

Comparative Effects of Pyrolyzed Oil Shale and Pyrolyzed Burned Oil Shale Used as Fillers in Poly(ethylene-co-vinyl alcohol)

Ronilson Vasconcelos Barbosa,^{1,2} Ricardo Baumhardt-Neto,¹ Raquel Santos Mauler,¹ Eder Cláudio Lima,¹ Cláudia Gazzana Schneider¹

¹Instituto de Química, Universidade Federal do Rio Grande do Sul, Departamento de Química Orgânica, Avenida Bento Gonçalves, 9500, Porto Alegre (Caixa Postal: 15003), Rio Grande do Sul, Brasil

²Departamento de Química, Universidade Federal do Paraná, Centro Politécnico, Jardim das Américas, Curitiba (Caixa Postal 19081), Paraná, Brasil.

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ABSTRACT: Pyrolyzed oil shale (POS) obtained from the pyrolysis of bituminous rock was burned in a normal atmosphere (POSB) to remove the organic phase and then used as a filler in poly(ethylene-co-vinyl alcohol) (EVAL). The effects of vinyl alcohol content, POSB particle size, and POSB concentration on the composite were investigated through measurement of mechanical properties. Composites were prepared in a rotor mixer at 180°C. Stress-strain plots of compression-molded composites showed synergic behavior of the mechanical properties with low concentrations (1–5 wt %) of POSB, regardless of particle size or type of EVAL. Such behavior suggests close packing and strong interactions between inorganic filler and polymer, with the effects rein-

forced by the mechanical properties. It was observed that the absence of the organic phase in the modified material improved the mechanical properties of the composites. Increasing the vinyl alcohol content improved the compatibility between polymer and filler in the EVAL/POS but did not affect the compatibility in EVAL/POSB composites. The relationship of mechanical and morphological behavior in the EVAL/POS and EVAL/POSB composites indicated that different factors were at play to explain the compatibility between the EVAL and the inorganic phase. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1859–1864, 2006

Key words: composites; EVAL; EVA

INTRODUCTION

Pyrolyzed oil shale (POS) is an inorganic material originating from the extraction of oil from bituminous rock through pyrolysis at approximately 400°C. During the pyrolytic process the organic material in the rock is transformed into oil and gas, and another part produces a coke that is retained in the mineral matrix. Pyrolyzed oil shale (POS) is consolidated with the inorganic material in an organic phase, with most of the inorganic part being composed of silicates. Many of the minerals fillers currently used in plastics, clay, mica, and talc, also consist of silicate.¹ The polymer industry mostly uses minerals as filler in polymeric materials for economic reasons, to reduce production costs; the most important of these minerals are alumina, calcium carbonate, talc, and clay. The use of POS as filler in polymer materials is new, and there are few published works in the specialized literature that refer to this subject.^{1–5}

In a previous work we showed the role of surface organic compounds on pyrolyzed oil shale in promoting a better interaction between high-density polyethylene (HDPE) and POS.⁴ These interactions also were responsible for better phase dispersion but were not enough to improve the ultimate tensile strength and elongation at break with a decrease in particle size of pyrolyzed oil shale.⁴ In another work,⁵ we related the mechanical properties of EVA-8/POS and EVA-18/POS to three factors. First was POS particle size. The smaller the particle size, the better were the mechanical properties of the composites compared to the pure polymer. This behavior could be explained by the best dispersion of the particle in the polymer matrix. Second was POS concentration. The amount of POS or any other filler was very important for the mechanical properties. Increased filler content tended to determine loss in mechanical properties, mainly when the polymer/filler interface showed poor interaction. The third factor was the polarity of the polymer. Compared with what occurred in the pure polymer, with increasing polarity (VA content) of the composites, the mechanical properties remained almost the same as with a higher filler content.

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

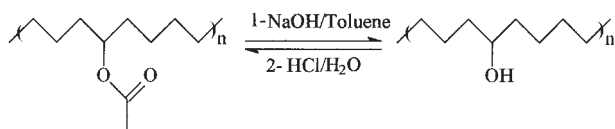


Figure 1 Scheme of the hydrolysis reaction of EVA-8 and EVA-18 to obtain EVAL-8 and EVAL-18.

