1

Overview of Rubber Rheology and Dynamic Property Tests

1.1 Introduction to the Uniqueness of Rubber Rheology

The rheology for a given raw rubber and its respective rubber compounds (formulations) are significantly different and unique compared to the rheology of polymer melts of plastics. Typically, the raw rubber used is an amorphous ultra-high molecular weight polymer with a low glass transition temperature (T_g) range well below the intended rubber product's operating temperature, see Figure 1.1. The raw rubber used in formulating the rubber compound must be of sufficiently high molecular weight for strength in order to provide effective chain entanglements on the rubbery plateau of a modulus-temperature master curve in order to impart its "rubbery nature" to the rubber product at operating temperatures.

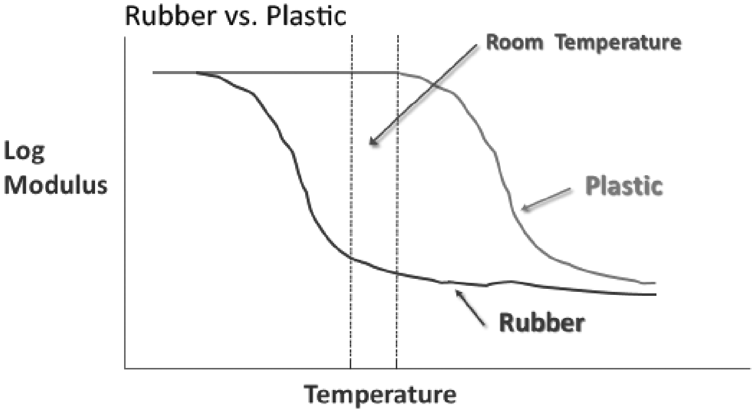

Figure 1.1 The modulus curves of rubber and plastic versus temperature show the location of the glass transition temperature T_g. The modulus always rapidly changes to lower values at the T_g. The T_g of rubber is below room temperature while the T_g of plastic materials is above room temperature

Also, typically rubber compounds are filled with colloidal particle size fillers, such as carbon black and silica. These very small particles are typically between 20 to 60 nanometers in diameter, and form differing degrees of a filler network while under different stages of deformation during processing (before cure) and in use in a given rubber product after cure. This results in differing degrees of a strain softening effect (called the Payne effect), involving differing degrees of filler particle-particle interaction, rubber-filler interaction, and hydrodynamic effects, depending on the final state of mix (before cure) and the physical and chemical characteristics of the compounding ingredients that make up the rubber compound. Certainly, this too is somewhat unique to the rubber industry as well. The changes in the compound compositions not only affect the rheology of the uncured stock, but, in most cases, have a great influence on the after-cure dynamic properties of these compounds as well. For example, rubber compounds that tend to have more viscous heating during mixing also tend to run hotter (more hysteretic) as cured products (such as tires) when used in severe dynamic property applications (Figure 1.2).

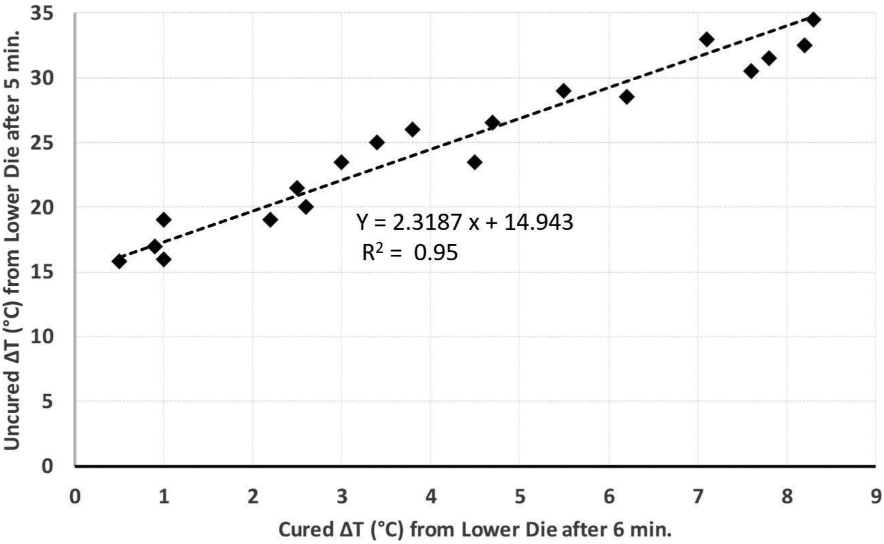

Figure 1.2 There is often a correlation between the heat build up in a cured rubber product and viscous heating in its uncured state. RPA cured measurement is after 6 minutes of movement at ±38.9% and 12 Hz starting at 40 °C. RPA uncured measurement is after 6 minutes of movement at ±1256% and 0.33 Hz starting at 50 °C; Adapted and printed with permission from Alpha Technologies.

