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Analysis of the Mechanical Properties and Characterization by Solid State ^{13}C NMR of Recycled EVA Copolymer/Silica Composites

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The incorporation of micrometer sized silica particles on poly (ethylene-co-vinyl acetate) – EVA - residues from the footwear industry was evaluated. The effects of the processing parameters – temperature and mixing ratio – on the mechanical behavior of molded plates of neat recycled EVA and EVA/silica composites were also investigated. The mechanical properties measured by the tensile test, the fractographic analysis by scanning electron microscopy (SEM), and the ^{13}C Nuclear Magnetic Resonance (NMR) showed a reduced EVA to silica compatibility. Therefore, incorporation of untreated silica to recycled EVA copolymer produced a slight decrease on the mechanical performance of EVA/silica composites in respect to neat EVA copolymer. The NMR analysis also shows that the crosslinking process on recycled EVA may be occurring at the carbonyl group.

Keywords: *EVA, composite, recycling, NMR*

1. Introduction

Nowadays, the environmental pollution produced by industry residues is one of the largest concerns of human society. Polymers play a key role in this respect, since the demand of polymeric artifacts increased over the last decades due to their many possible applications. As synthetic polymers do not decompose easily, their residues constitute a serious problem to the environment. Together with the society's concern, considerable legislative effort has been created to minimize the impact of polymeric residues as well as all kinds of leftover materials[1].

The copolymer poly(ethylene-co-vinyl acetate), EVA, is a very flexible polymer suitable for films, flexible tubes and catheters[1]. This copolymer of moderate price is also largely used by the footwear industry as a material for shoes' sole. The incorporation of inorganic particles, such as silica in recycled EVA, has an important role in the improvement of shoes' sole mechanical properties[2-4]. The incorporation of inorganic fillers to polymers has, in fact, many advantages when one wants to increase hardness[5,6] and wear resistance[7], for example. However, the structure of the composites developed can be difficult to analyze.

NMR spectroscopy is an extremely powerful technique to characterize the material's structure and dynamics. This method can supply information to the chemical structure, chemical composition, tacticity, crystallinity and molecular dynamics[8,9]. Carbon-13 CP/MAS NMR, for example, can be employed to measure individual proton spin-lattice relaxation time in the rotating frame (T_1H_ρ) for protons attached to different kinds of carbons. Proton $T_{1\rho}$ relaxation can be characterized by means of matched spin-locked, cross polarization transfer experiments in which the carbon signal tracks the proton polarization as a function of proton high field decoupler contact time and thus follows its decrease via a $T_{1\rho}$ process[8,9].

Since solid state NMR provides a way to study the dynamics down to a molecular size scale, it was employed in this work to evaluate molecular motion and flexibility of recycled EVA filled with silica particles. The structural information from the NMR analysis was matched with the tensile mechanical properties and scanning electron microscopy analysis performed on the tensile fracture surfaces of the composites.

2. Experimental

2.1. Manufacture

The recycled EVA (19% VA) and silica particles (1% and 5% w/w), with sizes ranging from 5 to 100 µm were mixed in a Haake plastograph at two different temperatures (160 °C and 200 °C) and two mixing velocities (60 rpm and 100 rpm). The mixed material was then submitted to a pressure of 3.5 MPa for 15 minutes at 200 °C and cooled to room temperature. Plates with nominal dimensions of 150 x 150 x 1 mm were thus obtained. Tensile specimens were then machined from the plates according to ASTM standard D 638M-77a[10]. The dimensions of the specimens were in agreement with the standard test method for type M-V specimens, with an overall length (L_0) of 63.5 mm, distance between grips of 25.4 mm, gage length of 7.62 mm, width of narrower section of 3.18 mm, width (W_0) of 9.53 mm and thickness of 1mm. Neat EVA plates, from recycled and virgin copolymer, were manufactured using the same procedure.

2.2. Mechanical measurements

The tension testes were performed on a universal testing machine using a load-cell of 1 kN (100 kgf), following the procedures recom-

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mended by the ASTM standard D 638 M. The tests were conducted using pneumatic grips, and the velocity of the test was 10 mm/min.

2.3. Scanning electronic microscopy

The SEM observations were performed on gold-palladium coated specimens with secondary electrons imaging and acceleration of the electron beam ranging from 10 to 20 kV[11].