On the basis of the results obtained with the HDPE/POS⁴ and EVA/POS⁵ mixtures, we decided to verify the effects of polarity and the interaction by hydrogen bonds in the compatibilization of the EVAL/POS.⁶ The reported experiments suggest that organic compounds on the surface of pyrolyzed oil shale can promote a better interaction between the filler and the EVAL-8 or EVAL-18, improving the mechanical properties. Such improvement was not associated with particle size, as was observed in the EVA-18/POS⁵ system. However, different than what was 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 for the morphology but has no effect on the mechanical or dynamic properties. It was not possible to dissociate the effects of hydrogen bonding and polarity of the EVAL/POS interactions. To find out if groups like —COOH, —OH, and —SH, all part of the coke in POS, could have stronger interactions with higher-polarity polymers, we decided to remove the organic phase of the POS (coke) by burning it in the presence of oxygen and to study its effects as a new filler for EVAL.

EXPERIMENTAL

Materials

TECPOL (Tecnologia em Polímeros S.A., Curitiba, Brasil) and Petrobras S.A. (Rio de Janeiro, Brasil) supplied the POS. It was dried at 100°C, milled, and fractionated according to particle size: 125, 88.9, 53.3, and 44.5 μm . The POSB was prepared by burning the POS (with defined particles size) at 500°C for 5 h in the presence of oxygen. Petroquímica Triunfo S.A. (Porto Alegre, Brasil) supplied the two grades of EVA, one with 8 wt % vinyl acetate content (VAc), EVA-8, and the other with 18 wt % VAc (EVA-18).

Poly(ethylene-co-vinyl acetate) hydrolysis

EVAL with 8 mol % (EVAL-8) and EVAL with 18 mol % (EVAL-18) vinyl alcohol (VA) were obtained from EVA (8 and 18 mol %) hydrolysis (Fig. 1). A solution of EVA in toluene (10 wt %) with 0.06 mol % sodium hydroxide (5.0 wt % methanol solution) was kept under reflux for 2 h. Then the material was neutralized with an aqueous HCl solution (5.0 vol %) at 80°C for

30 min. Next the aqueous phase was eliminated, and the polymer (organic phase) was precipitated into methanol, filtered, washed several times with methanol, and dried under vacuum. In such conditions the resulting EVAL showed a degree of hydrolysis of 100 mol % (related to the acetate content) according FTIR results.⁴

Composite preparation and characterization

Composites of EVAL-8/POSB and EVAL-18/POSB 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 composites 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.

Chemical analysis of cadmium, arsenic, and lead

An atomic absorption spectrometer (Model AAS5EA; Zeiss, Jena, Germany) equipped with a deuterium lamp background correction system, a transversely heated graphite tube atomizer (TGA), and an MPE 5 auto sampler was used to perform the chemical analysis. The TGA tubes (IC graphite tubes, Part No. 07-8102525) with pin platforms were used with thermal treatment for permanent modifier deposition, using the procedure reported previously by Lima et al.^{7,8} Tungsten-rhodium permanent modifier was used throughout.

Measurements were made at the following analytical wavelengths and slit settings: As—193.7 nm, slit 0.7 nm; Cd—228.8 nm, slit 0.7 nm; Pb—283.3 nm, slit 0.7 nm. Hollow cathode lamps (Imaging and Sensing Technology, Horseheads, NY) of As, Cd, and Pb were utilized according to the instrument recommendations.

The heating programs employed for the different analyses and samples using the permanent modifier were described previously.⁸ All measurements were carried out with at least three replicates and were based on integrated absorbance. Argon (White Martins, Esteio-RS, Brazil) was used as a protective gas throughout.

