

Use of Pyrolyzed Oil Shale as Filler in Poly(ethylene-co-vinyl acetate) with Different Vinyl Acetate Contents

RONILSON VASCONCELOS BARBOSA, RICARDO BAUMHARDT-NETO, RAQUEL SANTOS MAULER, CARLOS JOSÉ PEREZ GORGA, ADRIANA TEDESCO

Instituto de Química, Universidade Federal do Rio Grande do Sul, Departamento de Química Orgânica, Avenida Bento Gonçalves, 9500, Porto Alegre, Rio Grande do Sul, Brasil

Received 29 March 2001; accepted 27 August 2001

ABSTRACT: Pyrolyzed oil shale (POS) obtained from the pyrolysis of bituminous rock was used as filler in poly(ethylene-co-vinyl acetate) (EVA). The effects of the VA content of EVA and the particle size of POS on the mechanical properties were investigated. The composites were prepared in a rotor mixer at 180°C with a concentration of POS of up to 30 wt %. The stress-strain plots of the compression-molded composites are similar to the EVA (18% VA content) behavior for low concentrations (1–5 wt %) of POS with a particle size lower than 270 mesh. It was observed that decreasing the POS particle size and increasing the VA content of EVA produced better compatibility between the polymer and filler. The mechanical properties, differential scanning calorimetry, and dynamic mechanical analysis also demonstrated the compatibility between EVA and POS under the increase of the VA content in the EVA. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1544–1555, 2002; DOI 10.1002/app.10494

Key words: blend; poly(ethylene-co-vinyl acetate); pyrolyzed oil shale; filler; mechanical properties

INTRODUCTION

Pyrolyzed oil shale (POS) is an inorganic material originating from the oil extraction of bituminous rock through pyrolysis at approximately 400°C. The POS with low oil concentration goes back to the mines after it is extracted, increasing production cost and the need for appropriate environmental control in the areas close to the mining. During the pyrolysis process the organic material contained in the rock is transformed into oil and gas, and another part is transformed into 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 being constituted of silicates. Many of the minerals fillers currently being used in plastics, such as clay, mica, and talc, also consist of silicates.¹ The use of minerals as fillers in polymeric materials is an economic practice in the polymer industry today. Most mineral fillers are used in industry to reduce production cost and, among them, the most important are alumina, calcium carbonate, talc, and clay. The use of POS as a filler in polymer materials is new and few works referring to the subject are found in the specialized literature.¹ According to the two studies, the objective of blending oil shale with polymers is to promote the decomposition of the oil shale in the pyrolysis process.^{2,3} In this case, the use of POS as a filler in polymers is important because it is possible to take advantage of this

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

Contract grant sponsors: CNPq; FAPERGS; ANP/CTPE-TRO; Tecnologia em Polímeros.

Journal of Applied Polymer Science, Vol. 84, 1544–1555 (2002)
© 2002 Wiley Periodicals, Inc.

mineral residue and at the same time generate new materials.

It is known that in polymeric mixtures and composites the compatibility among the phases depends on the miscibility among each one of the components. Filling poly(ethylene-co-vinyl acetate) (EVA) with inorganic materials is the better way to attain materials with a low cost and improve the tensile properties and stiffness. Some studies in this direction have already been reported in recent years on systems such as the addition of a rigid filler like CaCO_3 in high-density polyethylene (HDPE).^{4,5} After the 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 phase in a compound of EVA/POS. It would also enhance some mechanical properties of the compound.

With the aim of studying the POS application as a filler for EVA and to understand the effect of filler on the properties of the compounds, mixtures of EVA with POS were obtained while varying the filler concentration and its particle size.

EXPERIMENTAL

Materials

The TECPOL Tecnologia em Polímeros S.A. and Petrobras S.A. supplied the POS. It was dried at 100°C, milled, and classified as 115, 170, 270, and 325 mesh. Petroquímica Triunfo S.A. supplied the EVA and two different grades were used: one sample with 8% VA content (EVA-8) and another one with 18% VA content (EVA-18).

Compound Preparation and Characterization

Compounding of EVA-8/POS and EVA-18/POS were performed in a Haake Rheomix 600 mixer at 180°C. The rotor speed was fixed at 20 rpm for 15 min. The compounds were compression molded at 180°C for 3 min at 4000 lb in a Carver Monarch press. The tensile properties were measured at room temperature in accordance with ASTM D 882-83 using a Wolpert TZZ 771 testing machine at a crosshead speed of 10 mm/min. Differential scanning calorimetry (DSC) measurements were performed in a Polymer Laboratories DSC instrument under an N_2 atmosphere. The samples were heated from 40 to 180°C and cooled to 40°C at a heating and cooling rate of 10°C/min. The melting

temperature (T_m) values were taken from the second heating curve.

Dynamic Mechanical Analysis (DMA)

For the DMA measurements the samples were melt pressed at 180°C for 3 min at 4000 lb and allowed to cool at room temperature. Rectangular films were used that averaged 10 mm wide, 12 mm long, and 0.1–0.2 mm thick. The dynamic mechanical experiments were performed on a Polymer Laboratories dynamic mechanical thermal analysis (DMTA) MK II Instrument in the tensile mode. The measurements were carried out at a heating rate of 2°C/min at a frequency of 1 Hz. The temperature ranged from –125°C to the melting point of each compound (100–150°C, depending on the sample used).

RESULTS AND DISCUSSION

Compound Preparation

Figures 1 and 2 show the graphs of torque during the processing of the EVA-8/POS and EVA-18/POS composites with different POS particle sizes. It can be observed that when the POS was added to the EVA, there was a tendency for the torque to increase, which has a slight dependence on the particle size.

Tensile Properties

The tensile properties of the EVA-8, EVA-8/POS, EVA-18, and EVA-18/POS as a function of filler are listed in the Table I. For the EVA-8/POS composites the ultimate tensile strength (UTS) is smaller than that for pure EVA-8 (Fig. 3). The same happens for EVA-18 (Fig. 4), and in both cases the POS 30 wt % filled samples showed a UTS that was 40% lower than for pure EVA samples. With respect to the elongation at break (EB), samples of EVA-8/POS (Fig. 5) quickly collapse under the test, while an EVA-18/POS (Fig. 6) sample still maintains a plastic deformation even under high POS content. Considering only samples filled with 1% POS, there is a reinforcing effect when the particle size is 270 and 325 mesh.

