Use of TD-NMR and Mini DeMattia-Crack-Growth for Characterization of EPDM Hose Compounds

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Abstract

The state-of-cure and property changes of an EPDM hose compound were studied as a function of cure and aging history. Time domain (TD)-NMR was used for tracking changes to the state of cure. Mini DeMattia was used to characterize the changes in cut growth resistance. TD-NMR is useful also for quality assurance because it is fairly simple and robust. Mini DeMattia is particularly useful when only small samples can be extracted from a molded rubber component. These techniques were useful for EPDM hose compound. The property changes as a function of cure and aging (air-oven) of the EPDM hose compound were quantified.

Introduction

Dynamic mechanical testing is a powerful predictive tool that can provide valuable insight into the performance of various compounds. Certain compound characteristics correlate with dynamic mechanical properties measured under defined frequency, strain (or stress) conditions, and temperature on a Dynamic Mechanical Thermal Analyzer (DMTA), which can be used to quickly differentiate a series of experimental compounds.

Time domain nuclear magnetic resonance (TD-NMR) is a useful tool for tracking changes in the state of cure, i.e. crosslink density, of the compound. A Hahn Spin Echo experiment is conducted to determine the relaxation time of the compound. This relaxation time is the time required for all of the protons in the compound to return to their original position.

This study will investigate state-of-cure and property changes of an EPDM hose compound as the extent of cure and the total aging time were varied. The cure was varied from 25% to 100% cure and the compound was tested unaged as well as after 1, 3, 6, and 13 days of air oven aging at 155°C. The testing included DMA strain sweep, TD-NMR, Mini DeMattia, and Tensile.

Experimental

Compounding/Mixing

The EPDM hose compound was mixed using an upside down mixing procedure. The procedure is summarized in Table 1 below. The compound was cured at 160°C for 14 min for the 100% cure condition and for 4, 5, or 6 min for the 25%, 50%, and 75% cure conditions, respectively.

Starting Temperature		65°C
Starting Rotor Speed, rpm		60
Fill Factor		80%
Ram Pressure		50
Mix Sequence		Mix Upside Down
		Sweep at 87.8°C (190°F)
Dump Conditions		At 104.4°C (220°F)
Royalene 512	EPDM Rubber	100 phr
N650	Carbon Black	100 phr
N762	Carbon Black	100 phr
Sunpar 2280	Oil	120 phr
Zinc Oxide	Cure Activator	5 phr
Stearic Acid		0.5 phr
DTDM	Accelerator	1.7 phr
ZDBC	Accelerator	2.5 phr
ZDMC	Accelerator	2.5 phr
TMTD	Accelerator	2.5 phr
Sulfur	Crosslink Agent	0.5 phr

Table 1: Compound Formulation for EPDM hose compound

The compound was molded into 2mm tensile slabs for unaged properties and into 1mm tensile slabs for all aged properties. For the Mini DeMattia testing, the compound was molded into 0.762mm (0.030in) slabs.

Dynamic Mechanical Analysis

A Metravib DMA +150 dynamic mechanical thermal analyzer with the attached 150N load cell was employed using tension grips. A sinusoidal cyclic deformation was applied to the samples. One 2mm thick tensile sheet per cure condition and one 1mm thick tensile sheet per aging condition had one strip cut to a width of 12.7mm stamped out of it using an ASTM die.

Two successive strain sweeps (double strain sweeps) were carried out at a frequency of 1 Hz at 30°C. The testing followed the following sequence of static/dynamic strain ratios: (0.001/0.0005, 0.001704/0.0009334, 0.002904/0.001716, 0.004949/0.003118, 0.008433/0.005611, 0.01437/0.01002, 0.02449/0.01779, 0.04173/0.03140, 0.07112/0.05519, 0.1212/0.09665, 0.2065/0.1687, 0.3521/0.2936, 0.60/0.51). The distance between the tension grips was 5mm for this testing. The data used for comparison was obtained at approximately 5% dynamic strain during the second strain sweep.

Tensile

Tensile was conducted following ASTM D412. Five die C dumbbells were cut out of one 2mm tensile slab per cure condition and out of one 1mm tensile slab per aging condition using an ASTM die. The samples were elongated at 508mm/min (20in/min).

Time Domain NMR

A Bruker Minispec mq20 solid state TD-NMR was used to determine state of cure differences. Buttons 6.35mm (1/4in) in diameter were punched out of one 2mm tensile slab per cure condition and out of one 1mm tensile slab per aging condition using a Mayhew Hollow Punch. These buttons were placed into NMR tubes and allowed to warm to 90°C. A Hahn Spin Echo experiment was then conducted on these samples to obtain the relaxation times for the compound at the various cure and aging conditions.

Mini Demattia

In the interest of measuring fatigue properties of small samples extracted from engineered rubber components such as tires, belts, hoses, etc., ARDL, Inc. has developed the Mini DeMattia test. This test is based upon the standard DeMattia test (ASTM D813) which is used to evaluate the fatigue life of lab-cured compounds. The specimen dimensions have been reduced by a factor of 8 to 1.

Results and Discussion

All of the final DMTA testing results, NMR results, and tensile results are included in the figures below. The results from all of the tests compliment each other.

DMA Strain Sweeps

Figures 1 – 4 show the results from the DMA strain sweep. Figures 1 and 2 show how amount of cure affects storage modulus and tangent delta, respectively. Figures 3 and 4 show how amount of aging affects storage modulus and tangent delta, respectively. It is seen that storage modulus appears to be dependent on the amount of strain put on the compound during curing. It is also seen that storage modulus appears to increase greatly after a short period of aging and then decreases as expected after longer aging.

