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Compounding and Testing for Performance

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3 Vulcanizate Physical Properties, Performance Characteristics, and Testing

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3.1 Introduction

The physical properties of cured rubber compounds are major determinants of product performance. The following physical properties are discussed as follows in this chapter:

- Density (in Section 3.2)
- Hardness (in Section 3.3)
- Stress Strain Properties Under Tension (in Section 3.4)
- Stress Strain Properties Under Compression (in Section 3.5)
- Stress Strain Properties Under Shear (in Section 3.6)
- Dynamic Properties (in Section 3.7)
- Low Temperature Properties (in Section 3.8)
- Stress Relaxation, Creep, and Set (in Section 3.9)
- Gas Permeability (Transmission) (in Section 3.10)
- Adhesion (in Section 3.11)
- Tear Resistance (in Section 3.12)
- Degradation Properties (in Section 3.13)
 - Flex Fatigue Resistance (in Section 3.13.1)
 - Heat Resistance (in Section 3.13.2)
 - Ozone Resistance (in Section 3.13.3)
 - Weathering Resistance (in Section 3.13.4)
 - Resistance to Liquids (in Section 3.13.5)
 - Abrasion and Wear Resistance (in Section 3.13.6)

Not all of these cured physical properties are optimized at the same point on the cure curve (see Chapter 2). As shown in Fig. 3.1, the optimum properties for tear resistance, rebound, ultimate tensile strength, hysteresis, etc. do not occur at exactly the same time during vulcanization.

3.2 Density

Density is simply weight (or mass) divided by volume at a specified temperature. This property determines the mass (weight) of a given rubber compound required to fill a specific mold cavity. Compounds with higher densities require greater weights of the

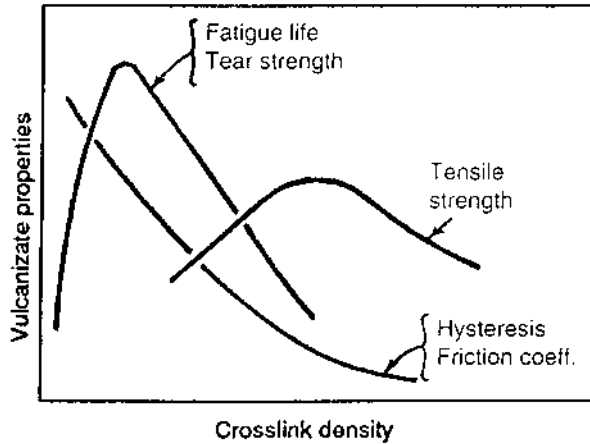


Figure 3.1 Optimum cure profiles for different vulcanizate properties (courtesy John Sommer, Elastech).

compounded stock to fill a given size mold cavity. Because raw materials are usually purchased by unit weight and molded rubber products are produced from a mold cavity with a fixed volume, knowing the compound density is very important in product cost calculations. Usually, increasing compound filler loading, such as carbon black, silica, or clay, results in a higher compound density. However, many times increased filler concentration still reduces the product's cost. Also, measuring compound density is an effective quality procedure to detect variations in the rubber compound composition resulting from changes in ingredient weighing and mixing, among other reasons.

The density of a vulcanized rubber compound specimen can be measured and calculated by Archimedes' Principle in which the specimen is weighed in water and weighed in air. ISO 2781 [1] gives detailed procedures for calculating the density of a cured specimen. Additionally, special cases are also addressed. For example, if cured tubing or cable insulation is tested with trapped air, this may lead to erroneous results. To overcome this problem, Method B of ISO 2781 calls for the specimen to be cut up into small pieces and tested in a density bottle, using an analytical balance.

3.3 Hardness

Hardness is a simple, inexpensive, and fast test used throughout the rubber industry. Hardness is measured from the cured rubber's resistance to deformation when a force is applied to a rigid indenter. This results in a measure of "a modulus" of a rubber compound under very limited deformation (strain). When the force is applied to the indenter with a dead-load, this method is called the International Hardness in IRHD units (International Rubber Hardness Degrees), which is described in ASTM D 1415 or ISO 48. This test normally uses a hemispherical indenter.