From the results of the mechanical properties of EVA-8/POS and EVA-18/POS, it can be observed that three factors were related to the mechanical properties of the mixtures of polymer and POS:

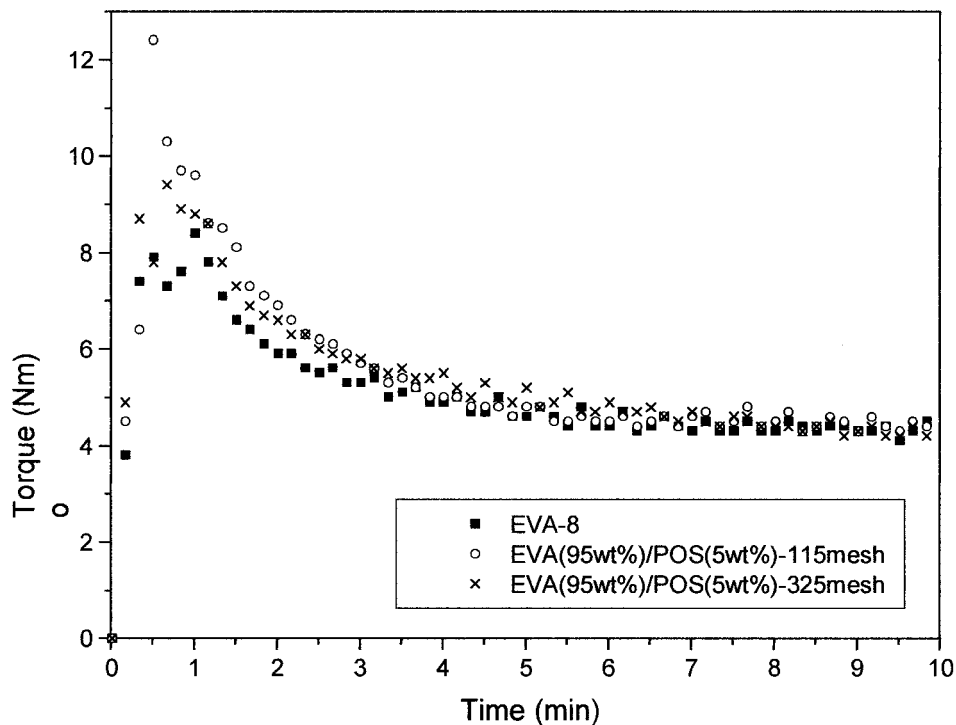


Figure 1 The torque versus time of mixing of EVA-8 and POS (115/325 mesh).

1. The POS particle size: the smaller the particle size the better are the mechanical properties of the composites when com-

pared to the pure polymer. This behavior may be explained by the best dispersion of the particle in the polymer matrix.

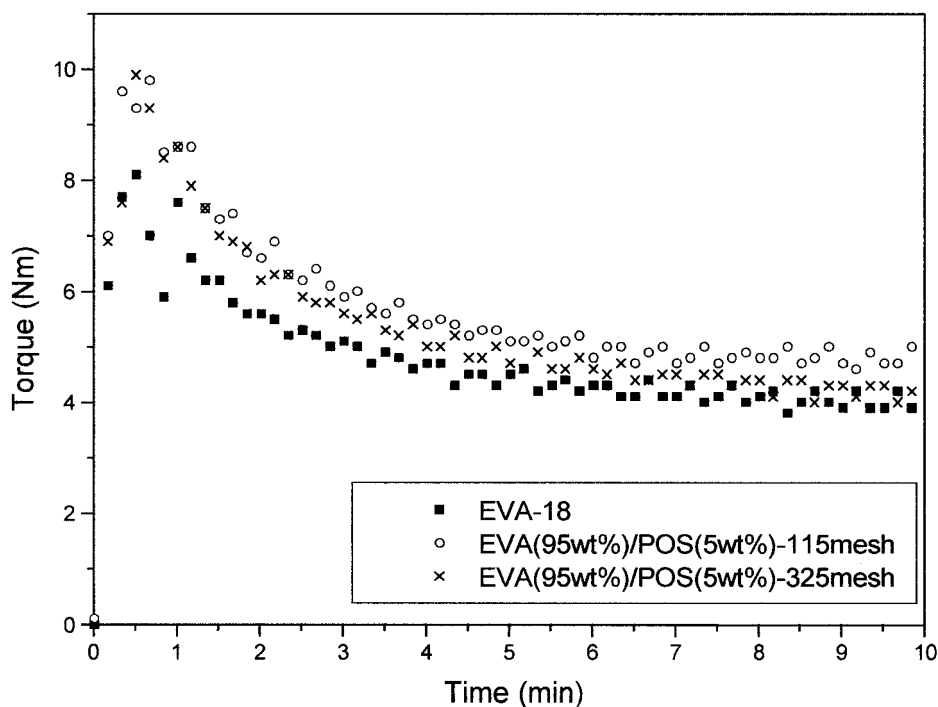


Figure 2 The torque versus time of mixing of EVA-18 and POS (115/325 mesh).