High-purity deionized water (resistivity 18.2 M Ω cm) was used throughout. Analytical—reagent-grade HNO₃ and HCl (Merck, Rio de Janeiro-Brazil) were distilled in quartz sub-boiling stills (Kürner, Rosenheim, Germany). Hydrofluoric acid (Merck, Rio de Janeiro, Brazil) was used without purification.

Five replicates of each pyrolyzed oil shale were decomposed according to the following procedure. A 0.2-g sample was accurately weighed into a Teflon digestion bomb (Tecnal, Piracicaba-SP, Brazil), and 2

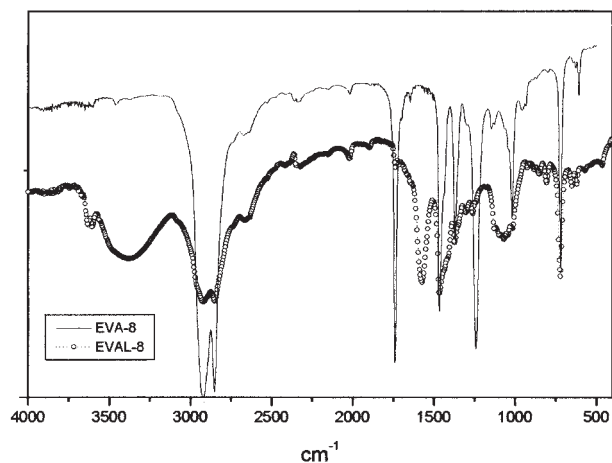


Figure 2 Infrared spectrum of EVA-8 and EVAL-8.

mL of HNO_3 , 6 mL of HCl , and 5 mL of HF were added to the bomb, which was capped and placed in an aluminum digestion block with a capacity for 15 bombs (Tecnal, Piracicaba-SP, Brazil). The samples were heated at 150°C for 8–10 h. Afterward, the bomb caps were removed, a new aliquot of the acid mixture was added, and the heating procedure was repeated in order to completely dissolve the sample. After the bombs reached room temperature, the caps of the bombs were removed, 1 mL of H_2SO_4 (Merck, Darmstadt, Germany) was added to the digestion bombs, and the sample solutions were boiled to near dryness in order to eliminate excess HF . Then the small amount of sample digest was transferred quantitatively to a 25- to 100-mL volumetric flask, adjusting the final acidity with 1% (v/v) HNO_3 .

RESULTS AND DISCUSSION

The hydrolysis of EVA was confirmed by FTIR, and the spectrum is shown in Figures 2 (EVA-8 and EVAL-8) and 3 (EVA-18 and EVAL-18). EVAL-8 and EVAL-18 were used in the composite after drying at 70°C for 3 h under nitrogen.

Chemical analysis of cadmium, arsenic, and lead

It was important to determine the concentrations of heavy metals in the POS in order to certify that it was possible for this product to be used as filler in polymers because such metals are harmful to health above certain values.

The analyses detected values of $0.49 \mu\text{g/g}$ for cadmium, $11.6 \mu\text{g/g}$ for lead, and $49.6 \mu\text{g/g}$ for arsenic. Taking as a reference the concentrations of heavy metals allowed for the packaging of foods in Brazil, which are $3 \mu\text{g/g}$ for arsenic, $2 \mu\text{g/g}$ for cadmium, and $10 \mu\text{g/g}$ for lead, only the arsenic had a value above the

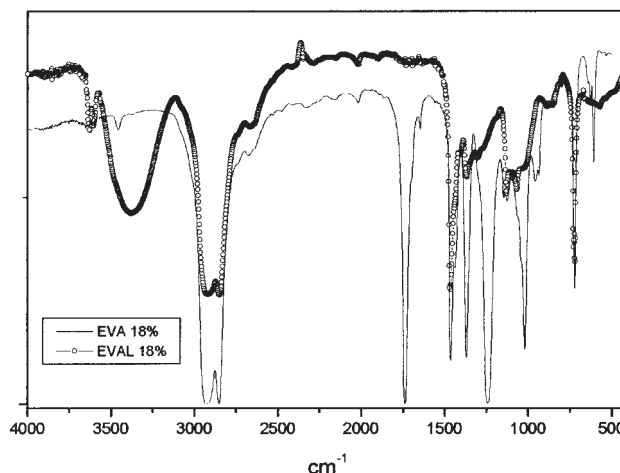


Figure 3 Infrared spectrum of EVA-18 and EVAL-18.

limit. As the concentration of the POS used in the composite was 5 wt %, the concentration of the metal in the composite would be below the allowed limit. However, as the samples were prepared by POS thermal decomposition and not by extraction, it was possible to verify that the metal released from the composite should have been smaller than the detected values.

