Evaluation of Aging Effect on NR/CEL II Nanocomposites by Solid State ^{13}C NMR

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Abstract: Elastomeric systems are important classes of industrial materials. They are often used in many critical service applications. Rubber performance decreases with time due to aging, which depends on many factors such as operating temperature, chemical environment, loading conditions and type of rubber. As a result, the estimation of elastomer behavior under aging is a subject of great importance to technologists working with these materials. In this work, the influence of aging caused by heating on vulcanized nanocomposites of natural rubber (NR) and cellulose II (Cel II) was studied by solid state ^{13}C NMR. The amount of Cel II varied from 0 to 30 phr. The composites were submitted to accelerated aging in an air-circulating oven at 70°C during 72 hours. Solid state ^{13}C NMR showed the occurrence of a physical rubber-filler interaction and the nanocomposite with 15phr of Cel II. This sample presented the best mechanical performance, before and after aging. The dynamic molecular evaluation of NR/Cel II systems by NMR correlated strongly with their mechanical properties.

Aging in elastomeric materials is a complex chemical process, which occurs under the influence of heat, oxygen or mechanical stress, resulting in a time-dependent change in their chemical and physical properties. Aging is a very important factor in terms of cost and reliability. Thermal aging is mostly studied because of its practical importance and also because it can easily be controlled under laboratory conditions. At the molecular level, aging is dominated by two competing processes: molecular scission, which results in shorter chains and more dangling ends, and crosslinking, which leads to a more tightly networked structure. Elastomers have been the object of intensive study by NMR, a powerful technique that has the additional advantage of being non-destructive. [1,2]

In this work, the influence of aging caused by heating on vulcanized nanocomposites of natural rubber (NR) and cellulose II (Cel II) was studied by solid state ^{13}C NMR. The amount of cellulose II (Cel II) varied from 0 to 30 phr.

Natural rubber and cellulose II nanocomposites were prepared by the co-coagulation process, and the composites were submitted to accelerated aging in an air-circulating oven at 70°C during 72 hours. NR/Cel II nanocomposites were examined using ^{13}C high resolution solid-state NMR with cross polarization (CP) and magic angle spinning (MAS). These tests were conducted at room temperature using a Varian INOVA-300 (7.1T) NMR spectrometer operating at 75.4 MHz for ^{13}C. A pulse width of 90° (5.5 μs)

was applied with a delay time of 1s, and 1024 transients were accumulated. A spectral width of 50 kHz and an acquisition time of 0.05s were used for data collection. The contact time was 5000 μs. The spectra were referenced to the hexamethylbenzene (methyl peak at 17.3 ppm from TMS). Pulse power was calibrated to achieve Hartmann-Hahn conditions. The samples were spun at 4.5kHz of MAS in a 7mm zirconia rotor. The ^{1}H relaxation times in the rotating frame ($T_{1\rho}{}^H$) were measured using a standard procedure based on a variable spin lock period preceeding a constant cross-polarization time. Twelve points were acquired in the range of 800 μs to 25 ms.

Tables 1 and 2 present $T_{1\rho}{}^H$ relaxations detected by the protonated main chain carbons of NR/Cel II nanocomposites. From Table 1 three different features can be observed: (1)

NR/10 and NR/20 composites show a heterogeneous phase, characterized by distinct $T_{1\rho}{}^H$ values between the olefinic and the aliphatic carbon peaks; (2) NR/30 composite shows a homogeneous phase since $T_{1\rho}{}^H$ values for both domains (olefinic at 127ppm and aliphatic at 34-25ppm) are similar. This composite presents higher molecular mobility than the other filled ones, much closer to the unfilled NR. This suggests that cellulose II no longer affects the NR molecular motion when it is present in the amount of 30 phr; and (3) that NR/15 composite presents a unique behavior. Among the filled composites, it shows a more homogeneous phase, and the lower $T_{1\rho}{}^H$ values indicate a decrease in NR molecular mobility. These results are consistent with the ones obtained for the mechanical properties.

Table 1. $T_{1\rho}{}^H$ values for NR/Cel II nanocomposites before aging

NR/Cel II (phr)	$T_{1\rho}{}^H$ (ms)						
	136 ppm[a]	127 ppm[b]	106 ppm[c]	76 ppm[d]	34 ppm[e]	28 ppm[f]	25 ppm[g]
NR	(15.6)	16.3	---	---	17.4	19.1	23.0
NR/10	(25.4)	17.3	---	14.7	9.6	8.4	8.5
NR/15	(17.7)	9.4	---	12.3	8.8	7.4	7.8
NR/20	(17.7)	18.4	---	10.9	8.1	7.2	7.7
NR/30	---	24.4	7.6	9.3	19.3	22.1	22.7

Shifts: (a) α Carbon of NR; (b) β Carbon of NR; (c) C1 Carbon of Cel ring; (d) C2,C3,C4 and C5 Carbons of Cel ring, (e) δ Carbon of NR; (f) ε Carbon of NR; (g) γ Carbon of NR

After aging (Table 2) there is a severe decrease in the molecular mobility of rubber domains, mainly at the olefinic part. NR and NR/30 present a similar behavior, *i.e.*, a decrease in $T_{1\rho}{}^H$ values, which can be

explained by the poor mechanical properties of these samples. Once again, NR/15 shows a different behavior, much closer to that found before aging.

Table 2. $T_1\rho^H$ values for NR/Cel II nanocomposites after aging at 70°C; 72h

NR/Cel II	$T_1\rho^H$ (ms)						
(phr)	136 ppm	127 ppm	106 ppm	76 ppm	34 ppm	28 ppm	25 ppm
NR	9.0	6.5	-	-	6.0	8.8	8.3
NR/10	7.1	5.3	-	7.0	6.1	5.7	6.5
NR/15	7.4	6.3	4.5	10.4	8.4	7.1	9.4
NR/20	5.1	7.4	4.8	6.1	6.4	4.3	4.6
NR/30	11.1	8.7	6.1	7.7	7.3	6.8	7.4

The natural rubber nanocomposite containing 15 phr of cellulose II was found to have the best mechanical performance, before and after aging. Solid state ^{13}C NMR showed the occurrence of a physical rubber-filler interaction. The dynamic molecular evaluation of NR/Cel II systems by NMR corroborated very well with the mechanical properties measurements, before and after aging.

References

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