Technical

Molecular characteristics of elastomers measured with modern rheological tools

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Executive summary

With the introduction of DMRTs containing a sealed and pressurized sample chamber, rheological characterization of elastomers has evolved over the last few decades into many more complex tests that provide much more molecular information about elastomers. These methods can provide a better understanding of the behavior of elastomer grades used in rubber production in a reasonable period of time.

This study used a variety of these methods on a series of elastomers with known molecular differences. The trends in the molecular nature of these elastomers and their corresponding changes in rheological data were compared.

The Mooney viscometer has been in use since the 1930s to measure the viscosity of raw elastomers.[1] The effort to get molecular properties from rheological tests in the factory included the Mooney viscometer. The Mooney viscometer was intended to provide a measure for the average molecular weight, or Mn, of raw elastomers.

The introduction of the rubber process analyzer, or RPA 2000, in the early 1990s expanded the type of routine rheological

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tests that could be done rapidly in the rubber laboratory. The RPA is actually four instruments in one: rheometer for raw elastomers or dynamic mechanical rheological tester (DMRT); processability tester for mixed stocks; curemeter for materials with curatives; and a dynamic mechanical analyzer or DMA for cured rubber materials.

This presentation discusses the DMRT capability of the RPA. The flexibility of the RPA was rapidly accepted by many rubber scientists due to the amount of information that could be provided in a short period of time. Since that time, there have been many studies and ASTM standards designed to show the capability of the RPA in estimating molecular characteristics of raw elastomers.

Another way to measure the viscosity of raw elastomers is with a capillary rheometer. This is rarely done with raw elastomers, but this study explored some of the capability in measuring molecular characteristics on a capillary rheometer in spite of the problems.

Overall, this study explores the capabilities of the Mooney, RPA and the capillary rheometer in characterizing the MW and MWD of raw elastomers. The correlation of data among these instruments also is explored.

Instrumentation

Mooney viscometer

The sample cavity of the Mooney viscometer is shown in **Fig. 1**. The rotor is embedded in a sample and the torque required to move the rotor at 2 rpm is measured. A typical Mooney viscosity measurement is the ML1+42.

This test uses a 1 minute preheat with the motor off and then 4 minutes with the motor on at 2 rpm. The result used is the lowest viscosity value in the last 0.5 minutes.

The Mooney viscometer in this study was a Premier MV from Alpha Technologies. This model has the capability of testing materials at rotor speeds from 0.01 rpm to 20 rpm. This study also used other rotor speeds to determine some of their benefits to characterize raw elastomers.

RPA

The RPA die system is shown in **Fig. 2.** Two biconical dies form the sample cavity. The die surface is grooved to hold the specimens in place and prevent slippage during testing. The outer edge of the sample cavity contains two seal plates and two seals that completely seal the sample in the chamber under high pressure.

A pressurized chamber and the grooves help to reduce slippage during a test. An elastomeric sample is prepared by loading sufficient volume of material. The sample is placed onto the lower die and then the upper die is lowered, forming the sample geometry as excess material is squeezed out.

The lower die is oscillated sinusoidally at a programmable frequency and strain. The torque transducer attached to the upper die measures the force required to strain the sample under the specified conditions.

A Fourier Transform of the sinusoidal S* torque and strain data separates the torque signal into elastic and viscous components. The torque signal that is in phase with the strain is the elastic component, or S'. The torque signal that is 90 degrees out of phase with strain is the viscous component, or S".

The die dimensions, and strain are used with appropriate rheological equations to convert torque to shear modulus (G', G" and G*). The G' is a measure of the elastic or solid behavior, while the G" is a measure of the viscous or liquid behavior. The complex shear modulus G* is a measure of both the solid and liquid behavior.

The RPA used in this study was the Premier RPA from Alpha Technologies. This system has excellent low signal capability and the ability to do large angle oscillatory shear, or LAOS.

The samples were tested using the following test configurations:

1. ASTM D6204AB3—The test conditions for the D6204AB test are shown in **Table 1**. The first condition in Part A should correlate to the Mooney viscosity ML1+4 and to Mn.
2. Frequency sweep from 0.005 Hz to 50 Hz at 10 percent strain and 100°C.
3. Strain Sweep from 0.1 percent strain to 1,000 percent strain.
4. LAOS test at 0.1 Hz, 100°C and 1,000 percent strain.

Capillary rheometer

The capillary rheometer in this study was the ARC 2020 from Alpha Technologies. **Fig. 3** shows the schematic of a capillary rheometer. The force and/or pressure required to push the material through the orifice is measured at a specific speed or shear rate and the resulting viscosity is calculated. Typically, raw elastomers are rarely tested with a capillary rheometer due to high shear stresses in the barrel and melt fracture of the extrudate.

However, it is possible to get a viscosity measurement by using a short die. The short die does increase the size of the entrance effects in the capillary rheometer measurement, but it may be useful when testing a group of similar raw elastomer as was done in this study.

Experimental

This study used a series of seven EPDMs with known values for average molecular weight (Mn) and weight average molecular weight (Mw). These EPDMs were tested on a Mooney viscometer, RPA and a capillary rheometer. The trends in the actual results were compared to the expectations for those methods.

Where applicable, additional tests were done with six more EPDMs from different sources. These materials were used to verify some of the findings from those with known molecular characteristics.

In addition, where applicable, tests were run at experimental conditions in order to find test conditions that at least appear to correlate to molecular characteristics.

Results and discussion

Fig. 4 shows the correlation of the Mooney viscosity at 125°C to the Mn for seven EPDMs. This Mooney viscosity at

See **Elastomers**, *page 16*

Fig. 1: Schematic of the Mooney viscometer rotor and dies.

