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Monitoring the vulcanization of elastomers: Comparison of curemeter and ultrasonic online control

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ABSTRACT

The vulcanization of elastomeric materials has a high impact on the properties of the final product. Therefore, it is important to monitor and control this crosslinking process. A common technique to attain the necessary curing time is the use of a curemeter in accordance with ISO 6502 in order to determine the time for full cure of a sample with a standardized geometry. Based on this result and a lot of practical experience, the required curing time for a given product geometry is estimated. Within the scope of this work, a new analysis technique will be compared with the standard procedure. The ultrasonic online control employs ultrasound waves to measure the changes in material properties caused by vulcanization. For this study, a natural rubber compound with a conventional curing system was investigated by both techniques. It was found that the results of the ultrasonic technique show good agreement with the results of the curemeter.

1. Introduction

Elastomers form one of the most widely used material classes today. Their typical material properties, such as high elasticity and high damping, are what make these materials so important. The fields of application are manifold including vehicles parts, tires, tubing, shoes, gloves, seals, adhesives, drive and conveyor belts.

To reach the unique material properties, the raw material, which is generally a mixture of rubber, crosslinking agent, fillers and several additional ingredients, must be crosslinked to form an insoluble and shape persistent material. Due to the chemical crosslinking, a thermoset material with a low crosslinking density, compared to e.g. epoxy resins, is formed. The crosslinking or vulcanization of elastomeric materials is a complex process, which is crucial to the final material properties. During vulcanization, "the properties of a rubber compound change" and, therefore, "the vulcanization characteristics can be determined by measuring properties as a function of time and temperature" [1].

It is a common technique to measure vulcanization isotherms with a curemeter according to ISO 6502 to determine typical characteristic times of the curing process of a compound. A drawback of these measurements is that they are performed off-line with samples of defined shape that are not related to the actual product geometry and the processing conditions within the mould. To date, a direct measurement of the crosslinking process within the production mould is not employed.

For the cure monitoring of crosslinking resins such as epoxy resins, amino resins or unsaturated polyesters an ultrasonic technique is available. This technique, which uses ultrasound waves to measure the property changes within a curing material, was described by Alig et al. [2–6], Döring et al. [7,8] and several other authors in more detail [9–11]. It is based on the ultrasound wave propagation in polymers already described in 1948 by Nolle and Mowry

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[12]. This technique can be used for the online control within the production process as shown by Schmachtenberg et al. [13], Maffezzoli et al. [14], Rath et al. [15] and also for DMA-measurements shown by McHugh [16].

For the investigation of elastomers, a rather similar technique was used by Eckert-Kastner and later Kroll [17,18] as a spectroscopy technique for the study of high frequency properties of elastomers. In their work, only the end properties of fully cured rubbers are investigated and not the vulcanization process itself.

In this work, the use of the ultrasonic online control with the US-Plus system produced by Iserlohner Kunststoff-Technologie GmbH (ISK) Germany is tested for suitability for monitoring cure of a natural rubber compound in a compression mould. The results obtained by this technique are compared to the results of the conventional curemeter.

2. Methods and equipment

The employed curemeter was a Monsanto Moving Die Rheometer (MDR2000). As indicated by the name, the lower half of the die oscillates through 0.5° which leads to a torsional deformation of the rubber sample. The resulting torque is measured by a torque transducer and recorded during the measurement. In vulcametry, several characteristic times of the curing process are determined according to ISO 6502. Examples are the scorch time t_{s2} which is the time at which the crosslinking reaction shows an influence on the measured torque and 2% of the total increase in torque is reached. The scorch time can be used as a measure of the processing safety of the compound. From the measured torque the shear modulus (G^*) can be calculated according to:

$$G^* = \frac{\tau}{\gamma} \tag{1}$$

The shear modulus is, therefore, given by the ratio of the shear stress (τ) and the strain (γ). The stress can be calculated from the torque and the sample geometry.