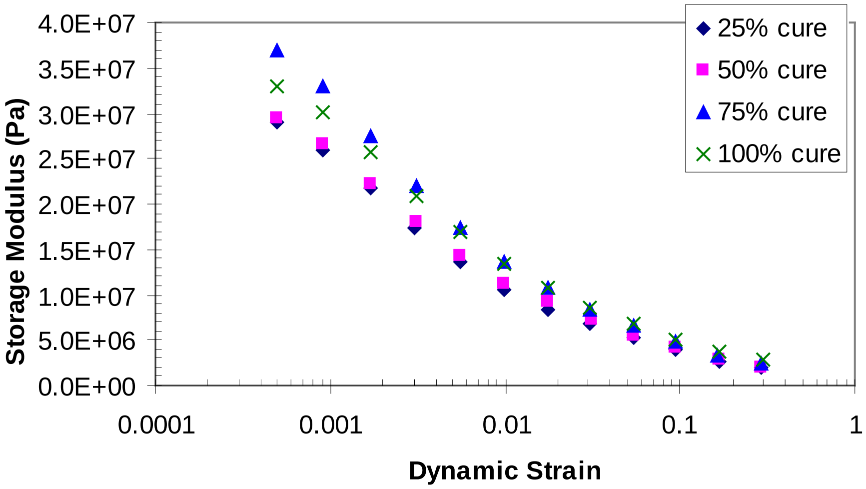


Fig. 1 – Storage Modulus vs. Amount of Cure

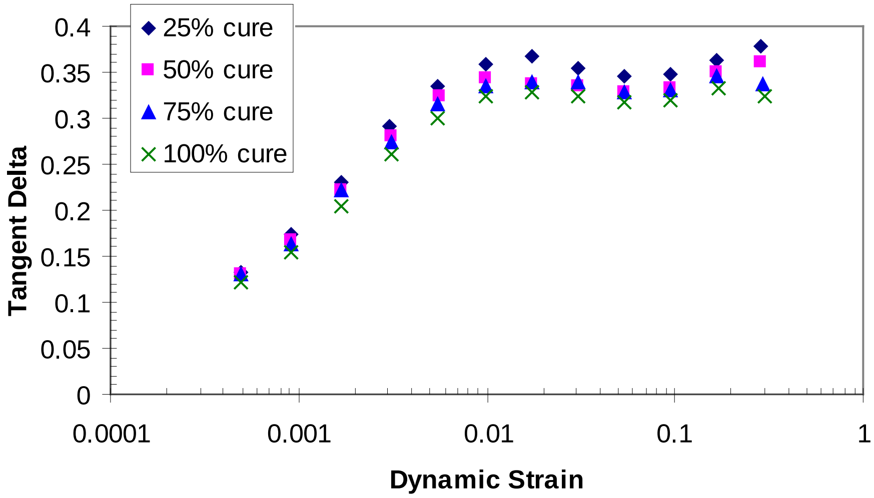


Figure 2 – Tangent Delta vs. Amount of Cure

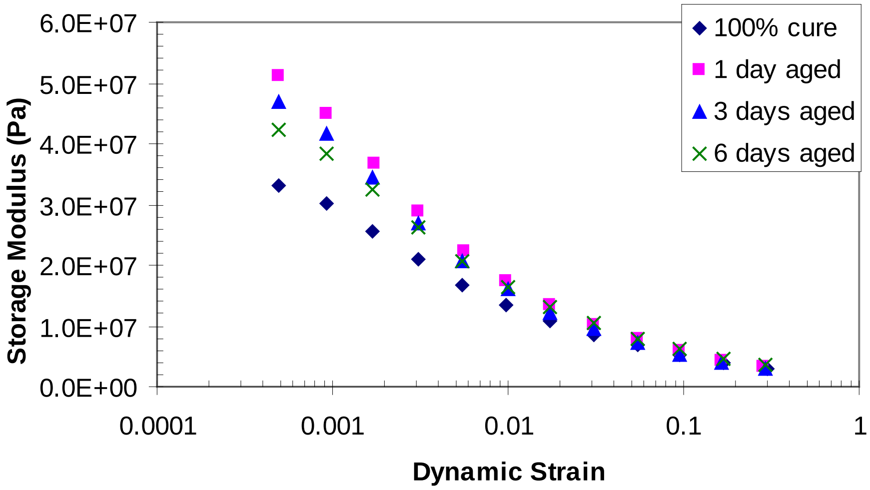


Figure 3 – Storage Modulus vs. Amount of Aging

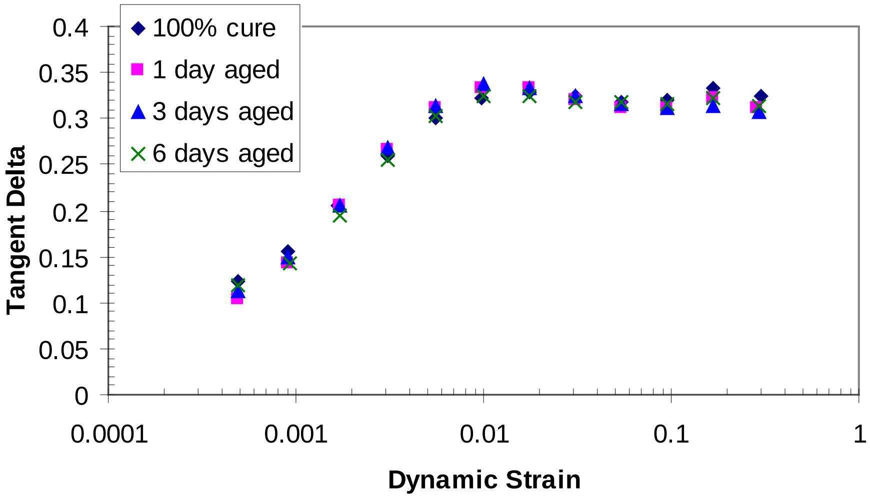


Figure 4 – Tangent Delta vs. Amount of Aging

Time Domain NMR

The NMR results are shown in Figures 5 – 10, and Table 2. Table 2 shows the results from the T_2 relaxation bi-exponential fit. The A(1) and A(2) values are the coefficients of the first and second component, respectively, of the bi-exponential fit. The time constant $T_2(1)$ and $T_2(2)$ values are the exponents for the first and second component, respectively, of the bi-exponential fit. Figure 5 shows an example of a Hahn Echo experiment. Figure 6 shows a typical T_2 relaxation curve. Figure 7 shows how the average value for the exponent $T_2(1)$ is affected by the amount of cure. Figure 8 shows how the ratio between A(1) and $T_2(1)$ is affected by the amount of cure. Figure 9 shows how the average value for the exponent $T_2(1)$ is affected by the amount of aging. Figure 10 shows how the ratio between A(1) and $T_2(1)$ is affected by the amount of aging. The error bars in these four figures are the 95% confidence limits for each value shown. $T_2(1)$ and the ratio $A(1)/T_2(1)$ are useful indicators for crosslink density. Samples with shorter $T_2(1)$ relaxation times and higher $A(1)/T_2(1)$ ratios have higher crosslink density. It is seen that crosslink density increases as amount of cure increases and as amount of aging increases.