2.4. High-resolution solid-state NMR

High-resolution solid-state carbon-13 (^{13}C) NMR experiments were carried out on a Varian INOVA 300 spectrometer equipped with a Cross Polarization-Magic Angle Spinning (CP/MAS) solid state probe operating at resonance frequency of 74.5 MHz (7.1T) for ^{13}C. The ^{13}C MAS (spinning at magic angle) spectra were acquired with the following experimental parameters: 90° pulse (5.5 μs); pulse delay of 1 s; acquisition time of 0.05 s.

Measurements of the proton spin-lattice relaxation in the rotating frame (T_1H_ρ) were performed using the following experimental conditions: pulse angle of 90° (5.5 μs) with 1 second pulse interval. All measurements were made at room temperature. A proton RF field of 45 kHz and a contact time of 1 ms were employed throughout the experiments. The spinning speed at the magic angle was about 4 kHz. The pulse sequence used in the experiments was the Delayed Contact Time[5]. In this pulse sequence, the contact time is fixed and the time τ from the beginning of the carbon contact time is varied, and acquisition is made after the contact while the proton decoupler is on. This method works in the same manner of the conventional variable CP experiment in measuring T_1H_ρ of crystalline samples and makes itself essential when $T_{IS} \geq T_1H_\rho$. For each sample, 10 to 12 data points were collected and a 30 Hz line broadening applied. All the relaxation data were fitted with a spreadsheet program on a personal computer, assuming single-exponential (first order) decay.

3. Results and Discussion

3.1. Mechanical characterization

Table 1 presents the experimental data from the tension tests performed on neat EVA specimens. These tests were used to determine the optimum processing parameters, establishing the variation of the tensile properties of neat recycled EVA matrix as a function of the temperature (160 °C or 200 °C) and the mixing speed (60 rpm or 100 rpm). The values of neat virgin EVA were obtained only for the following experimental conditions: 160 °C and 100 rpm.

The results on Table 1 show that at 160 °C, and at a rotation speed of 100 rpm, the best compromise between the evaluated properties was obtained. A small increase of the ultimate stress, and a moderate increase of toughness and ultimate strain were obtained in respect to the other processing conditions. The increase of the ultimate strain and, particularly, of toughness, is an interesting aspect for the footwear industry. Figure 1 shows a representative curve of the tensile specimens of the recycled EVA polymer.

This behavior has shown to be dependent of the mixture's experimental processing conditions, since the properties evaluated – mainly the ultimate strain – vary over fairly large bounds, confirmed in Table 1.

When compared with the recycled EVA, on the same conditions of processing, 160 °C and 100 rpm, pure EVA presents a less rigid but tougher behavior, which may happen due to the formation of crosslinking in the recycled EVA structure.

Table 2 shows the results of the tension tests for recycled EVA-silica composites. The values of the processing parameters – temperature (160 °C and 200 °C) and mixing speed (60 rpm and 100 rpm) – were maintained. It can be observed that the values of the Young's modulus did not present significant differences, as a function of the processing parameters. In comparison to the neat recycled EVA (Table 1), the composites showed a slightly decrease of up to 20% on modulus for the same processing parameters. The crosslinking formed in the EVA copolymer structure, known as EVA rubber, during the manufacturing process[12] of shoes' sole, produces a certain degree of molecular immobility. From Table 2, it can be seen that the main effect of reprocessing was a decrease of the molecular rigidity of the polymeric matrix, probably caused by the shear rate imposed to the material, with consequent reduction of some mechanical properties. This effect is more intense when hard particles, such as silica, are present and considerable more time of residence is employed[13-16].

A decrease on the average value of the ultimate stress with the increase of the fraction of silica was also observed. In fact, it was not observed a significant influence on the mechanical properties of the composites with 1% of silica in respect to the neat recycled EVA. However, for the recycled materials composites with 5% of silica the mechanical properties showed a clear tendency to decrease. This behavior strongly suggests that the silica to EVA compatibility is weak.

Comparing the results of the neat virgin EVA, Table 1, and its composite (5% silica), it is possible to observe a slight increase on

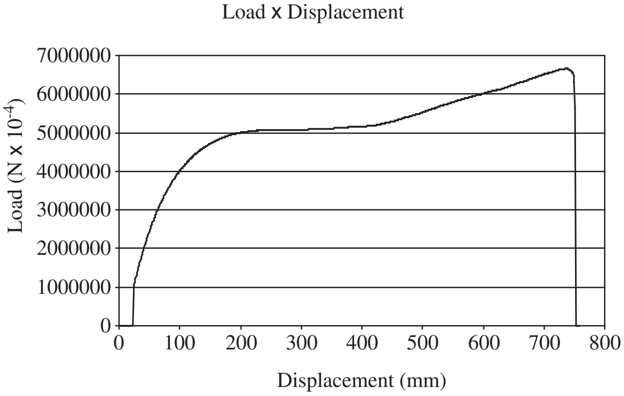

Figure 1. Representative load-displacement curve of recycled EVA specimen (160 °C and 100 rpm).