Composite preparation

Figure 4 shows the plot of torque as a function of time during the processing of the EVAL-18/POSB (5 wt %) composites with different-sized POSB particles. It was observed that after 5 min the torque was stable, showing that processing occurred without decomposition of the EVAL under such experimental conditions.

Tensile properties

The tensile properties of the EVAL-8, EVAL-8/POSB, EVAL-18, and EVAL-18/POSB as a function of filler

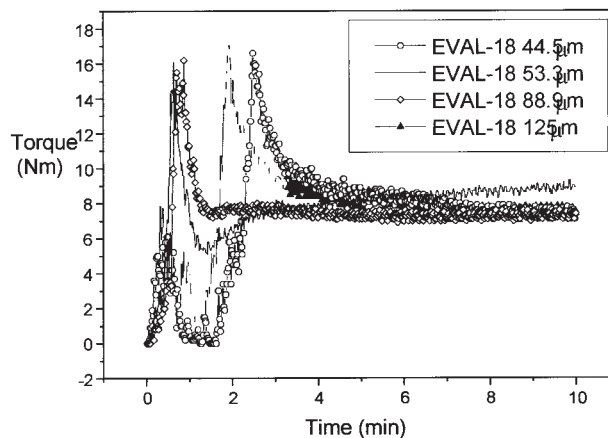


Figure 4 Torque versus time during the processing of the EVAL-18/POSB.

TABLE I
Mechanical Properties of EVAL/POSB

EVAL (wt %)	POSB (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 \pm 0.9	8.6 \pm 1.6	26.1 \pm 14	33.9 \pm 15	219 \pm 49	373 \pm 40
99	1, 125	10.7 \pm 0.4	14.5 \pm 0.4	18.3 \pm 6.5	78.6 \pm 20	291 \pm 95	537 \pm 111
95	5, 125	9.7 \pm 0.4	13.6 \pm 0.7	14.2 \pm 2.0	45.3 \pm 28	389 \pm 28	484 \pm 129
99	1, 88.9	8.6 \pm 1.7	14.2 \pm 0.3	13.2 \pm 3.3	31.2 \pm 7.2 25.8 \pm	410 \pm 92	554 \pm 124
95	5, 88.9	8.3 \pm 0.4	12.3 \pm 0.6	12.8 \pm 2.7	5.5	223 \pm 49	454 \pm 41
99	1, 53.3	8.6 \pm 0.8	14.3 \pm 1.1	13.9 \pm 3.3	44.9 \pm 20	401 \pm 87	511 \pm 87
95	5, 53.3	9.3 \pm 0.2	13.5 \pm 0.6	23.5 \pm 7.7	74.9 \pm 17	200 \pm 98	459 \pm 83
99	1, 44.5	10.4 \pm 0.4	14.1 \pm 0.6	15.5 \pm 0.9	62.8 \pm 24	305 \pm 35	519 \pm 109
95	5, 44.5	9.1 \pm 0.5	11.4 \pm 5.2	8.2 \pm 2.0	87.6 \pm 64	433 \pm 70	403 \pm 196