Table I Mechanical Properties of EVA/Filler Contents

EVA (wt %)	POS (wt % – Mesh)	Ultimate Tensile Strength (MPa)		Elongation at Break (%)	
		EVA-8	EVA-18	EVA-8	EVA-18
100		12.6 ± 1.9	16.2 ± 2.5	572.1 ± 74.3	620.9 ± 67.9
99	01-115	10.7 ± 2.6	9.1 ± 1.5	468.1 ± 102.8	417.8 ± 86.2
95	05-115	7.8 ± 1.2	13.6 ± 3.8	350.2 ± 133.5	554.9 ± 143.9
90	10-115	6.3 ± 2.0	12.4 ± 1.4	213.7 ± 194.2	536.8 ± 56.19
80	20-115	2.9 ± 1.3	9.5 ± 1.6	65.3 ± 45.1	488.7 ± 77.3
70	30-115	5.2 ± 1.1	7.4 ± 1.6	24.9 ± 5.6	365.6 ± 177.3
99	01-170	11.0 ± 0.6	13.0 ± 7.3	537.4 ± 22.8	462.2 ± 352.7
95	05-170	10.3 ± 0.8	13.7 ± 3.3	518.7 ± 43.0	563.1 ± 90.4
90	10-170	8.0 ± 2.0	12.7 ± 2.0	353.4 ± 176.2	528.2 ± 51.3
80	20-170	8.1 ± 1.2	11.8 ± 0.5	340.0 ± 139.8	472.1 ± 17.7
70	30-170	5.7 ± 0.4	9.0 ± 0.9	37.9 ± 22.8	417.9 ± 36.6
99	01-270	10.8 ± 1.4	16.8 ± 0.6	520.3 ± 21.4	627.0 ± 28.5
95	05-270	10.5 ± 1.3	12.7 ± 1.8	518.0 ± 70.0	534.9 ± 65.3
90	10-270	9.8 ± 1.2	13.4 ± 2.3	505.2 ± 62.9	533.3 ± 78.4
80	20-270	7.7 ± 1.2	10.6 ± 2.1	341.3 ± 132.2	489.5 ± 94.0
70	30-270	6.0 ± 0.3	8.0 ± 0.8	47.2 ± 32.6	371.9 ± 46.8
99	01-325	10.8 ± 0.8	16.6 ± 1.3	539.7 ± 53.0	642.2 ± 55.4
95	05-325	11.7 ± 0.6	15.0 ± 1.1	563.5 ± 17.5	601.3 ± 44.4
90	10-325	9.8 ± 2.0	13.5 ± 1.3	416.98 ± 195.8	569.7 ± 40.8
80	20-325	8.7 ± 0.6	8.9 ± 3.5	396.3 ± 90.6	412.0 ± 263.5
70	30-325	5.7 ± 3.2	10.0 ± 1.8	152.2 ± 133.68	464.7 ± 84.7

- The 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 the losses in the mechanical properties, mainly when the interface of the polymer–filler shows poor adhesion.
- The polarity of the polymer: when increasing the polymer polarity (VA content), the mechanical properties remained almost the same at higher filler content if compared with the pure polymer.

Factorial Analyses

All results may be rearranged to produce factorial designs as illustrated in Table II, which allows the calculation of the factor effects on the mechanical properties. Four factorials were developed with three factors (% VA, % POS, and POS size) and two levels to contemplate the four percentages of POS in the compound and the four different POS sizes. It is important to emphasize that in this case the pure EVA properties were not included in the designs; only the effects of changing the POS size and its amount in the composites were analyzed.

From these designs the effects on the UTS and EB were calculated (Table III).

The effects in the white cells in Table III were significant and the effects in the gray cells were pooled in the experimental error. Factorial designs D1–4 are described in Table III.

These analyses of the factorial suggested the following:

- The increase of the VA content in the EVA increased the UTS and EB in all cases, except for factorial design number one. In this case the observed value (positive) was smaller than the experimental error. The other results (D2, D3, and D4) were in agreement with the expected behavior: when increasing the VA fraction, the UTS and EB increase with the strength of the intermolecular interactions.
- Increasing the POS content caused the UTS to decrease, as expected, but it took place only when the POS content was higher than 10%. From 1 to 5% there was no effect on the UTS (D1 and D2). At the same time, the EB was decreased by increasing the POS content, except for design

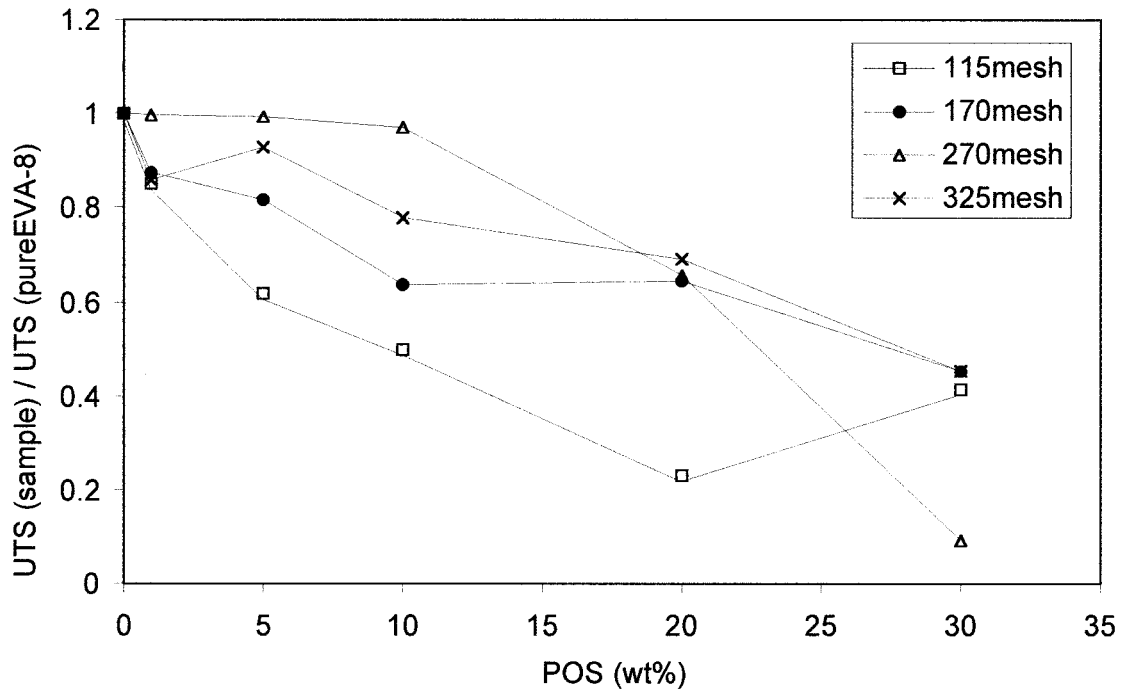


Figure 3 The ultimate tensile strength (UTS) ratios (composites/pure EVA-8) as a function of the POS content for different particle sizes.

number one, where the effect was pooled in error.

