

# Use of Pyrolysed Oil Shale as Filler in Poly(ethylene-co-vinyl Alcohol)

Ronilson Vasconcelos Barbosa, Ricardo Baumhardt-Neto, Raquel Santos Mauler, Carlos José, Perez Gorga, Cláudia Gazzana Schneider

*Instituto de Química, Universidade Federal do Rio Grande do Sul, Departamento de Química Orgânica, Avenida Bento Gonçalves, 9500, Porto Alegre, Rio Grande do Sul, Caixa Postal 15003, CEP 91501-970, Brazil*

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**ABSTRACT:** The pyrolysed oil shale (POS) obtained from the pyrolysis of bituminous rock was used as filler in poly(ethylene-co-vinyl alcohol) (EVAL). The effects of vinyl alcohol content in the EVAL and the particle size of pyrolysed oil shale in the mechanical properties were investigated. The EVAL was prepared by hydrolysis of poly(ethylene-co-vinyl acetate) (EVA) with 8 and 18 wt % of vinyl alcohol content. The composites were prepared in a rotor mixer at 180°C with concentration of pyrolysed oil shale up to 5 wt %. Stress-strain plots of compression-molded composites showed a synergic behavior in the mechanical properties for low concentrations (1–5 wt %) of POS in all particle sizes and EVAL used. Such behavior indicates a close packing and

strong interactions between the inorganic filler and the polymer. Increasing of the vinyl alcohol content of EVAL improved the compatibility between the polymer and filler, but decreasing the POS particle size had no effect on the properties. The modulus and the ultimate tensile strength also increased in all concentrations of POS for both EVAL. Mechanical properties and dynamic mechanical analysis also demonstrated the compatibility between EVAL and POS. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1658–1665, 2004

**Key words:** composites; fillers; mechanical properties

## INTRODUCTION

Pyrolysed oil shale (POS) is an inorganic material that originates from the oil extraction of bituminous rock, through pyrolysis at approximately 400°C. POS, with low oil concentration (between 12% wt), goes back to the mines after extraction, increasing production costs and requiring appropriate environmental control. During the pyrolysis process the organic material contained in the rock is transformed into oil and gas, and another part produces a coke that is retained in the mineral matrix. POS is a black mineral consisting of a consolidated organic-inorganic mixture with most of the inorganic part constituted of silicates. Many of the mineral fillers currently being used in plastics, such as clay, mica, and talc, also consist of silicate.<sup>1</sup> The use of mineral as fillers in polymeric materials is an economic practice in the polymer industry today. Most mineral fillers are used in industry to reduce production costs; among them the most important are alumina, calcium carbonate, talc, clay, and others. The use of POS as filler in polymer materials is new and few works referring to the subject are found in the

specialized literature.<sup>1</sup> According to the literature, the objective of blending oil shale with polymer is to promote the decomposition of the oil shale in the pyrolysis process.<sup>2,3</sup>

In previous work we showed the role of surface organic compounds on pyrolysed oil shale in promoting a better dispersion between high-density polyethylene (HDPE) and POS.<sup>4</sup> These interactions are also responsible for better phase dispersion and the lost of ultimate tensile strength and elongation at break with the decrease of particle size of pyrolysed oil shale.<sup>4,5</sup> The results of mechanical properties of poly(ethylene-co-vinyl acetate) (EVA)-8/POS and EVA-18/POS showed that three factors were related to the mechanical properties of the mixtures of polymer/POS: (a) POS particle size: the smaller the particle size, the better the mechanical properties of the composites compared to the pure polymer. This behavior may be explained by the best dispersion of the particle in the polymer matrix; (b) concentration of POS: the amount of POS or any other filler is very important for the mechanical properties. The increase of filler content tends to determine losses in the mechanical properties, mainly when the interface polymer/filler shows poor dispersion; (c) the polarity of the polymer: when the polymer polarity (vinyl alcohol (VA) content) was increased, the mechanical properties remained almost the same at higher filler content compared with the pure polymer.

Correspondence to: R. V. Barbosa (Ronilson@iq.ufrgs.br).

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Based on the results obtained with the mixture of HDPE/POS<sup>4</sup> and EVA/POS,<sup>5</sup> we decided to verify the effect of polarity and the interaction with the hydroxyl bond in the compatibilization of the composites of poly(ethylene-co-vinyl alcohol) EVAL/POS. If the residual coke in it POS has groups like -COOH, -OH, and -SH, among others, we could have better results in the mechanical properties due to the simple fact that a polymer of larger polarity would have a better dispersion with an inorganic load and association with the hydrogen bond can increase the adhesion of the phases.