content are shown in Table I. For all composites the ultimate tensile strength, elongation at break, and modulus increased with the addition of 1 or 5 wt % POSB, if compared with the results of the pure EVAL. For EVAL-8/POSB the ultimate tensile strength increased more than 53% [with EVAL-8/POSB 125 μm (99:1), the ultimate tensile strength increased around 90%]. The ultimate tensile strength and modulus of the samples with 5 wt % POSB were higher than those of the pure EVAL-8, but this effect was not linear with respect to the particle size. For EVAL-18/POSB samples, the ultimate tensile strength increased more than 28% [with EVAL-18/POSB 125 μm (99:1), the ultimate tensile strength increased about 69%]. This behavior of the mechanical properties indicated strong interactions between the filler and the polymer, but it was not possible to establish any correlation between such parameters and particle size. For the samples filled with 1% and 5% POSB, there was a reinforcing effect regardless of particle size. Both particle concentrations, 1 and 5 wt %, generated composites with better mechanical performance than that in pure polymer, except for elongation at break. Higher amounts of POS resulted in poorer mechanical properties relative to the 5 wt %

samples, in the same way as what was found for the properties of HDPE/POS,⁴ EVA/POS,⁵ and EVAL/POS.⁶ The elongation at break of the EVAL-18/POSB composites was higher than that of the EVAL-18/POS composites, suggesting that the particle interacted with the polymer.

The results showed that the mechanical properties of EVA/POSB were better than those of the EVA/POS⁶ composites, but this improvement could not be attributed only to the removal of the coke from the filler. A comparison of the results for EVAL-8/POS and EVAL-18/POS shown in Table II⁶ confirmed that the organic compounds on the POS surface were responsible for, by different mechanisms, the interaction between POS and EVAL, compared with that between POSB and EVAL.

It has been suggested that the diameter of POS particles in HDPE⁴ have some influence on the yield stress and elongation at yield stress of HDPE/POS composites. This behavior arises from loss of the ability of the polymeric chains to reorganize when submitted to a deformation, and it is intimately linked to the existence of a polymer/POS phase interaction, promoted by the organic residue of the mineral filler.

TABLE II
Mechanical Properties of EVAL/POS

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 \pm 0.9	8.6 \pm 1.6	26.1 \pm 14	33.9 \pm 15	219 \pm 49	372 \pm 40
99	1, 125	7.4 \pm 0.9	8.8 \pm 1.6	26.4 \pm 10	28.0 \pm 11	336 \pm 36	448 \pm 78
95	5, 125	7.0 \pm 0.4	10.7 \pm 0.8	18.2 \pm 5.7	23.6 \pm 4.4	278 \pm 22	417 \pm 45
99	1, 88.9	8.8 \pm 0.7	9.8 \pm 0.6	21.7 \pm 5.3	16.5 \pm 3.2	357 \pm 52	347 \pm 98
95	5, 88.9	8.4 \pm 0.3	9.7 \pm 0.2	11.0 \pm 1.6	25.8 \pm 3.4	298 \pm 18	246 \pm 83
99	1, 53.3	9.9 \pm 0.7	9.9 \pm 0.1	23.5 \pm 20.2	30.8 \pm 6.6	305 \pm 37	274 \pm 85
95	5, 53.3	8.2 \pm 0.4	9.7 \pm 0.2	10.8 \pm 0.9	25.8 \pm 3.4	291 \pm 22	246 \pm 83
99	1, 44.5	7.6 \pm 0.6	9.7 \pm 1.1	37.8 \pm 9.6	34.4 \pm 8.0	330 \pm 35	527 \pm 47
95	5, 44.5	6.2 \pm 0.5	8.5 \pm 1.1	36.8 \pm 10.4	17.5 \pm 1.6	247 \pm 30	440 \pm 35

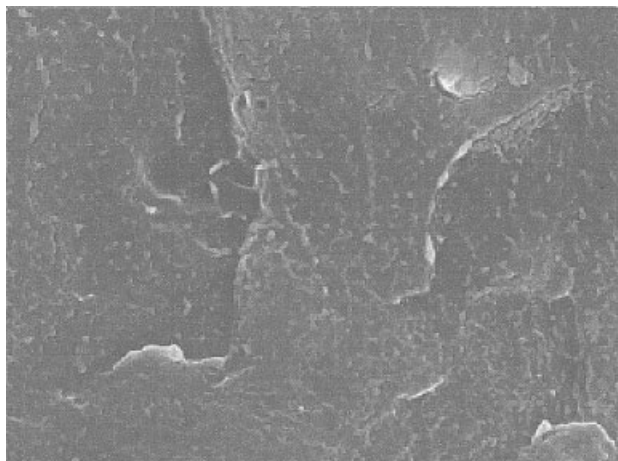


Figure 5 SEM micrographs of EVAL-8/POSB 125 μm (95:5). Magnification: 10,000.