If the force is applied to the indenter by a spring, it is called the Durometer Hardness Method (usually a small pocket-size apparatus), described in ASTM D2240 and ISO 7619.

This method uses the Shore A scale, which is similar, but not identical, to the IRHD scale, and the Shore D scale, which is used for testing rubber vulcanizates with high hardness. Also, these methods refer to other hardness scales, as well. There is no completely accepted conversion between a Shore A and a Shore D scale, just a crude approximation. Also, the Shore type indenter has a different geometry from the IRHD indenter: truncated cone vs. hemispherical. Shore hardness is the more popular method because the hand held durometer is more portable and can be used in the laboratory or in the factory.

These hardness tests are somewhat crude and measure only under very limited deformations that may not relate to end product applications. Also, data from these tests can show much scatter. This variability and poor repeatability can be the result of variations in sample thickness, operator dwell time, how the instrument is set up and applied, sample edge effects (readings taken too close to the sample edge), or differences in sample geometry, to name a few. Therefore, these hardness tests should *not* be considered a reliable measure of a design or engineering property, but a quick and simple method of detecting gross differences in cured compound properties.

3.4 Tensile Stress–Strain

Tensile stress–strain is one of the most commonly performed tests in the rubber industry. These tests are performed on tensile testing instruments where a cured, dumbbell-shaped rubber specimen is pulled apart at a predetermined rate (usually 500 mm/min.) while measuring the resulting stress. Figure 3.2 shows a commonly used dumbbell shaped specimen. ASTM D412 and ISO 37 detail the standard procedures used to measure tensile stress–strain properties of a cured rubber compound.

Generally, (1) ultimate tensile strength, (2) ultimate elongation, and (3) tensile stress at different elongations are reported. Ultimate tensile strength is the maximum stress when the dumbbell specimen breaks during elongation. Ultimate elongation is the applied strain when the break occurs. The tensile stress is usually measured and reported at different predetermined strains (such as 100 and 300%) before the break occurs.

Figure 3.3 shows a stress–strain curve for a “typical” rubber compound. Unlike metals, this stress–strain curve shows no (or a very limited) linear portion. Therefore, it is usually not practical to calculate Young’s modulus, which would be the slope of a straight line drawn tangent to the curve and passing through the origin. Instead, stress at selected elongations is usually reported. These stress values for different elongations are erroneously reported by some rubber technologists as 100% modulus, 300% modulus, etc. However, these measures are not actually modulus values.



Figure 3.2 Rubber dumbbell test specimen.

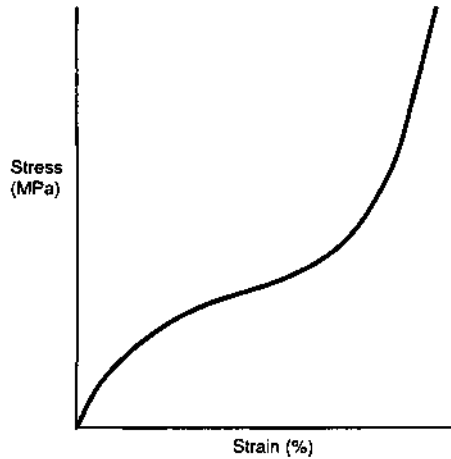


Figure 3.3 Typical stress strain curve for rubber.

Stress-strain properties, such as ultimate tensile strength can be easily affected by poor mixing and dispersion, the presence of contamination, under-curing, over-curing, and porosity, among other factors. Undispersed particles of different compounding ingredients, such as carbon black agglomerates, cause stress concentrations during the stretching of a rubber dumbbell, causing premature breaks at lower stresses. Impurities, such as dirt or paper fragments, can also cause the dumbbell to break at a lower stress. Likewise, volatile compounding ingredients can cause porosity to form during cure. These voids can also cause lower tensile strength [2]. Lastly, laboratory-mixed batches usually have higher tensile strength than factory-mixed batches because laboratory mixes often are better dispersed.