Since the interaction between polymer and filler must be strongly dependent on polarity, we investigated the use of a more polar polymer to verify such behavior. In addition, after oil shale pyrolysis some residual oil remains in the inorganic matrix, and it can be useful as a compatibilizing agent between the inorganic and organic phases in compounds of EVAL/POS. It would also enhance some mechanical properties of this kind of composite, as we observed in earlier results<sup>4,5</sup>. Besides the fact that better dispersion can modify the mechanical properties with synergism of these properties, and the synergism of mechanical properties is associated with particle size and concentration of POS in the compound, we decided to use no more than 5 wt % of POS in the compounds. The effect of polarity is important, as seen in the compounds EVA/POS, but this effect can be pronounced in the presence of hydroxyls of EVAL.

With the aims of studying the POS application as a filler for EVAL and understanding the effect of the filler on the mixtures of EVAL with pyrolysed oil shale, EVAL/POS compounds were obtained with different filler concentration and particle size. The mechanical properties, dynamic mechanical thermal analyses, and morphology of the compounds were investigated.

## EXPERIMENTAL

### Materials

TECPOL—Tecnologia em Polímeros S.A. and Petrobras S.A. supplied the POS. It was dried at 100°C, milled, and fractionated according to particle size: 125, 88.9, 53.3, and 44.5  $\mu\text{m}$ . Petroquímica Triunfo S.A. supplied the EVA and two different grades were used: one sample with 8 wt % of vinyl acetate (VAc) content (EVA-8) and another one with 18 wt % of VAc content (EVA-18).

### Poly(ethylene-co-vinyl acetate) hydrolysis

EVAL with 8 wt % (EVAL-8) and 18 wt % (EVAL-18) of VA was obtained from EVA hydrolysis: a solution of EVA (10.0 wt %) in toluene with 0.06 mol % of

sodium hydroxide (5.0 wt % methanol solution) was kept under reflux for 120 min. After this period, the material was neutralized with aqueous HCl solution (5.0 vol %), at 80°C for 30 min. Then, the aqueous layer was eliminated and the polymer (organic layer) was precipitated into methanol, filtered, washed several times with methanol, and dried in vacuum. Under these conditions the EVA copolymer obtained exhibited a hydrolysis degree of 100 mol % (related to the acetate content), according FTIR results.<sup>4</sup>

### Compound preparation and characterization

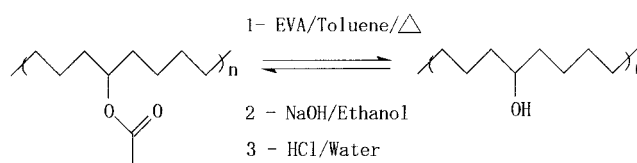
Compounds of EVAL-8/POS and EVAL-18/POS were prepared in a Haake Rheomix 600 mixer at 180°C. The rotor speed was 20 rpm and the mixing time was 15 min. The compounds were molded by compression at 180°C for 3 min under 4000 lb in a Carver Monarch press. The tensile properties were measured at room temperature in accordance with ASTM D882–83, using an EMIC 10.000 testing machine, at a crosshead speed of 10 mm/min.

### Dynamic mechanical analysis (DMA)

For the DMA measurements, the samples were pressed at 180°C for 3 min at 4000 lb and allowed to cool at room temperature. Rectangular films averaging 10  $\times$  12 mm and 0.1–0.2 mm thick were prepared and submitted to the dynamic-mechanical experiments with the help of a Polymer Laboratories Dynamic Mechanical Thermal Analyzer MK II Instrument (DMTA) in the tensile mode. The measurements were carried out at a heating rate of 2°C/min, with a frequency of 1 Hz. The temperature ranged from -125°C to the melting point of each component (160 to 180°C, depending on the sample).

### Morphology

For scanning electron microscopy analysis, the samples were immersed in liquid nitrogen for about 20 min and then fractured and the surface was coated with gold vapor. Micrographs were taken by a JEOL Model JSM 5800 scanning electron microscope (SEM). The samples for this test were prepared by compression