Table 1. Tensile mechanical properties of recycled and virgin EVA as a function of the processing temperature and velocity.

Material	Young's Modulus (MPa)	Toughness (MPa)	Ultimate Stress (MPa)	Ultimate Strain (%)
Recycled EVA (160 °C/ 60 rpm)	39.02 ± 0.46	22.62 ± 3.86	8.10 ± 0.24	301.10 ± 47.60
Recycled EVA (160 °C/100 rpm)	36.70 ± 1.26	33.27 ± 3.41	8.90 ± 0.35	433.00 ± 37.80
Recycled EVA (200 °C/60 rpm)	35.16 ± 2.42	27.56 ± 1.42	8.11 ± 0.34	383.20 ± 29.68
Recycled EVA (200 °C/100 rpm)	45.67 ± 2.85	19.29 ± 6.62	7.85 ± 0.57	253.60 ± 83.78
Virgin EVA (160 °C/100 rpm)	26.32 ± 1.57	49.64 ± 4.72	15.48 ± 1.96	587.39 ± 37.84

Table 2. Mechanical properties of the composites as a function of the processing variables.

Material	Young's Modulus (MPa)	Toughness (MPa)	Ultimate Stress (MPa)	Ultimate Strain (%)
R. EVA/Silica (1%) (160 °C/60 rpm)	35.87 ± 4.51	18.49 ± 1.83	8.75 ± 0.37	247.80 ± 29.90
R. EVA/Silica (1%) (160 °C/100 rpm)	30.57 ± 1.69	24.69 ± 1.57	9.24 ± 0.58	319.30 ± 47.60
R. EVA/Silica (1%) (200 °C/60 rpm)	34.84 ± 1.03	15.48 ± 2.95	7.99 ± 0.54	207.40 ± 36.10
R. EVA/Silica (1%) (200 °C/100 rpm)	32.22 ± 1.87	25.30 ± 3.82	8.49 ± 0.58	345.40 ± 44.80
R. EVA/Silica (5%) (160 °C/60 rpm)	34.19 ± 1.97	20.03 ± 3.33	7.73 ± 0.59	282.30 ± 38.17
R. EVA/Silica (5%) (160 °C/100 rpm)	33.10 ± 1.37	26.85 ± 2.91	7.50 ± 3.49	343.90 ± 33.10
R. EVA/Silica (5%) (200 °C/60 rpm)	30.12 ± 1.15	18.73 ± 2.76	7.75 ± 0.52	269.10 ± 27.90
R. EVA/Silica (5%) (200 °C/100 rpm)	33.54 ± 0.96	15.78 ± 1.86	7.59 ± 0.50	222.60 ± 31.10
EVA/Silica (5%) (160 °C/100 rpm)	28.36 ± 2.71	47.98 ± 4.23	16.25 ± 2.76	574.37 ± 35.58

modulus for the same processing parameters. A decrease on the values of the toughness and ultimate strain may suggest a certain degree of compatibilization between the silica (polarized structure) and virgin EVA.

The virgin EVA composite shows a reduced value of modulus when compared with the recycled EVA composite, on the same processing conditions and percentage of second phase, 160 °C/100 rpm and 5% silica, although it has a smaller difference between these modulus. This smaller difference is a consequence of the compability of the virgin EVA and silica, besides the mechanical degradation of molecular structure of the recycled EVA during reprocessing, as mentioned previously.

3.2. Scanning electronic microscopy characterization

Figure 2 presents aspects of the fracture surface of a neat recycled EVA sample. The surface is covered by stretched material, which is a characteristic of a great deformation capacity, as it would be expected for the highly flexible EVA copolymer, and it also corroborates with the large strains experimentally determined, Table 1.

Figure 3 shows a characteristic aspect observed at the fracture surface of the composites. It can be observed that the majority of the dispersed silica particles are not adhered to the recycled EVA matrix. The lack of adhesion between phases can create internal defects - voids, delaminated areas, broken interfaces – that cause a weakness of the material. The aspect observed corroborates the non-reinforcing behavior of the silica particles, as shown in Table 2.