So rubber rheology is truly unique and different than what is observed in plastic melts, coatings, food, cosmetics, oil drilling “muds”, concrete mix, textiles during melt spinning, metals in the melt state, etc. It is actually the type of rheology you get when you use very high molecular weight amorphous polymers with large amounts of colloidal particle sized fillers and other additives that interact with the polymers.

Basically, commercial rubber compounds consist of typically 9 to 24 different compounding ingredients [1]. Most all rubber compounds are based on at least four systems, i.e., (1) the rubber system [2, 3], (2) the filler/oil system [4, 5], (3) the curative system [6–8], and (4) the AO system (antioxidant/antiozonant) [9]. Also, there are three other systems that are optional depending on the need. These include possibly (5) an in situ adhesive system [10], (6) an in situ blowing agent system (only for sponge rubber compounds) [11], and (7) a flame retardant system [12], if required by the market. All seven of these systems can significantly affect the rheology of the uncured rubber compound and its cured dynamic property performance as a product. The rubber system (either a single raw rubber or a blend of raw rubbers) and the filler/oil system have the greatest rheological effects. All these systems have significant effects on the cured rubber product's dynamic performance as well.

■ 1.2 Basic Tensile Testing

In early rubber technology before there were any rheological tests for rubber, tensile testing (or tensile stress-strain testing) was used. This type of testing has been used for over 100 years in the rubber industry. Some of the oldest standard test methods for performing this procedure are found in ASTM D412 and ISO 37. This method applies a deformation by pulling apart a cured die C dumbbell at the rate of 500 mm/min. The resulting stress is recorded as a function of the applied strain. This rate of separation is important for consistent measurements of cured rubber properties because even when cured the compound properties vary with the speed of testing. Cured rubber is still a viscoelastic material.

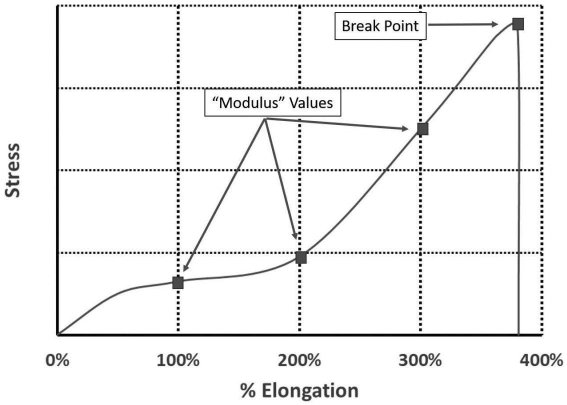

Figure 1.3 Typical results from pulling a cured rubber dumbbell specimen. This type of test has been done for many years

Three important rubber compound properties that are measured with this method are (1) stress at a given percent strain, (2) stress when the sample breaks or ultimate tensile strength, and (3) the ultimate strain or elongation at break. These measurements are illustrated in Figure 1.3. The stress values are often called “modulus” but the values are not true modulus values. The stress values are not divided by the true strain nor are they compensated for changes in sample thickness during a test. Rubber compounders (formulators) can still use this information to judge the quality of their new compounds and to determine if a compound was properly mixed. Poor dispersion from mixing will result in lower ultimate tensile strength, for example. The greatest problem with tensile testing as a quality control tool is that the entire procedure from the completion of the mix until data is available is too long to allow it to keep up with a series of factory mixes (as in a factory mixing campaign) [13, 14].

From a rubber rheology perspective, a stress-strain tensile strength test can be used to measure a property called “green strength”, which is the uncured strength of a rubber compound. A certain amount of green strength is needed in rubber fabrication for many different rubber products. For example, rubber compounds with higher green strength in the construction of a tire may be more resistant to blow-outs in the second stage of the building of an uncured radial tire, which must be blow-out resistant (containing the air without rupturing and ruining the “green tire”). Also, green strength of mixed rubber stock is needed in extruding a rubber tube to be used to make a rubber hose, for example. A tube made of rubber with high green strength will be more collapse-resistant from the force of gravity [15].

Green strength can be measured by ISO 9026 using a tensile tester with the proper load cell range. One example of such a tensile tester is illustrated in Figure 1.4. Uncured dumbbells can be used to measure green strength directly. However, green strength measurements are different from extensional viscosity measurements because green strength typically is measured from a constant rate of separation, while extensional viscosity must be measured from an accelerating rate of separation.