**Figure 1** Scheme of the hydrolysis reaction of EVA-8 and EVA-18 to obtain EVAL-8 and EVAL-18.

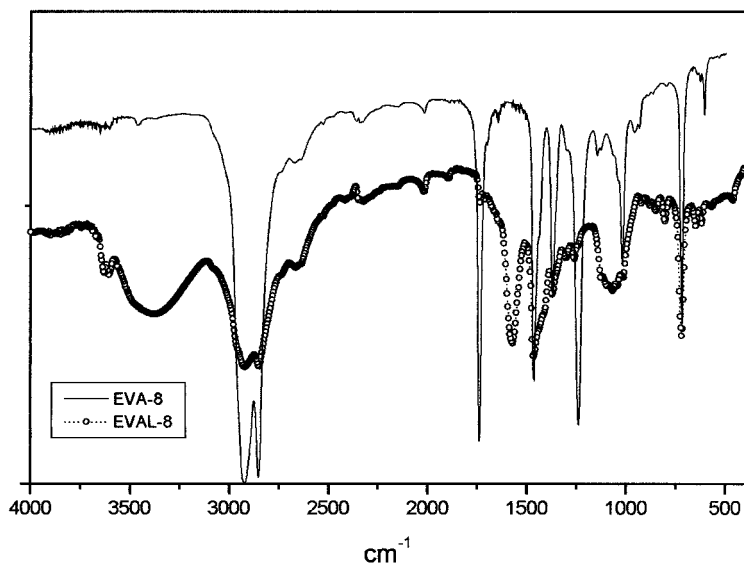


Figure 2 Infrared spectrum of EVA-8 and EVAL-8.

sion at 180°C for 3 min under 4000 lb in a Carver Monarch press.

EVAL-18 were used in the compound after being dried at 70°C for 3 h under nitrogen.

## RESULTS AND DISCUSSION

The EVA hydrolysis described in previous work<sup>6</sup> and the scheme of the reaction are shown in Figure 1. Hydrolysis was confirmed by FTIR and the spectrum is shown in Figures 2 (EVA-8 and EVAL-8) and 3 (EVA-18 and EVAL-18). The peak at 1780  $\text{cm}^{-1}$  in EVA-8 and EVA-18 disappears (carboxylic ester group) and a new band appears at 3200–3700  $\text{cm}^{-1}$  in EVAL-8 and EVAL-18 (hydroxy group). EVAL-8 and

### Composite preparation

Figure 4 shows the graph of torque during the processing of the EVAL-18/POS composites with different POS particle size. It can be observed that when the concentration of POS was 5 wt %, the torque after 5 min is stable, showing that the processing occurred without decomposition of EVAL under the conditions used.

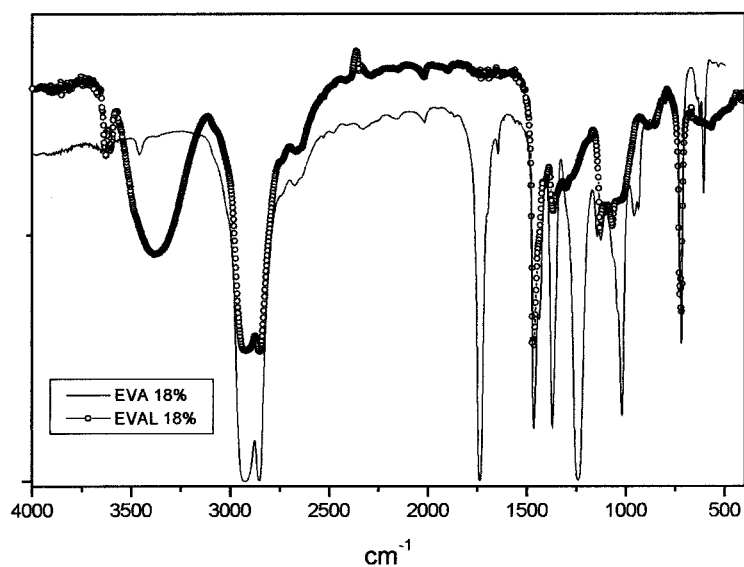


Figure 3 Infrared spectrum of EVA-18 and EVAL-18.

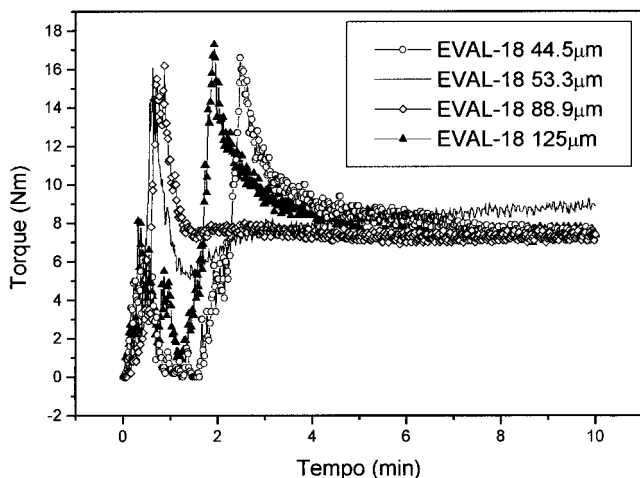


Figure 4 Graphs of torque versus time during the processing of EVAL-18/POS.