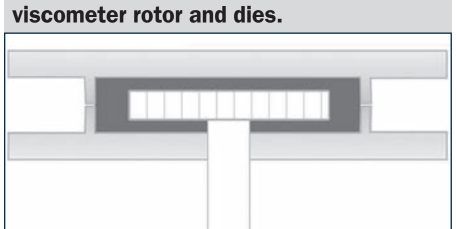


Fig. 2: Schematic of the RPA biconical die system.

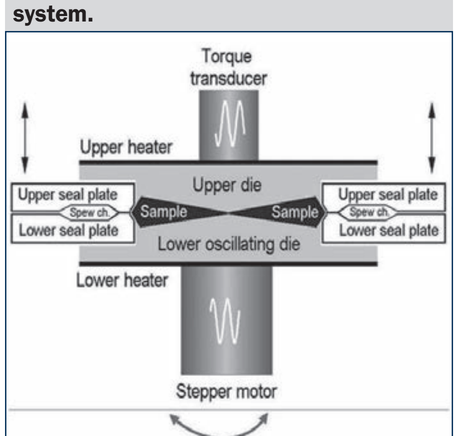
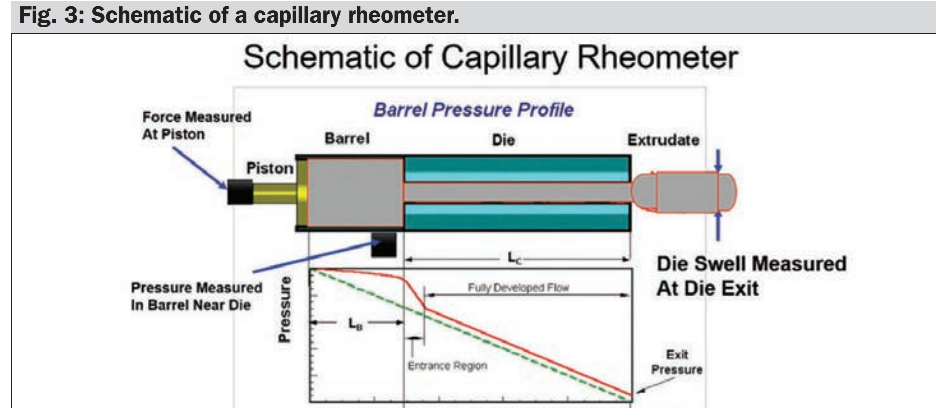


Fig. 3: Schematic of a capillary rheometer.



Pawlowski Hanzlik

The authors

Since Henry Pawlowski graduated from Case Western University, he has spent more than 40 years developing test equipment used in the biochemical and material sciences areas. These include instruments as diverse as spectrophotometers and rheometers.

His most significant accomplishment was the development of systems at Monsanto I&E (later known as Alpha Technologies) to measure properties of rubber using dynamic mechanical methods. These instruments are known all over the world today in the rubber industry as the Premier MDR curemeter and the Premier RPA.

Due to the significant progress made by the rubber industry to improve their products with these instruments, he was honored by the Akron Section of the Society of Plastics Engineers by induction into their Hall of Honor in 2001. Later he received a national award for his rheometer developments by becoming a co-recipient of the ACS Rubber Division's Banbury Award in 2013.

Pawlowski also has written many articles in the area of rubber and plastic testing.

Richard Hanzlik is a graduate from Cleveland State University in chemical engineering and has more than five years of experience in the polymer industry. He started his career as a formulations chemist dealing with ultraviolet curable thermosets.

He currently is an applications engineer with Alpha Technologies. In this position, Hanzlik has worked with customers in the rubber and thermoset composites industries to analyze materials and provide solutions for compounding and processing issues. Some of his work has been published in the U.S. and Latin America. He also is a teacher of rheology courses in the U.S.

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Elastomers

Continued from page 14

125°C was provided by the elastomer supplier. The results show that the ML1+4 at 125°C does follow the trend with the Mn with some scatter in the data.

Fig. 5 shows the measured ML1+4 value at 100°C from this study versus the Mn. The results look similar to those in **Fig. 4** as expected. These tests were run at 100°C to increase the signal to noise ratio on the EPDMs with low Mooney viscosity values.

Fig. 6 shows the scatter plot of the Mn of these materials versus the weight average molecular weight. The results show a poor correlation. In **Fig. 7** the ML1+4 at 125°C was plotted against the Mw. The results show a slightly better correlation than was seen with Mn in **Fig. 5**. This was surprising considering that a recent study claimed that the Mooney viscosity measured at 0.05 rpm should correlate better to Mw4. **Fig. 8** shows a plot of ML1+4 at 0.05 rpm and 100°C to the Mw. The results are much worse than **Fig. 7**.

The best correlation of the Mn to the Mooney viscosity is shown in **Fig. 9** with the ML1+4 obtained at 10 rpm and 100°C. This improvement was not expected at such a high speed due to possible sample slippage issues on the rotor.

The first condition in the RPA test configuration D6204 Part A has been correlated to the Mooney viscosity (or Mn) since the introduction of the RPA5. The correlation of the G* at 0.1 Hz, 7 percent strain and 100°C versus the ML1+4 at 100°C is shown in **Fig. 10** using the seven EPDMs with known Mn. The result is an excellent correlation. **Fig. 11** shows the same correlation when ML1+4 is done at 100°C with all 13 EPDMs. The result also shows an excellent correlation, but one EPDM is an outlier.

The correlation in **Fig. 11** was repeated at different rotor speeds in the Mooney viscometer. The best correlation is shown in **Fig. 12** for a rotor speed of 0.5 rpm. One interesting feature of **Fig. 12** is that the maximum G* value appears to have an upper limit of 170 kPa. The EPDMs with values below this upper limit show a very linear behavior between the G* value and the ML1+4 at 0.5 rpm.