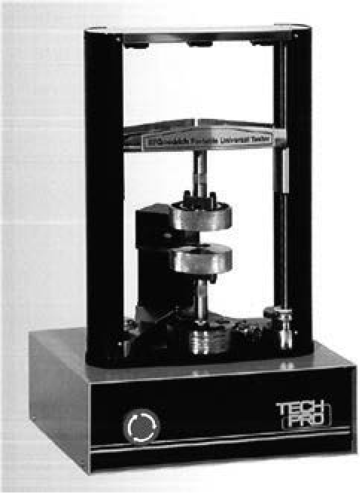

Figure 1.4
An example of a small tensile tester that can handle the small signal measured during a test for “green strength”. Note that a test for green strength requires the dumbbell grips. Adapted and printed with permission from Alpha Technologies.

The tensile tester is probably the most common testing instrument used to appraise the quality of rubber compounds. No matter how small a rubber testing laboratory might be, it probably has a tensile tester.

■ 1.3 Hardness Testing

The rubber hardness test was developed by Albert Ferdinand Shore in the 1920s, resulting in the Shore hardness measurement. Shore hardness has become part of the language of rubber. Shore durometers are ubiquitous in the rubber industry and are used everywhere. Compounders often formulate new cured compounds to a durometer hardness target. The Shore A scale used for softer compounds is much more common than the Shore D scale which is used for much harder compounds. Both the Shore A and Shore D scales are logarithmic. The durometers used to measure hardness do so by measuring the resistance to deformation of the cured rubber surface by the instrument’s indentor [16]. An example of a durometer is illustrated in Figure 1.5. When manual measurements are made using a durometer, it is important to keep the same pressure and same dwell time applied to the sample to ensure good repeatability (with the same operator) and reproducibility (for precision among different operators). Cured rubber hardness is discussed in ASTM D1415 and D2240 as well as ISO 48. To help reduce variation in hardness measurements, it is recommended to use a durometer mounted on an operating stand that takes readings automatically after a timeout. This can reduce test-to-test variation by a factor of three [17].

Figure 1.5
A manual durometer tester. The lower part of the instrument maintains the specimen in a repeatable flat position to improve the precision of the data

1.4 Density

Density measurements have become one of the more common practical quality tests in the rubber industry (for both uncured and cured rubber compounds) because they are simple and quick. The concept of using density measurements (weight per unit volume) as a measure of material quality dates back to the *Archimedes' Principle*, which was developed about 220 BC [18]. Density measurements were used as a measure of quality in the rubber industry over 100 years ago.

Density measurements verify that a mixed compound was mixed properly with all ingredients at their respective quantities. Raw rubber often has a typical density between 0.90 and 1.00 g/cm^3 unless it is halogenated. By comparison, the fillers used in a rubber formulation have densities that are much higher (for example, 1.8 g/cm^3 for carbon black, 2.0 g/cm^3 for silica, and 2.6 g/cm^3 for hard clay) [19]. The density of a mixed compound can be estimated from the factory recipe which gives the concentration of every compounding ingredient in parts per hundred rubber (phr) and their respective density values [20]. Since the density of the rubber component is often significantly less than the fillers used for a typical compound, deviations from the actual measured density of the mixed rubber compound from the calculated compound density usually represents weighing error(s) in the raw materials going into the mixing process. This type of error can lead to inferior cured physical properties for the subject compound and can affect the processing rheology of the mixed stock downstream in the rubber factory.

The test methods for measuring the density of cured rubber are quite different from the methods used to measure the density of uncured mixed rubber stock. For measuring the density of cured rubber, typically *Archimedes' Principle* is used, which is based on weighing the cured rubber specimen in air and immersed in water. Density can be calculated in accordance with ISO 2781 as shown in Equation 1.1.

$$\text{Density} = m_1 / (m_1 - m_2) \tag{1.1}$$

Where m_1 = Net mass of rubber compound (in air) and m_2 = Mass of rubber compound less mass of an equal volume of water (determined by weighing in water, both at standard temperature).

However, this method cannot be used to measure the density of uncured mixed rubber compound because the mixing process not only disperses fillers but also mixes air into the rubber batch as well. Since air is compressible but rubber is not, the actual density of mixed, uncured rubber compound can be measured with a compressed volume densimeter as described in ASTM D297.

■ 1.5 Mooney Viscosity

What is now known as the Mooney viscometer was developed in the 1930s by Dr. Melvin Mooney of US Rubber Co. (later to become Uniroyal) [21]. Before its introduction, the rubber industry had no effective way of measuring processability. After its introduction over 80 years ago, rubber technologists were able to quantify processability for the first time. The Mooney viscometer was (and still is) used to measure processability of mixed rubber batches and to crudely correlate to the average molecular weight of the raw rubber.