This effect was not evident in EVA-8, was pronounced in the EVA-18 compounds,⁵ but was not observable in EVAL.

Morphology of compounds

The role of the interface on the filler dispersion and mechanical properties occurring in this system, was similar to that found in other studies. Nagata et al.¹⁰ showed by scanning electron micrographs that BaTiO₃ particles were more easily dispersed in the EVA matrix (7 and 15 mol % vinyl acetate) than in LDPE. It was observed that the polar groups introduced into nonpolar LDPE improved the interaction between BaTiO₃ particles and the polymer. These results suggested that the degree of dispersion of the BaTiO₃ particles was based mainly on hydrogen bonding and/or dipole–dipole interaction between the particle

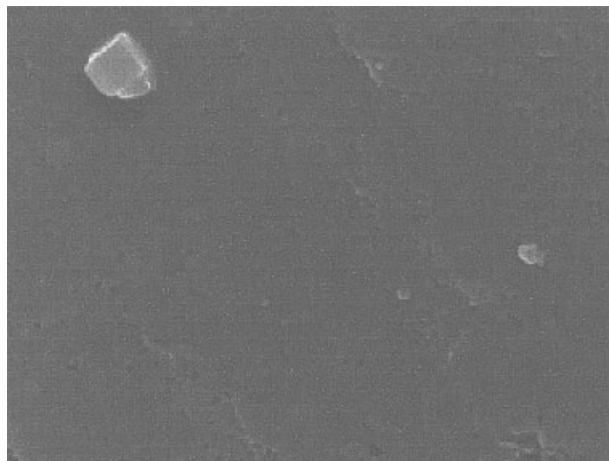


Figure 7 SEM micrographs of EVAL-18/POSB 125 μm (95:5). Magnification: 18,000.

surface and the vinyl acetate groups of EVA. A similar mechanism probably would explain our results.

The effect of POSB on the morphology of EVAL was investigated. It was observed in the micrographs that the etched surface of EVAL/POSB was different than that of EVAL/POS,⁶ showing holes and particles of different sizes linked to the polymer matrix. Figure 5 shows a micrograph of EVAL-8/POSB 125 μm (95:05), in which the continuous and the dispersed (POSB) Phases can be distinguished. It can be seen from the EVAL-8/POSB 44.5 μm (95:5) composite (Fig. 6) that holes and particles in the superficies of the structure. It can be observed in both Figures 5 and 6 that the POSB was not completely involved by EVAL, which is different than what was observed with EVAL/POS, indicating that another mechanism of compatibility between the two phases was occurring in this system. Figures 7 and 8 show the micrographs of EVAL-18/POSB 125 μm (95:5) and EVAL-18/POSB 44.5 μm

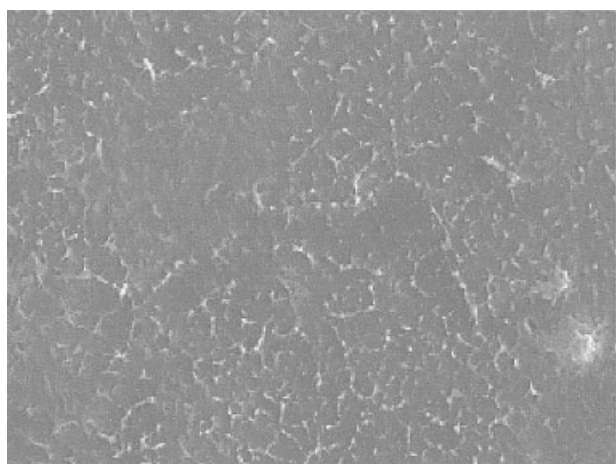


Figure 6 SEM micrographs of EVAL-8/POSB 44.5 μm (95:5). Magnification: 10,000.