A newer study found that the correlation of G* to ML1+4 is improved if the RPA strain is increased to 140 percent strain instead of 7 percent strain.[6] This strain is not part of the D6204 standard. **Fig. 13** shows the correlation for G* at 140 percent, 0.1 Hz and 100°C versus the ML1+4 at 100°C. These results show that there is no improvement in the correlation to the Mooney viscosity when using the higher strain with these samples compared with **Fig. 11**.

Fig. 14 shows the correlation of G* at 7 percent strain and 100°C to Mn. The results show the correct trend with scatter. When the same correlation was applied to Mw in **Fig. 15**, the results improved significantly.

The slope of the three-point frequency sweep of D6204A in a log-log plot is expected to indicate the Mw or the Mw/Mn of raw elastomers. The slope results are plotted versus Mw in **Fig. 16**. The results do appear to show some correlation between the slope and Mw for these EPDMs.

There have been numerous studies showing that the G' & G" crossover point in a frequency sweep can estimate the MW and MWD of a linear raw elastomer. The crossover point is illustrated in **Fig. 17**.

The one weakness of this approach is what to do if there is no crossover point?

Fig. 4: Correlation of Mooney viscosity ML1+4 at 125°C to Mn.

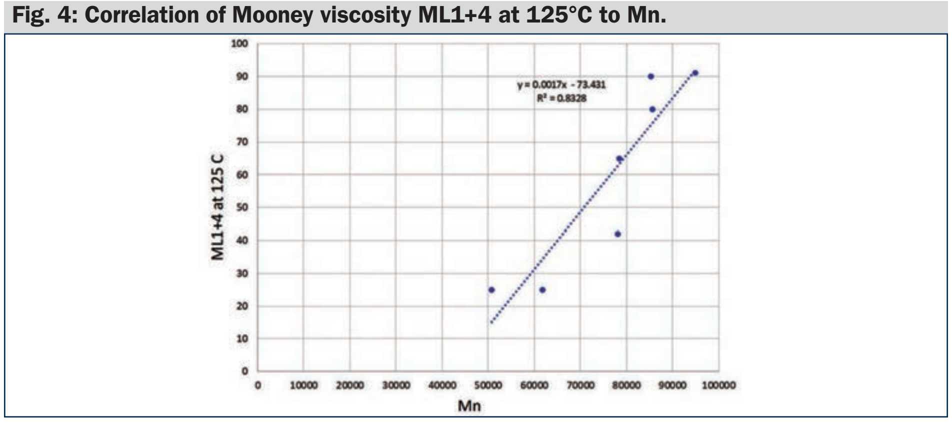


Fig. 5: Correlation of Mooney viscosity ML1+4 at 100°C to the Mn.

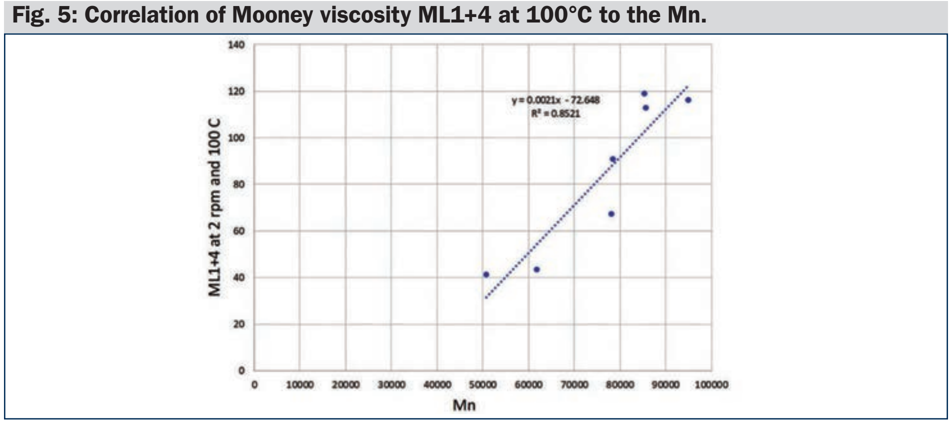


Fig. 6: Correlation of Mw to Mn for the EPDMs tested. The correlation is poor.

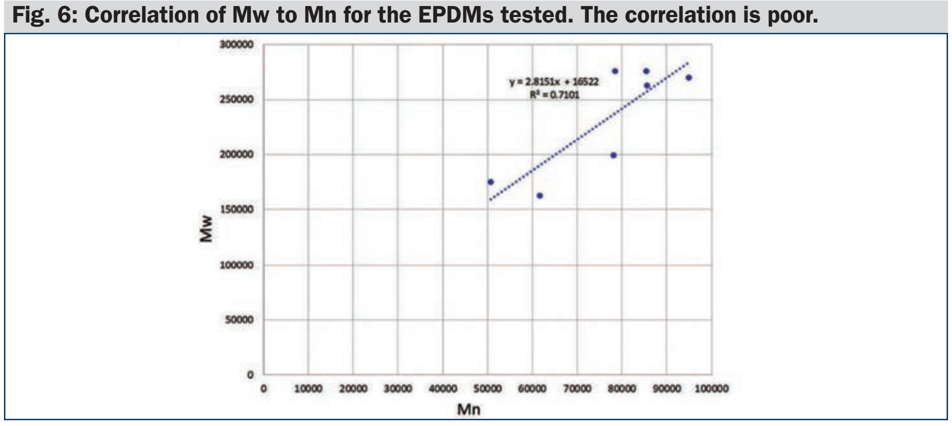


Fig. 7: Correlation of ML1+4 at 125°C to the Mw. The correlation is better than Mn, which is not expected.

