2 Compound Processing Characteristics and Testing

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2.1 Introduction

The processing of a rubber formulation is a very important aspect of rubber compounding. Also, it is important to understand the rubber properties needed for good processability and the tests performed to measure these properties.

2.2 Manufacturing Process

Uncured rubber, whether natural or synthetic, behaves as a viscoelastic fluid during mixing. Under processing conditions, various rubber chemicals, fillers, and other additives can be added and mixed into the rubber to form an uncured “rubber compound.” These compounding ingredients are generally added to the rubber through one of two basic types of mixers, the two roll mill or the internal mixer.

2.2.1 Two Roll Mill

The two roll mill in Fig. 2.1 consists of two horizontal, parallel, heavy metal rolls which can be jacketed with steam and water to control temperature. These rolls turn towards each other with a pre-set, adjustable gap or nip to allow the rubber to pass through to achieve high-shear mixing. The back roll usually turns at a faster surface speed than the front roll; this difference increases the shear forces. The difference in roll speeds is called the friction ratio. The rubber generally forms a “band” around the front roll. Mill mixing is the oldest method of rubber mixing, dating back to the very beginning of the rubber industry; however, it is a relatively slow method and its batch size is limited. Internal mixers overcome these problems.

2.2.2 Internal Mixers

Internal mixers were first developed by Fernley H. Banbury in 1916. Today, these internal mixers are commonly used because they are much more productive than two roll mills. Internal mixers consist of two rotors or blades turning toward each other in an enclosed
metal cavity. These rotors can be either tangential or intermeshing in arrangement (Fig. 2.2). The cavity is open to a loading chute through which rubber, fillers, and various chemicals are placed. Upon completion of the mix cycle, the mixed rubber stock is discharged through a door in the bottom of the mixer.

Mixing time is determined by the shape and size of the rotors, the rotor speed, and horsepower of the motor turning them. The rotors generally turn at a high friction ratio. Some internal mixers can handle batches in excess of 1000 pounds (greater than 455 kg), and in some cases, can completely mix a compound in less than two minutes. Of course, with so much energy being absorbed by the rubber stock, the batch temperature can rise well above 120 °C (250 °F) before it is dumped and cooled. The temperature rise that results from viscous heating of the rubber compound often means the compounds must pass through the internal mixer more than once to disperse fillers and other compounding
ingredients. Batches are usually dumped from an internal mixer onto a mill where they may be further worked while being cooled. Sometimes additional compounding ingredients, such as curatives, are added at this point.

2.2.3 Further Downstream Processing

After the rubber stock is mixed, it may be remilled and fed into either a calender or extruder. A three or four roll calender (Fig. 2.3) is generally used when uncured rubber is applied to a textile fabric or steel cord as a coating. Calenders are also used to form sheets of rubber. Extruders (Fig. 2.4) are used when the uncured rubber stock is to be shaped into a tire tread, a belt cover, or a hose tube, for example. A screw rotating in a cylinder transports the rubber compound from the feed port to the die of the extruder. During this process, additional heat and work histories usually affect the viscoelastic behavior of the compound and how it extrudes through the die. Extruders with lower screw length to screw diameter (L/D) ratios are considered “hot feed” extruders while ones with high ratios are considered “cold feed” extruders.

After calendering or extrusion, the uncured rubber parts may be brought together in a building step. For example, uncured tire components are put together by hand or automatically on a tire building machine where the calendered carcass plies are placed over the innerliner; then, the belt and sidewalls over the carcass, etc. In a similar manner, conveyor belts are constructed on large building tables on which each calendered ply is
manually placed over another, followed by the extruded cover stock. Some hose may be hand built as well. Other rubber products may require that the mixed compound be preshaped and molded.

2.2.4 Curing Process

After the shaping and/or construction of the uncured (‘green’) rubber product, it goes through the cure process. With tires, the uncured constructed assembly is placed in a special tire press, such as a Bag-O-Matic press, where it is shaped in a tire mold and cured at elevated temperatures under pressure. Other products, such as hose and rollers, are sometimes cured in autoclaves with steam pressure. Many automotive rubber parts are also cured through compression molding, transfer molding, or injection molding. Rubber cure temperatures can generally range from as low as 100 to more than 200 °C. The higher cure temperatures mean shorter cure cycles. Many rubber products are therefore cured at higher temperature ranges for greater productivity, provided that reversion or thermal degradation is not a problem at these higher temperatures. Most rubber products are cured under pressure as well to avoid gas formation and porosity.

2.2.5 Factory Problems

If rubber compound processability characteristics are not controlled for the different stages of the manufacturing process, various factory quality problems can result. Poor control can
Table 2.1  Examples of Factory Problems

<table>
<thead>
<tr>
<th>Mixing</th>
<th>Stock bin storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long black incorporation times (BIT)</td>
<td>Scorch</td>
</tr>
<tr>
<td>Lower filler dispersion</td>
<td>Green strength</td>
</tr>
<tr>
<td>Higher compound viscosity</td>
<td>Sticky slabs</td>
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<tr>
<td>Crumbly batches</td>
<td></td>
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<tr>
<td>Lumpy stocks</td>
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<tr>
<td>Slow mixing</td>
<td></td>
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<tr>
<td>Milling</td>
<td>Compression/transfer/injection molding</td>
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<tr>
<td>Back rolling</td>
<td>Poor appearance</td>
</tr>
<tr>
<td>Bagging</td>
<td>Shrinkage</td>
</tr>
<tr>
<td>Poor mill release</td>
<td>Cured hardness</td>
</tr>
<tr>
<td>Thickness control</td>
<td>Porosity</td>
</tr>
<tr>
<td>Extrusion</td>
<td>Mold release</td>
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<tr>
<td>Rough surface (not smooth)</td>
<td>Mold fouling</td>
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<tr>
<td>Poor dimensional stability</td>
<td></td>
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<tr>
<td>Uncontrolled extrudate shrinkage</td>
<td></td>
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<tr>
<td>High die swell</td>
<td></td>
</tr>
<tr>
<td>Low extrusion rate</td>
<td></td>
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<tr>
<td>Pin holes</td>
<td></td>
</tr>
<tr>
<td>Scorch</td>
<td></td>
</tr>
<tr>
<td>Calendering</td>
<td>Autoclave cures</td>
</tr>
<tr>
<td>Scorch</td>
<td>Appearance</td>
</tr>
<tr>
<td>Bare spots, holes</td>
<td>Mandrel release</td>
</tr>
<tr>
<td>Poor dimensional stability, width, thickness</td>
<td>Shrinkage</td>
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<tr>
<td>Heat blisters</td>
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<tr>
<td>Trapped air</td>
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<tr>
<td>Calender release (from rolls)</td>
<td></td>
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<tr>
<td>Rubber fabric penetration</td>
<td></td>
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<tr>
<td>Liner release</td>
<td></td>
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</tbody>
</table>

result in higher scrap rates, higher internal and external failure costs, and lost plant productivity, all of which can command a great deal of the rubber compounder’s attention as daily plant problems. Some examples [1] of these problems are given in Table 2.1.

