortar and reactive processing and its blends with the elastomer ethylene–propylene-diene (EPDM) prepared by mechanical mixture were investigated. The effect of the

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PAni–DBSA doping method was analyzed. The aim of this study is to obtain an electrically conductive rubber material by reactive processing.

2. Experimental

2.1. Polyaniline preparation

HCl doped PAni was prepared by a pilot-plant scale adaptation [14] of a previously published work [15]. The product was neutralised with an aqueous NH_4OH solution, resulting in PAni emeraldine base (EB). Doping was carried out using three methodologies: (i) stirring EB for 24 h in a 1.5 $\mathrm{mol\,l^{-1}}$ solution of DBSA; (ii) grinding in a mortar EB and DBSA in a 1:2 ratio and (iii) doping EB with DBSA (1:2) by reactive processing in an internal mixer chamber of a Haake rheometer 600 (cam rotors) at 150°C and 50 rpm for 10 min.

2.2. Blend preparation

Blends of EPDM and PAni–DBSA doped using the three above cited methods were prepared in an internal mixer at 150°C and 50 rpm in the following sequence: (a) addition of EPDM; (b) 2 min later addition of PAni–DBSA; (c) processing until constant torque and (d) unloading and calendering.

Flat sheets of $0.2 \times 80 \times 50$ $\mathrm{mm^3}$ were prepared for characterization by compression molding at 150°C and 5 MPa of pressure during 15 min in a Jasco hot press model HP3. The corresponding name of blends in agreement with the doping method is: EPDM/PAni–DBSA-S for solution doping, EPDM/PAni–DBSA-M for grinding in a mortar and EPDM/PAni–DBSA-R for reactive processing.

2.3. Characterization

Optical microscopy (OM) was made using an Olympus-CBA-K equipment with 200× magnification. Stress–Strain tests were done in an EMIC DL 2000 equipment, according to ASTM D412-92 standard using a crosshead speed of 500 $\mathrm{mm\,min^{-1}}$ and a cell of 50 N. Electrical conductivity was measured by an adaptation of the Coleman method [16], using a Keithley 617 programmable electrometer and a four-probe sensor with gold contacts. Soluble fraction (Sf) determination was done by swelling measurements at room temperature in cyclohexane during eight days.

3. Results and discussion

PAni doping was done by the three methods described, blends were prepared and the materials were characterised. EPDM/PAni–DBSA blends using PAni doped by the three different methods were prepared in the same mixer in the conditions described in the experimental part and the variation of the torque as a function of processing time for the preparation was measured (Fig. 1). The difference observed in the curves depend on the PAni used and can be discussed in terms of the interaction among the blends components. The torque versus time curves were divided in four regions, giving the following information about the processing: (a) EPDM plasticization; (b) addition of PAni–DBSA; (c) mixing, homogenization and reaction among the components; and (d) equilibrium of the reaction. Stage (a) and (b) show the expected behavior. For stage (c) we have three possibilities to explain the torque increase: (i) PAni–DBSA dispersion in the EPDM matrix; (ii) PAni–DBSA curing and its physical entanglement with EPDM and (iii) chemical reaction between PAni–DBSA and EPDM (formation of a graft copolymer between PAni and EPDM [17]). There is also an increase in the temperature in the stage (c), indicating the presence of an exothermic reaction. This reaction can be related with the curing processing.

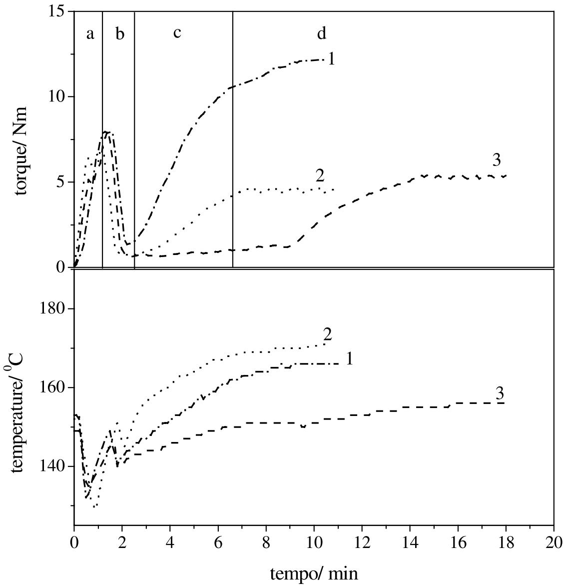

Fig. 1. Torque and temperature curves as a function of processing time for EPDM/PAni–DBSA blends with (1) PAni–DBSA-R, (2) PAni–DBSA-M and (3) PAni–DBSA-S. Stages (a) EPDM plasticization, (b) addition of PAni–DBSA, (c) mixing, homogenization and reaction among the components and (d) equilibrium of the reaction.