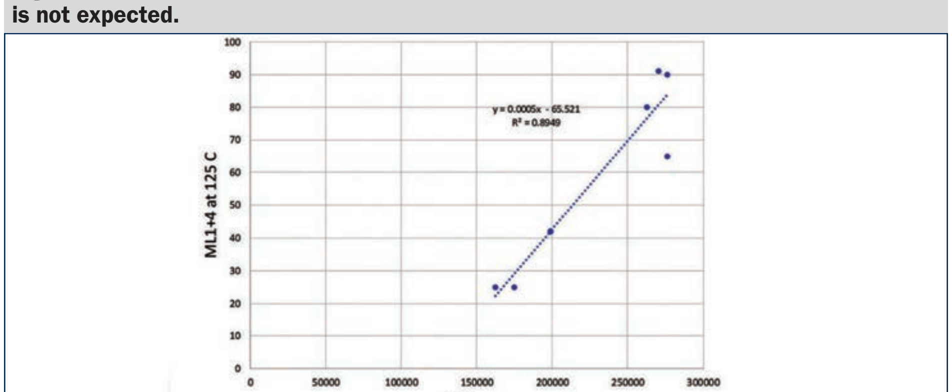


Fig. 8: Correlation of Mooney viscosity at 0.05 rpm to the Mw. Some investigators have claimed that this should be a very good correlation, but it was not for the EPDMs tested.

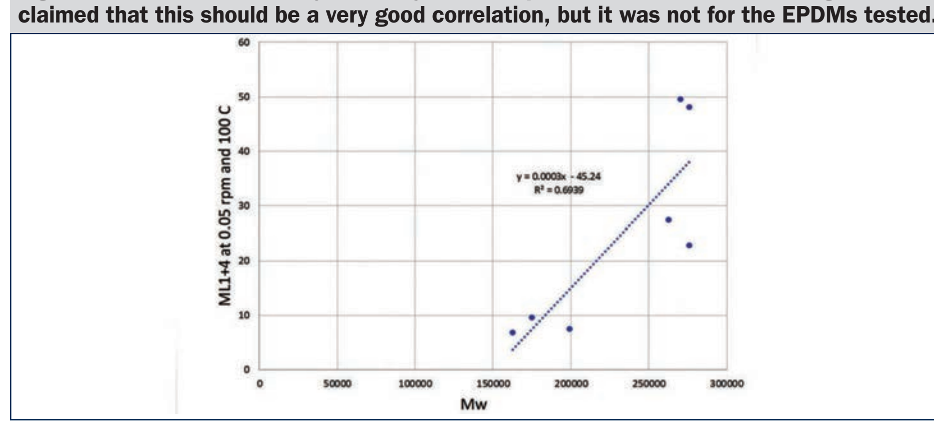


Fig. 9: Correlation of ML1+4 at 10 rpm and 100°C. Results were much better than expected even though slippage is often observed under these conditions.

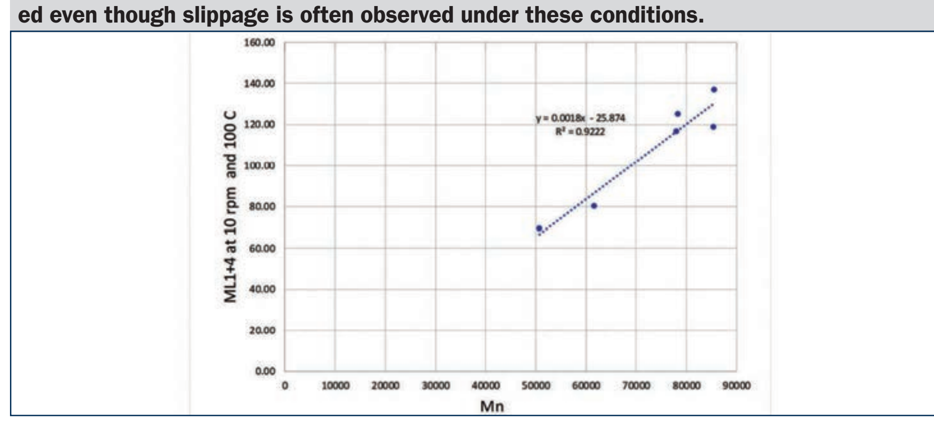


Fig. 10: Corrrelation of RPA G* at 0.1 Hz, 7% strain and 100°C (1st Condition in D6204A) versus ML1+4 at 2 rpm and 100°C. This good correlation confirmed previous observations.

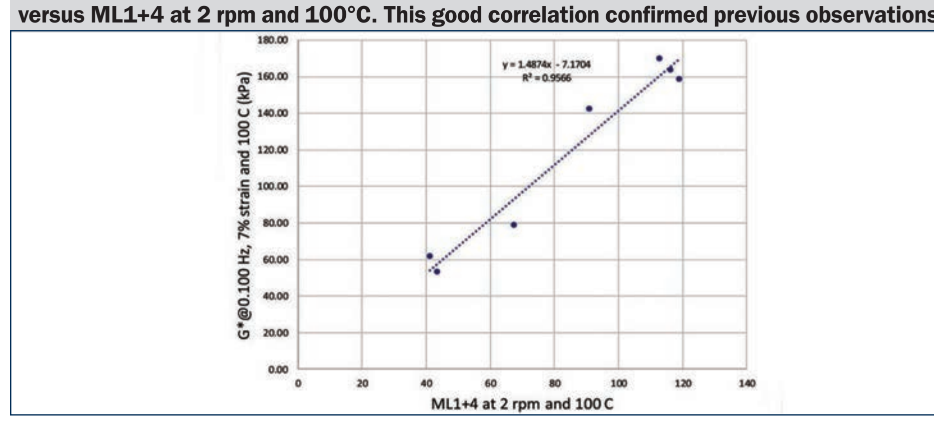
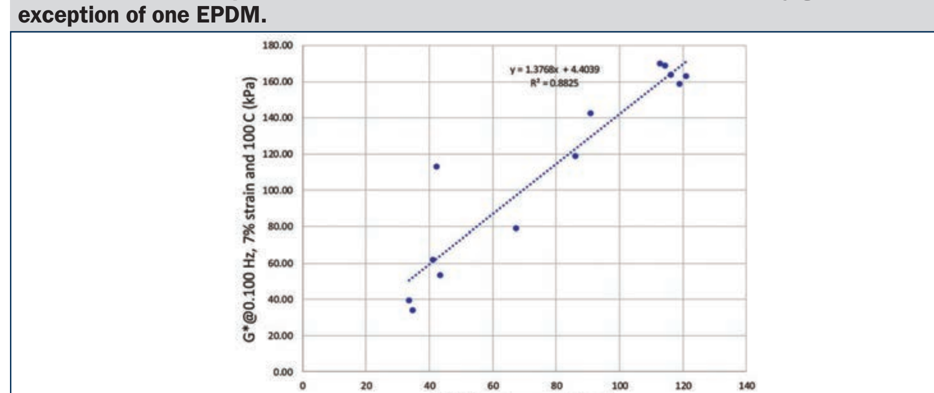