Lord Kelvin once said that “applying numbers to a process makes for the beginnings of a science.” If rubber processability characteristics can be measured effectively, then the rubber compounder can find the cause of many of the factory problems given in Table 2.1. Various test methods help determine the cause of many problems and aid in the design of new compounds and/or better processing conditions to reduce factory problems.

2.3  Processability Characteristics and Measurements

The following are rubber compound processability characteristics that determine how well a given compound processes:
1. Viscosity
2. Shear Thinning
3. Elasticity (or V/E Ratio)
4. Time to Scorch
5. Cure Rate
6. Ultimate State of Cure
7. Reversion Resistance
8. Green Strength
9. Tack
10. Stickiness
11. Dispersion
12. Storage Stability
13. Mis-Compounding (Compound Variation)
14. Cellular Rubber Blow Reaction

2.3.1 Viscosity

Viscosity is the resistance of a fluid, such as rubber, to flow under stress. Mathematically, viscosity (\( \eta \)) is shear stress divided by shear rate as shown below in Eq. (2.1).

\[
\eta = \frac{\text{shear stress}}{\text{shear rate}}
\]  

(2.1)

Viscosity is very dependent on temperature; at higher temperatures materials are less viscous. The viscosity of rubber can be measured by four methods:

1. rotational viscometers
2. capillary rheometers
3. oscillating rheometers
4. compression plastimeters

2.3.1.1 Rotational Viscometers

By far, the most commonly used rotational viscometer in the rubber industry is the Mooney viscometer. Melvin Mooney of U.S. Rubber Co. developed this instrument in the 1930s [2]. Since then, it has become one of the most widely used test methods in the industry. It is used for testing both raw rubber and mixed stocks.

This method is described in detail in ASTM D1646 or International Standard ISO 289, Part 1. Two precut rubber test pieces with a combined volume of 25 cm\(^3\) are placed into a two-part compression cavity mold. With the dies closed, a sealed, pressurized cavity is formed, in which a special rotor is imbedded in the rubber. This rotor and the dies are grooved to help prevent the rubber from slipping at the rotor or die interface while the rotor is turning.

Usually there is a pre-heat time after the dies are closed to allow the rubber to approach the set temperature of the instrument. Then the test specification calls for the rotor to turn at two revolutions per minute (2 rpm) for a specified time period. The instrument records
viscosity in Mooney Units (MU), which are arbitrary units based on torque. Generally, the measured viscosity of the rubber under test decreases with running time because of the thixotropic effects of the rubber tested. However, depending on the type of rubber and the test temperature, the rate of decrease in the measured Mooney viscosity with time should slow down greatly (Fig. 2.5). Usually, the Mooney viscosity test is performed with a one minute preheat and a run time of either four or eight minutes. The final Mooney viscosity value is reported as the lowest value recorded in the last 30 seconds of the test.

As an example, a Mooney viscosity value may be reported as 55 ML (1 + 4). This is in accordance with the convention recommended by the ASTM standard cited above. The term “ML” indicates a large standard rotor was used. “55” represents the measured Mooney viscosity value reported for the specified conditions of the test. The “1” represents the preheat time before the rotor starts to turn. The “4” indicates the running time of actual rotation of the rotor before the final Mooney viscosity measurement is made.

Mooney viscosity crudely relates to the average molecular weight of a raw rubber and to the state-of-mix or quality-of-mix for a masterbatch or final uncured rubber stock. If the Mooney viscometer with a large rotor is measuring values well above 80 MU, it can be somewhat insensitive to subtle differences among raw polymers or mixed stocks. When the rubber specimen is too tough, slippage and tearing may occur. One method to avoid this is to simply run the test at a higher temperature. For example, many EPDM polymers do not test well at 100°C. Instead, they are tested at 125°C. However, a higher temperature can be a problem for rubber compounds containing curatives that are “scorchy.” Also, if a rubber has a high Mooney viscosity from the large rotor (ML), then repeating the test with a small Mooney rotor (MS) should be considered. One basic problem with the Mooney viscometer is that it measures viscosity at a low shear rate of only 1 s⁻¹, which is far lower than many rubber manufacturing processes.

2.3.1.2 Capillary Rheometer

The capillary rheometer measures the viscosity of mixed rubber stocks at relatively high shear rates. ASTM D5099 describes this method for rubber testing. There is no ISO
International Standard for the capillary rheometer’s use with rubber. The ASTM method consists of placing (or packing) cut pieces of a rubber sample in a heated barrel. Then, a special piston pushes the rubber out of the barrel through an orifice of a special die (with a given capillary length to orifice diameter ratio or L/D) to form an extrudate. The apparent shear rate is determined from the speed of the piston traveling in the barrel (the ram speed). The apparent shear stress is determined from the resulting barrel pressure measured by a transducer (Fig 2.6). From Eq. (2.1), the apparent viscosity $\eta_{\text{app}}$ can be calculated. This apparent viscosity can be converted to “true” viscosity by applying the Rabinowitsch correction to obtain the “true” shear rate and the Bagley correction to obtain the “true” shear stress [3,4].

