

Characterization of Recycled EVA Copolymer/Silicon Composites by Solid State Carbon-13 NMR

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Abstract: *The problem of environmental pollution produced by industrial residues is one of the largest concerns of society. As for polymeric materials, they do not decompose easily, and thus the great amount of residues constitutes a serious threat to the environment. Considerable legislative effort has been made to minimize the impact of industrial rejects. The copolymer poly(ethylene-co-vinyl acetate) (EVA) is widely used at the footwear industry as a material for shoes' sole. The incorporation of such inorganic particles such as silicon dispersed in recycled EVA's matrix plays an important role in the improvement of the shoes' sole mechanical properties. Carbon-13 CP/MAS NMR was employed to measure individual proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}^H$'s) 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. This relaxation time is sensitive to motion at low frequency and was used to characterize the composites' compatibility. Since solid state NMR makes it possible to study the dynamics on the molecular size scale, it was thus employed to evaluate molecular motion and composites' compatibility and establish a correlation with the information supplied by other methods such as tension test, adhesion and scanning electron microscopy (SEM).*

The copolymer poly(ethylene-co-vinyl acetate), (EVA), is widely used at the footwear industry as a material for shoes' sole. The incorporation of such inorganic particles such as silicon dispersed in recycled EVA's matrix plays an important role in the improvement of the shoes' sole mechanical properties. Carbon-13 CP/MAS NMR was employed to measure individual proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}^H$'s) at low frequency and was used to study the dynamics¹ on the molecular size scale, in

addition to other methods such as tension test, adhesion and scanning electron microscopy.

High-resolution solid-state ^{13}C NMR experiments were carried out on a Varian INOVA 300 spectrometer equipped with a Cross Polarization-Magic Angle Spinning (CP/MAS) probe operating at resonance frequency of 74.5 MHz (7.1T). ^{13}C MAS spectra were acquired with the following experimental parameters: 90° pulse (5.5 μs); pulse delay of 1s; acquisition time of 0.05s. The spinning rate at magic angle (MAS) was 4kHz. Measurements of the proton spin-lattice

relaxation in the rotating frame ($T_{1\rho}^H$) were performed using the following experimental conditions: a pulse angle of 90° ($5.5\mu\text{s}$) and a 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. 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 a single-exponential (first order) decay.

Figure 1 shows the SEM image of the fractured surface of recycled EVA/silicon composite, where it can be observed that the great part of the dispersed silicon particles in the EVA seems to be not adhered to the polymer matrix. This finding substantiates what was previously observed by tension tests measurements. Table 1 displays proton $T_{1\rho}^H$ relaxations detected by the protonated main chain carbons of high molecular weight recycled EVA and composites.

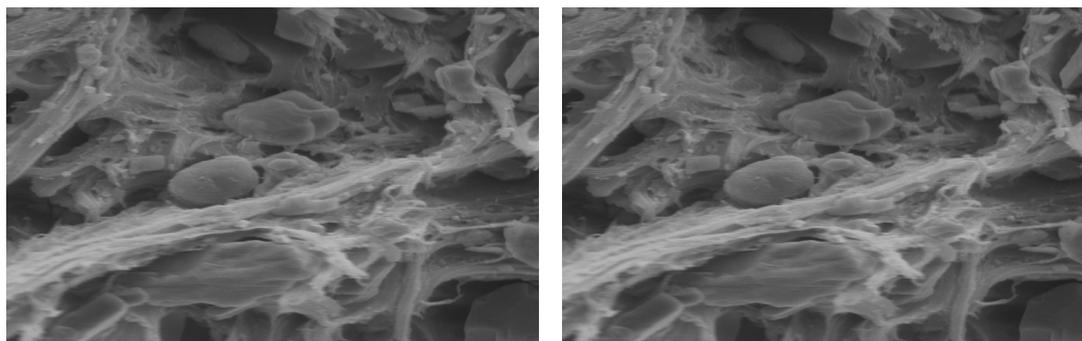


Figure 1. Detailed surface fracture of recycled EVA with 5% silicon.

It was observed that the molecular motion of all samples shows no difference as compared to that of recycled EVA. The fact that protons $T_{1\rho}^H$ do not change between samples indicates that EVA relaxation has not been affected by silicon. However, it is known that a crosslink reaction takes place at the acetate part of EVA copolymer during the recycling process, which can affect the adherence of silicon to the sample. Figure 2 shows the ^{13}C MAS NMR spectrum of recycled EVA.

Table 1. Proton $T_{1\rho}^H$ relaxation times results.

SAMPLE	$T_{1\rho}^H$ (ms) 31ppm peak
EVA (recycled)	2,0
EVA/1% silicon	2,1
EVA/5% silicon	2,3

The lines a,b,c,d and e were assigned to the methylene, methyne, carbonyl and methyl groups of EVA structure, respectively.

It was observed that the ratio of lines c/d of the acetate part of EVA has changed between the two samples ($c/d \cong 1$ for the commercial EVA and $c/d \cong 4$ for the recycled EVA). The recycled EVA presented a loss of carbonyl

groups compared to the commercial EVA. This was attributed to the fact that the crosslinking process of the recycled EVA may have occurred at the carbonylic carbon.

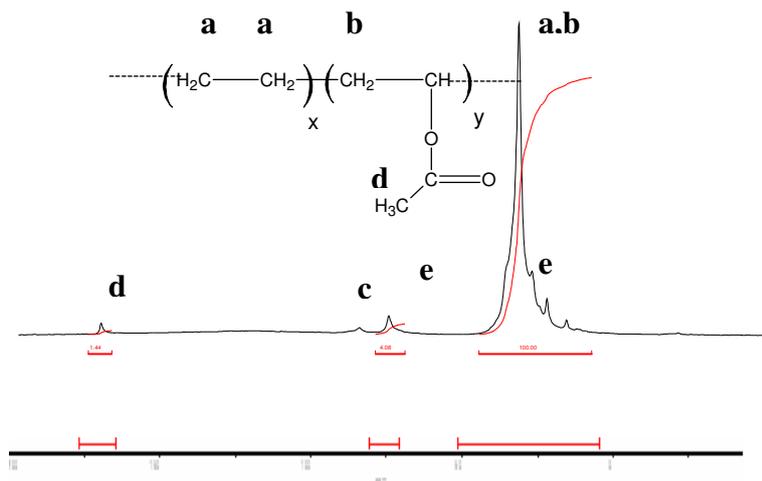


Figure 2. MAS spectrum of recycled EVA.

The tension tests and the scanning electron microscopy analysis evidenced that recycled EVA has no compatibility with the silicon particle.

NMR data substantiates that EVA/silicon composites are non compatible whereas the other methods used seemed to agree.

Reference

1. W. Dierkes. *Int. Polym. Sci. Technol.* **22** (1995) 17.