3. When the POS size was decreased, the UTS and EB showed a tendency to in-

crease, but only the EB value at D2 was significant. In addition, it may be observed that all effects (significant or not) of the POS size were positive, as expected.

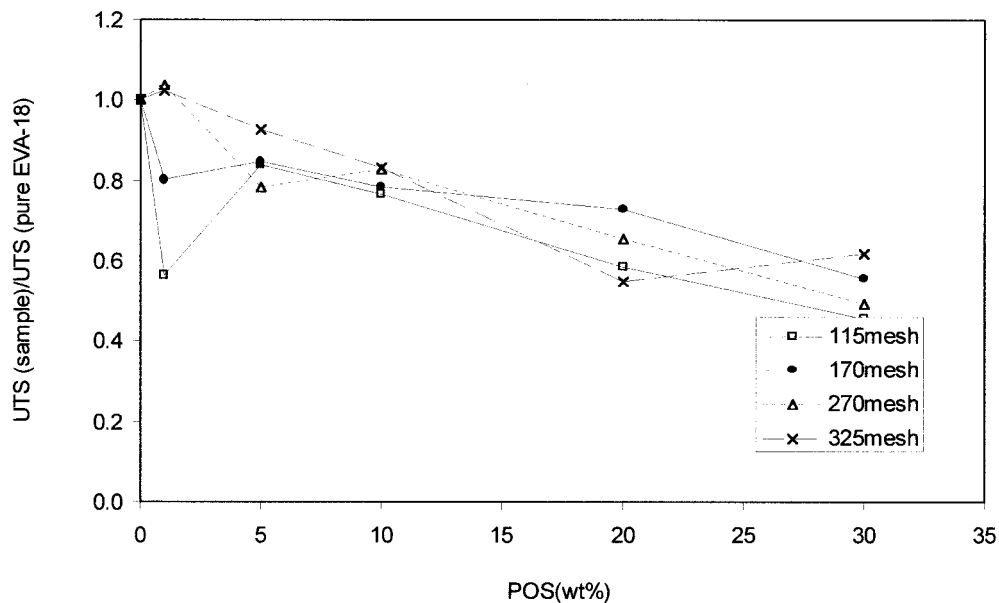


Figure 4 The ultimate tensile strength (UTS) ratios (composites/pure EVA-18) as a function of the POS content for different particle sizes.

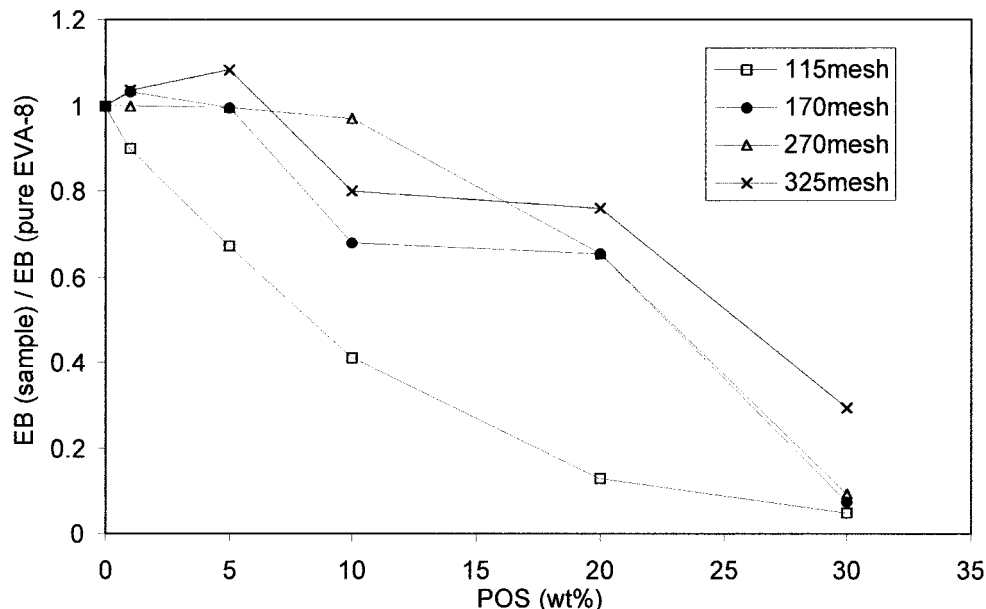


Figure 5 The elongation at break (EB) ratios (composites/pure EVA-8) as a function of the POS content for different particle sizes.

4. There was only one significant interaction effect, which was due to the VA and POS content (effect 1 × 2 in Table III) acting on the EB in D2 and D4. When the VA (8–18%) and POS (1–5%) content increased simultaneously, the EB decreased 39%. On the other hand, when the VA was varied from 8 to 18% and the POS from 10 to 30%,

the EB increased 114%. This means that at higher POS content the polymer–filler chemical interactions were able to promote the increase in the EB, which did not happen at low filler content. Figure 7 shows this effect. The interaction between acetate units and the POS affected the EB. In other words, the interaction between the