Figure 1.6
The Mooney viscometer was developed in the 1930s. Manufacturers have continued to apply new technology to the design of the Mooney viscometer as illustrated here. However, the basic design of the rotor and dies are only slightly changed; Reprinted with permission from Alpha Technologies.

The Mooney viscometer, which is still used today as a standard rubber test instrument, is a rotational viscometer. A modern Mooney viscometer is illustrated in Figure 1.6. The sample cavity of a Mooney viscometer consists of a standard, serrated rotor imbedded in the rubber specimen, which rotates always in the same direction at a speed of 2 revolutions per minute (rpm) in a standardized grooved die cavity. Two rpm gives a theoretical shear rate calculation of only 1.6 s^{-1}, which is a very low shear rate compared to some of the much higher shear rates imparted to rubber compounds downstream in the factory (such as extrusion, calendering, injection molding, etc.). Typically, a Mooney rubber sample size is around 26 grams.

Mooney viscometers were used extensively in the Reserve Rubber Company that was created by the US government during World War II. Synthetic rubbers such as SBR and NBR were routinely tested on the Mooney viscometer. “Mooney viscosity” became part of the language of rubber and is still very much used today. Today we have more than 30 different types of synthetic rubber; however, just about all of these types use Mooney viscosity as the characterizing parameter because it so closely relates to average molecular weight (AMW). Rheologically there are better and faster methods with the Rubber Process Analyzer (RPA) to relate to this property, but a “predicted Mooney” from the RPA testing is the more accepted application because rubber compounders still think in terms of Mooney units. Incidentally, Mooney units are not true viscosity units, they are actually arbitrary units as defined in ISO 289 or ASTM D1646 [22, 23].

In addition to characterizing raw elastomers, the Mooney viscometer is also used as a “processability tester” for mixed batches of a rubber compound. The Mooney viscosity measurements of mixed stock give a rough measure of the amount of mechanical breakdown that has occurred in the mixing process. This can crudely relate to degree of filler dispersion, downstream ease of extrusion, quality of calendering, and/or the quality of molding.

If one were to apply a much faster rotational speed to create higher shear rates, then the resulting viscous heating would make this test very non-isothermal, affecting the validity of these test results [24, 25]. In spite of this fact, instrument manufacturers have recently introduced Mooney viscometers with multi-speed capability. One investigator has claimed that the Mooney viscosity measured with the rotor speed at 0.05 rpm correlates to the weight average molecular weight [26]. Other studies have also shown that testing at high speeds can produce slippage of the rotor on the sample and thereby reduce the expected viscosity value. The speed at which slippage occurs may vary with the viscosity of the sample. In addition to viscosity measurements, Mooney viscometers can also be used to measure time-to-scorch (which is the time to onset of vulcanization or time to incipient formation of crosslinks) for a “final” stock (compound containing curatives). When the vulcanization agent (usually sulfur) and accelerators are added during the mixing process, the so-called “scorch clock” begins. If the downstream work history and heat history use up all the scorch safety time, then this “final” rubber batch is ruined. After a final rubber batch reaches the scorch point, it can no longer be extruded, calendered, or molded properly for curing. The final compound should reach time-to-scorch while it is in the mold, not before. When using a Mooney viscometer in the scorch mode, one simply runs the Mooney test at a higher temperature such as 120 to 135 °C instead of the usual 100 °C for raw polymer testing. Modern Mooney viscometers can run in scorch mode at temperatures up to 200 °C. Scorch time is usually measured with the Mooney viscometer through the ASTM parameter t5 (time to five Mooney units rise above the minimum or low point of the curve). While the Mooney viscometer can measure scorch time quite well, it is not that effective at measuring the cure rate and final state of cure. This is because as rubber goes through the curing (vulcanizing) process, it is transitioning from a fluid to a solid. Since the Mooney rotor is always rotating 360° in the same direction, it is going to slip and tear when rubber transitions from a fluid to a solid. It is not possible to rotate the Mooney 360° in cured rubber without it slipping and tearing the specimen. This slippage problem is the reason why the Mooney viscometer is a terrible curemeter, because it cannot measure the cure rate or state of cure accurately. In the 1960s, several investigators saw the need for a new instrument design with sinusoidal oscillations instead of a 360° rotation. This need resulted in the development of the oscillating disc rheometer or ODR, discussed in Section 1.6 [27].

1.6 ODR Curemeter

In the early 1960s, both BFGoodrich and Monsanto developed the oscillating disc rheometer (ODR, Figure 1.7), which was used as the world's first practical rubber curemeter. The rotor of the ODR is smaller than the Mooney rotor. Also, this ODR rotor is not flat like the Mooney rotor, but has a biconical shape. This shape produces a uniform strain on the sample regardless of the location from the center of the die or disc.