Fig. 11: Correlation of RPA G* at 0.1 Hz, 7% strain and 100°C (1st Condition in D6204A) versus ML1+4 at 2 rpm and 100°C. with all 13 EPDMs. Results were very good with the exception of one EPDM.



There were five elastomers in this study with crossover points, but the correlation was very poor between the frequency of oscillation in the crossover point (ωc) and Mn. The Gc or modulus at the crossover point should correlate to the Mw or Mw/Mn (Polydispersity Index). **Fig. 18** shows the correlation of Gc and the polydispersity index or Mw/Mn. The results show the expected trend with some scatter. This plot is similar to those done for the inverse or [=1e6/Gc] in the literature.[7]

These results appeared to be unsatisfactory for getting good correlation between molecular characteristics and rheological data. The frequency sweep results are expected to indicate the molecular characteristics of the raw polymers. So a study was done to determine the best correlation between results at any one oscillation frequency and average molecular weight.

The G* at 0.270 Hz and 10 percent strain had the best correlation, and is shown in **Fig. 19** plotted against the Mn value. The best result for Mw was G* at 0.058 Hz shown in **Fig. 20**. The latter appeared to be reasonable since the Mw is dominated by the higher molecular components, and these are best determined at lower oscillation frequencies.

Recently, LAOS has become more popular to determine the amount of long chain branching.[8] This is a relatively quick and easy measurement with current RPAs. The method applies a large strain to an elastomeric sample at low frequencies—usually 0.1 Hz. When the strain approaches 1,000 percent, the torque/shear stress sine wave becomes distorted. The application of a Fourier Transform to the data calculates the harmonics in the result.

In this study, the EPDMs were predominately linear and did not contain long chain branching. However, one interesting result from the measurement of the harmonics is shown in **Fig. 20** where the third G* Harmonic, or G*3, was plotted against the Mw. The result showed a very good correlation, and as Mw increased, the value of G*3 also increased. This should be expected because the value of G*3 should be the most sensitive to the distortion in the sine wave at 1,000 percent strain and has been demonstrated for polystyrene.[9] This suggests that the value of G*3 may be a good measure to verify the average molecular weight of raw elastomers.

The linear viscoelastic region is expected to be determined by the MWD. However, for the EPDMs tested in this study, it was not possible to see a correlation between the Mw or the polydispersity index with the linear viscoelastic region.

However, another measure that should correlate with the MWD is slope of a strain sweep at high strains. **Fig. 22** shows the area of interest. As the Mw/MWD becomes larger/broader, the slope should be less negative. **Fig. 23** shows the plot of the slope for all seven EPDMs versus Mw. The results show that the slope becomes more negative as Mw increases. However, one possible reason for this observation is that the G* value is only the first harmonic. **Fig. 20** showed that the G*3, or third harmonic, value increases with increasing Mw. As G*3 increases G*1 decreases. That would explain the more negative slope with the greater Mw. The value still can be used to characterize the Mw of raw elastomers.

Capillary rheometers are rarely used

See **Elastomers**, *page 18*

Fig. 12: Correlation of RPA G* at 0.1 Hz, 7% strain and 100°C versus ML1+4 at 0.5 rpm. This was the best correlation to the first condition of D6204A.

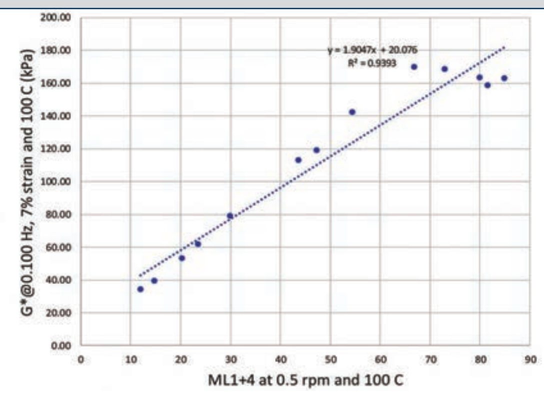


Fig. 13: RPA G* at 0.1 Hz, 140% strain and 100°C versus ML1+4 at 2 rpm and 100 C for all 13 EPDMs. These conditions did not seem to be better than those in Fig. 11.

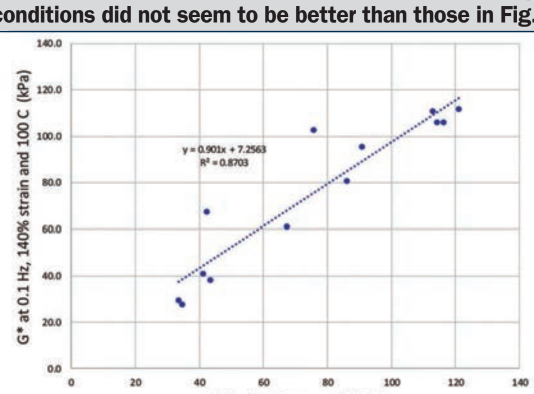


Fig. 14: Correlation of G* at 0.1 Hz, 7% strain and 100°C to the Mn. The results show the correct trend with a lot of scatter.