**Tensile properties**

The tensile properties of EVAL-8, EVAL-8/POS, EVAL-18, and EVAL-18/POS as a function of filler content are shown in Table I. For all composites the ultimate tensile strength, elongation at break, and modulus increase with the addition of 1 or 5% wt of POS compared with the results of the pure EVAL. In the case of EVAL-8/POS the ultimate tensile strength increases more than 30% and the modulus increase more than 35% for all composites when only 1% wt of POS was added to EVAL-8. The ultimate tensile strength and modulus of samples with 5% wt of POS are higher than that of the pure EVAL-8, but this effect is not linear. In the case of EVAL-18/POS samples, the ultimate tensile strength and the modulus do not reach the EVAL-8/POS values for those properties. It is important to observe that the filler particle size does not influence the mechanical properties of the composites. Considering samples filled with 1 and 5% POS, there is a reinforcing effect regardless of particle size. The

concentration of the particle is optimum at 1 wt %, and besides the increase of the result when 5 wt % was put in the compounds, the results of the properties were smaller than that of the compounds with 1 wt %. Because of this and based on the results of mechanical properties of HDPE/POS<sup>4</sup> and EVA/POS<sup>5</sup>, we do not make compounds with POS concentration of greater than 5 wt %. The optimum filler concentration is around 1%. Higher amounts of POS resulted in poor mechanical properties when compared to the 1% samples.

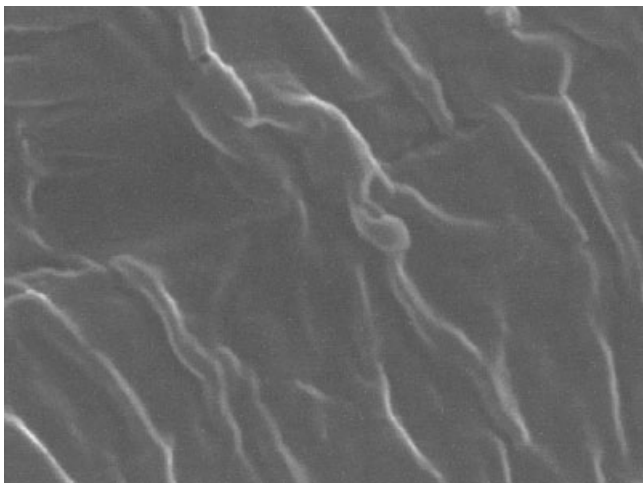
From these results, as expected, we have reached better mechanical properties than those observed for the EVA/POS<sup>4</sup> composites, but is not possible to attribute this effect only to the polarity of both polymers or to the hydrogen bond in the EVAL polymer and the POS or to both effects.

These results suggest the role of organic compounds on the POS surface in promoting a better adhesion between POS and EVAL. They may contribute to the dispersion development between filler and EVAL by two mechanisms: first, a better spreading of the polymer on the filler surface, due to the chemical interactions, and/or *in situ* plastification of EVAL by the organic adsorbed phase being released during processing.

The interface role on the filler dispersion and mechanical properties is taking place in this system, in a similar way as studied by other authors. Nagata et al.<sup>7</sup> showed by SEM that the BaTiO<sub>3</sub> particles were more easily dispersed in the EVA matrix (7 and 15 mol % of vinyl acetate) than in LDPE. It was observed that the polar groups introduced into a nonpolar LDPE improved the dispersion between BaTiO<sub>3</sub> particles and the polymer. These results suggest that the degree of dispersion of the BaTiO<sub>3</sub> particles was mainly based on the hydrogen bonding and/or dipole-dipole interaction between the particle surface and vinyl acetate groups of EVA. We suppose that a similar mechanism would explain our results.

**TABLE I**  
Mechanical Properties of EVAL/Filler contents

EVAL (wt%)	POS (wt% - µm)	Ultimate tensile strength (MPa)		Elongation at break (%)		Modulus (MPa)	
		EVAL-8	EVAL-18	EVAL-8	EVAL-18	EVAL-8	EVAL-18
100		5.6 ± 0.9	8.6 ± 1.6	26.1 ± 14	33.9 ± 15	219 ± 49	372.8 ± 40
99	01-125	7.4 ± 0.9	8.8 ± 1.6	26.4 ± 10	28.0 ± 11	336 ± 36	448.6 ± 78
95	05-125	7.0 ± 0.4	10.7 ± 0.8	18.2 ± 5.7	23.6 ± 4.4	278 ± 22	417.6 ± 45
99	01-88.9	8.8 ± 0.7	9.8 ± 0.6	21.7 ± 5.3	16.5 ± 3.2	357 ± 52	347.5 ± 98
95	05-88.9	8.4 ± 0.3	9.7 ± 0.2	11.0 ± 1.6	25.8 ± 3.4	298 ± 18	246.0 ± 83
99	01-53.3	9.9 ± 0.7	9.9 ± 0.1	23.5 ± 20.2	30.8 ± 6.6	305 ± 37	274.5 ± 85
95	05-53.3	8.2 ± 0.4	9.7 ± 0.2	10.8 ± 0.9	25.8 ± 3.4	291 ± 22	246.2 ± 83
99	01-<44.5	7.6 ± 0.6	9.7 ± 1.1	37.8 ± 9.6	34.4 ± 8.0	330 ± 35	527.2 ± 47
95	05-<44.5	6.2 ± 0.5	8.5 ± 1.1	36.8 ± 10.4	17.5 ± 1.6	247 ± 30	440.2 ± 35