Figure 1.7 The Monsanto Model R100 Oscillating Disc Rheometer with a flat bed chart recorder. This curemeter revolutionized cure testing in the rubber industry and was the recipient of a Trilogy Award in 2000; Reprinted with permission from Alpha Technologies.

The ODR oscillates sinusoidally through a preselected strain of ±1, ±3, or ±5 degrees arc. The ODR was built with one eccentric that contained locations for all three strain angles. Since the ODR rotor is oscillating back and forth through a predetermined arc (instead of rotating 360° in the same direction as with the Mooney rotor), the ODR can much more accurately and precisely record the cure transition from a fluid to the "scorch" state (like a low modulus "solid" or "gel"). The ODR can continue to monitor changes in the mechanical properties of rubber compounds until the compound reaches the ultimate state of cure and there is no more reactivity possible, that is, the highest hardness for the rubber compound being tested. The Mooney viscometer can measure processability and the scorch point until slippage and tearing become a problem. The ODR can follow these two properties as well, but can continue to measure the cure rate and the state of cure until all of the reactants are used up. A comparison of the Mooney and ODR rotors is given in Figure 1.8.

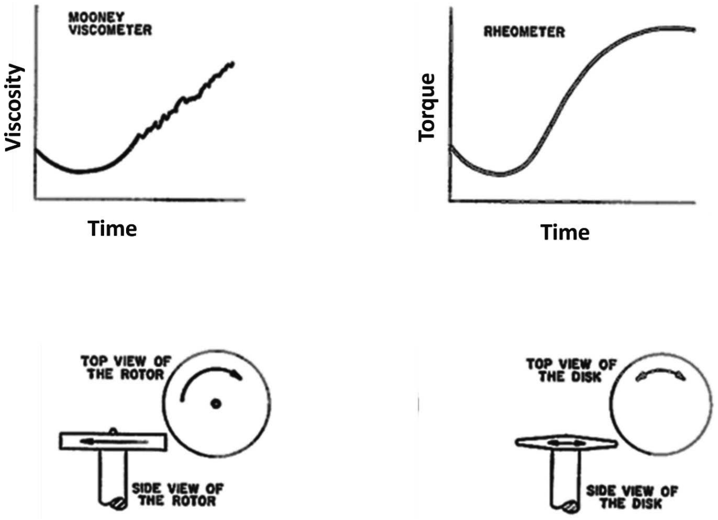

Figure 1.8 Comparison of the rheological measurements made by rotating a rotor versus oscillating a rotor. In the transition from a high viscosity fluid to a solid, the rotating rotor starts to destroy the specimen. The oscillating rotor produces a smooth transition from the fluid to the solid state; Adapted and printed with permission from Alpha Technologies.

The invention of the ODR in the mid-1960s revolutionized testing in the rubber industry. In a relatively short period of time, more than 10,000 of these instruments were made and sold globally. Also an ASTM standard (D2084) was created to standardize this method [28]. In the year 2000, Alpha Technologies (formerly Monsanto Instruments & Equipment) received the *Trilogy Award* for one of the most important technological achievements for the rubber industry in the 20th century [29]. Since then, many ODRs have been replaced by more modern MDRs and RPAs; however, there are still many ODRs in operation today throughout the world [25].

■ 1.7 Capillary Rheometer

It was well recognized that the problem with the Mooney viscometer as a rubber processability tester was that the Mooney only takes measurements at low shear rates of 1.6 s^{-1} at its standard rotational speed of 2 rpm. However, various factory processes in a rubber plant, such as mixing, extruding, calendering, and injection molding, have much higher shear rates, sometimes as high as 1000 s^{-1}. Rubber compounds have differing degrees of shear thinning profiles. Increasing the applied shear rate causes a given percent drop in the compound's viscosity (resistance to flow). Rubber compounds are naturally shear thinning (also called non-Newtonian flow) because of different chemical structures of elastomers and different types and loading levels of various colloidal particle size fillers such as carbon black and silica.

Capillary rheometers were introduced into the plastics industry in the second half of the 20th century. These rheometers were modified to improve their ability to test rubber compounds more effectively. Monsanto I&E introduced their version of the capillary rheometer in the 1970s designed specifically for rubber compound testing, called the MPT (Monsanto Processability Tester). The MPT was limited, but there were still investigators that published research using this device.

Laboratory capillary rheometers are like small "piston extruders" in the laboratory, which can measure the viscosity changes with the application of controlled piston speed which increase the applied shear rates. Thus, they can produce a shear thinning profile for a given rubber compound under steady state shear conditions, and more effectively representing actual flow conditions experienced in the factory. A modern version of a rubber capillary rheometer is the ARC2020 shown in Figure 1.9.