The tensile stress-strain testing discussed here involves non-prestretched specimens. However, if the dumbbell specimen is prestretched, for example, to more than 400% of its original length, and then tested in a normal manner, stress-strain would probably be significantly affected. This is particularly true of compounds containing high reinforcing filler loadings such as carbon black [3]. Prestretching causes “stress softening,” which results from breakdown of the carbon black agglomerates. Many times, if prestretched dumbbells are allowed to rest, their modulus (or tensile stress) increases. Because many rubber products are exposed to repetitive stress-strain cycling, this phenomenon can affect end use performance.

Many rubber products are not extensionally deformed more than 30%. So tensile stress-strain is usually not of great importance for product design, unless the product is a rubber band. On the other hand, tensile stress-strain testing of a given compound can be a valuable quality assurance tool to detect compounding mistakes in the factory and is very useful in compound development [4].

3.5 Stress-Strain Properties under Compression

Compression stress-strain testing often relates to actual product service conditions better than extension testing. Usually, test methods involve measuring the stress resulting from a

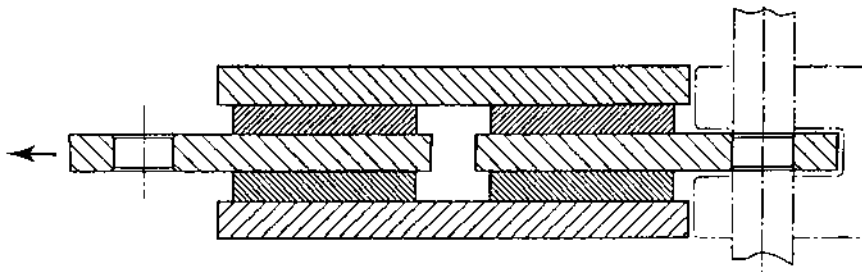


Figure 3.4 Quadruple lap shear test piece (ISO 1827).

compressive deformation applied to a standard, cured cylindrically-shaped rubber specimen between two plates. Compression test results depend on such factors as the shape of the rubber specimen, preconditioning, rate of deformation, and the degree of bonding or slippage of the specimen to the two metal surfaces. The more slippage experienced with the test piece means less “barrelling.” The degree or lack of “barrelling” greatly affects the test results [5,6]. ASTM D575 and ISO 7743 are both standard methods for measuring stress–strain properties under compression, although they are quite different. The ASTM method uses sandpaper to prevent slippage, while one part of the ISO method allows a lubricant to be used, and another part requires the samples to be bonded to the parallel metal plates. Of course, these different conditions result in different results.

3.6 Stress Strain Properties under Shear

Measuring the stress–strain properties under shear can also be very relevant to some rubber product applications. Generally, most rubber product applications do not exceed a strain of 75% [7]. The resulting stress–strain curve may be linear up to about 100% for “soft” compounds and up to 50% for “hard” rubber compounds [8]. ISO 1827 is a commonly used test method for measuring the stress–strain properties of a rubber compound under shear. Figure 3.4 shows the quadruple shear test piece which is separated, as noted by the arrow.

3.7 Dynamic Properties

Rubber products are used in many dynamic applications such as tires, belts, isolators, dampers, etc. The best way to measure and quantify the cured dynamic properties of a rubber compound is to mechanically apply a sinusoidal strain to a cured rubber specimen and measure the complex stress response and the resulting phase angle (δ), as was illustrated in Fig. 2.8. As discussed earlier in Section 2.3.1.3, this phase angle δ and

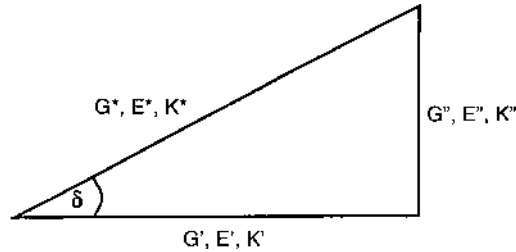


Figure 3.5 Vector diagram for dynamic properties.

complex modulus response (either G^* for shear or E^* for compression or extension) are used to calculate the storage modulus (G' or E') and the loss modulus (G'' or E''). Also, $\tan \delta$ is calculated by dividing G'' by G' or E'' by E' . In addition, the same principles can be applied to determine spring rates k^* , k' , and k'' . The vector analysis for these complex, elastic, and loss functions is shown in Fig. 3.5. Standards that define dynamic properties are ISO 2856, ASTM D2231 and the newer ASTM D5992.