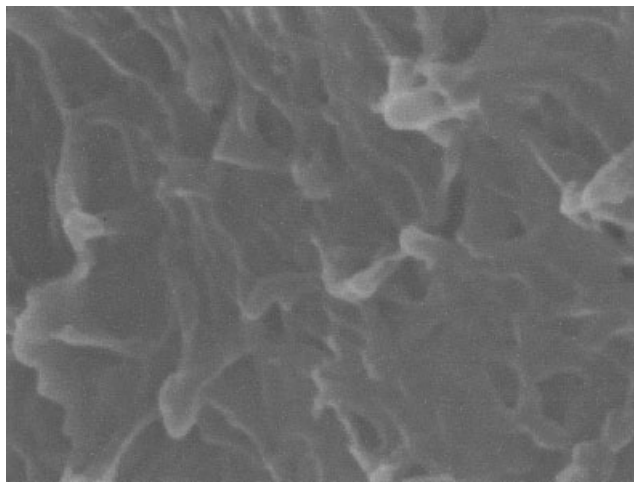


**Figure 5** SEM micrographs of EVAL-8/POS 125  $\mu\text{m}$  (95/05). Original magnification: 30,000 $\times$  (1 cm/4.4  $\mu\text{m}$ ).

It has been suggested that the diameter of POS particles in HDPE<sup>4</sup> has some influence in the yield stress and elongation at yield stress of HDPE/POS composites. This behavior arises from the loss of ability of the polymeric chains to reorganize when submitted to a deformation and it is intimately linked to the existence of adhesion between the polymer/POS phase, promoted by the organic residue of the mineral filler. The effect is not evident in EVA-8 and is pronounced in EVA-18 compounds,<sup>5</sup> but in the case of EVAL it is possible to observe this effect.

#### Morphology of the compounds

The effect of POS on the morphology of EVAL was investigated. The micrographs of the etched surface of EVAL/POS composites do not show any hole, indicating that POS is bonded to EVAL. Figure 5 presents the micrographs of cryogenically fractured surface EVAL-8/POS 125  $\mu\text{m}$  (95/05) and it is impossible to distinguish the continuous and the dispersed phase. Figure 6 presents the micrographs of EVAL-8/POS 44.5  $\mu\text{m}$  (95/05) composite and also in this case it is not possible to see holes or any other kind of structure. In Figures 5 and 6 it is seen that the POS is completely involved by EVAL, indicating a great compatibility between the two phases. Figures 7 and 8 present the micrographs of EVAL-18/POS 125  $\mu\text{m}$  (95/05) and EVAL-18/POS 44.5  $\mu\text{m}$  (95/5) samples. The micrographs shows the same behavior as observed for the composites with EVAL-8, but a different topography with respect to the amount and size of the structures. They are bigger than those observed for EVAL-8. This behavior indicates that the increase of polarity and the hydroxyl groups in the EVAL improve the filler dispersion in the polymer matrix.

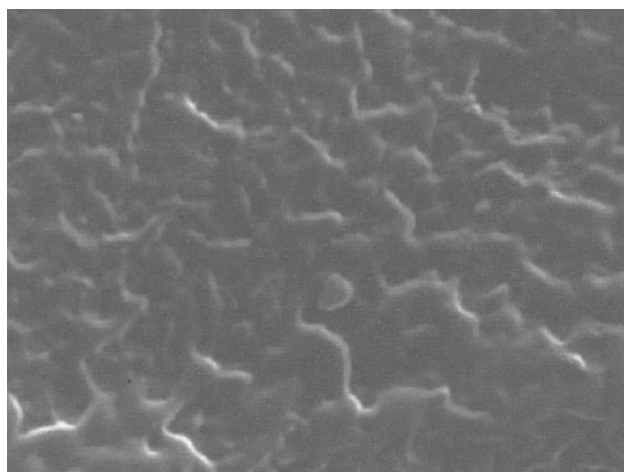


**Figure 6** SEM micrographs of EVAL-8/POS 44.5  $\mu\text{m}$  (95/05). Original magnification: 30,000 $\times$  (1 cm/4.4  $\mu\text{m}$ ).

