Analysis Method

A simple NMR method to measure crosslink density of natural rubber composite

Young Kee Chae, Woo Young Kang, Joong-Hee Jang, Sung-Seen Choi*

Department of Chemistry and Institute for Chemical Biology, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul 143-747, South Korea

ABSTRACT

The crosslink density of carbon black-reinforced natural rubber (NR) was correlated with ^{1}H chemical shift by liquid-state ^{1}H NMR spectroscopy. Instead of observing the rubber directly with the solid-state NMR technique, we used toluene molecules in the liquid state as probes to explore the inner cavities of the rubber sample. Four NR composites with different carbon black contents of 20, 40, 60, and 80 phr were tested. The toluene signals were split into two: one from the bulk solvent and the other from inside the rubber. The chemical shift difference between those two split signals was observed to be in linear relationship with the carbon black content. The samples thermally aged at 70 °C for 100 days showed larger chemical shift differences than the unaged sample. Furthermore, the chemical shift difference was directly proportional to the apparent crosslink density obtained independently by the conventional swelling method. This result offers by far the simplest method to measure the apparent crosslink density in rubber.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

NMR spectroscopy is the method of choice when it comes to the investigation of molecular structures. One of the many advantages it carries is its non-destructive nature, so the same sample can be removed from the NMR tube and used in other types of analysis. Many investigations on rubber have been made using solid-state NMR spectroscopy and microscopy [1–6]. A practical application of NMR is the estimation of the crosslink density responsible for important mechanical characteristics of polymers. The crosslink density is related to the size of pores or cavities inside solid polymers. There are several useful NMR parameters to get the information on the crosslink density, for example magnetic relaxation [7] and the dipolar correlation effect [8]. These methods directly observe the NMR parameters of the polymer itself. On the other hand, one can use small particles to look inside the polymer, thus observing it indirectly through the behaviors of those probes. Some researchers have been using [129]Xe to determine the pore sizes and their distribution in mesoporous silica gels [9,10]

As an important elastomer for industrial applications, natural rubber (NR) has been the subject of extensive research. Curatives, such as sulfur, cure accelerators and reinforcing fillers, such as carbon black and silica, are added to enhance the chemical and mechanical properties. Carbon black is the most popular reinforcing filler of rubber compounds. Carbon black content of a rubber compound affects the cure characteristics, bound rubber content and crosslink density [11–13]. Crosslink density of a rubber vulcanizate determines the physical properties such as modulus, hardness, resilience, elongation at break and heat build-up [14]. Crosslink densities of rubber composites were reported to be changed by thermal aging [14–19].

Although several useful parameters could be extracted from solid-state NMR experiments, the correlation between the crosslink density and such parameters as T_1 and T_2 was seldom demonstrated explicitly. One rare case is the report from Sakdapipanich et al. [20] who explicitly

* Corresponding author. Tel.: +82 2 3408 3815.
  E-mail address: sschoi@sejong.ac.kr (S.-S. Choi).

showed such a relationship, although no clear tendency was visible, based on the intensity ratio between two small ^{13}C signals. The [129]Xe NMR could draw some linear relationship between the chemical shift and degree of solvent swelling, but the linearity only held for the subset of their data. We have been trying to devise a much simpler way to determine the crosslink density by applying one-dimensional ^{1}H NMR in the liquid state and avoid any sophisticated machinery or special conditions that some of the previous works have employed. The solid-state NMR would seem to be the obvious choice since the sample is solid but, if the same information can be obtained in the liquid-state, liquid-state NMR could yield a simpler solution with better sensitivity and resolution. In this work, we present by far the simplest method of estimating the crosslink density of an NR composite based on the chemical shift differences between the bulk solvent and trapped molecules.

2. Experimental

Four carbon black-reinforced compounds were made using natural rubber (STR OL), carbon black (N330), anti-degradants (N-phenyl-N′-(1,3-dimethylbutyl)-p-phenyl-enediamine (HPPD) 1.5 phr and wax 2.0 phr), cure activators (stearic acid 2.0 phr and ZnO 3.0 phr), and curatives (N-tert-butyl-2-benzothiazole sulfenamide (TBBS) 1.8 phr and sulfur 1.2 phr). The carbon black contents were 20.0, 40.0, 60.0, and 80.0 phr. Mixing of the compounds was performed using an internal mixer and the vulcanization was performed at 160 °C for 30 min in a compression mold of $140 \times 140 \times 2$ mm^3. The samples were aged at 70 °C for 100 days in a convection oven.