Table 2: Bi-exponential fit data

Sample	Run	A(1)	$T_2(1)$	$A(1)/T_2(1)$	A(2)	$T_2(2)$
jemnb1-70-1_25%	1	47.5	1.78	26.7	55.5	18.5
“	2	47.4	1.79	26.5	55.6	18.6

“	3	47.7	1.79	26.6	55.6	18.6
Average		47.5	1.79	26.6	55.6	18.6
Standard Deviation		0.153	0.00577	0.109	0.0577	0.0577
95% Confidence		0.245	0.00925	0.175	0.0925	0.0925
jemnb1-70-1_50%	1	48.2	1.71	28.2	54.7	18.5
“	2	48.3	1.72	28.1	55.0	18.6
“	3	48.3	1.73	27.9	54.8	18.6
Average		48.3	1.72	28.1	54.8	18.6
Standard Deviation		0.0577	0.0100	0.135	0.153	0.0577
95% Confidence		0.0925	0.0160	0.216	0.245	0.0925
jemnb1-70-1_75%	1	48.4	1.68	28.8	54.7	18.9
“	2	48.4	1.70	28.5	54.9	19.0
“	3	48.3	1.71	28.2	54.8	19.0
Average		48.4	1.70	28.5	54.8	19.0
Standard Deviation		0.0577	0.0153	0.284	0.100	0.0577
95% Confidence		0.0925	0.0245	0.455	0.160	0.0925
jemnb1-70-1_100%	1	49.0	1.62	30.2	54.2	19.1
“	2	49.0	1.64	29.9	54.3	19.1
“	3	48.9	1.65	29.6	54.4	19.1
Average		49.0	1.64	29.9	54.3	19.1
Standard Deviation		0.0577	0.0153	0.307	0.100	0.00
95% Confidence		0.0925	0.0245	0.493	0.160	0.00
jemnb1-70-1_1day	1	48.5	1.54	31.5	55.1	17.5
“	2	48.4	1.54	31.4	54.9	17.5
“	3	48.4	1.53	31.6	55.1	17.5
Average		48.4	1.54	31.5	55.0	17.5
Standard Deviation		0.0577	0.00577	0.105	0.115	0.00
95% Confidence		0.0925	0.00925	0.168	0.185	0.00
jemnb1-70-1_3days	1	47.4	1.51	31.4	55.8	17.0
“	2	47.7	1.52	31.4	55.4	17.1
“	3	47.7	1.51	31.6	55.6	17.1
Average		47.6	1.51	31.5	55.6	17.1
Standard Deviation		0.173	0.00577	0.117	0.200	0.0577
95% Confidence		0.278	0.00925	0.188	0.321	0.0925
jemnb1-70-1_6days	1	46.7	1.48	31.6	56.2	18.0
“	2	46.8	1.47	31.8	56.2	18.0
“	3	46.5	1.48	31.4	56.1	18.0
Average		46.7	1.48	31.6	56.2	18.0
Standard Deviation		0.153	0.00577	0.213	0.0577	0.00
95% Confidence		0.245	0.00925	0.342	0.0925	0.00
jemnb1-70-1_13days	1	43.7	1.33	32.9	58.1	15.9
“	2	43.5	1.31	33.2	58.3	15.8
“	3	43.7	1.31	33.4	58.4	15.9
Average		43.6	1.32	33.1	58.3	15.9
Standard Deviation		0.115	0.0115	0.257	0.153	0.0577

95% Confidence		0.185	0.0185	0.412	0.245	0.0925

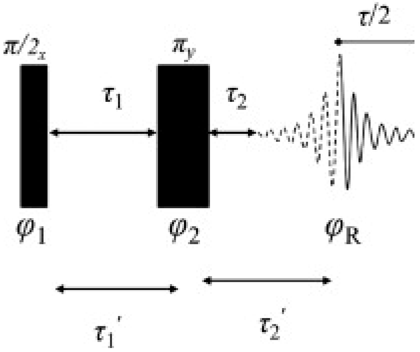


Figure 5 – Example of Hahn Echo Time Domain NMR experiment[1]