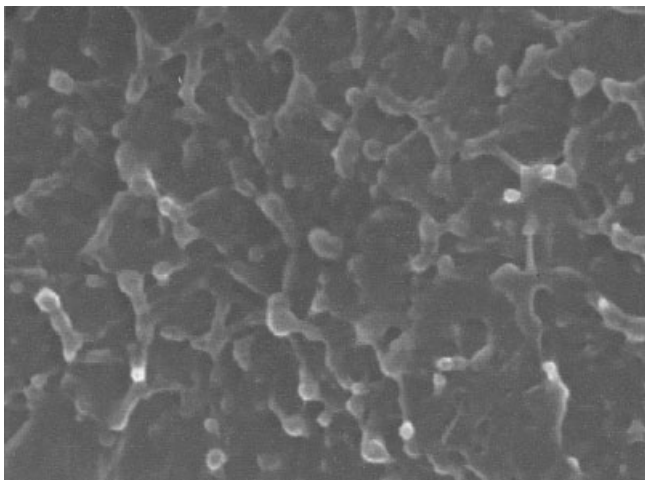
In the case of samples that were broken at the cryogenic temperature the resulting surface suggests that the polymer has experienced some flow during the fracture process. This type of breakage was observed in another work,<sup>8</sup> but at room temperature, and it would be additional evidence of the good adhesion between polymer and filler.

#### DMTA analysis

Figures 9 and 10 show the logarithm of the storage modulus versus temperature for EVAL-8/EVAL-8/POS (95/05) and EVAL-18/EVAL-18/POS (95/05) (particle size of 44.5  $\mu\text{m}$ ), respectively. In general, the storage modulus for both systems was the same. The absence of change in the storage modulus could not necessarily be linked to mechanical properties of the composites. The EVAL-8 and EVAL-8/POS systems



**Figure 7** SEM micrographs of EVAL-18/POS 125  $\mu\text{m}$  (95/05). Original magnification: 30,000 $\times$  (1 cm/4.4  $\mu\text{m}$ ).



**Figure 8** SEM micrographs of EVAL-18/POS 44.5 μm (95/05). Original magnification: 30,000× (1 cm/4.4 μm).

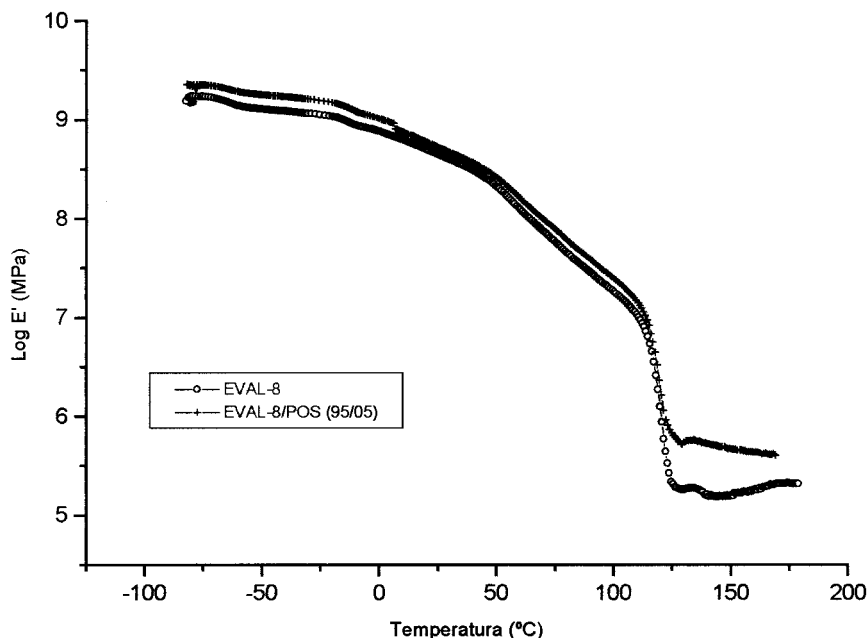
had the same behavior with respect to storage modulus, but the mechanical properties of the EVAL-8/POS (95/05) mixtures were better than that of EVAL-8, and the same behavior was observed for EVAL-18/POS (95/05) and EVAL-18.