Capillary rheometers can measure rheological properties over a much wider range of applied shear rates than the Mooney viscometer. Thus, the rubber capillary rheometer (ASTM D5099) is a much better rubber processability tester, but is rarely used in quality control testing because it takes significantly longer to perform tests than the Mooney viscometer [30–34].

Figure 1.9
The model ARC 2020 shown here is a modern capillary rheometer designed to test rubber compounds over a wide temperature and shear rate range. A computer is used to set up tests, perform calculations and review data; Reprinted with permission from Alpha Technologies.

■ 1.8 Moving Die Rheometer (MDR)

In the late 1980s, Monsanto Instruments introduced a new, improved curemeter, called the Moving Die Rheometer (MDR), to take the place of the older ODRs. While the ODR was a large improvement over the Mooney viscometer, its design had some fundamental problems. One of the major problems was with the unheated rotor of the ODR. The fact that the rotor was unheated caused it to act as a “heat sink” when the instrument closed on the uncured rubber specimen. This delayed the time necessary for the rubber specimen to reach the set temperature of the dies after the closure of the dies. In addition, the mass of the ODR dies and platens required a relatively long period of time for the temperature to recover after a room temperature sample was loaded. The MDR dies had significantly less mass and so a faster recovery. A faster temperature recovery time in a curemeter is very important to produce a more isothermal test and to improve test productivity. Test cycle time is reduced significantly if the temperature recovery time for the rubber specimen is relatively short especially when testing at elevated temperatures. When cure tests were run at temperatures in excess of 190 °C (374 °F), two new MDRs could replace three operational ODRs for a significant economic savings to the rubber factory. In fact, this is very consistent with historic trends in the rubber industry. Typically, the rubber industry comes close to doubling its labor productivity every 20 years (Figure 1.10).

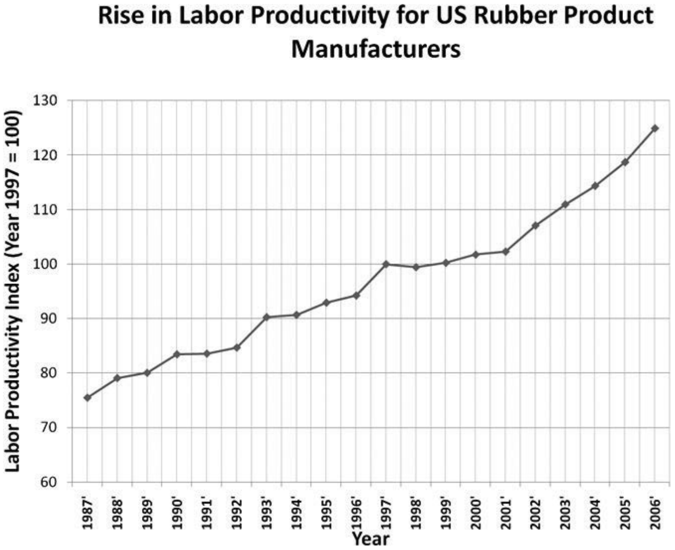

Figure 1.10 The improvement in productivity of the rubber factory with time showing a 67% improvement in 20 years

In addition to the economic benefits of the MDR vs. the ODR, the new design of the MDR significantly reduced the signal coming from instrument components, such as seals and bearings, which often added to the ODR signal coming from the rubber compound under test. This often resulted in improved test sensitivity of the MDR to real compound changes in a given formulation. The repeatability and reproducibility values are also often better for the MDR as well. The moving or oscillating die of the MDR replaced the unheated rotor of the ODR design and allowed the measure of nearly true isothermal cure properties. The complex torque S^* is measured in an MDR from a reaction torque transducer mounted to the upper die. The quality improvement in the MDR S^* measurement is very significant because all of the contributions from ODR items that do not indicate rubber properties of the sample under test, such as seal and bearing frictions, are located at the lower die. The result is a very good complex torque signal-to-noise ratio even when measuring low rubber viscosity. The complex torque is very repeatable and can be split into an elastic or storage torque component (S'), and a loss or viscous torque component (S''). This allows a much more accurate measure of tan delta in a curemeter, which is the ratio of S''/S'. This value is very important in uncured and cured rubber compounds. Due to the lack of a good signal-to-noise ratio and the presence of seal and bearing friction, the ODR could not accurately measure dynamic properties such as S'' or tan delta [35–37].

