Rubber Testing with DMA Instruments

Dynamic (oscillatory) Rubber Testing

Traditionally, pure gum rubber rheological properties are tested and certified using the well-known Mooney viscometer according to ISO 289. This test is, in most of the cases, used for polymer choice for a specific recipe. Most rubber technologists recognize that this method fails to provide compound flow behavior information, especially when comparing polymers of identical ML(1+4) from various sources. Money Stress Relaxation has improved polymer source discrimination but is not widely adopted by polymer users although an increasing number of polymer suppliers are now providing this characteristic.

With the introduction of closed cavity oscillatory rheometers (known variously as Moving Die Rheometers, Dynamic Mechanical Analyzer, and Rubber Process Analyzers), descriptive testing of gum rubber is now easy and repeatable. These instruments provide the ability to test polymeric materials' mechanical properties as a function of frequency at many controlled temperatures.

When plotting G′ and G″ (storage and loss shear modulus) versus frequency, a large number of polymers exhibit a response as per Fig.1.
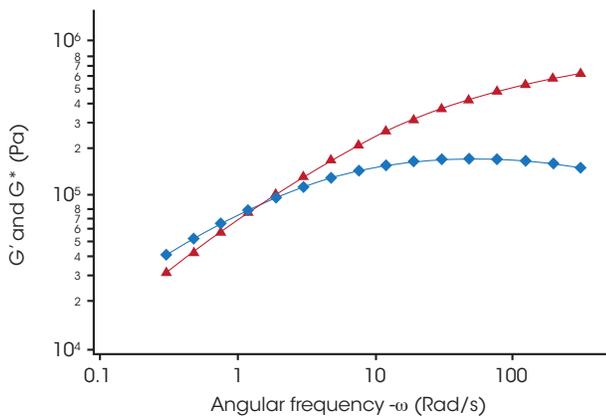
Figure 1

G′ curve is crossing G″ curve at a typical value of frequency. This crossing point is called "cross-over" point. This point is very interesting for polymer characterization as its modulus and frequency coordinates (G_c and ω_c respectively) can be mathematically correlated to polymer MWD (Molecular Weight Distribution) and AMW (Average Molecular Weight). This mathematical relationship is ONLY valid for strictly linear

polymers such as IIR, PDMS (Silicone), and some EPDM's.
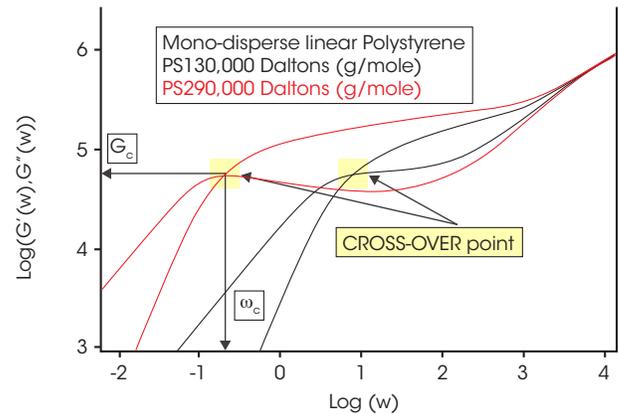
Figure 2

This relationship is well illustrated in Fig.2 showing the result of two samples of mono-dispersed PS (Poly-Styrene) with different AMW. From this example, we can observe that G_c is identical for both samples while ω_c is largely different. In general, ω_c is inversely proportional to AMW while G_c is inversely proportional to MWD. This has been found particularly true and useful for PP (Poly-Propylene) so this test can replace lengthy and tedious SEC (Size Exclusion Chromatography) for MWD measurement with the following relationship: PI (Poly-Dispersity Index) = Mw/Mn = $10000/G_c$.

For polymers with unknown LCB (Long Chain Branching) level, this mathematical relationship is not valid any longer. Nevertheless, computing and reporting the cross-over point coordinates for these materials is very efficient and extremely sensitive in case of polymer discrimination or quality control at least much more than Mooney. In this case, it can possible that for ultra-high level of LCB or very low viscosity, no cross-over point can be observed. In this case, test temperature needs to be changed. According to Time Temperature Superposition principle, if the cross-over point seems to exist towards higher frequency, test temperature shall be decreased while it shall be increased if the cross-over point is towards lower frequency. In case of fully automated DMA's, this type of analysis can be organized at minimum labor cost.

Conclusion

To perform this analysis, the oscillatory rheometer needs to be programmed as follow:

1. Close instrument at test temperature (ex: 100° C)
2. Oscillate at very low strain and moderate frequency to stabilize material behavior (ex: 0.5% and 2 Hz for 3 to 5 minutes). Record S' and S" to verify that stationary conditions are reached (constant or quasi constant S' and S").
3. Perform a frequency sweep at strains not exceeding 15% over two to three decades of frequency (ex: 0.3 to 300 Rad/s). In most cases, it is highly recommended to vary test strain at each frequency with high strain for low frequency and low strain at high frequency. This technique largely increases S/N ratio at low torque reading (low frequency) and reduces material heat-build-up at high frequency. Dissipated energy per oscillation is proportional to strain squared.
4. Plot G' and G" versus frequency on a double logarithmic scale.
5. Perform a second order regression on both G' and G" versus frequency and solve both equations to get G_c (85082 Pa) and ω_c (1.39 Rad/s).

The general rule is illustrated in Fig3.
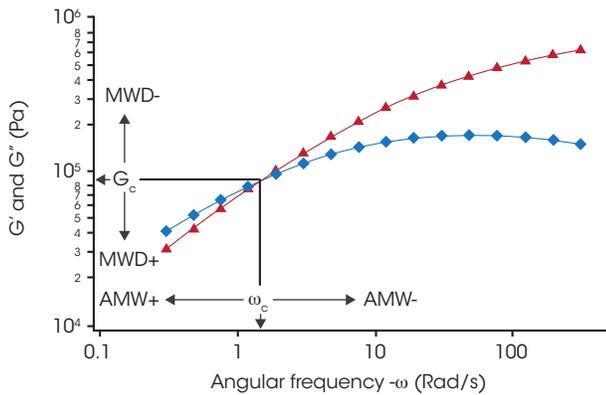
Figure 3

For more information or to place an order, go to http://www.tainstruments.com/ to locate your local sales office information.