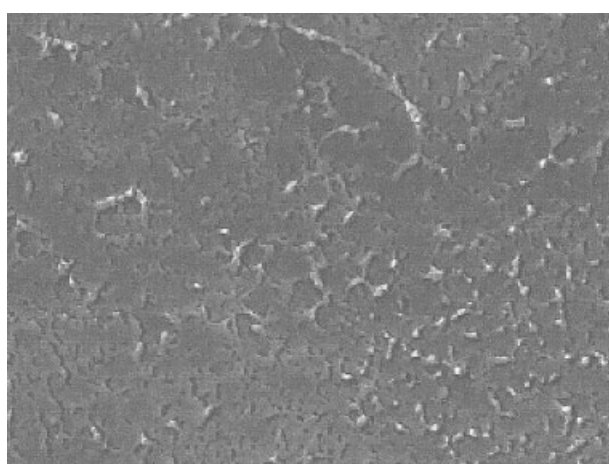


Figure 8 SEM micrographs of EVAL-18/POSB 44.5 μm (95:5). Magnification: 18,000.

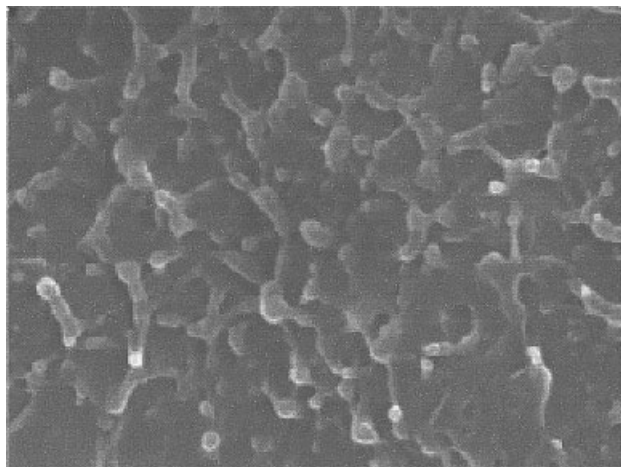


Figure 9 SEM micrographs of EVAL-18/POS 44.5 μm (95:5).⁶ Magnification: 30,000.

(95:5) samples, respectively, in which the same behavior can be observed as that seen for the composites with EVAL-8, but the topography was different in the amount and size of the POSB.

The micrographs of the etched surface of EVAL/POS showed a different morphology than that of EVAL/POSB. For EVAL-18/POS 44.5 μm (95:5; Fig. 9) broken at the cryogenic temperature, the resulting surface suggested that the polymer experienced some flow during the fracture process, which did not happen to the EVAL/POS system. This type of breakage was observed in another study,¹¹ but at room temperature, providing additional evidence of the good interaction between polymer and filler.

It was found that different mechanisms were taking place in the EVAL/POS and EVAL/POSB composites. In EVAL/POS, the presence of coke in the POS was responsible for the flow in morphology, shown in the micrographs, and also for the improved mechanical properties. In the EVAL/POSB composites the absence of coke was able to provide holes to anchor the polymer on the filler surface. This could explain the better mechanical properties and the modification of the morphology structure of the EVAL/POSB composites.

CONCLUSIONS

The experimental results suggested that the removal of organic compounds from the surface of pyrolyzed oil shale (coke) can promote better interaction between the fillers in both polymers EVAL-8 and EVAL-18, probably because of the formation of holes, to which polar polymer could be attached. The better interaction between polymer and filler improved the mechanical properties and modified the morphology of the composite. Such improvement in mechanical properties was not associated with particle size, as was observed in the EVA-18/POS system. However, different from what was observed for EVA, the concentration of vinyl alcohol was not an important factor for the mechanical properties.

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