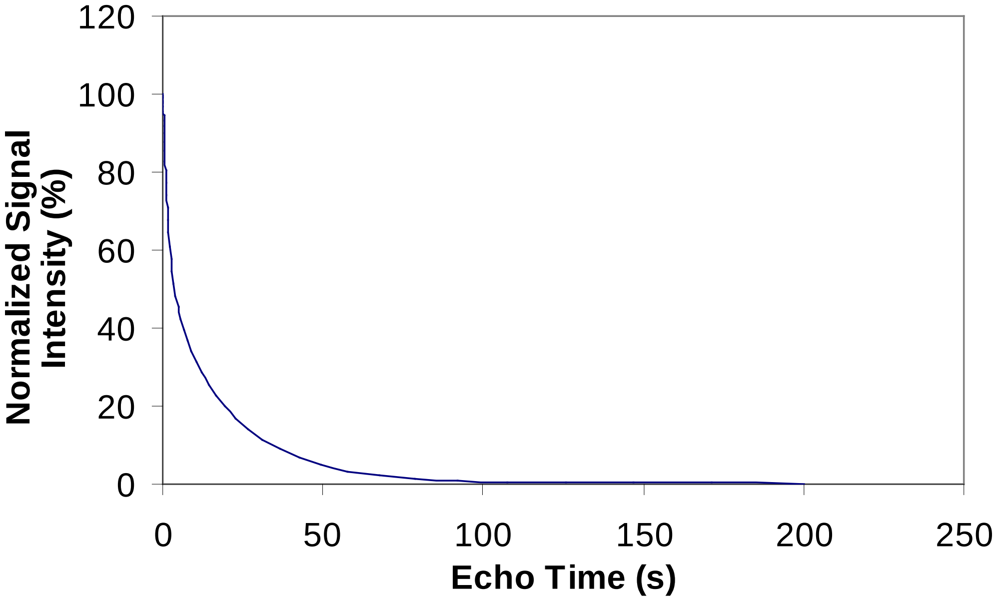


Figure 6 – Example Time Domain NMR T_2 relaxation curve

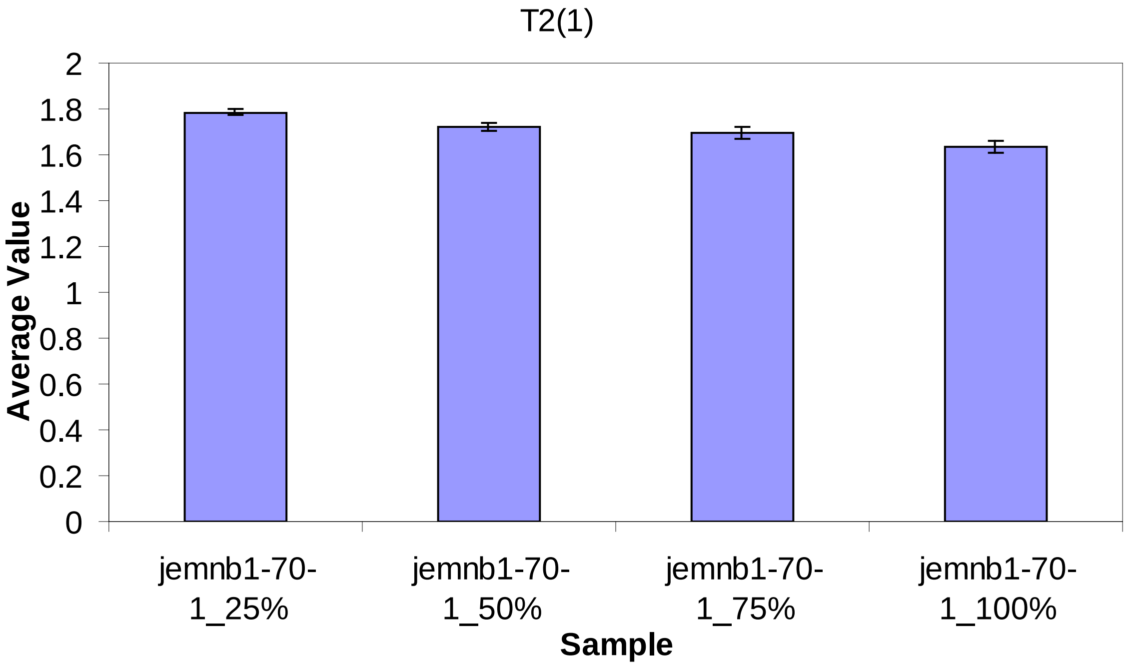


Figure 7 – Average $T_2(1)$ Value vs. Amount of Cure

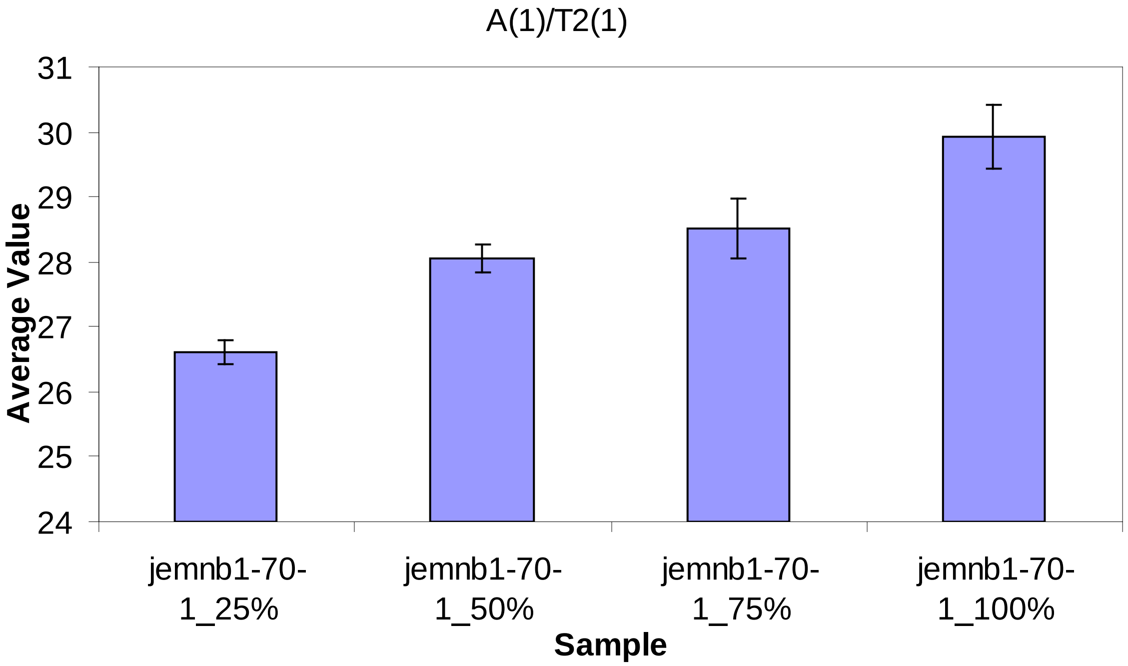


Figure 8 – Average $A(1)/T_2(1)$ Value vs. Amount of Cure

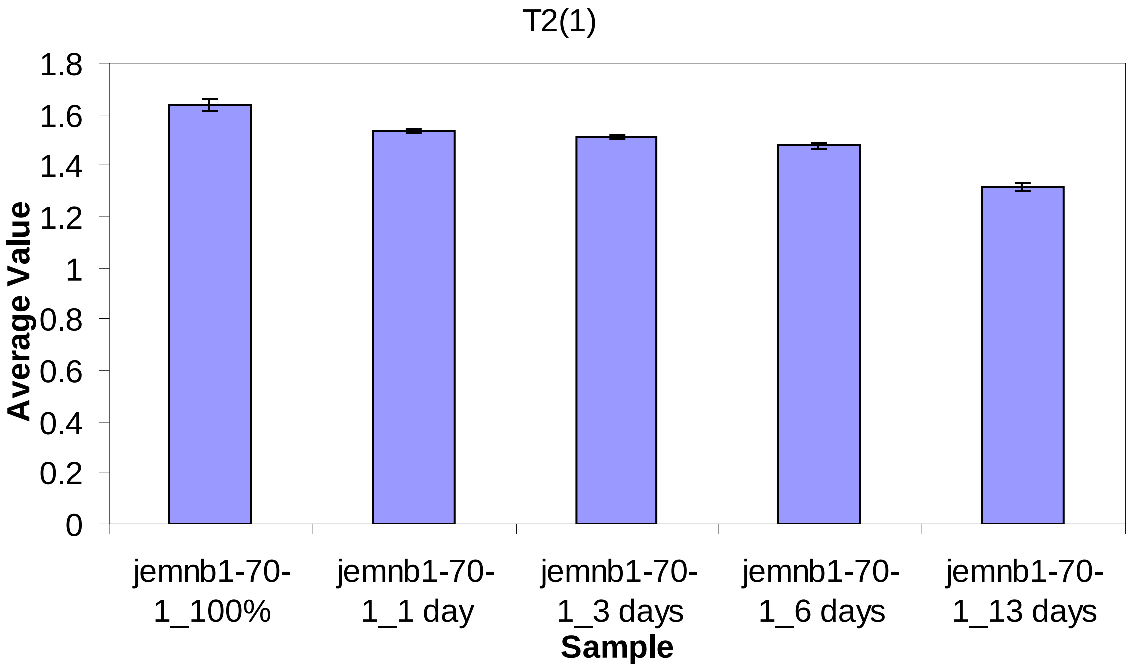


Figure 9 – Average $T_2(1)$ Value vs. Amount of Aging

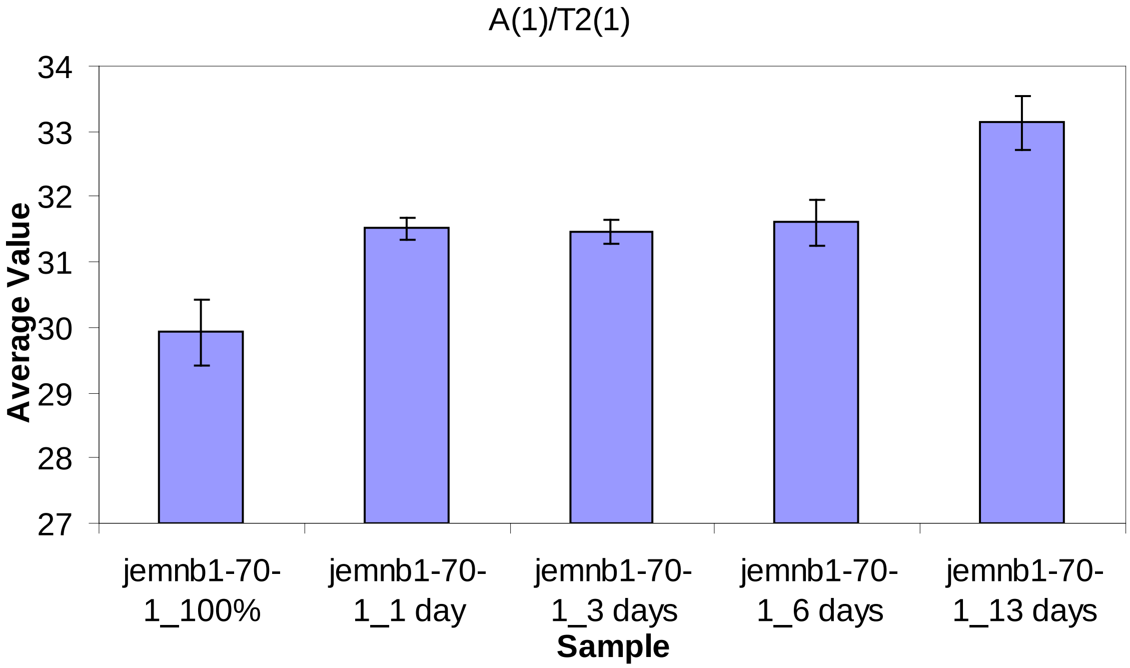


Figure 10 – Average $A(1)/T_2(1)$ Value vs. Amount of Aging

Tensile

Figures 11 and 12 show how the stress-strain curve is affected by amount of cure and amount of aging, respectively. It is seen that the peak stress increases as the amount of cure in increased, but elongation to break decreases as amount of cure is increased. It is also seen that peak stress and elongation to break decrease as amount of aging is increased.