The dynamic mechanical thermal analysis test only determines the response of the polymeric phase to a vibratory tension, and the tensile properties determine the capacity of the compound to support a tension at the fracture. Because of this it is impossible to find a relationship between these tests. The test was sensitive to interactions between the phases, as in the case of EVAL-8, EVAL-18, and their composites. The capacity

of the system in storing energy was harmed with the introduction of POS.

Figures 11 and 12 show the loss tangent versus temperature curves for the systems EVAL-8/EVAL-8/POS (95/05) and EVAL-18/EVAL-18/POS (95/05) (particle size: 44.5 μm), respectively. Two regions should be considered in the analysis. The first one at 125°C for both EVAL-8 and EVAL-18 that normally corresponds to the α-transition apparently was not affected by the addition of pyrolysed oil shale. The second is at -60 and 90°C for EVAL-8 and EVAL-18, respectively, corresponding to the β transition. Both α and β transitions of EVAL-8 and EVAL-18 compounds showed the same behavior.

The β transition corresponds to the glass transition of both EVAL, and it is known that it is associated with the relaxation of a main chain in the amorphous phase of the EVAL vinyl unit. Nagata et al.<sup>7</sup> showed that β-peak shift about +5°C in EVA/BaTiO<sub>3</sub> composite systems and the β-peak temperature for EVA/graphite composite systems were independent of the filler concentration. The polarity of POS is closer to graphite than to BaTiO<sub>3</sub>, in agreement with the results presented by the EVA-8/POS system. However, for the EVA-18/POS<sup>5</sup> system the decrease in modulus and the shift of α,β-peak temperature suggest an interaction between EVA-18 and POS (as observed by Nagata et al.<sup>7</sup> in EVA/BaTiO<sub>3</sub> composite systems). This anomalous behavior suggests that there is a critical concentration of acetate group in EVA starting from which the system shows some polar interaction, decreasing the elastic response and inducing a shift of the α,β-



**Figure 9** Storage modulus versus temperature curves for EVAL-8 polymer and EVAL-8/POS 44.5 μm (95/05) composite.

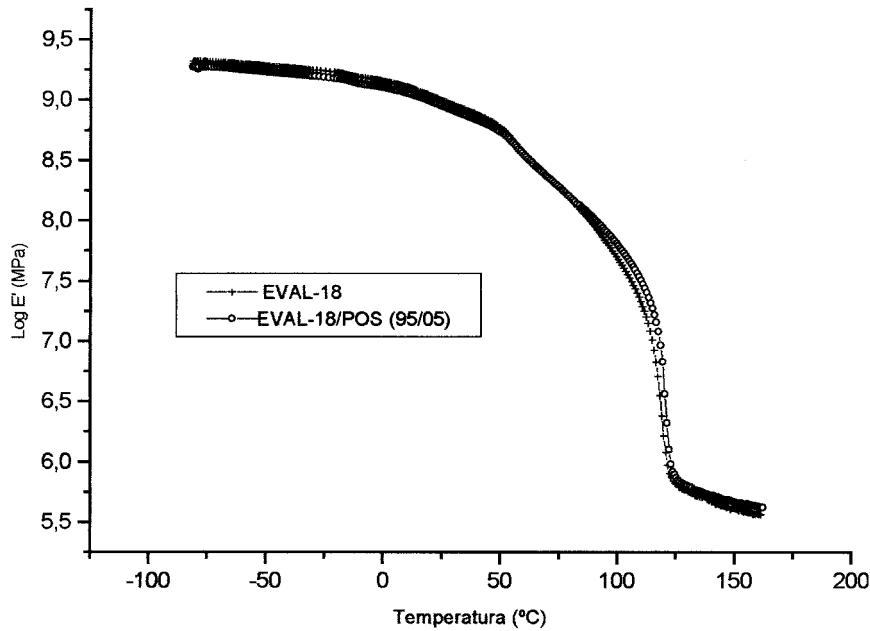


Figure 10 Storage modulus versus temperature curves for EVAL-18 polymer and EVAL-18/POS 44.5  $\mu\text{m}$  (95/05) composite.

peak temperatures. But for EVAL-8 and EVAL-18 this behavior was not observed. The difference in these three systems is the possibility that EVAL can establish hydrogen bonds with POS.

It is known that fillers and reinforcing agents may have viscoelastic characteristics in plastic materials. On the other hand, they can work as purely elastic systems while the polymer and the filler/polymer interface shows a viscoelastic behavior. The addition of a filler or a reinforcing agent to a polymer increases

the modulus of the system.<sup>8</sup> This behavior was not observed in the EVAL system, perhaps because the pyrolysed oil shale also acts as a lubricant.