The following are definitions for some common dynamic property terms used in the rubber industry.

- Storage Normal Modulus E' (Elastic Normal Modulus) is the component of normal stress exactly in phase with the normal sinusoidally applied strain, divided by the strain.
- Loss Normal Modulus E'' (Viscous Normal Modulus) is the component of normal stress exactly 90° out-of-phase with the normal sinusoidally applied strain, divided by the strain.
- Complex Normal Modulus E^* is the resultant normal stress divided by the resultant normal strain. By vector analysis, $(E^*)^2 = (E')^2 + (E'')^2$ (see Fig. 3.5).
- Storage Shear Modulus G' (Elastic Shear Modulus) is the component of shear stress exactly in-phase with the sinusoidally applied shear strain, divided by the strain.
- Loss Shear Modulus G'' (Viscous Shear Modulus) is the component of shear stress exactly 90° out-of-phase with the sinusoidally applied shear strain, divided by the strain.
- Complex Shear Modulus G^* is the resultant shear stress divided by the resultant shear strain. By vector analysis, $(G^*)^2 = (G')^2 + (G'')^2$ (see Fig. 3.5).
- Phase Angle δ (Loss Angle) is the angle by which dynamic force leads the dynamic sinusoidal deflection (see Fig. 2.8).
- $\tan \delta$ (Loss Factor) is the ratio of loss modulus to storage modulus. For normal stresses, $\tan \delta = E''/E'$; while for shear stresses, $\tan \delta = G''/G'$. Higher $\tan \delta$ values usually denote a more hysteretic compound at a given complex modulus.
- Hysteresis refers to a process occurring within the rubber in which there is a loss of mechanical energy as heat from an applied cyclical deformation of a rubber body.
- Hysteresis Loop refers to the closed curve formed from a plot of dynamic force vs. dynamic deflection in a complete cycle.
- Damping refers to a component of a complex dynamic force which is 90° out-of-phase with the strain.

When designating test conditions for dynamic testing of rubber, it is extremely important that the exact temperature, frequency, strain amplitude, type of strain, preconditioning, and strain history be specified. Other factors, such as test piece shape, can also affect test results. Typically, but not always, the elastic modulus for a vulcanizate decreases with a rise in temperature or a decrease in applied frequency. Rheologically, the effects of increasing the temperature while dynamically testing rubber are usually equivalent to decreasing the frequency and vice versa. This is the principle of the time-temperature superposition, which can be performed on the elastic modulus, loss modulus and loss factor, $\tan \delta$ using the Williams, Landel, and Ferry (WLF) equation [9].

The applied strain amplitude and the strain history on a test specimen are also very important, particularly for rubber vulcanizates containing fillers because of the filler-filler and filler-polymer interactions affected by applied strains [10]. Because of these filler effects, the elastic modulus generally decreases when the amplitude of the applied strain is increased, the well known Payne effect [11]. Also, prior strain history and preconditioning can have a great effect on the dynamic properties measured [12].

Futamura [13] and Gatti [14,15] have published extensively on the use of cured dynamic properties measured on tire tread compounds to predict tire rolling resistance, steering response, and dry, wet, and snow traction. These different tire properties are usually measured at different conditions of temperature, frequency and strain. Warley [16], Novotny [17], Gregory [18], and others have researched the advantages of using dynamic property measurements in predicting the performance of rubber automotive parts, such as bushings, mounts, bumpers, dampers, caps, isolators, and drive belts. Calculating percent *transmissibility* for a rubber part in forced vibration (the ratio of transmitted force to applied force) is reviewed by Warley and Novotny [16,17].