The main advantage of the capillary rheometer for measuring rubber viscosity is the wide shear rate range it can apply to the rubber specimen. Many capillary rheometers can measure viscosity shear rates at over 1000 s$^{-1}$. The disadvantages of these rheometers are that they are difficult to operate, require more time to run a single test, and require extensive time to clean the barrel and set up for the next test.
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2.3.1.3 Oscillating Rheometers

An instrument called the Rubber Process Analyzer (RPA) by Alpha Technologies [5] measures dynamic viscosity through the application of a sinusoidal strain to an uncured rubber specimen molded in a sealed, pressurized cavity. ASTM D6204 describes this unique method for measuring processability. Figure 2.7 shows the instrument used for this method. Figure 2.8 shows a sinusoidal strain being applied to the rubber test specimen. The complex torque response ($S'$) is observed to be out-of-phase with the applied strain because of the viscoelastic nature of the rubber being tested. The phase angle $\delta$ quantifies this out-of-phase response.

![Figure 2.7 RPA 2000® rubber process analyzer.](image)

![Figure 2.8 Applied sinusoidal strain and resulting stress response.](image)
From the complex torque $S^*$ response and the phase angle $\delta$, the elastic torque $S'$ (in-phase with the applied strain) and the viscous torque $S''$ (90° out-of-phase with the applied strain) can be derived (Fig. 2.8). The elastic response $S'$ is a function of the amplitude of the applied strain while the viscous torque is a function of the rate of change of the applied strain.

The storage shear modulus ($G'$) is calculated as follows:

$$G' = k \cdot S' / \text{strain} \quad (2.2)$$

The loss shear modulus ($G''$) is calculated as follows:

$$G'' = k \cdot S'' / \text{strain} \quad (2.3)$$

where $k$ is a constant that takes into account the unique geometry of the die cavity.

The complex shear modulus ($G^*$) is equal to the square root of the sum of $G'$ squared and $G''$ squared.

$$G^* = [(G')^2 + (G'')^2]^{1/2} \quad (2.4)$$

The complex dynamic viscosity $\eta^*$ is calculated as follows:

$$\eta^* = G^* / \omega \quad (2.5)$$

where $\omega$ is the frequency of the sinusoidal strain in radians/second.

The real dynamic viscosity $\eta'$ is also calculated in the following manner:

$$\eta' = G'' / \omega \quad (2.6)$$

The complex dynamic viscosity $\eta^*$ from the Rubber Process Analyzer is analogous to the apparent viscosity ($\eta_{\text{app}}$) from the capillary rheometer, while the real dynamic viscosity $\eta'$ is analogous to the “corrected” viscosity from the capillary rheometer.

Cox and Merz in the early 1950s published the following empirical relationship between capillary rheometer viscosity $\eta_{\text{app}}$ measured under conditions of steady shear rate and dynamic complex viscosity $\eta^*$, which is measured through sinusoidal deformation (and constantly changing shear rates) applied by a dynamic mechanical rheological tester [6]:

$$\eta_{\text{app}}(\dot{\gamma}) = \eta^*(\omega)|_{\omega = \dot{\gamma}} \quad (2.7)$$

- $\eta_{\text{app}}$ is the apparent (uncorrected) capillary rheometer viscosity at a steady shear rate (in s$^{-1}$)
- $\eta^*$ is complex dynamic viscosity measured at an oscillatory frequency of $\omega$ (in radians per second).

This empirical relationship sometimes works, but not every time [7,8]. Sometimes the success of this empirical relationship is based on the nature and concentration of the reinforcing fillers used.

The important advantages of the Rubber Process Analyzer in measuring rubber viscosity over the other methods discussed are its versatility in measuring viscosity at both low and high shear rates, ease of use, and excellent repeatability.

2.3.1.4 Compression Plastimeters

While viscosity is defined as the resistance to plastic deformation, the term plasticity refers to the “ease of deformation” for a rubber specimen. In a way “plasticity” and
“viscosity” define the same property, but have the opposite meaning. A plastimeter measures the plasticity of an uncured rubber specimen. Plastimeters are very simple, crude methods for measuring the flow of a rubber sample. The main problem with most plastimeters is that they operate at extremely low shear rate ranges of only 0.0025 to 1 s\(^{-1}\), much lower than even the Mooney viscometer [9]. To reinforce this point, the Rubber Process Analyzer can be correlated to these methods but only when very low frequencies (very low shear rates) are applied to the rubber specimen [10]. The principle of plastimeter procedures is basically to measure the deformation of a cylindrically cut, uncured rubber specimen after it has been subjected to a constant compressive force between two parallel plates for a specified time period at a specified test temperature.

The initial part of ASTM D 3194 (the standard describing the Plasticity Retention Index for natural rubber) and International Standard ISO 2007 describe the use of the Wallace rapid plastimeter method. The Williams plastometer parallel plate method is described by ASTM D926 and ISO 7323.

2.3.2 Shear Thinning

Shear thinning is the characteristic of non-Newtonian fluids (such as rubber compounds) to decrease in measured viscosity with an increase in applied shear rate. Not only is it important to measure the compound viscosity, it is also important to know how rapidly viscosity decreases with increasing shear rate. All rubber compounds are non-Newtonian in their flow characteristics and their viscosity usually decreases according to the power law model. If the log of viscosity is plotted against the log of shear rate, a straight line usually results. Rubber compounds with different reinforcing filler systems have different log-log slopes. These different slopes can be quite important because compounds are commonly processed at different shear rates. As shown in Fig. 2.9, the ordinal relationship of Compound 1 vs. Compound 2, for example, can change between a low shear rate to high shear rate. So, Compound 2 might have higher viscosity than Compound 1 in an

![Figure 2.9 Comparison of two compounds with different shear thinning profiles from capillary rheometer viscosity measurements with increasing applied shear rates.](image)
injection molding operation, but Compound 2 might have lower viscosity than Compound 1 in the mold after injection.

Two effective methods of measuring shear thinning behavior are the capillary rheometer and oscillating rheometer.

2.3.2.1  Shear Thinning by Capillary Rheometer

The capillary rheometer can apply a wide range of shear rates. As discussed earlier, according to ASTM D5099, the piston can be programmed to travel in the barrel at a series of faster and faster speeds which result in higher and higher shear rates. Figure 2.10 shows the log-log plot for a capillary rheometer. The applied shear rate for a capillary rheometer can be more than 1000 s\(^{-1}\).