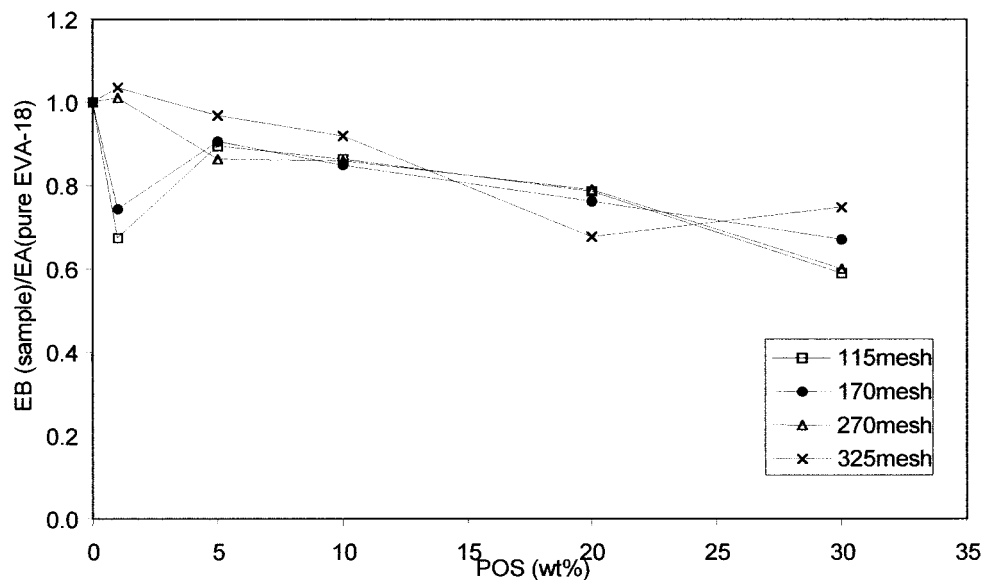


Figure 6 The elongation at break (EB) ratios (composites/pure EVA-18) as a function of the POS content for different particle sizes.

Table II Factorial Designs (D) Built from EVA-8/POS and EVA-18/POS Composites

D1					D2				
VA (%)	POS (%)	POS Size	UTS	EB	VA (%)	POS (%)	POS Size	UTS	EB
8	1	115	10.7	468.0	8	1	270	10.8	520.0
18	1	115	9.1	418	18	1	270	16.8	627
8	5	115	7.8	350.0	8	5	270	10.5	518.0
18	5	115	13.6	555	18	5	270	12.7	535
8	1	170	11.0	537.0	8	1	325	10.8	540.0
18	1	170	13	462	18	1	325	16.6	642
8	5	170	10.3	518.0	8	5	325	11.7	564.0
18	5	170	13.7	563	18	5	325	15	601
D3					D4				
VA (%)	POS (%)	POS Size	UTS	EB	VA (%)	POS (%)	POS Size	UTS	EB
8	10	115	6.3	214.0	8	10	270	9.8	505.0
18	10	115	12.4	537	18	10	270	13.4	533
8	30	115	5.2	25.0	8	30	270	6.0	47.0
18	30	115	7.4	366	18	30	270	8	372
8	10	170	8.0	353.0	8	10	325	9.8	417.0
18	10	170	12.7	528	18	10	325	13.5	570
8	30	170	5.7	38.0	8	30	325	5.7	152.0
18	30	170	9	417	18	30	325	10	464

VA and POS contents could not increase the strength of the composite, but it could promote a new flow behavior under load.

These results suggested the role of organic compounds on the surface of POS in promoting a better adhesion between the particle and EVA-18. Such compounds may contribute to the adhesion development between the filler and EVA by two

mechanisms: a better spreading of the polymer on the filler surface due to the chemical interactions and *in situ* plastification of EVA by the organic compost on the surface of the POS, which was fixed in the mineral filler during the pyrolysis process. The fixed mineral filler was prone to develop adhesions during the processing and affected the mechanical properties; if the particle size of the POS was smaller than 270 mesh, the

Table III Calculated Effects of Factors on Ultimate Tensile Strength (UTS) and Elongation at Break (EB)

Factors	Ultimate Tensile Strength (MPa)				Elongation at Break (%)			
	D1	D2	D3	D4	D1	D2	D3	D4
EVA (1)	2.4	4.3	4.1	3.4	31	66	304	205
POS (%), (2)	0.4	-1.3	-3.0	-4.2	25	-28	-197	-248
POS SIZE (3)	1.7	0.8	1.0	0.4	72	37	48	36
1 × 2	2.2	-1.6	-1.3	-0.2	94	-39	56	114
1 × 3	0.3	0.2	-0.1	0.6	-46	4	-27	28
2 × 3	-0.4	0.9	0.0	0.4	16	19	-17	62
1 × 2 × 3	-1.5	0.3	0.6	0.6	-34	6	47	-34

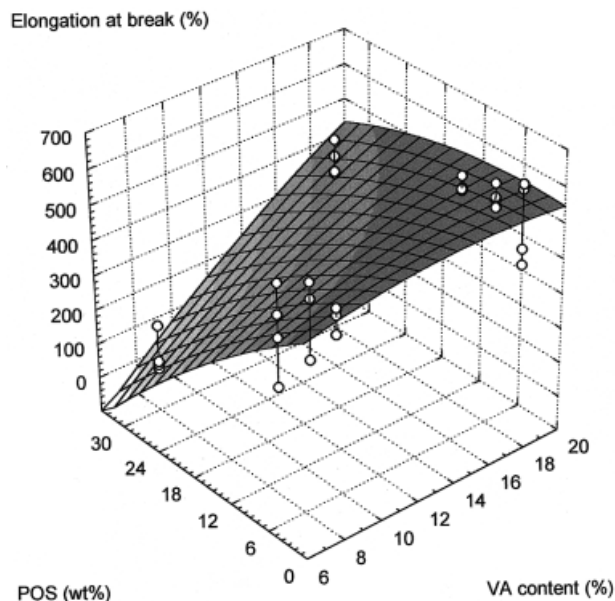


Figure 7 A plot of the elongation at break as a function of the POS and VA content.

concentration of POS in the polymer was up to 5 wt % and the content of VA in the EVA was 18 mol %.

The experiment suggested that polar organic chains from the pyrolysis process of bituminous rock were available on the surface of the POS and these polar chains were responsible for the improvement of the adhesion among the phases of the polymer with a larger polarity (EVA-18). This better adhesion consequently resulted in an improvement in the mechanical properties. Nagata and colleagues⁶ used scanning electron micrographs to show that the BaTiO₃ particles were more easily dispersed in the EVA matrix (7 and 15 mol % VA) than in LDPE. It was observed that the polar groups introduced into a nonpolar LDPE improved the adhesion between BaTiO₃ particles and the polymer. These results suggest that the degree of dispersion of the BaTiO₃ particles was mainly based on the hydrogen bonding and/or dipole–dipole interaction between the particle surface and VA groups of EVA.