1.9 Rubber Process Analyzer (RPA)

In 1992, Monsanto I&E (now Alpha Technologies) introduced a new class of rheometer especially designed for testing rubber in many stages of manufacture. This instrument was the Rubber Process Analyzer.

The RPA evolved from the MDR curemeter design created by Monsanto in the late 1980s. In fact, the early RPAs have the same die design as the original MDR. However, the MDR motor and linkage system produced a sinusoidal amplitude at one strain and frequency. The RPA had a digital direct drive motor so that the amplitude and frequency of oscillation could be directly controlled from a computer. The MDR was designed to operate with or without a computer, whereas the RPA required a computer. The RPA design proved to be a very versatile oscillating rubber rheometer which could do much more than the MDR. They both had the advantage of having a sealed, pressurized cavity which molds and conditions the rubber specimen. Pressurized sample chambers improve repeatability and provide more accurate measurements of viscosity and modulus.

The RPA can operate as four different types of rubber testers. A schematic of these four different rubber testers is shown in Figure 1.11. The four testers are described in more detail below:

- Viscometer – measures raw rubber viscosity (similar to the information provided by a Mooney viscometer).
- Dynamic Mechanical Rheological Tester (DMRT) – measures processability of raw elastomers and mixed stocks. This is done by the measurement of the viscoelastic properties of raw elastomers or mixed stocks under a wide range of oscillation frequencies, strain amplitudes, shear rates, and time at temperature. The latter can also measure scorch time which is also a measure of processability.
- Advanced Curemeter – provides cure measurements under isothermal, nonisothermal (for example, a temperature ramp and hold), or mold simulation.
- Dynamic Mechanical Analyzer (DMA) – measures the viscoelastic properties of cured rubber compounds to predict performance of rubber products. The modulus and damping properties after cure are very important in specific products.

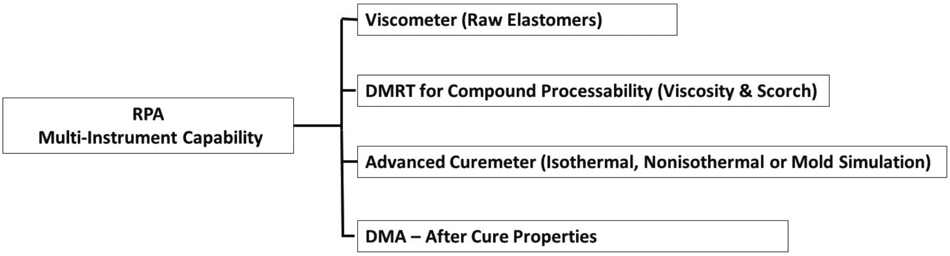

Figure 1.11 Unlike many rubber instruments, the RPA can operate as four distinct instruments to provide data from rubber before, during, and after cure under many different test conditions; Adapted and printed with permission from Alpha Technologies.

When RPAs were first introduced to the rubber industry in 1992, they were mostly used in centralized research and development laboratories all over the world. Then with the emergence of quality programs such as *Six Sigma* in the late 1990s, it was discovered that RPAs possessed much better statistical test sensitivity and could actually measure rubber properties with much better repeatability and test sensitivity than most other rubber tests discussed in this chapter. The RPA evolved in the rubber industry because it was considered a more sensitive gage at a wide range of test conditions. Since the year 2000, there has been a lot of activity amongst standards organizations to establish RPA standards to improve quality assurance tests with over nine new standards based on the RPA [38–43].

■ 1.10 Dynamic Mechanical Analyzer (DMA)

The RPA just discussed is considered another version of a DMA [44]. However, the RPA, unlike most other DMAs, possesses a sealed and pressurized cavity and prepares (or molds) the uncured rubber sample for processability testing and/or curing and/or after-cure dynamic testing. However, most other DMAs require a cured rubber sample to be cut or molded to proper dimensions and sinusoidally tested under shear, extension, or compression for cured dynamic properties. These systems test at different temperatures, strains, and frequencies. Many DMAs have an advantage over the RPA in that they can measure the change in tan delta, storage modulus, and loss modulus over a very wide temperature range [45]. They can perform these temperature sweeps from well below −100 °C to very high temperatures in excess of 1000 °C. In performing these temperature sweeps, the DMA is very effective at measuring both first order (T_m melt points for any crystalline content) and second order (T_g glass transitions) for both raw elastomers and mixed stocks. The various transitions present in rubber can be observed by either a very wide temperature sweep or a very wide frequency sweep using many decades. In DMA tests, changes in frequency and temperature produce similar changes in the data. These rubber transitions are illustrated with a wide range frequency sweep in Figure 1.12.