As is discussed in other chapters, specific formulating ingredients have profound effects on the dynamic properties of the vulcanizate. For example, base elastomers which have higher glass transition temperatures (T_g) may impart higher hysteresis to a compound [19]. Also the addition of a specific plasticizer to a compound can lower the compound's T_g and affect dynamic properties of the compound by reducing hysteresis. The type and concentration of a plasticizer are important factors in determining the rubber vulcanizate's dynamic properties [20]. The specific grade and loading of carbon black also have profound effects on the compound's dynamic performance [21]. The type of crosslinks and the crosslink density can affect dynamic properties of a rubber compound, as well [22].

The dynamic properties discussed here are usually measured by forced vibration methods because the strain amplitude is controlled. ISO 4664 specifically gives a method for determining dynamic properties by forced sinusoidal shear strain. Other methods for measuring the dynamic behavior of cured rubber compounds include *rebound resiliency* and *free vibration* methods. Generally, when a compound is formulated to have lower hysteresis, it also has a higher rebound. Specific rebound test methods are discussed in ASTM D1054 (Goodyear-Healey Rebound Pendulum method), ASTM D2632 (falling weight method), and ISO 4662 (which mentions apparatus designs based on the Lupke Pendulum, the Schob Pendulum, and the Zerbini Pendulum). The free vibration methods are given by ASTM D945 (Yerzley Oscillograph) and ISO 4663, which includes three different methods. While the rebound resiliency and free vibration methods are generally

not recommended as sources of engineering data, they are usually simpler to perform than forced vibration methods.

3.8 Low Temperature Properties

As the temperature of a rubber vulcanizate is decreased, the material becomes stiffer and its modulus increases. If the temperature is decreased enough, there is no longer sufficient energy for molecular rotation of the vulcanized rubber. The material takes on the properties of a glass, and becomes very hard and brittle. Figure 3.6 shows a log plot of the vulcanizate modulus vs. temperature for a typical rubber compound. As can be seen, the modulus can increase over 1,000 times when the material is exposed to low temperatures. Rubber behaves as a glass at very low temperatures because of a lack of thermal kinetic energy. With an increase in temperature, the thermal energy increases the material's flexibility, as shown in Fig. 3.6, where the modulus drops off the glassy plateau. At these temperatures, the rubber takes on characteristics similar to leather. Here, there is enough thermal energy to allow chain rotation and flexibility, but not enough energy for complete chain mobility and the good resiliency commonly associated with vulcanized rubber. As the temperature increases further, the vulcanizate finally reaches what has been called the "rubbery plateau" where normal rubber behavior is seen. So unlike what is shown in Fig. 3.6, in an unvulcanized rubber, the modulus would drop off this rubbery plateau because, at higher temperatures, the thermal kinetic energy is sufficient to disentangle rubber chains that are not chemically crosslinked.

When the temperature of a vulcanized rubber compound is so low that no further molecular rotation can occur, then it has reached the compound's glass transition temperature (T_g). The T_g of a rubber compound is greatly dependent on the chemical structure of the base elastomer. Structural aspects such as polarity, bulkiness, and

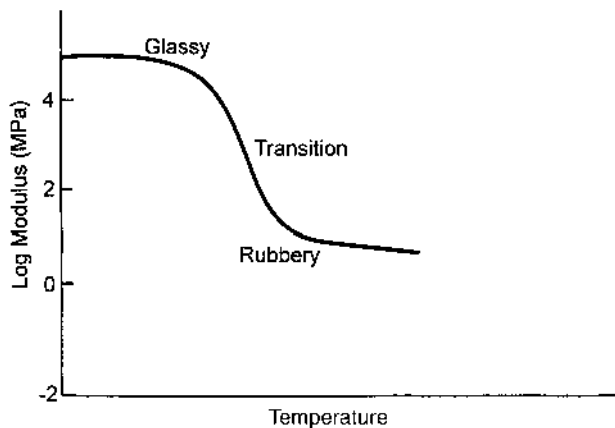


Figure 3.6 Vulcanized rubber modulus vs. temperature.