In a previous article⁷ we suggested that the diameter of the POS particles in HDPE influenced the yield stress and elongation at yield stress, and the mechanical properties of HDPE/POS compounds were a function of the particle size and their concentration in compounds. This behavior was caused by the loss of the capacity of the polymeric chains to get organized when submitted to a deformation and it was intimately

linked with the existence of adhesion between the polymer/POS phase, which is promoted by the existence of an organic residue intimately linked to the bonded mineral filler. The effect was not evident in EVA-8 and was pronounced in the EVA-18 compounds.

DSC Analyses

The DSC curves of the EVA-8, EVA-18, EVA-8/POS, and EVA-18/POS composites are shown in Figures 8 and 9. EVA-8 and EVA-18 exhibited a melting temperature (T_m) in the range of 80 and 63°C, respectively. A physical compound of EVA-8/POS with a different composition and particle size presented a T_m range identical to the EVA-8. However, the physical compound of EVA-18/POS showed a small displacement in the melting temperature (63–66°C), which was independent of the concentration or particle size of the POS used in the mixture.

DMTA Measurements

Figure 10 shows the logarithm of the storage modulus (E') versus temperature curves for EVA-8/POS with different compositions. In general, the storage modulus of EVA-8, EVA-8/POS-115 mesh (95/05), and EVA-8/POS-325 mesh (95/05) were the same and the behavior of the storage modulus was independent of the particle size and POS concentration in EVA-8. The absence of change in the storage modulus could not necessarily be linked to the mechanical properties answer for the compounds. The EVA-8 and EVA-8/POS systems had the same behavior in terms of the storage modulus, but the mechanical properties of the mixtures were inferior to the pure EVA-8. Figure 11 shows the log E' of EVA-18 and EVA-18/POS with different compositions. The EVA-18/POS system showed that the loss in storage modulus was dependent on the particle size if compared with the storage modulus of pure EVA-18. It is important that the mechanical properties of the compounds were better in these compounds.

The DMTA test only determines the answer capacity of the polymeric phase to a vibratory tension. The test was sensitive to interactions among phases, as in the case of EVA-18 and its compounds. The capacity of the system to store energy was harmed with the introduction of the POS, and the module decreased with the decrease of the particle size in the EVA-18 systems.

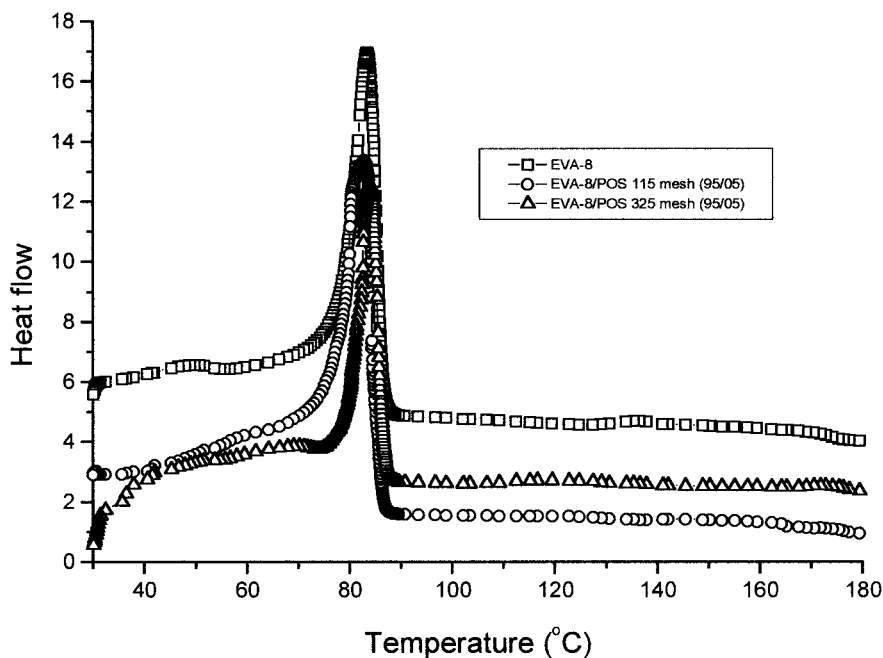


Figure 8 DSC curves of the EVA-8 polymer and EVA-8/POS composites.

Figure 12 shows the loss tangent ($\tan \delta$) versus temperature curves for the EVA-8/POS, EVA-8/POS-115 mesh (95/05), and EVA-8/POS-325 mesh (95/05). Two regions should be considered in the analysis. The first one at 52°C normally corre-

sponds to the α transition and it was apparently not affected by the addition of POS. The second region is at -19°C and corresponds to the β transition. Both the α and β transition of the EVA-8 and EVA-8/POS compounds showed the same behavior.

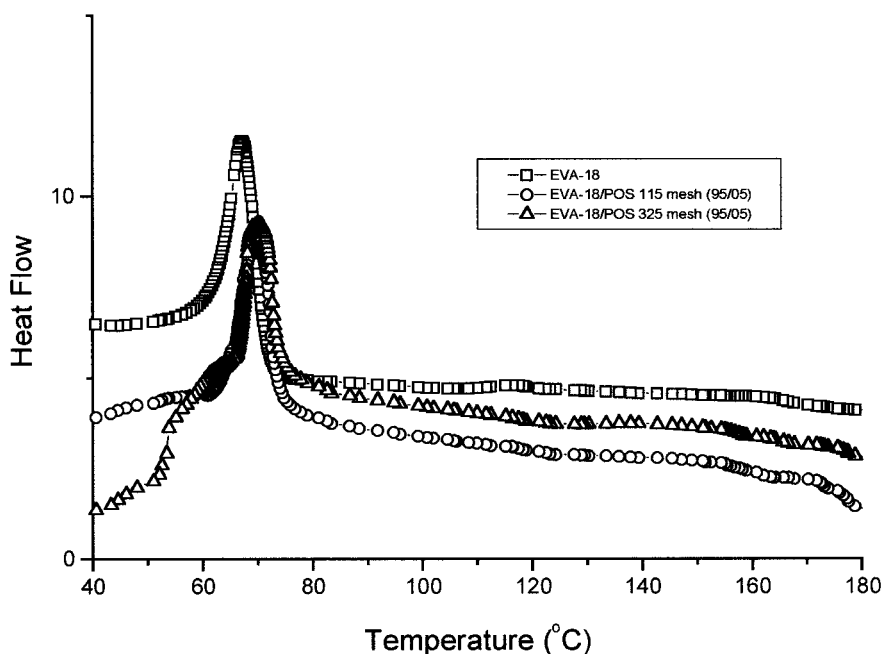


Figure 9 DSC curves of the EVA-18 polymer and EVA-18/POS composites.