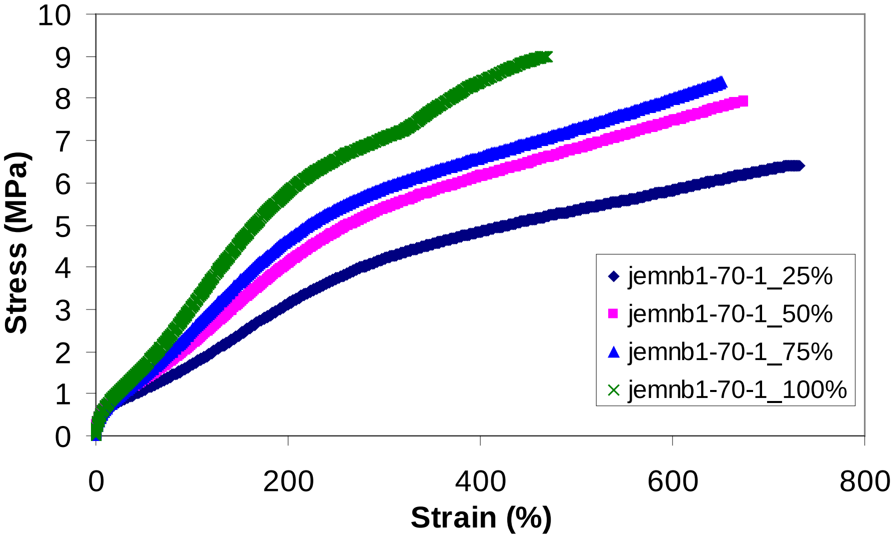


Figure 11 – Stress-Strain Curve vs. Amount of Cure

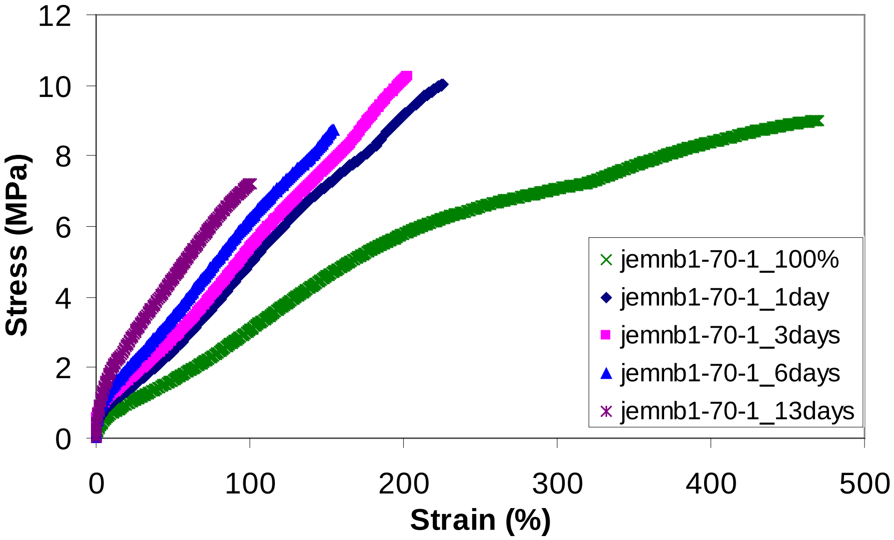


Figure 12 – Stress-Strain Curve vs. Amount of Aging

Conclusions

In summary, modulus, crosslink density, and peak stress increased as the cure time increased, but elongation to break decreased as cure time increased. Also, modulus, peak stress, and elongation to break decreased with aging time, but crosslink density increased with aging time.

References:

1. Perras, F. A., Viger-Gravel, J., Burgess, K.M.N., Bryce, D. L., Signal enhancement in solid-state NMR of quadrupolar nuclei, Solid State Nuclear Magnetic Resonance, Volumes 51–52, April–May 2013, Pages 1-15, ISSN 0926-2040, http://dx.doi.org/10.1016/j.ssnmr.2012.11.002. (http://www.sciencedirect.com/science/article/pii/S0926204012001130)

Section II - Mini Demattia

In the interest of measuring fatigue properties of small samples extracted from engineered rubber components such as tires, belts, hoses, etc., ARDL, Inc. has developed the Mini DeMattia test. This test is based upon the standard DeMattia test (ASTM D813) which is used to evaluate the fatigue life of lab-cured compounds. Once samples are extracted, both surfaces are buffed parallel and to uniform thickness at very low rates to minimize any material degradation due to heating the samples. The nominal sample dimensions were 38.1mm (1.50in) long by 3.18mm (0.125in) wide by 0.762mm (0.030in) thick. For this particular study, there was no need to extract samples, as we were working with cured slabs. Once buffed smooth, grooves of a nominal depth 0.381mm (0.0150in) were cut into the samples.

Finally, a pre-crack was placed in each sample. The pre-crack was crescent-like in shape. Once all samples were prepared in this manner, they were mounted on the Mini DeMattia frame shown in Fig. 1.