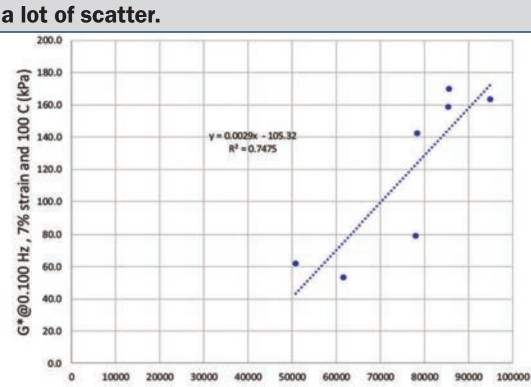


Fig. 15: Correlation of G* at 0.1 Hz, 7% strain and 100°C to the Mw. The results show a very good correlation but there are two clusters.

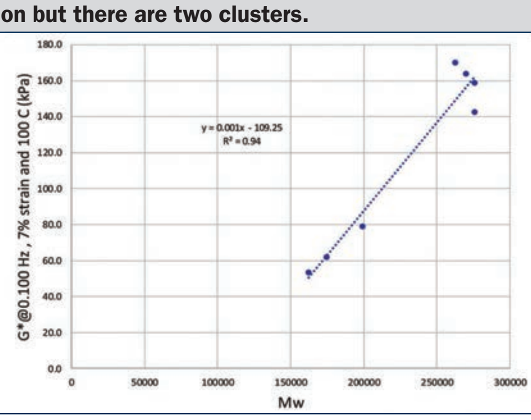


Fig. 16: The Log-Log slope of G* and the oscillation frequency versus the Mw value. The results look promising.

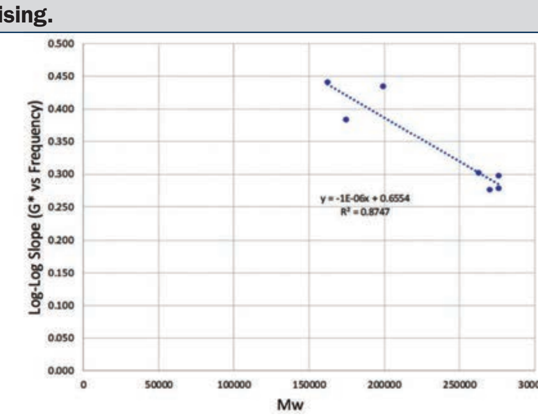


Fig. 17: Illustration of the use of the G' & G" crossover point in a frequency sweep to characterize the MW and MWD of linear elastomers. This method requires that the Tan(Delta) value must be greater than 1.000 somewhere in the sweep.

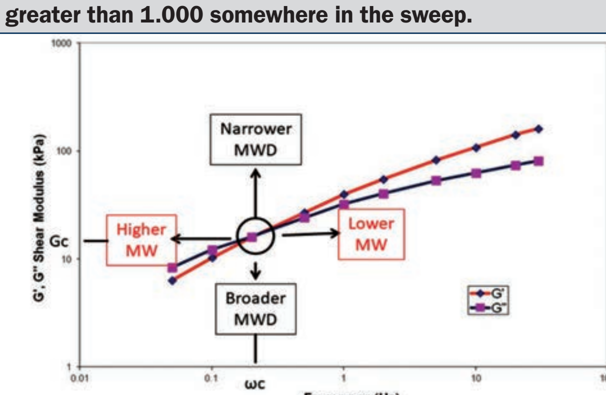


Fig. 18: The crossover modulus Gc versus the polydispersity index. The results show the correct trend.

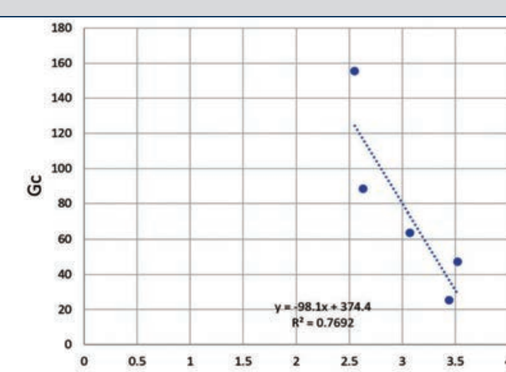
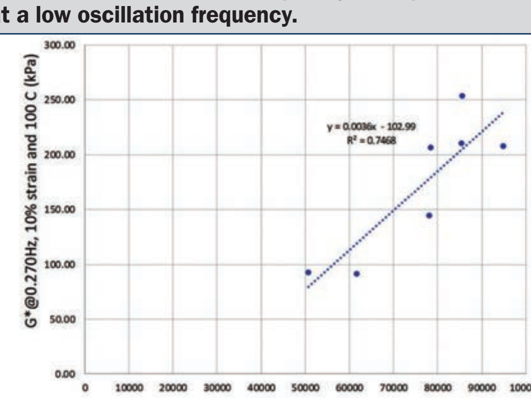


Fig. 19: The best correlation of G* in a frequency sweep versus Mn. The relatively poor correlation was at a low oscillation frequency.



Elastomers

Continued from page 17

to characterize raw elastomers. One reason being that such tests produce melt fracture (**Fig. 24**). This always calls into question about the quality of the data.

Several EPDMs were selected for capillary rheometer tests. Rheologists like to use capillary rheometers with long L/D values to minimize entrance effects and improve the accuracy of the viscosity measurements.