3.3. NMR characterization

To measure T_1H_ρ in the composites and neat EVA formulations the sharper line in the NMR spectra at 31 ppm was monitored. This is not a pure line, and corresponds to the CH_2 groups from the ethylene and the vinyl acetate portion of EVA at the main chain. The relaxation behavior was modeled in the composites, considering that silica particles are attached to the recycled EVA matrix by a surface polymer-silica interaction. Therefore, any changes detected in the T_1H_ρ parameter of the composites, in comparison to the values presented by the neat recycled EVA relaxations, were discussed. The NMR analysis was performed for samples processed at 160 °C and 100 rpm.

Table 3 displays proton T_1H_ρ relaxations detected by the protonated main chain carbons of high molecular weight recycled EVA and composites. It was observed that the molecular motion of all samples do not have any significant differences when compared to recycled EVA. This was attributed to the fact that protons T_1H_ρ did not change between samples, which also suggests that EVA relaxation has not been affected by the incorporation of silica particles. Even though the results showed that the overall motion did not change, this may not imply that an interaction has not occurred at the interface. However, it could be pointed out that the matrix is dominating

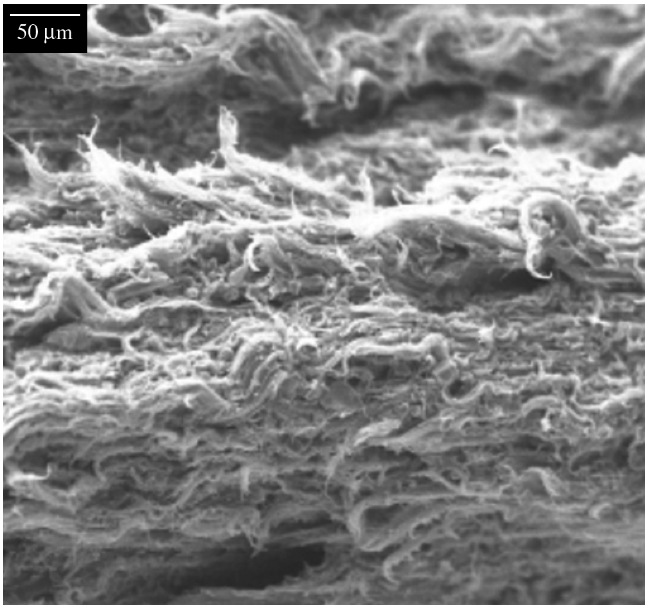

Figure 2. Typical aspects of the fracture surface of the recycled EVA samples.

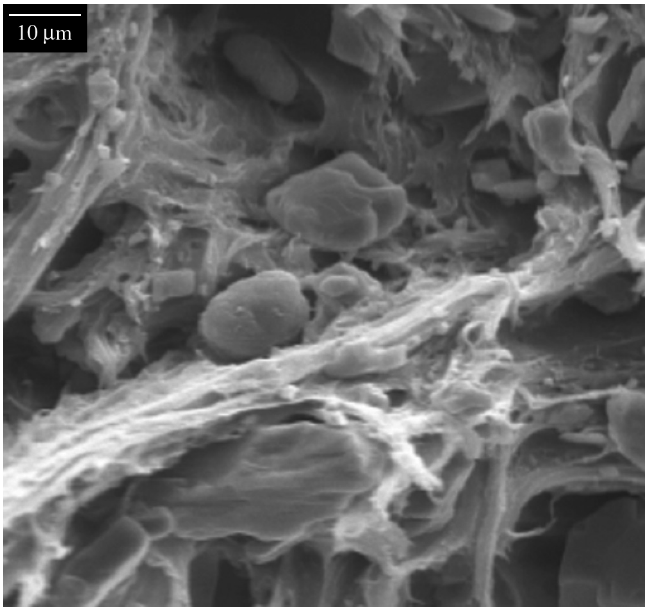

Figure 3. Characteristic aspects of the fracture surface of the silica-EVA composites. The silica particles are detached from the matrix, without signs of any EVA copolymer adhered to them. Recycled EVA sample with 5% silica, processed at 160 °C and 100 rpm.

proton T_1H_ρ relaxation process in these samples since it is, by far, the major component.

Figure 4 shows the ^{13}C MAS NMR spectrum of recycled EVA and Figure 5 shows the spectrum of virgin commercial EVA. Lines a, b, c, d and e were assigned to the methylene (a and b), methyne, carbonyl and methyl groups of EVA structure, respectively. It was observed that the carbon chemical shifts at the recycled EVA spectrum did not change when compared to that of the commercial EVA spectrum. This was interpreted as an absence of chemical modification at EVA structure during the recycling process. However, one can also analyze if the ratio of lines c/d, at the acetate part of EVA, would change between these two samples. From the results obtained, it can be seen that recycled EVA presented loss of the carbonyl groups compared to commercial EVA.