2.3.2.2  Shear Thinning by Oscillating Rheometer

As discussed earlier, the Rubber Process Analyzer (which is defined in ASTM D6204) increases shear rate by increasing the frequency of the sinusoidal strain. Figure 2.11 shows a log-log plot of the complex dynamic viscosity vs. shear rate (frequency in radians/second) for the same set of compounds shown earlier in the figure for capillary rheometer measurements. In fact, Fig. 2.12 shows how the power law slopes from these measurements for capillary rheometer vs. Rubber Process Analyzer agree quite well [11].

Shear rate with the Rubber Process Analyzer can also be increased by using a higher applied strain. Sometimes applying higher strains to achieve higher shear rates may have some advantages over higher frequencies because these higher strains may more effectively destroy carbon black aggregate-aggregate networks which form in the rubber compound while in storage. Figure 2.13 shows the very good correlation achieved between a capillary rheometer shear stress values measured at 100 s\(^{-1}\) and Rubber Process Analyzer \(G'\) values at very high applied strain [12].
Figure 2.11 Log-log plot of RPA dynamic complex viscosity $\eta'$ vs. rad./s (frequency sweep).

Figure 2.12 Comparison of power law slopes for shear thinning as measured with a capillary rheometer vs. an oscillating rheometer (RPA).

The Rubber Process Analyzer is very simple to operate and versatile in applying different shear rates by either varying the frequency or varying the strain. It is a unique instrument because it can apply very high strains to an uncured rubber specimen in a sealed pressurized cavity and achieve very repeatable results. Also, the Rubber Process Analyzer has an advantage over the capillary rheometer in that it can more effectively test raw rubber samples for shear thinning behavior and achieve better repeatability.

2.3.3 Elasticity

Elasticity is that material property that conforms to Hooke’s Law. A purely elastic material, such as some metals at low strains, conforms perfectly to Eq. (2.8) below [13]:

$$\sigma = E\gamma$$

(2.8)
where:

- $\sigma =$ stress, or force per unit area
- $\gamma =$ strain (displacement) as measured from change in length
- $E =$ the static modulus of elasticity

With a perfectly elastic material, the rate of applied deformation has no effect on the measured stress response. Of course, rubber is not perfectly elastic even in the cured state. Rubber is viscoelastic, possessing both viscous and elastic qualities in both the uncured and cured states. However, the ratio of the viscous quality to the elastic quality (the V/E ratio) decreases greatly when a rubber compound is cured.

Uncured rubber possesses an elastic quality mainly as a result of chain entanglements. Uncured rubber with a high elastic quality has what is commonly called nerve. Rubber with high "nerve" (high elasticity) resists processing. It is not uncommon for two rubbers to have the same viscosity, but one is "nervier" (has more elasticity) than the other. This elastic quality difference affects how well the rubber processes. This higher elastic quality affects how well a rubber mixes, how well it incorporates fillers, the length of a mix cycle, and the viscoelastic properties imparted to the final batch. For example, a mixed stock with a higher elastic quality may have greater die swell, poorer dimensional stability during a downstream extrusion process, or mold differently from a stock with higher nerve.

The elasticity of rubber can be measured by five test methods:

1. Mooney stress relaxation
2. oscillating rheometer
3. capillary rheometer die swell
4. compression plastimeter elastic recovery
5. direct shrinkage measurements.

2.3.3.1 Mooney Stress Relaxation

In 1996, a new Part B for measuring stress relaxation was added to ASTM D1646, the Mooney Viscosity Standard. This new method is widely used in the rubber industry because it can measure Mooney viscosity as well as stress relaxation decay rates. Stress relaxation tests are run on the same specimen immediately after completing viscosity measurements. For example, an ML 1 + 4 test (large rotor, 1 minute preheat, 4 minutes run) can be performed on a raw rubber sample followed by a two minute stress relaxation at the end of the test. The total test time is seven minutes. Mooney stress relaxation can be performed automatically after the “final” Mooney viscosity measurements by very rapidly stopping the rotation of the rotor and measuring the power law decay of the Mooney viscosity output with time. Mathematically, this power law decay is described in Eq. (2.9).

\[ M = kt^{-\alpha} \] (2.9)

where

- \( M \) is the torque value in Mooney units
- \( k \) is the torque value at 1 second
- \( t \) is the time in seconds
- \( \alpha \) is the rate of relaxation (the slope of the relaxation function)

In a log-log plot, this expression takes the following form:

\[ \log M = -\alpha \log t + \log k \] (2.10)

The slope \( \alpha \) is commonly used as a measure of the stress relaxation for raw rubber and rubber compounds. Figure 2.14 illustrates how this slope \( \alpha \) can be used to quickly compare the elasticity of two EPDM polymers. These two EPDMs have the same Mooney viscosity.

![Figure 2.14 Mooney stress relaxation for two EPDM polymers using the MV2000® Mooney viscometer.](image-url)
but different elasticity. A steeper slope (a faster rate of decay) indicates that the polymer has a higher V/E ratio and a lower elastic quality than the polymer shown with a flatter slope. Therefore, these two polymers are likely to process differently [14].

2.3.3.2 Elasticity by Oscillating Rheometer

ASTM D6204, which describes the Rubber Process Analyzer (RPA), can provide a procedure to measure the elasticity of rubber. As described in Section 2.3.1.3, the storage modulus $G'$ and loss modulus $G''$ are measured by this technique from the testing of raw rubber as well as uncured mixed stocks. $G'$ is a direct measure of elasticity. A higher $G'$ response means a higher elastic quality at a defined temperature, frequency and strain. Dividing $G''$ by $G'$ calculates a parameter known as $\tan \delta$ as shown in Eq. (2.11).

$$\tan \delta = \frac{G''}{G'}$$  \hspace{1cm} (2.11)

Tan $\delta$ is the tangent of the phase angle discussed in Section 2.3.1.3 (see also Fig. 3.5). A higher uncured $\tan \delta$ for a raw elastomer or mixed stock implies a higher V/E ratio, which is also analogous to a steeper slope from a stress relaxation test. The $\tan \delta$, as a processability parameter, has been found to be at least twice as sensitive to real differences in rubber processability than the $\alpha$ slope from the Mooney Stress Relaxation test discussed earlier [15]. Also, an RPA $\tan \delta$ as a parameter is more reliable and can be measured at a wider range of shear rates than the $\alpha$ slope. Therefore, $\tan \delta$ and $G'$ are both very effective processability measurements. An example of comparing viscoelastic properties with the RPA is shown in Fig. 2.15. Here, two different sources of SBR 1006 have almost exactly the same Mooney viscosity but have quite different $\tan \delta$ values. Other studies have shown similar differences [16,17].