For this study, it was decided to investigate the data produced by a 1 mm diameter with a short L/D of 5:1. This allows the operation of the capillary rheometer through a wider shear rate range before reaching the upper limit of the sensors.

Fig. 25 shows the capillary viscosity versus the Mooney viscosity ML1+4 at 2 rpm and 100°C. The results show an excellent correlation for the five EPDMs tested. **Fig. 26** also shows an excellent correlation for the RPA G* at 0.1 Hz, 7 percent strain and 1,000°C to the capillary viscosity. These results show that with the right set of test conditions, the Mooney viscometer, RPA and the capillary rheometer follow the same trends for all EPDMs. This means that they should all be a function of the Mn or Mw value.

Conclusion

Several rheological methods were used to measure the viscosity of several EPDMs with known Mn and Mw values. These methods utilized a multi-speed Mooney viscometer, an RPA and a capillary rheometer. These methods were evaluated on their ability to predict or correlate to Mn and Mw.

The results showed that some of the methods which should work very well did not work as well as expected. In addition, some test conditions that were not expected to work well, showed very good correlations.

The results indicate there is need for more studies to determine the best methods to determine Mn and Mw with these instruments.

References

1. M. Mooney, "A Shearing Disk Plastometer for Unvulcanized Rubber." Rubber Chemistry and Technology 7.3 (1934): 564-75.
2. ASTM D1646-15, Standard Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer), ASTM International, West Conshohocken, PA, 2015.
3. ASTM D6204-15, Standard Test Method for Rubber—Measurement of Unvulcanized Rheological Properties Using Rotorless Shear Rheometers, ASTM International, West Conshohocken, PA, 2015.
4. C. Kim, M. Morel, J. Beuve, S. Guilbert, F. Bonfils, "Better characterization of raw natural rubber by decreasing the rotor speed of Mooney viscometer: Role of macromolecular structure." Polymer Engineering and Science, 50.2 (2009): 240-48.
5. H. Pawlowski and John Dick, "Viscoelastic Characterization of Rubber with a New Dynamic Mechanical Tester." Akron Rubber Group (1992).
6. E. Norton, "Processability Measurements for Improved Characterization of Synthetic Polymers by Dynamic Oscillatory Shear Rheometers and Rotating Shear Viscometers." Rubber Division (2016).
7. Zeichner and Patel, "Proceedings of the Second World Congress of Chemical Engineering," (1981), p. 333.
8. H. Burhin, H. Pawlowski, N. Rossion C. Bailly, A. Leygue, and R. Keunings. "A Study of Polymer Architecture with FT-Rheology and Large Amplitude Oscillatory Shear (LAOS)." XVth International Congress on Rheology (2008).
9. K. Hyun, M. Wilhelm, C. Klein, K. Cho, J. Nam, K. Ahn, S. Lee, R. Ewoldt, G. McKinley, "A Review of Nonlinear Oscillatory Shear Tests: Analysis and Application of Large Amplitude Oscillatory Shear (LAOS)," Progress in Polymer Science, Vol. 36, Issue 12, December 2011, Pages 1,697-1,753.

Fig. 20: The best correlation of G* in a frequency sweep to Mw. The results were at a relatively low oscillation frequency.

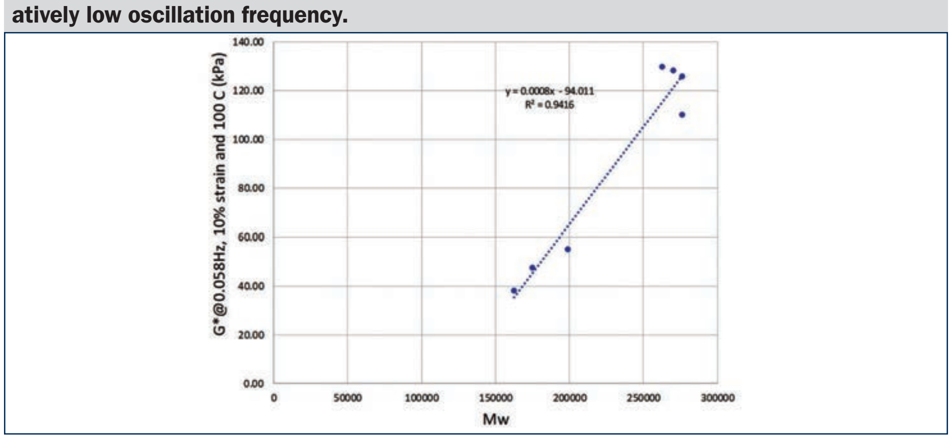


Fig. 21: The 3rd Harmonic for G* at 6 cpm, 1,000% strain and 100°C versus Mw. The value of G*3 indicates the level of distortion in the sine wave signal. Results show an increase in distortion with an increase in Mw. This is expected due to more elasticity in the material as Mw increases.

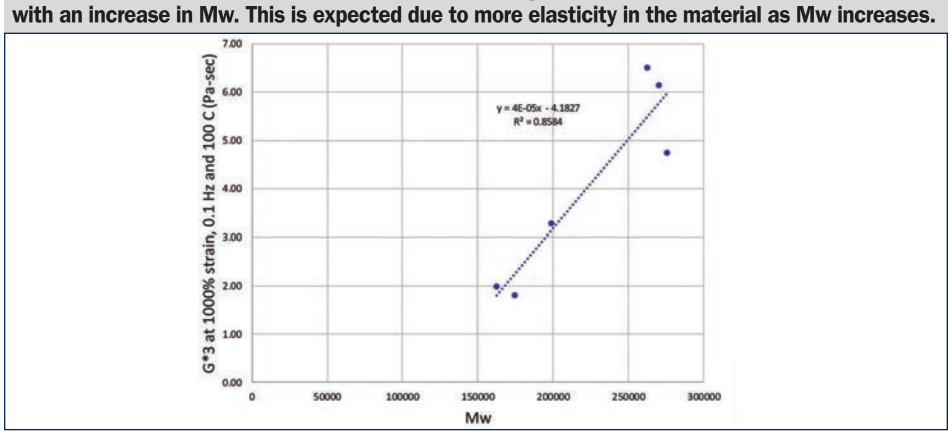


Fig. 22: G* versus strain for an EPDM. At low strains, the EPDM is in the linear viscoelastic region. At high strains, the EPDM is in the non-linear region.