Table 3. Proton T_1H_ρ relaxation data.

Sample	T_1H_ρ (ms) 31 ppm peak
EVA (recycled)	2.0
EVA/1% silica	2.1
EVA/5% silica	2.3

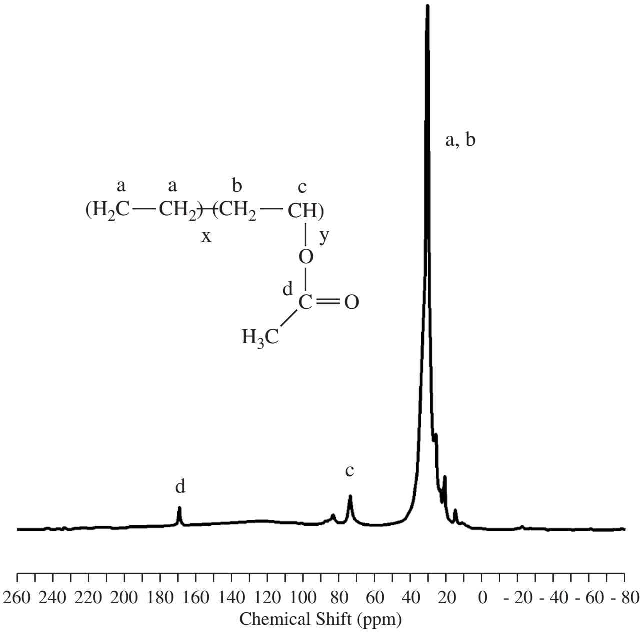

Figure 4. ^{13}C MAS spectrum of recycled EVA.

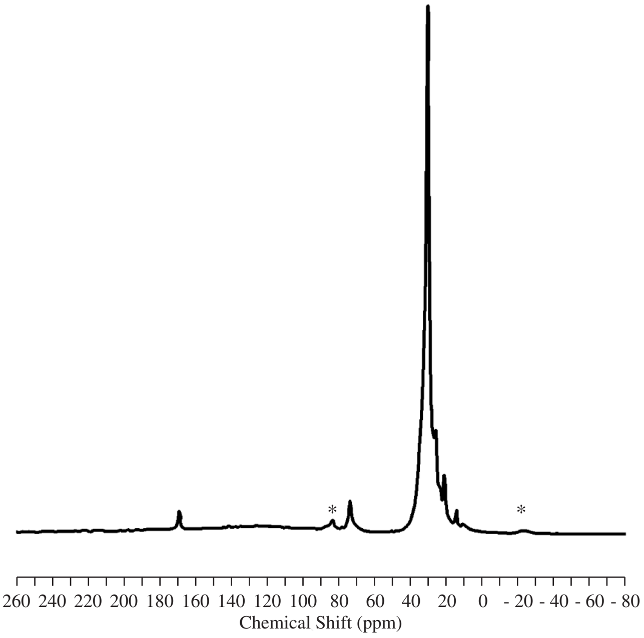

Figure 5. ^{13}C MAS spectrum of commercial EVA.

It is well known that in the reticulation process of EVA is possible to use peroxides or silanes as crosslinking agents. However, in most of the cases, crosslinking is carried out through a transesterification reaction between the ester groups of EVA and the groups of crosslinking agents[12,17,18].

The fact that recycled EVA presented loss of the carbonyl groups, compared to commercial EVA, was attributed to the crosslinking process of recycled EVA. This behavior was attributed to the fact that it may have occurred at the carbonyl carbon. This result indicates that recycled EVA presented a crosslinking formation compared to commercial EVA and this may be the major difference between both recycled and commercial EVA.

4. Conclusions

The experimental results have shown that both temperature and mixing rate can alter the mechanical properties of neat recycled EVA copolymer and EVA-silica composites. The best compromise between the mechanical properties evaluated was obtained when the material was mixed at 100 rpm at 160 °C.

The tension tests and the scanning electron microscopy analysis showed evidences that recycled EVA and hydrofilic silica particles are not compatible. ^{13}C NMR data corroborate these results, since the proton T_1H_ρ relaxations have not been affected by the incorporation of silica. An opposite behavior was observed in the composite of virgin EVA, where an increase in the value of modulus indicated a certain degree of compatibility between polymer matrix and silica.

The NMR analysis shows that the crosslinking process on recycled EVA may be occurring at the carbonyl group. The presence of crosslinking is responsible for the higher rigidity and lower deformability of recycled EVA in comparison to virgin EVA when submitted to tensile test.

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