![Figure 2.15](image)

Figure 2.15 Uncured $\tan \delta$ response from the RPA for two SBR 1006 polymers with the same Mooney viscosity.
2.3.3.3  *Capillary Rheometer Die Swell*

As discussed earlier, ASTM D5099 describes the use of the capillary rheometer for testing the viscosity of rubber compounds at different shear rates. When the rubber compound is extruded through a standard die orifice, it swells from its elastic memory. A rubber compound with high elasticity usually displays greater die swell. ASTM Test Method D5099 does not describe a method for measuring this die swell. However, a capillary rheometer, such as the Monsanto Processability Tester, can measure die swell directly using a special optical detector. This method has a disadvantage in that its statistical test sensitivity and repeatability are not nearly as good as the RPA method described earlier. Also, the capillary rheometer is not normally effective for testing raw rubber.

2.3.3.4  *Compression Plastimeter Elastic Recovery*

As discussed earlier, the principle of these plastimeter procedures is to measure the deformation of a cylindrically cut, uncured rubber specimen after it is subjected to a constant compression force between two parallel plates for a specified time period at a specified test temperature. This relates to plasticity, or the viscous component, as discussed earlier. However, these plastimeter methods usually have an additional procedure for elastic recovery, which is measured dimensionally in a given time period after the deformational load has been removed. This elastic recovery is supposed to relate to the elasticity of the rubber specimen. Some problems with these procedures in measuring elasticity are that they are performed at low strain, low shear rate, and at a temperature that is usually much lower than the factory processing temperature. Because of these conditions, the data may not be relevant to plant processes. Variations in sample preparation also greatly affect test results. Recovery data can be quite variable.

2.3.3.5  *Direct Shrinkage Measurements*

Another way of measuring nerve is to directly measure percent shrinkage. An example of this is presented in ASTM D1917, which is the standard method for measuring shrinkage of raw and compounded hot-polymerized SBR. Rubber strips from a mill are prepared and placed on a specified type of low-friction surface. The strips are exposed to elevated temperatures for specified lengths of time, and finally cooled, dimensionally measured, and their percent shrinkage calculated. Even though this is an old method, no precision statement has been published. This method is not widely used and some believe it is not very repeatable.

2.3.4  *Time to Scorch*

The time to scorch is the time required at a specified temperature (or heat history) for a rubber compound to form incipient crosslinks. When a scorch point is reached after a compound is exposed to a given heat history from factory processing, the compound cannot be processed further by milling, extruding, calendering, etc. Therefore, scorch
measurement is very important in determining whether a given rubber compound can be processed in a particular operation. The scorch time can be measured by:

1. Rotational viscometer
2. Oscillating rheometer
3. Capillary rheometer

2.3.4.1 Scorch by Rotational Viscometer

The Mooney Viscometer has been used to measure scorch since the 1930s. It was the first instrument method used to measure scorch safety of a mixed stock. ASTM D1646 and International Standard ISO 289, Part 2 describe how Mooney scorch time is reported. Usually, the Mooney viscometer is set at a temperature higher than 100 °C, such as 121°C or 135°C, for example. From a practical viewpoint, some rubber technologists consider the best scorch test temperature is selected when the compound routinely reaches scorch within 10 to 20 minutes. However, others feel the temperature for the Mooney scorch test should be close to the normal temperature of the factory process in question.

Mooney scorch is generally reported for a large rotor as the time required for the viscosity to rise five Mooney units above the minimum viscosity (referred to as \(t_s\)). However, when the small rotor is used, the scorch time is reported as the time required for viscosity to rise three Mooney units above the minimum (referred to as \(t_3\)). It should be noted that the Mooney rotor is unheated, which means that Mooney Scorch values are not true isothermal measurements.

2.3.4.2 Scorch by Oscillating Rheometer

The oscillating disk rheometer (ODR) was introduced in 1963 and is considered a great improvement over the Mooney viscometer because the ODR measures not only scorch, but also cure rate and state of cure [18]. The ODR method is described in ASTM D2084 and in International Standard ISO 3417. Unlike the Mooney viscometer, which continuously rotates its rotor, the ODR oscillates its biconical disk (rotor) sinusoidally. This gives the ODR an advantage in that it can measure the complete cure curve.

ODR scorch time is usually defined as the time until one torque unit rise above the minimum is achieved (\(t_{s1}\) when 1° arc strain is applied, or time until two torque units rise above the minimum is achieved (\(t_{s2}\) when 3° or 5° arc strain is applied. Also, through the computer software used today with ODRs, it is relatively easy to calculate time to 10% state-of-cure (\(t_{c10}\)). This cure time \(t_{c10}\) also relates to scorch. The parameter \(t_{c10}\) may have an advantage over \(t_{s1}\) because it is not based arbitrarily on a one torque unit rise (which can be either dNm or in-lb torque units). Because the ODR measures the entire cure curve, it is usually performed at a higher temperature than the Mooney scorch test discussed earlier. As a result, the ODR may not be as sensitive to scorch differences as the Mooney Scorch test [19].

Even though thousands of ODRs have been used worldwide, the ODR itself has a design flaw which involves the use of the ODR disk itself. This is why the rubber industry
is shifting away from the ODR to rotorless curemeter designs (discussed next). The problems associated with the disk rotor are as follows [20]:

1. The ODR disk itself functions as a “heat sink,” preventing the rubber specimen from reaching the set temperature quickly. Because the rotor is not heated, this means that the ODR scorch values are not a true isothermal measurement.
2. The ODR torque signals must be measured through the shaft of the rotor. This design results in poor signal-to-noise response resulting from the friction associated with the rotor.
3. This same friction associated with the ODR rotor prevents true dynamic properties from being measured during cure.
4. After an ODR test, the cured specimen must be physically dried off the rotor. Because of the rotor shaft, it is not easy to use a barrier film. This also means that the ODR dies are easily fouled and require constant cleaning.
5. The ODR is very difficult to automate because the cured specimen must be removed from the rotor.