### CONCLUSION

The experiments here reported suggest that the organic compounds in the surface of pyrolysed oil shale can promote a better adhesion between that of

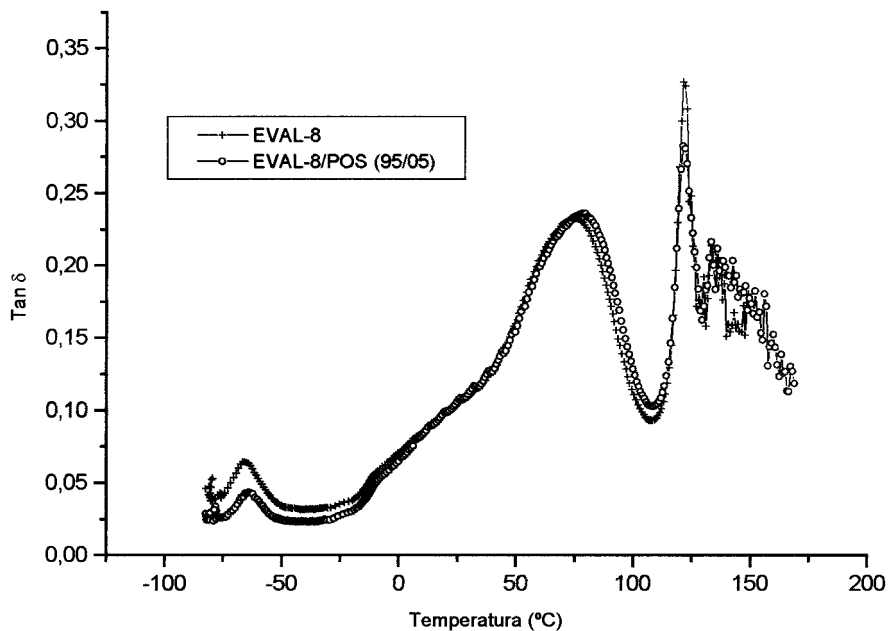
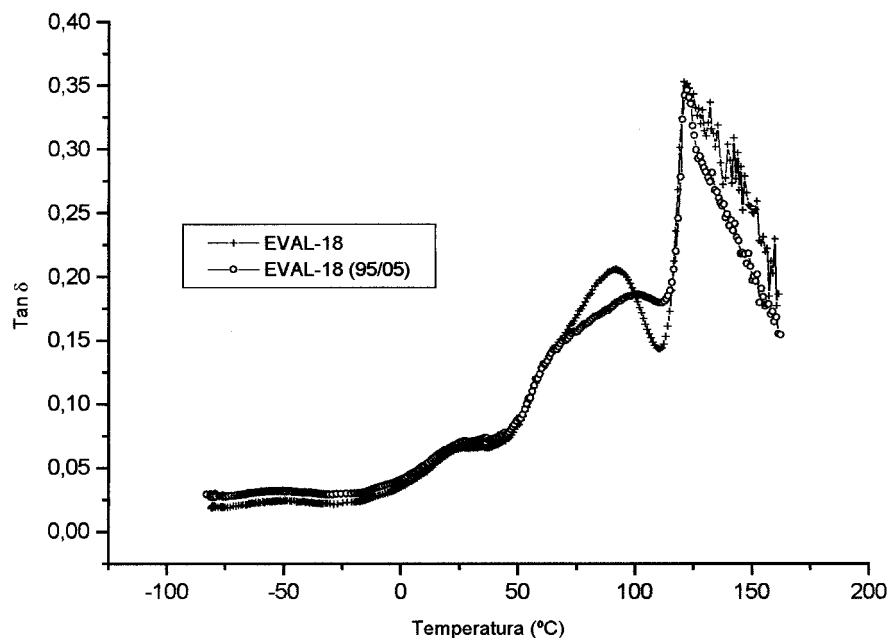


Figure 11 Loss tangent ( $\tan \delta$ ) versus temperature curves for EVA-8 polymer and EVAL-8/POS 44.5  $\mu\text{m}$  (95/05) composite.



**Figure 12** Loss tangent ( $\tan \delta$ ) versus temperature curves for EVA-18 polymer and EVAL-18/POS 44.5  $\mu\text{m}$  (95/05) composite.

the filler and both polymers, EVAL-8 and EVAL-18. Better dispersion between polymer and filler improves the mechanical properties. Such improvement of the mechanical properties is not associated with the particle size as was observed in the system EVA-18/POS. However, differently from that observed for EVA, the concentration of vinyl alcohol is not an important factor for the mechanical properties. The high content of vinyl alcohol is important to the morphology, but this behavior is not with the mechanical or dynamic properties.

It was not possible to dissociate the effect of hydrogen bonding and the polarity of EVAL with POS and its behavior with respect to the morphology and mechanical and dynamic response.

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