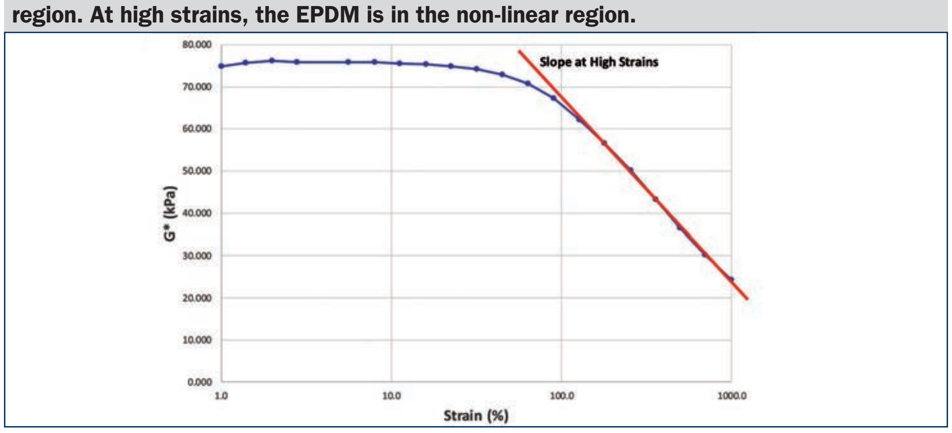


Fig. 23: The slope at high strains for all EPDMs correlates to the Mw value. The value becomes more negative at higher Mw values probably due to more distortion in the sine wave at higher strains which produces a loss of signal in the 1st Harmonic.

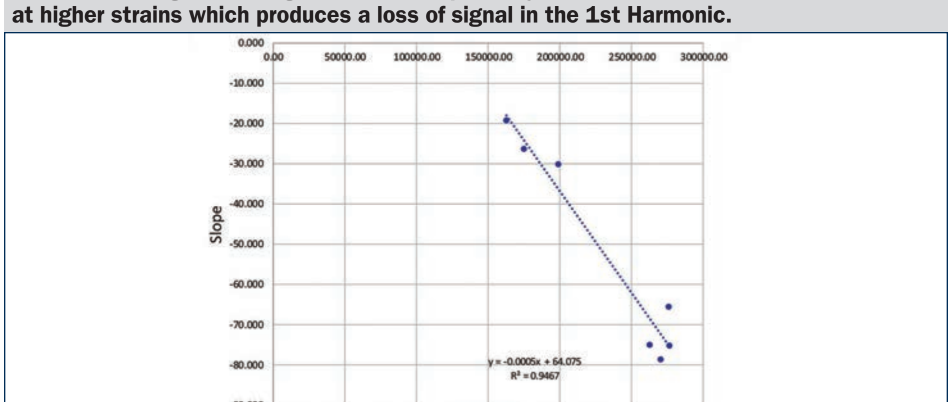


Fig. 24: The EPDM extrudate from a capillary rheometer. The extrudate shows clear signs of melt fracture.

Table 1: Description of the D6204AB test.

1. Timed subtest allows temperature and internal stresses to stabilize
   a. 100 C
   b. 4 minutes
   c. Motor Off
2. Frequency Sweep (Part A)
   a. 100°C
   b. 7% Strain
   c. Frequencies of
      i. 0.1 Hz (correlates to Mooney Viscosity
      ii. 2 Hz
      iii. 20 Hz
3. Frequency Sweep (Part B)
   a. 100°C
   b. 100% Strain
   c. Frequencies
      i. 0.1 Hz (Determination of gel in NR)
      ii. 1 Hz

Fig. 25: In spite of the presence of melt fracture, the measured capillary rheometer viscosity correlated very well to the traditional Mooney viscosity (ML1+4 at 2 rpm and 100°C) for the samples tested.

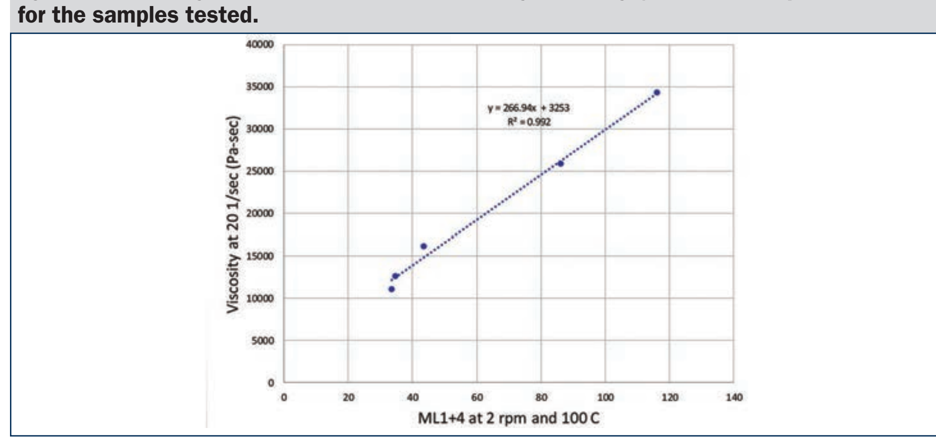


Fig. 26: Again with melt fracture, the capillary rheometer viscosity correlated very well to the RPA G* at 0.1 Hz, 7% strain and 100°C (D6204A 1st test condition) for the samples tested.