LA-UR- 00 - 3 5 9 1

SOLID-STATE NMR - PROGRESS REPORT

January - April, 2000

Tom Stephens - ESA-WMM

tstephens@lanl.gov

Andrea Labouriau - CST-18

andrea@lanl.gov

It is well established that the zero shear bulk viscosity of all amorphous polymers is directly proportional to the molecular weight below a critical low molecular weight M_c , and above this molecular weight increases as the 3.5 power of M_w . This effect manifests itself on the NMR proton spin-spin relaxation time (T_2). For polydimethyl siloxane the break in the proton T_2 -molecular weight curve occurs at about $M=50000$ g/mol and M_c is about 30000 g/mol from viscosity measurements. Thus, there is a direct connection between the critical molecular weight representing the influence of entanglements on the bulk viscosity and other properties and the spin-spin relaxation time of amorphous polymers. Therefore, the entanglements must modulate the segmental motions so that even in the amorphous state they are a major reason for the incomplete motional narrowing. This effect would then be further accentuated with cross-links, filler, etc. For high molecular weights in the amorphous state, polymer chains exhibit both liquid-like and solid-like properties from the point of view of NMR measurements. The liquid-like properties are manifested in the high frequency segmental motions. The solid-like properties are a result of residual dipolar couplings caused by incomplete motional narrowing.

We have applied spin-spin relaxation time measurements to probe the dynamics of PDMS chains having different amounts of cross-links and filler. The spin-spin relaxation decay curves are shown in Figure 1. As we can see, the transverse magnetization decay is a function of the cross-link density as well as the filler concentration. It decays faster for the sample containing the highest cross-link density and filler concentration than for the sample containing no filler and a low cross-link density. This result is just an indication of a more 'solid-like' behavior for the sample containing more constraints, and a more 'liquid-like' behavior for the sample containing fewer constraints.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Next, we carried out T_2 measurements for the counterparts of these samples that have been aged under thermal treatments and that have shown changes in their mechanical properties. Figure 2 shows the magnetization decay for the sample with high cross-link density and 10% of filler aged at 90°C for 60 days. As we can see, the decay became faster for the aged sample compared to the unaged one. This effect is explained in terms of a reduction in the polymer chain dynamics, which translates to a stiffer sample. This result is in agreement with mechanical tests done for these samples. From the ^{29}Si MAS NMR spectrum obtained for the unaged sample, we have detected two small peaks at -3 and -6 ppm. These resonance lines have been identified as the ones from catalyst that was used to vulcanize these samples. However, these two peaks are not present in the ^{29}Si MAS NMR spectrum obtained for the aged sample. Consequently, we infer that the aged sample became stiffer as a result of a small amount of catalyst left over during the curing process. As the sample was heated at 90°C for 60 days, the catalyst reacted to form a few more cross-links. With respect to the sample with a low cross-link density and 10% filler, the magnetization decay for the aged sample shows the opposite behavior (see Figure 3). Or in other words, the magnetization decay became slower for the aged sample when compared to the unaged one, which implies that the former sample became softer. Once more, it is worth mentioning that this result is in conformity with the latest mechanical tests done for this sample. From ^{29}Si MAS NMR spectrum, we propose that the aged sample underwent degradation by cleavage of the Si-C bonds.

Subsequently, we have carried out spin-spin relaxation measurements for S5370 and two stockpile return parts. The magnetization decay curves are shown in Figure 4, and they are very similar. ^{29}Si MAS NMR spectra obtained for these samples show that their chemical composition is also very similar (see Table 1). We have also investigated the effect of thermal treatment for S5370. The magnetization decay as a function of the time that the sample was heated at 115°C in air is shown in Figure 5. As we can see, no 'aging' effects were detected for S5370 under these conditions.

The next set of NMR tests that we have started is the cross-polarization experiment (CP). Up to now, we have applied this technique for investigating the ^{29}Si magnetization for silanol species present in fumed silica. The dependence of the ^{29}Si magnetization on the contact time for silanol species is shown in Figure 6. The rise of the

magnetization is due to the cross-polarization by protons. We propose to perform CP experiments for the DC745u sample, where fumed silica is one of the fillers. The presence of near by protons from the polymer chains to the surface of the filler should influence the ^{29}Si magnetization growth, when compared to the one for the filler alone. Consequently, this technique should allow us to directly probe the interface polymer/filler. These experiments as well as T_2 measurements, ^{29}Si , ^{13}C MAS NMR are under way for DC745u.

Overall, this study shows that solid state NMR is a valuable tool for determining structure as well as changes in the chain dynamics of solid polymers.

Figure 1- PDMS GELS

Figure 2 - Aged PDMS (high cross-link density and 10% filler)

Figure 3 - aged PDMS (low cross-link density and 10% filler)

Figure 4 - S5370 and two return parts.

Figure 5 - S5370 aged at 115C in air for a total of 53 hours.

Figure 6 - Cross-polarization for fumed silica

Table 1. Chemical composition calculated from ^{29}Si MAS NMR:

Si species	Chemical shift δ (ppm)	% of total signal S5370	% of total signal 'none'	% of total signal aged '83'
$\begin{array}{c} \text{Me} \\ \\ \text{HO}-\text{Si}-\text{O}- \\ \\ \text{Me} \end{array}$	~ -11			
$\begin{array}{c} \text{Me} \\ \\ \text{MeO}-\text{Si}-\text{O}- \\ \\ \text{Me} \end{array}$	~ -12			
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{Me}-\text{Si}-\text{O}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	(From -10.3 to -12.2 ppm) ~ -12	2.7% (this could also come from the other two groups listed above)	2% (same)	2.6% (same)
$\begin{array}{c} \text{Me} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{Me} \end{array}$	-21.9	75%	80%	77%
$\begin{array}{c} \text{O} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{Me} \end{array}$	-66.8 (~ -66)	9%	7%	7%
$\begin{array}{c} \text{OH or} \\ \text{O}(\text{CH}_2\text{CH}_3) \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{Me} \end{array}$	-58 (~ -57)	Small amounts	no	Small amounts
Filler	-110 broad peak	13%	12%	12%

Table 2. Chemical composition calculated from ^{29}Si MAS NMR for DC745:

Si species	Chemical shift δ (ppm)	% of total signal DC745 new	% of total signal DC745 aged*
$\begin{array}{c} \text{Me} \\ \\ \text{-O-Si-O-} \\ \\ \text{Me} \end{array}$	-22.1	82%	82%
$\begin{array}{c} \text{O} \\ \\ \text{-O-Si-O-} \\ \\ \text{Me} \end{array}$	-66.8 (~ -66)	Small amounts	Small amounts
$\begin{array}{c} \text{Ph or vinyl} \\ \\ \text{-O-Si-O-} \\ \\ \text{Me} \end{array}$	-33.9	About 2%	About 2%
Filler	-110 broad peak -107.4 sharp peak		About 12% fumed silica and 3% quartz

* The aged sample was heated at 250C for a total time of 59.5 hours in air. T2 experiments show an decrease in the dynamics.