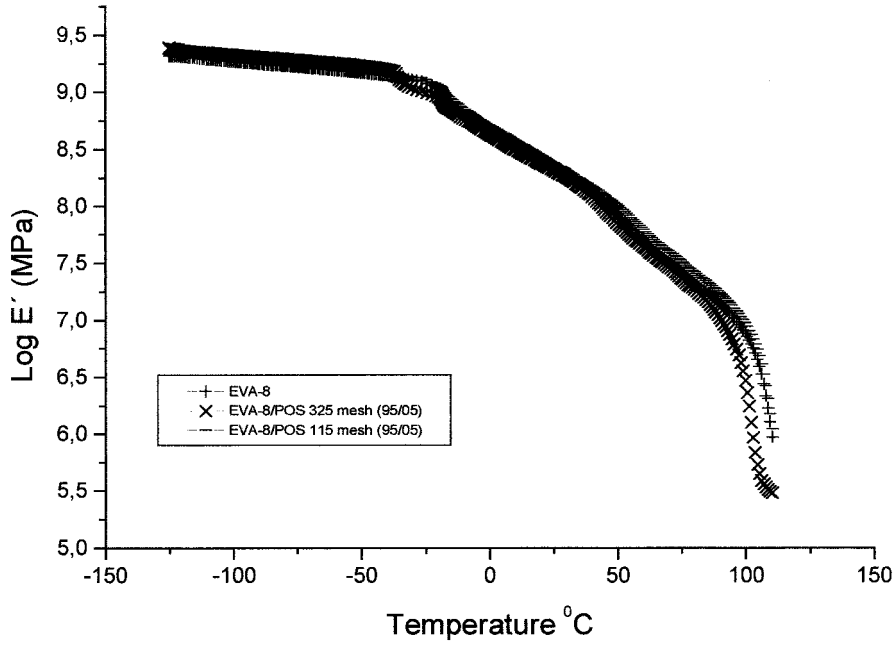


Figure 10 The storage modulus versus temperature curves for EVA-8/POS, EVA-8/POS-115 mesh (95/05), and EVA-8/POS-325 mesh (95/05).

In the loss tangent versus temperature curves shown in Figure 13 for the EVA-18/POS, EVA-18/POS-115 mesh (95/05), and EVA-18/POS-325 mesh (95/05), two regions should be considered in

the analysis, the α transition at 20°C and the β transition at -11°C. Both the α and β transition of EVA-18/POS showed a shift of about -20°C in regard to EVA-18.

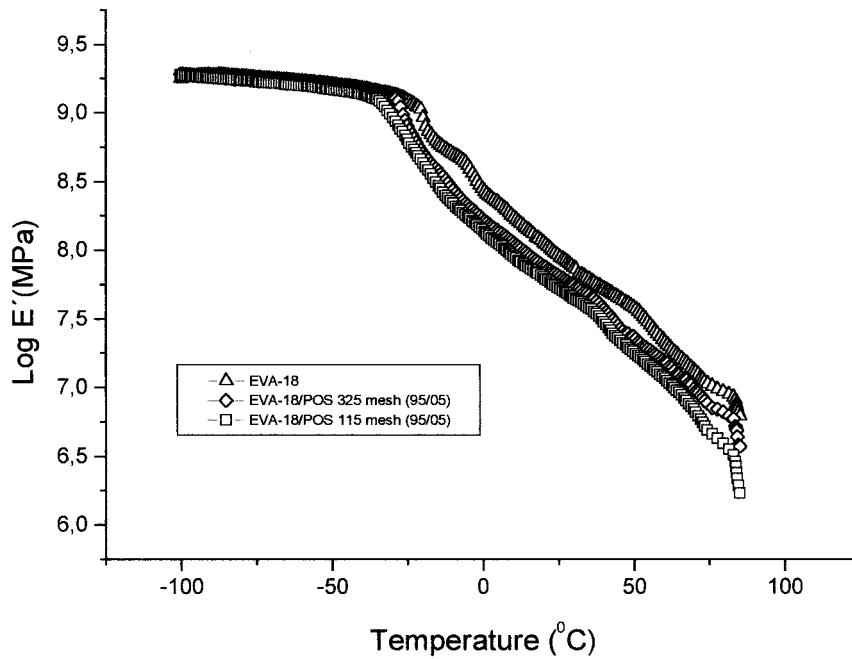


Figure 11 The storage modulus versus temperature curves for EVA-18/POS, EVA-18/POS-115 mesh (95/05), and EVA-18/POS-325 mesh (95/05).