These problems were greatly reduced with the introduction of new rotorless curemeters such as the Moving Die Rheometer (MDR) [21]. ASTM D5289 and International Standard ISO 6502 describe the use of rotorless curemeters. In an instrument such as the MDR, the lower die oscillates sinusoidally, applying a strain to the rubber specimen which is contained within a sealed, pressurized cavity. The upper die is attached to a reaction torque transducer which measures the torque response. This design greatly improves the test sensitivity (signal-to-noise) measurements so that real changes in a rubber compound can be detected faster. Also, because there is no rotor, the temperature recovery of the test specimen is less than 30 seconds, compared to approximately 4 to 5 minutes for the older ODR design. Because curing a given rubber specimen in the MDR is closer to a true isothermal cure, the $t_\text{51}$ scorch time values from the MDR are significantly shorter than the $t_\text{51}$ scorch time values from an ODR for the same compound at the same test conditions. At higher cure temperatures, such as 190°C, scorch information from the MDR can be obtained in about one-half the time as from the ODR [22]. Also, barrier film can be used with rotorless curemeters which greatly reduces clean-up time.

With the MDR, two curves are produced during cure, as shown in Fig. 2.16. The elastic torque $S'$ is the traditional cure curve which is more commonly used as an indication of cure state (the ODR produces only an $S'$ cure curve). The viscous torque $S''$ curve is a second curve generated simultaneously. Sometimes, the $S''$ peak can be used as an alternate method for measuring scorch. Studies have shown that the percent drop from this $S''$ peak as the cure progresses gives information regarding filler loadings as well as the ultimate crosslink density [23].

A more advanced rotorless curemeter is the Rubber Process Analyzer (RPA). Improved sensitivity to scorch is achieved by increasing the applied shear rate. When the applied frequency or strain is increased, the resulting shear rate is increased. When a rubber compound is tested at higher shear rates, the sensitivity to subtle scorch differences is increased (which is also true in factory processes which apply higher shear rates to a rubber compound). Studies have shown that higher frequencies or strains applied to a rubber compound provide earlier warning of a scorch condition [24].
Another way to improve test sensitivity to scorch is to use the Variable Temperature Analysis feature of the RPA. This feature allows the user to program the RPA to linearly "ramp" the test temperature to achieve an increase in a very controlled way from, for example, 100 to 180 °C in 8.0 minutes. In this way, the RPA first measures processing properties at 100 °C, which is a temperature typically low enough to prevent any vulcanization. Then the temperature is "ramped" up to measure scorch and cure properties. This "ramping of temperature" results in better test sensitivity to scorch differences than measuring scorch under traditional isothermal conditions [25]. In one test, both viscoelastic processing behavior and scorch are measured with excellent precision and test sensitivity.

2.3.4.3 Scorch by Capillary Rheometer

As discussed earlier, tests performed at higher shear rates are more sensitive to the beginnings of scorch than tests at lower shear rates. A capillary rheometer used at a sufficiently high enough temperature (close to the temperature of the factory process), at a shear rate of 300 to 1000 s\(^{-1}\), and a capillary die with a length to diameter (L/D) ratio in excess of 10:1, has high test sensitivity to scorch. Studies have shown that capillary rheometer scorch values relate better to computer simulation of injection molding than do the lower shear rate ODR or Mooney scorch values [26,27]. One problem with the capillary rheometer is that it is more complex and time-consuming than other tests, which limits its use mainly to research and development.

2.3.5 Cure Rate

Cure rate is the speed at which a rubber compound increases in modulus (crosslink density) at a specified cure temperature or heat history. Cure time refers to the amount of
time required to reach specified states of cure at a specified cure temperature or heat history. An example of cure time is the time required for a given compound to reach 50% or 90% of the ultimate state of cure at a given temperature. Of course, determining what is the instrumental optimum cure time for a small curemeter specimen is not the same as determining what is the optimum cure time for a high mass, thick, rubber article cured in the factory. This is because usually an instrumental cure is closer to an isothermal cure (being cured at the same temperature), whereas the center portion of a thick rubber article sees a variable temperature heat history.

The rubber technologist must take into account other factors such as the temperature recovery time of the curemeter being used, the thickness of the rubber article cured in the factory, the compound thermal conductivity, the variable heat history of the center of the article, the compound cure kinetics, the compound overcure stability, etc., to determine the optimum cure temperature and time for a rubber article in the factory. Sometimes an empirical approach with test trials at different cure times and temperatures may be a practical way to determine the optimum cure temperature and time for a given rubber article. If the cure residence time is too short, then poor cured physical properties result, especially toward the center of a thick article, because it sees less heat history. On the other hand, if the cure residence time is too long for a thick article, then there is deterioration in the cured physical properties, especially at the surface of the article where it receives too much heat history. Also, a long cure time results in poor productivity. Thick articles made from a composite of different rubber compounds represent a “balancing act” by the R & D compounding in adjusting the cure properties for the different component compounds that receive different heat histories.

There are two methods which can be used for measuring cure profile properties such as cure rate and cure times:

1. rotational viscometers
2. oscillating rheometers

2.3.5.1 Cure Rate by Rotational Viscometer

As discussed earlier, Mooney Scorch with the large rotor is measured by the time required for the viscosity to rise 5 Mooney units above the minimum (referred to as \( t_5 \)), and when the small rotor is used, the scorch time is reported as the time required for viscosity to rise 3 Mooney units above the minimum (referred to as \( t_3 \)). ASTM D1646 describes what is called the “ASTM cure index.” These indices are expressed in Eqs. (2.12) and (2.13).

For small rotor \[ \Delta t_5 = t_{18} - t_3 \]  \hspace{1cm} (2.12)

For large rotor \[ \Delta t_L = t_{35} - t_5 \]  \hspace{1cm} (2.13)

A lower cure index means the cure is faster. However, the Mooney scorch test is not very effective at giving cure information above \( t_{18} \) (for small rotor) or \( t_{35} \) (for large rotor) because the rotor tears and slips at the rubber interface as the rotor rotates. The Mooney viscometer is not effective at providing a complete cure curve because it uses a rotating rotor, not an oscillating one. Also, the Mooney Viscometer uses large sample weights of
approximately 25 g and an unheated rotor which functions as a “heat sink.” Therefore, the temperature recovery of the Mooney viscometer (the time required for the temperature of the rubber specimen to reach the set temperature of the dies) is relatively long compared to an oscillating rheometer such as the MDR. This temperature recovery is more critical at higher cure temperatures.