Bound rubber content was determined by extracting the unbound materials such as unbound ingredients and free rubber with toluene at room temperature for 7 days and with n-hexane for 1 day, followed by drying at room temperature for 2 days. The weights of the samples before and after the extraction were measured and the bound rubber contents were calculated as $R_b(\%) = 100 \times \{W_{fg} - W_t[m_f/(m_f + m_r)]\}/\{W_t[m_r/(m_f + m_r)]\}$, where R_b is the bound rubber content, W_{fg} is the weight of filler and gel, W_t is the weight of the sample, m_f is the fraction of the filler in the rubber composite, and m_r is the fraction of the rubber in the rubber composite.

Apparent crosslink densities of the unaged and aged rubber composites were measured by the swelling method. Organic additives remaining in the samples were removed by extracting with THF and n-hexane for 3 and 2 days, respectively, followed by drying for 2 days at room temperature. The weights of the organic materials-extracted samples were measured. They were soaked in toluene for 2 days and the weights of the swollen samples were measured. The swelling ratio (Q) was calculated by the equation of $Q = (W_s - W_u)/W_u$, where W_s and W_u are the weights of the swollen and unswollen samples. The reciprocal swelling ratio (1/Q) was used as the apparent crosslink density.

The rubber composite strips were soaked in toluene for one day, and excess solvent was removed by gravity. The strips were put into the 5 mm NMR tube, and sufficient deuterated chloroform was added to submerge the strips.

All spectra were collected at 298 K with a Bruker Avance II 500 spectrometer (Bruker, Germany). The spectral width, total data points and number of scans were 10,000 Hz, 32,768, and 16, respectively. The cosine squared window function was applied before Fourier transform. After the phase correction, the spectra were referenced by setting the internal TMS frequency to 0 ppm. The chemical shifts of ring protons and methyl protons were measured. The spectral data were imported to Microsoft Excel, and the changes of chemical shifts were plotted against the carbon black content or the crosslink density. The peak width was measured by fitting the peak to a Lorentzian line shape after baseline correction.

3. Results and discussion

Since the NMR sample was heterogeneous, i.e., solid rubber composite in liquid chloroform, it was difficult to shim. For some samples, automatic gradient shimming (Top Shim) could be executed and performed although the resulting lock level did not increase as for normal liquid samples. For others, automatic shimming was not even possible and it had to be shimmed manually. Thus, we believe that the toluene resonances were broadened partly due to the low level of shimming. As will be mentioned later, the other source for peak broadening was the chemical exchange.

The aromatic and methyl regions of a stacked plot of four spectra obtained from the unaged rubber composite strips with different carbon black contents are shown in Fig. 1(a) and (b). Both the aromatic and methyl resonances were clearly split into two groups, corresponding to those resulting from toluene molecules outside and inside the rubber strip. It can also be readily noted that both the aromatic and methyl signals from toluene molecules moved further upfield as the carbon black content increased from 20 to 80 phr. Since the aromatic signals suffered more severe overlap, the methyl resonances were regarded more suitable to track as a function of the carbon black content and, therefore, were chosen for the later analysis. The methyl resonances from TMS showed the same trend as those of toluene (Fig. 1(c)), but they showed more complicated shapes than the toluene methyl groups. Fig. 2 explicitly shows this tendency. We could observe that the signal from the outside toluene also moved slightly upfield and broadened. This is partly due to the inhomogeneous magnetic field around the sample. In addition to this, the outside toluene could interact with the outer surface of the rubber strip, so might well be influenced by it. Therefore, when we measured the chemical shift change, we measured the difference between two methyl signals in the same sample, not between those of the sample and reference toluene liquid. The reference toluene liquid showed its methyl signal at 2.34 ppm, while outside toluene of the actual samples appeared between 2.29 and 2.33 ppm. The actual chemical shift values did not correlate with the carbon black content, which indicated the variation of the heterogeneity of both the samples and magnetic field at the time of the experiments.

The inside structures of the unaged and aged sample strips were observed with the toluene molecules as probes. The aged sample strips showed greater changes in the