In order to identify which process is occurring in stage (c) we determined the swelling parameters such as: soluble fraction, Sf, and relative soluble fraction, $\mathrm{Sf_r}$ (Table 1). These results provide information related to the crosslinking degree of the material. The ability of cyclohexane to dissolve EPDM associated with the long

Table 1
Electrical conductivity (σ), soluble fraction (Sf) and relative soluble fraction (Sf_r) for blends as function of PAni doping method

Doping method	% (w/w) of PAni–DBSA	Sf (%)	Sf_r (%)	σ/S cm^{-1} ($\times 10^{-6}$)
Solution	10	100 ± 2	100	0.08
	20	100 ± 3	100	0.2
	30	100 ± 3	100	0.8
	40	100 ± 4	100	0.8
Grinding in a mortar	10	80 ± 2	72	0.1
	20	70 ± 2	56	0.5
	30	50 ± 1	35	2
	40	50 ± 1	30	2
Reactive processing	10	68 ± 2	61	0.2
	20	56 ± 1.2	45	0.8
	30	30 ± 0.5	21	5
	40	28 ± 0.5	17	5

extraction period (eight days) allows the total extraction of the elastomeric phase if its is not crosslinked. As observed from Table 1, Sf_r values increase with the PAni doping method according to the sequence EPDM/PAni–DBSA-R < EPDM/PAni–DBSA-M < EPDM/PAni–DBSA-S. For EPDM/PAni–DBSA-S blends all EPDM was dissolved. In this case PAni–DBSA complex does not contain excess of DBSA, resulting in a system which consists basically in particles dispersed in a matrix without crosslinking. However, EPDM/PAni–DBSA-M and EPDM/PAni–DBSA-R blends show a partially insoluble EPDM phase. This behavior indicate a kind of crosslinking and physical entanglement or chemical reaction. Considering a blend prepared with 30% (w/w) of PAni–DBSA-M, the Sf_r is 35%. In this case PAni–DBSA is further doped during the homogenization process favoring an entanglement between the components (see stage (c) in Fig. 1). For EPDM/PAni–DBSA-R blends Sf_r is 21% for 30% (w/w) of PAni–DBSA, indicating higher crosslinking degree, entanglement or chemical reaction. The physic aspect of PAni–DBSA-R is like a paste. Due this fact its physical state improves the interaction with EPDM, favoring the curing process.

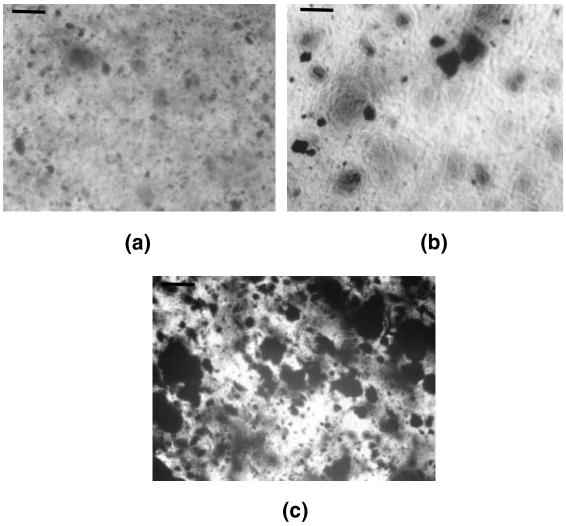

Fig. 2. Optical micrografies for (a) EPDM/PAni–DBSA-S, (b) EPDM/PAni–DBSA-M blends and (c) EPDM/PAni–DBSA-R blends.

To study the dispersion of the PAni phase in EPDM, we obtained the optical micrographies of the blends (Fig. 2). Differences in the viscosity, as seen in the torque curves, act on the dispersion of PAni–DBSA into the EPDM. Dispersion means more than simply distributing particles or mixing then in: it is in fact a matter of breaking down agglomerates and thereby creating large surface areas which have to be wetted by the matrix. This is on the whole an energy-intensive process. It is possible to distinguish different phases for the three PAni–DBSA doping methods. In EPDM/PAni–DBSA-S blends PAni is homogeneously dispersed into EPDM with particle sizes smaller than 50 μm. PAni–DBSA doped by grinding in a mortar and reactive processing forms non-miscible blends with EPDM. From Fig. 2 is possible to see two phases consisting in PAni–DBSA and EPDM/PAni–DBSA. However, from swelling measurements the system can be identified by three different phases: (1) PAni–DBSA; (2) EPDM/PAni– DBSA and (3) EPDM. This fact means that pure EPDM is inside of the EPDM/PAni–DBSA phase.