2.3.5.2 Cure Times and Cure Rate by Oscillating Rheometer

The ODR method as described in ASTM D2084 or ISO 3417 has been used since the 1960s to measure cure times and cure rate. The $t_{cX}$ is simply the time to reach a given percent $x$ state of cure (for example $t_{c50}$ is the time required to reach 50% of the state of cure). This is illustrated in Fig. 2.17. So, mathematically, $t_{cX}$ is calculated as follows:

$$t_{cX} = \frac{x}{100} \cdot (M_H - M_L) + M_L$$ (2.14)

where:

- $M_L$ = minimum torque
- $M_H$ = maximum torque
- $x$ = percent state-of-cure
- $t_{cX}$ = time to a given percent ($x$) state-of-cure

As discussed earlier, the unheated rotor used with the ODR is functioning as a heat sink when it is embedded in the rubber specimen. This can cause the temperature recovery time for the rubber specimen (the time required for the temperature of the specimen to reach the set temperature of the dies after the dies are closed) to be 4 to 5 minutes. Therefore the cure times from the ODR are generally inaccurate in that they do not truly reflect the cure times for a true isothermal cure.

Figure 2.17 Illustration of the calculation of $t_{c50}$ (time to 50% state-of-cure).
With computer software used today, the **maximum cure rate** as well as the average cure rate or the ASTM/ISO **Cure Rate Index** can easily be calculated. The maximum cure rate is the slope of the tangent line at the inflection point on the cure curve while the Cure Rate Index is calculated as follows:

\[
\text{Cure Rate Index} = \frac{100}{(\text{Cure Time} - \text{Scorch Time})}
\]

(2.15)

The user of this index can select preferred cure and scorch times, such as \(t_{c90}\) and \(t_{51}\).

Rotorless curemeters, such as the MDR, use essentially the same methods for calculating the cure times and cure rates as specified in ASTM D5289 and ISO 6502. However, the cure times from the rotorless curemeters are significantly shorter than those measured by the ODR for the same compound under the same set of test conditions. As mentioned before, this is because rotorless curemeters, such as the MDR, have a cure which is much closer to a true isothermal cure. The temperature recovery for the MDR [28] is only 30 seconds and the temperature drop when loading a sample is much less than for an ODR. Therefore, cure kinetic studies based on the German Standard DIN 53529 can be performed much better with the MDR [29]. If the ODR were used, there would be a high degree of error because of the ODR’s much longer temperature recovery.

While the MDR is curing a compound at near-isothermal conditions (the same temperature over time), thick rubber article cures are not isothermal. The center of a thick section of a rubber article cured in a mold is exposed to a variable heat history. A thermocouple in the center of a rubber article can measure the rise in temperature as the rubber article is cured. This time-temperature profile can be used by the RPA software to give the same heat history to the compound as measured by the thermocouple. Because the RPA has low mass dies and very efficient heaters, the temperature of the upper and lower dies can exactly match the required time-temperature profile. The RPA can also match a drop in temperature after demolding through the use of a forced air cooling system. This Variable Temperature Cure technique is an empirical way to estimate state-of-cure for the center of a thick section. It should be understood that the cool down portion of the test can introduce an error, i.e., the \(S'\) can increase from both crosslinking and the drop in temperature.

### 2.3.6 Ultimate State of Cure

Ultimate state of cure refers to the “ultimate crosslink density.” Strictly speaking, the “best” state of cure can be quite different for one rubber property, such as tear resistance, compared to another rubber property, such as rebound. When discussing processability, however, the ultimate state of cure is usually measured as the maximum elastic torque \(M_{el}\). This is not a perfect method of measuring the ultimate state of cure, but it is very practical. One problem with using maximum torque to measure ultimate state-of-cure occurs when the compound displays a “marching modulus.” This phenomenon occurs when the \(S'\) torque never reaches a plateau during cure. In this case, an arbitrary cure time must be set to measure the maximum \(S'\) torque response. This selected cure time should be located where the rate of \(S'\) increase has slowed significantly.
Figure 2.18  $S'$ and $S''$ cure curves for selected vibration isolator compounds.

There are two tests used in production to measure the ultimate state of cure:

1. ring testing
2. oscillating rheometer

2.3.6.1  Ring Testing

Ring testing can be used in a production setting provided the ring specimens can be cured fast enough. This method is discussed in Chapter 3 as ASTM D412 and ISO 37 for tensile testing.

2.3.6.2  Oscillating Rheometer

The most common and practical test to measure the “ultimate state of cure” is by using the maximum $S'$ torque ($M_H$) from the oscillating rheometer. The ODR (ASTM D2084 and ISO 3417) is commonly used to measure $M_H$. The MDR can also measure $M_H$ (Ref. ASTM D5289); however, it can measure the viscous torque $S''@M_H$, as well. This is illustrated in Fig. 2.18. As can be seen, the $S''$ response sometimes changes more from carbon black and oil variations than the $S'$ response. In addition, the RPA can give not only an $S'$ and $S''$ cure curve, but it can also quickly determine the die cavity temperature and measure after-cure dynamic properties at a designated lower temperature. These properties often relate better to product performance. An example of an RPA after-cure temperature sweep with the tan $\delta$ responses, is given in Fig. 2.19. In this example, the differences in the cured tan $\delta$ values are much greater at the lower temperature.

2.3.7  Reversion Resistance

Reversion resistance is the resistance of a rubber compound to deterioration in vulcanize properties usually as a result of extended curing times. This property is particularly
important when a rubber part or compound experiences too much heat history during curing. For example, the outside surface of a thick article may be exposed to an excessive heat history, causing reversion to occur. Rubber compounds based on natural rubber commonly revert at higher cure temperatures.