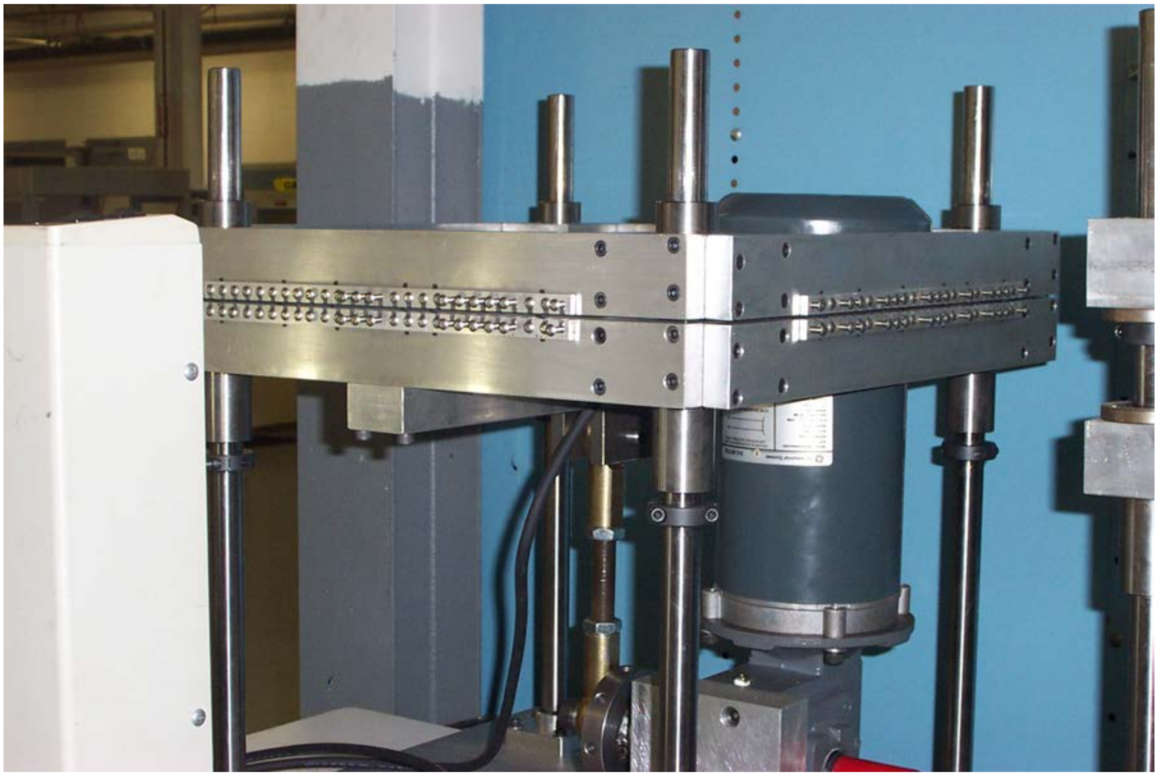


Figure 1: The Mini DeMattia instrument. Visible are the frame, electric motor and cam to drive the instrument.

This instrument is capable of testing 100 samples simultaneously (25 per side). It is driven at 5Hz using an electric motor attached to a steel cam to provide accurate displacement control and the sample crack lengths are measured using a vision system. Measurements are generally taken approximately every 9000 cycles, although the interval can easily be shortened for compounds which may be expected to have rapid crack growth rates. The crack lengths are reported as a percentage of the total sample width. Two examples from a prior paper (ACS Rubber Division Paper Number 68 October 2005) are described first to show the capabilities of this test.

Example Data and Analysis – Mini DeMattia

Figure 2 shows the crack length as a function of number of cycles for 4 different compounds: 1) a control compound which was a conventional cure; 2) a semi-EV cured compound; 3) an “efficient” cure; and 4) a peroxide cured compound. As expected, the control compound, with the highest level of polysulfidic crosslinks, performed the best, followed by the semi-EV cure which has less polysulfidic crosslinks. The poorest performing compounds were the efficient cure (mostly monosulfidic crosslinks) and the peroxide cure having carbon-carbon crosslinks. It should be noted that the recipes for these compounds were all adjusted to obtain nearly the same 100% modulus.

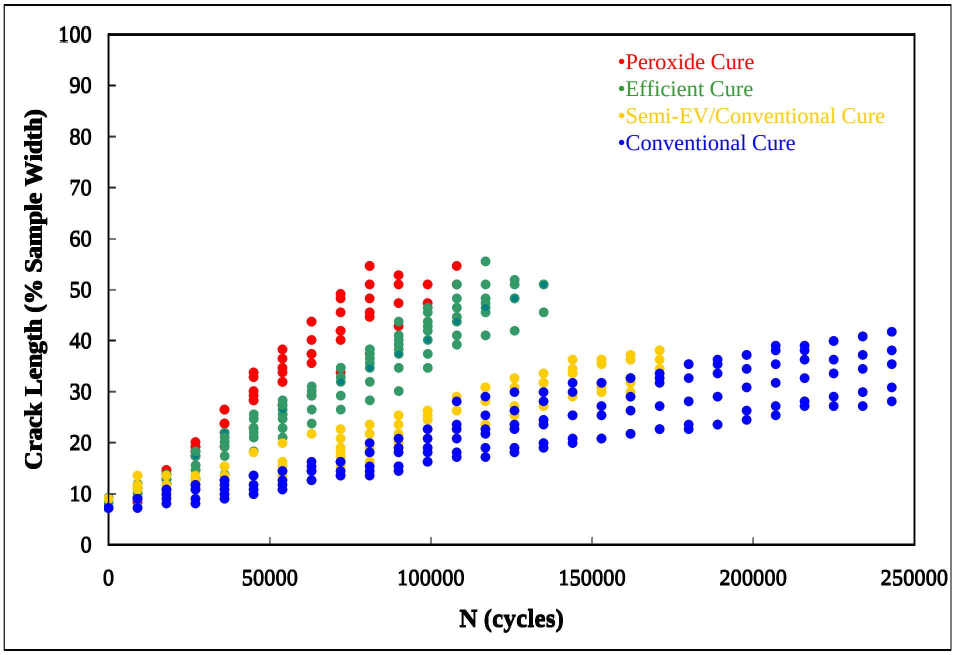


Figure 2: Crack length as a function of number of cycles for a control compound, semi-EV compound, efficient cure, and peroxide cure

Shown in Fig. 3 are the crack growth data for the control compound, which contains a standard antioxidant package, compared to a compound in which the antioxidant level was reduced to half its usual amount and a compound in which all the antioxidant was removed. Presumably, the observed difference in crack growth rates is a result of oxygen attack near the crack tip as the rubber molecules and crosslinks are broken.