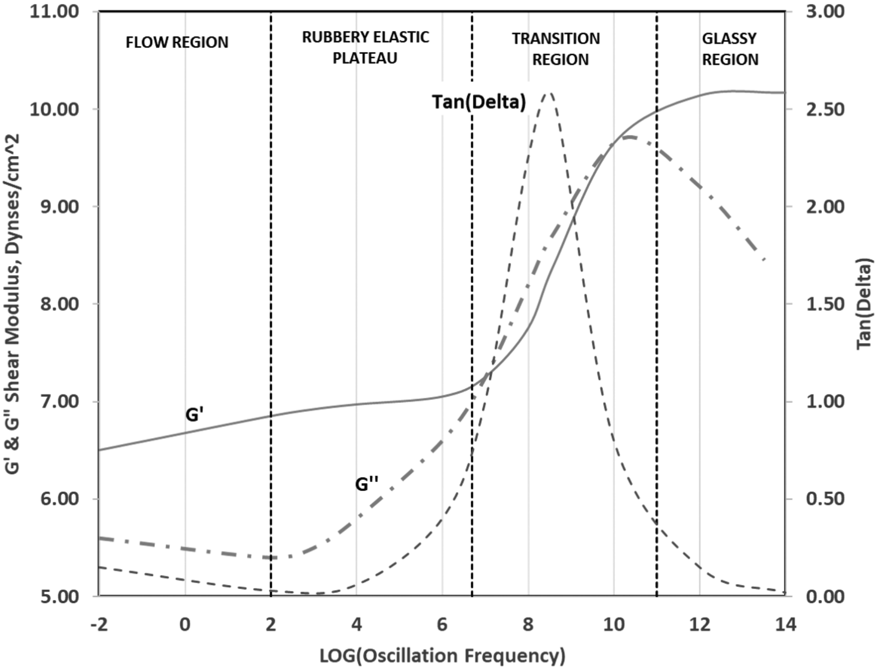

Figure 1.12 The dynamic properties of elastomers change dramatically when changing either temperature or oscillation frequency. This figure shows four distinct transition areas when viewing the results over a very wide range of oscillation frequencies

RPAs, on the other hand, can more effectively test uncured rubber under high percentage strain conditions than a traditional DMA; so RPAs are more effective in measuring in the non-linear viscoelastic region. This is due to the reduction in edge effects present in the RPA design. Edge effects often increase the variation of the data, which can make the data useless. While overall, dynamic properties from different types of DMAs (including the RPA) have been found to correlate well, values such as tan delta are not necessarily the same among different instruments. ASTM D5992 (which replaced ASTM D2231) defines many dynamic properties that are measured in rubber compounds. ISO 2856 is a good reference as well [46]. The RPA as a DMA is a non-destructive tester and does not correlate well with destructive test results.

1.11 Flex Fatigue Testers

Flex fatigue resistance of a cured rubber compound is measured by the time or cycles required for a subject compound to degrade, crack, or fail from repeated cyclical deformation under shearing, bending, or extension.

Rubber compounds based on higher ratios of accelerator to sulfur possess more mono- and di-sulfidic crosslinks than polysulfidics resulting in better heat aging resistance and poorer flex fatigue resistance. Of course, rubber compounds with lower ratios of accelerator to sulfur possess more polysulfidic crosslinks, which give better flex fatigue properties. So the accelerator/sulfur ratio is very important in predicting what flex fatigue properties a compound will possess. Other influences on the flex cracking resistance are the type and loading levels of the compound filler/oil system and the type of base elastomer used in the subject compound. The hardness of the cured rubber compound has a great influence on flex fatigue life as well.

In measuring flex cracking resistance, various standardized flex cracking tests have been developed. These tests usually make relative comparisons with a given "control" compound. All these flex fatigue methods have very poor repeatability and reproducibility. To show significant differences, one should run a large number of specimens with the same formulation. If multiple formulations are run, they should be done in random order [47].

The following are some of the standardized ASTM and ISO flex fatigue tests that have been used [48].

- *Scott* Flexer – ASTM D430 Part A
- *DuPont* Flexing Machine – ASTM D430, Part C
- *DeMattia* Tester – ASTM D430, Part B, ASTM D813, ISO 132
- *Ross* Flexing Machine – ASTM D1052
- *Texus* Flex Tester – ASTM D3629
- Fatigue to Failure Tester – ASTM D4482

All these methods have different sample shapes, which give very different results. They should only be used with a known control with many replicate specimens to prove any significant difference.

Probably the most popular of these tests is the DeMattia Tester which is still used widely.

Monsanto Instruments (now Alpha Technologies) introduced the Monsanto Fatigue to Failure Tester (FTFT) under tension, which some feel is more relevant. This method is now in ASTM D4482. This device can test many samples at the same

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