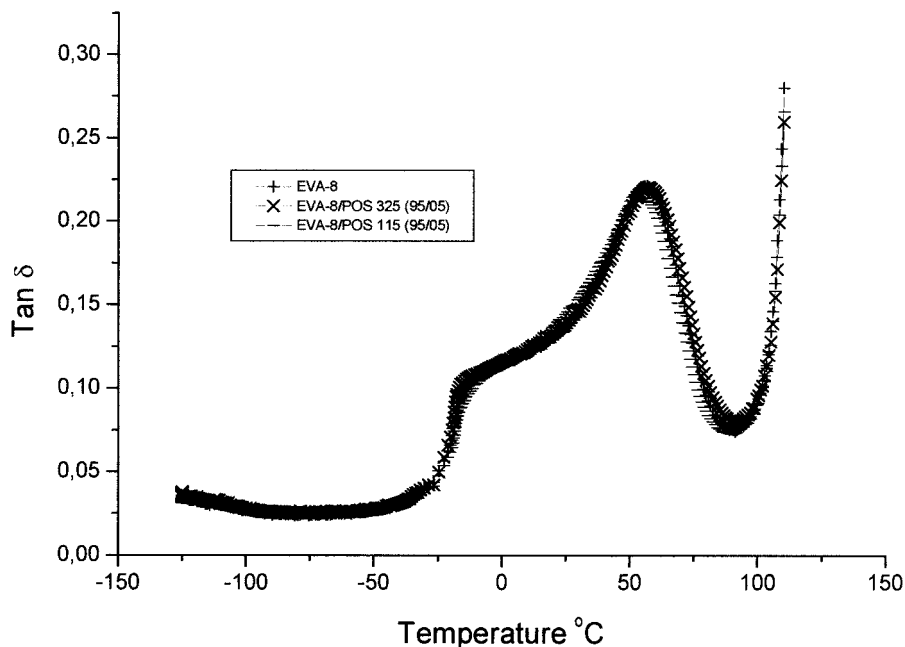


Figure 12 The loss tangent ($\tan \delta$) versus temperature curves for EVA-8/POS, EVA-8/POS-115 mesh (95/05), and EVA-8/POS-325 mesh (95/05).

The β transition corresponded to the glass transition of both EVAs, and it is known that the β transition is associated with the relaxation of a main chain in the amorphous phase of the vinyl

unit of EVA. Nagata et al.⁶ showed that the β -peak shift was about +5°C in the EVA/BaTiO₃ composite systems, and the β -peak temperature for EVA/graphite composite systems was inde-

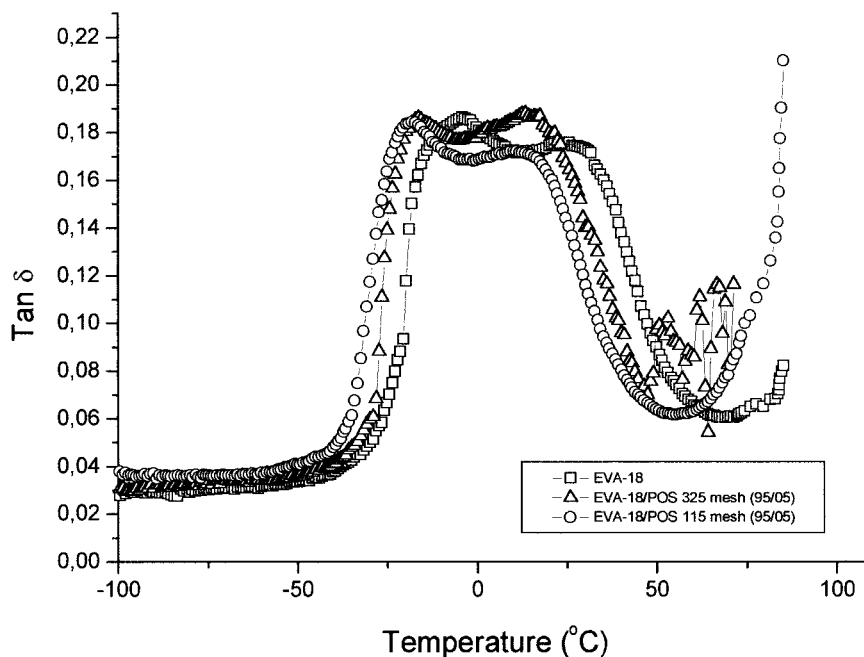


Figure 13 The loss tangent ($\tan \delta$) versus temperature curves for EVA-18/POS, EVA-18/POS-115 mesh (95/05), and EVA-18/POS-325 mesh (95/05).

pendent of the concentration of filler. The polarity of POS is closer to graphite than to BaTiO₃, and this was in agreement with the results presented by the EVA-8/POS system. However, for the EVA-18/POS system the decrease of the modulus and the shift of the α,β -peak temperature suggested an interaction between the EVA-18 and the POS, as observed by Nagata et al.⁶ in EVA/BaTiO₃ composite systems. This anomalous behavior suggested that there must be a critical concentration of the acetate group in EVA for the system to show some polar interaction, and this interaction with EVA-18 and the polar group in the POS decreased the elastic answer and induced a displacement of the α,β -peak temperature.

It is known that fillers and reinforcements have viscoelastic characteristics in plastic materials. Many fillers and reinforcements therefore respond as purely elastic systems while the polymer and the filler-polymer interface have viscoelastic behavior. The addition of filler or a reinforcement to a polymer increases the modulus of the system.⁸ This behavior was not observed in the EVA-18 system; perhaps POS also acted as a lubricant.

CONCLUSIONS

The experiments reported suggested that the organic compound in the surface of POS can pro-

mote better adhesion between EVA-18 and POS. The better adhesion can modify the mechanical properties with synergism of these properties, but this synergism is associated with the particle size and the concentration of POS in the polymer. However, the VA content of EVA is important for the property results.

The authors would like to thank CNPq, FAPERGS, ANP/CTPETRO, and TECPOL Tecnologia em Polímeros for their support.

REFERENCES

1. Nascimento, R. S. V. Ph.D. Thesis, Cranfield Institute of Technolog, 1987.
2. Gersten, J.; Fainberg, V.; Garbar, A.; Hetsroni, G.; Shindler, Y. *Fuel* 1999, 78, 987.
3. Ballice, L.; Yuksel, M.; Saglam, M.; Reimert, R.; Schulz, H. *Fuel* 1998, 13, 1431.
4. Haworth, B.; Jumpa, S. *Polym Compos* 1999, 28, 363.
5. Wang, Z. *J Appl Polym Sci* 1996, 60, 2239.
6. Nagata, K.; Kodama, S.; Kawasaki, H.; Deki, S.; Mizahata, M. *J Appl Polym Sci* 1995, 56, 1313.
7. Barbosa, R. V.; Baumhardt Neto, R.; Mauller, R. S.; Gorga, C. J. P. *Polym Test* 2001, 20, 357.
8. Sepe, M. P. *Dynamic Mechanical Analysis for Plastics Engineering*; Plastics Design Library: New York, 1998.