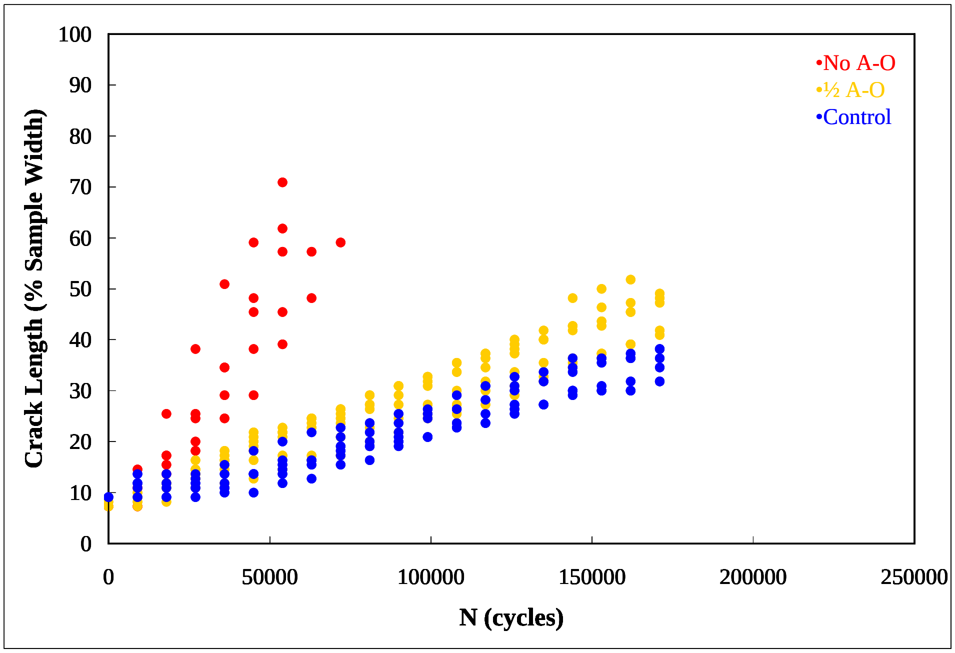


Figure 3: Crack length as a function of number of cycles for the control compound, one with half the usual antioxidant level, and a compound with no antioxidant.

Shown in Figure 4 are the crack growth rate results for the EPDM hose compound at various cure and aging conditions. The resistance to crack growth was affected by extent of cure and aging. Crack growth resistance was better at 100% of cure than partial cures. The crack growth resistance was better in the unaged material than the aged material. The crack growth rate as a function of aging time is shown in Figure 5.

Figure 4: Crack Growth Rate as a Function of Cure and Aging

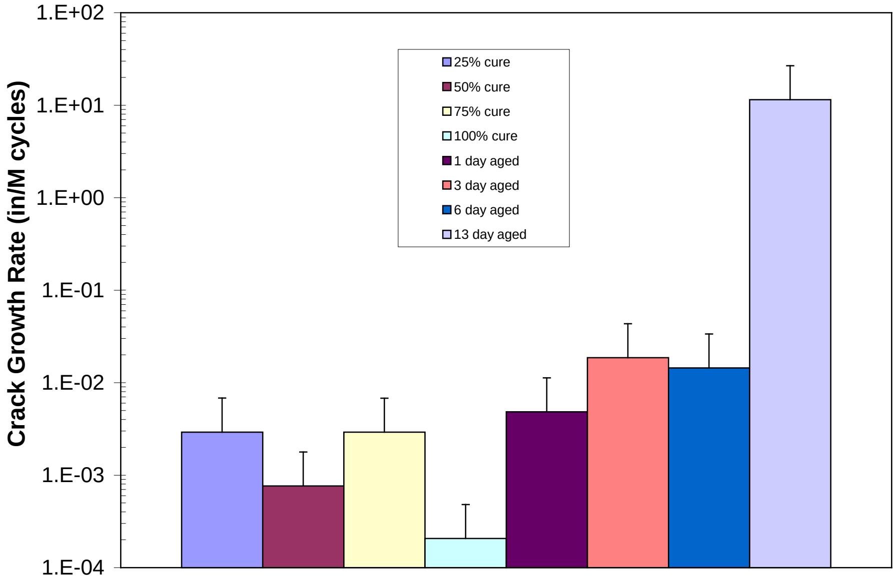
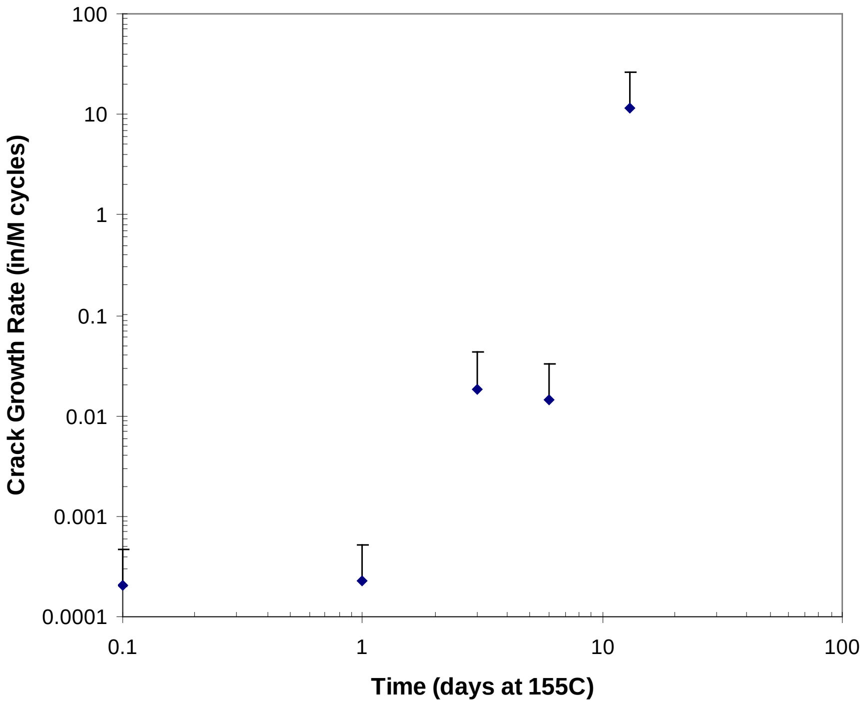


Figure 5: Crack Growth Rate as a Function of Aging Time at 155°C



Conclusions from Mini DeMattia

We have shown that the new methodology developed at ARDL for measuring crack growth in rubber compounds is quite effective. The method is capable of ranking materials and the effects due to key structural variables. We have shown the ability to differentiate between a variety of crosslink types and levels of antioxidant and show the effect these had on the fatigue properties of rubber compounds. The method is particularly useful for measuring the properties for small samples extracted from rubber articles, such as tires, belts, and hoses.