Doping methods of PAni–DBSA and the differences in the morphology can also affect the mechanical properties (Figs. 3 and 4). Young modulus (Fig. 3), increases with PAni–DBSA concentration independently of the doping method. This increase is related with the reinforcement effect of PAni–DBSA. The increase is less pronounced for EPDM/PAni–DBSA-S blends. This is assigned to the low viscosity of these blends, as seen in the torque curves. Higher modulus values are found for EPDM/PAni–DBSA-M blends and this is also due to

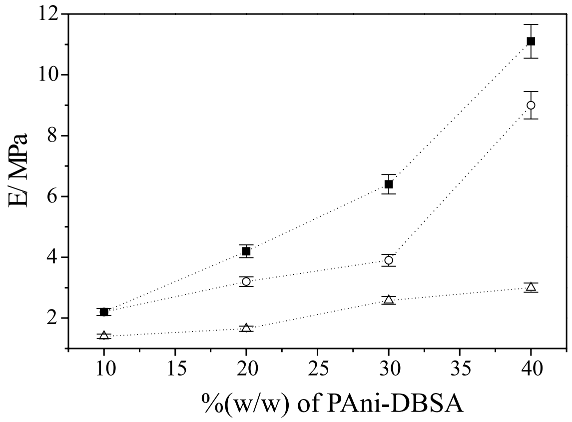

Fig. 3. Young modulus variation as a function of PAni concentration for: (△) EPDM/PAni–DBSA-S, (○) EPDM/PAni–DBSA-R and (■) EPDM/PAni–DBSA-M blends.

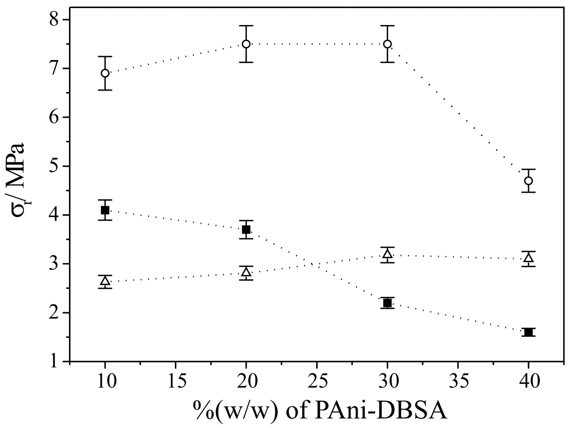

Fig. 4. Tension at rupture variation as a function of PAni concentration for: (△) EPDM/PAni–DBSA-S, (○) EPDM/PAni–DBSA-R and (■) EPDM/PAni–DBSA-M blends.

the viscosity (torque curves) and to the large PAni agglomerates present in the mixture, as observed by OM (Fig. 2).

EPDM/PAni–DBSA-R blends show higher tensile strength in comparison to the other blends, (Fig. 4). The presence of crosslinking produces more resistant materials. This fact, along with the insoluble fraction determination, makes evident the network formation. Tensile strength decreases for blends with 30% and 20% (w/w) of PAni–DBSA-R and PAni–DBSA-M, respectively. Tensile strength and elongation at break depends on the interfacial adhesion between the phases. If the adhesion is not perfect, the fissure that induces sample break originate in the interfacial region. The absence of this adhesion makes this region weaker. Thus, above these concentrations the mixture is more susceptible to imperfections which can be due to the large PAni–DBSA agglomerates.

Conductivity values of PAni–DBSA change with the doping method, being higher for PAni–DBSA doped by reactive processing. The values are 10^{-3}, 1 and 5 $\mathrm{S\,cm^{-1}}$ for PAni–DBSA doped by grinding in a mortar, solution and reactive processing, respectively. Conductivity of the blends increases linearly with PAni–DBSA concentration, independently of the PAni doping method, until ≈30% (w/w) (Table 1) however, the conductivity values depend on the doping method, being higher for blends prepared with PAni–DBSA doped by reactive processing. The level of interaction among the components (PAni, DBSA and EPDM) determines the PAni–DBSA fracturing, the mode of dispersion within the matrix polymer, the blend's morphology and, thus, its electrical conductivity. In agreement, Zilberman et al. [18] verified that blends of PS and PAni–DBSA doped by reactive processing have higher conductivity than those prepared with PAni doped by solution. They assign it to the acid excess in the first case facilitating the dispersion.

4. Conclusions

PAni–DBSA acts as reinforcement and conductive filler in blends with EPDM, contributing to the formation of a network which inhibits EPDM solubilization. Thus, a conductive rubber compound was prepared without the use of a crosslinking agent. The material presents mechanical properties suitable for use as reinforced rubber. Good conductive properties were found for blends with 30% (w/w) of PAni–DBSA, independently of the doping method used. This concentration threshold was previously observed for EPDM blends prepared by mechanical mixing using PAni doped by solution with toluene sulfonic acid [19].

Acknowledgements

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