Oscillating rheometers are the most practical method for measuring reversion. The ODR, MDR, and RPA can measure the drop in the $S'$ response after $M_{st}$. When the $S'$ elastic torque peaks and then drops because of reversion, the $S''$ torque response and the tan $\delta$ both rise with reversion. There is some evidence that these dynamic properties are more sensitive to reversion [30]. The RPA can increase the test sensitivity to reversion even more by performing an in situ post cure aging test at an elevated temperature such as 190°C and then measuring the percent change in the cured tan $\delta$ at a lower temperature such as 60°C [31].

2.3.8 Green Strength

Green strength is the tensile strength and/or tensile modulus of an uncured rubber compound. This important processing property relates to the compound’s performance in extrusions, calendering, and conveyor belt or tire building, particularly the second-stage building machine for radial tires. If tires are constructed with rubber compounds with poor green strength, they may fail to hold air during normal expansion in the second stage of tire building prior to cure. High molecular weight, strain crystallizing elastomers (such as natural rubber) tend to exhibit good green strength.

The only standardized test for measuring green strength is International Standard ISO 9026, which specifies the preparation of dumbbells for tensile testing. This method calls for testing five dumbbell specimens and reporting the medians and ranges found.

Research done in 1996 showed that high strain testing with the RPA could correlate to green strength for a series of natural rubber compounds [32].
2.3.9 Tackiness

Tackiness refers to the ability of an uncured rubber compound to stick to itself or another compound with a short dwell time and a moderate amount of applied pressure [33]. This property is very important whenever rubber products, such as tires or conveyor belts, are built by laying one calendared or extruded rubber ply on top of another. The uncured product must hold together before it is placed in a mold or press for cure. Usually compounds based on natural rubber have good building tack. Compounds based on EPDM, on the other hand, usually have poor building tack. Many times, tackifiers are added to a compound to improve tack.

Rubber compounds consist of many ingredients with differing degrees of solubility. Some of these ingredients may separate from the compound under certain cooling conditions, exuding to the compound’s surface to impart a surface bloom. Many times, this bloom destroys building tack. Some compounding ingredients which may bloom are sulfur, accelerators, antidegradants, petroleum oils, zinc stearate, and waxes.

There are no ASTM or ISO test standards for measuring the tack of rubber compounds. However, the most widely used tack testing instrument is the Tel-Tak Tackmeter, introduced by Monsanto in 1969 [34].

2.3.10 Stickiness

Stickiness refers to the nature of a rubber compound to stick to non-rubber surfaces such as metals or textiles. Too much stickiness to metal surfaces can result in poor mill and calender release and problems in other processing equipment. However, not enough stickiness can result in rubber compound slippage against metallic surfaces in extruders or internal mixer rotors. Adjusting temperature can sometimes control stickiness. Certain compounding ingredients such as external lubricants or release agents are sometimes used to control the stickiness level. These agents, however, should be used with caution because adhesion and other compounding properties might be affected.

There are no ASTM or ISO test methods developed to measure stickiness. However, the Tel-Tak Tackmeter developed by Monsanto in 1969 can be used to measure not only compound tackiness, but stickiness to a stainless steel surface as well [35].

2.3.11 Dispersion

Dispersion is a property which defines how well filler aggregates and particles are dispersed in a rubber compound from a mixing process. This property relates not only to percent carbon black dispersion, but also to non-black fillers such as clays, silica, titanium dioxide, calcium carbonate, etc. Rubber curatives, such as accelerators and sulfur, can also be poorly dispersed. Poor dispersion can sometimes be a particularly critical characteristic with curatives because they are commonly added late in the mixing cycle. Poor dispersion for a rubber batch can result in poor stock uniformity and highly variable cured physical properties such as ultimate tensile strength. It is well known that poor dispersion can decrease abrasion, tear, and fatigue resistance as well as hurt flexometer
heat buildup and other dynamic properties. Test method ASTM D2663 lists three different methods for quantifying percent carbon black dispersion [36].

2.3.12 Stock Storage Stability

Stock storage stability is defined as the period of time a given mixed stock can be stored on the factory floor and remain usable. Stock can be affected by scorch time [37]. Usually, but not always, the longer a mixed stock is stored, the lower its scorch safety. With storage, rheological properties change as a result of an increase in interaction between the rubber and carbon black (called bound rubber). This can be seen by a rise in compound’s Mooney viscosity or oscillating rheometer minimum torque $M_L$ (see Section 2.3.1). LeBlanc and Staehlaeve reported on the advantages of large strain RPA tests for improved sensitivity to storage maturation [38]. Not only mixed stocks, but raw elastomers, such as natural rubber, can manifest changes in their rheological properties with storage. For example, the storage of natural rubber can produce a rise in viscosity and storage hardening [39]. The RPA can also be used to measure the storage hardening properties of natural rubber [40].

2.3.13 Mis-Compounding

Mis-compounding occurs when an error is made in the labeling or weighing of compounding ingredients before mixing or when not all of the ingredients are properly loaded into the mixer. Establishing specifications for batch weight is one check for compounding ingredient weighing errors. Many processing tests are affected by such errors. The careful monitoring of dynamic property variations and pattern changes with the MDR or the RPA can help determine which compounding ingredient might have been weighed in error [41,42]. Also, the Compressed Volume Densimeter described in ASTM D297 can easily measure the density of unvulcanized rubber compounds. If, for example, the compound density did not change, but the dynamic properties from the MDR or RPA suggested a change in the fillers, this may indicate that the wrong type of carbon black was used.

2.3.14 Cellular Rubber Blow Reaction

This chemical reaction occurs as a result of the decomposition of one or more blowing agents which generate gas during the cure. The generation of this gas is necessary to produce a cellular rubber product (see Chapter 21). To achieve the proper cellular structure, the cure reaction and blow reaction must be in balance. Therefore, it is important to measure the blow reaction.

Currently there are no standards available for tests to monitor blow reactions. However, instruments, such as the MDR-P [43] from Alpha Technologies, measure both the cure reaction and the blow reaction simultaneously. This is important because if these two reactions are not balanced, then unacceptable cell size or structure may result.

Parameters somewhat analogous to what is used to describe the cure reaction are used for the blow reaction. For example, the minimum and maximum pressure as well as time to 50% of the maximum pressure are calculated automatically [44,45].