Other important characteristic values attained from a curemeter test are:

T_L minimum torque
T_H maximum torque
x reached percentage of full cure
t_x time to reach a defined percentage $\times$ of full cure

The reached percentage of full cure can be calculated according to the following equation:

$$x = \frac{T(t) - T_L}{T_H - T_L} \cdot 100\% \tag{2}$$

The ultrasound online control uses a transmission technique with a setup given in Fig. 1.

Two ultrasonic longitudinal wave transducers from ISK [19] are employed, one is used as an emitter the other as a receiver. Both transducers are suited for high temperature use up to 200 °C and have a middle frequency of 4 MHz. The dimensions of the transducers are approximately 8 mm diameter and 40 mm in length. In the configuration used, both transducers are mounted so that the sensor and the mould surface are parallel i.e. in direct contact with the rubber within the compression mould. Hidden sensors are also available that are mounted behind the wall of the mould surface and prevent sensor marks on the product [20].

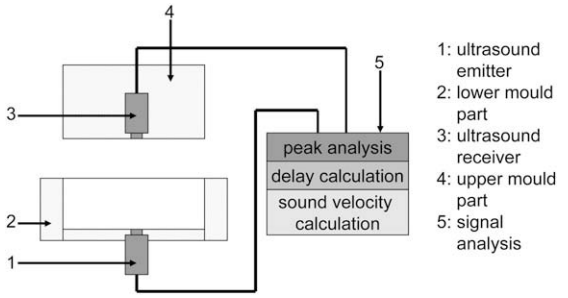

Fig. 1. Setup of the mould equipped with the ultrasonic online control.

The compression mould, Polystat 200S, was manufactured by Schwabenthan, Germany and is equipped with cavities for production of 60 mm diameter discs. The lower and upper mounting plates as well as the tool walls are individually temperature controlled.

The US-Plus system analyses the measured ultrasonic signal to determine the transmission time of the signal. Automatic signal analysis using cross correlation is performed [21] to locate a distinctive peak shape within the measured signal and determine the transmission time. The measured transmission time (t_m) is compared with the transmission time of a prior measured reference signal (t_r). The reference signal was measured with direct contact of both sensors to determine the delay caused by the sensor setup. The delay that is caused within the sample (t_s) is calculated as follows:

$$t_s = t_m - t_r \tag{3}$$

The ratio of the sample thickness (d) to the delay results in the sound velocity of the longitudinal waves (v_L) given in Eqs. (4):

$$v_L = \frac{d}{t_s} \tag{4}$$

The sound velocity is also related to the material properties of the investigated compound, namely the complex longitudinal modulus L^* by Eq. (5)

$$L^* = \frac{\rho v_L^2}{1 - i(\alpha v_L/\omega)} \tag{5}$$

where ρ is the density, α the attenuation and ω the angular frequency of the sound wave.

The complex longitudinal modulus can be expressed as the sum of the real and imaginary parts and also as a combination of the complex shear (G^*) and bulk modulus (K^*):

$$L^* = L' + iL'' = \frac{4}{3}K^* + G^* \tag{6}$$

According to Alig [22], the storage and the loss part of the longitudinal modulus can be expressed, under the assumption that $\alpha v/\varpi$ is much less than one, as follows:

$$L' = \rho v_L^2 \tag{7}$$

$$L'' = \frac{2\rho v_L^3 \alpha}{\omega} \tag{8}$$

Eqs. (6) and (7) show that a change in sound velocity can be directly correlated to a change in the storage modulus.

Due to the increase in shear modulus during vulcanization, the sound velocity is expected to increase such that it can be used to determine the vulcanization characteristics.

3. Material and processing conditions

The investigated material was a natural rubber compound from industry with a conventional sulphur curing system and filled with carbon black. The final material properties measured on samples taken from an additionally vulcanized plate with a thickness of 2 mm and a curing time of 10 min in a compression mould at 160 °C are given in Table 1.

The ultrasonic measurements were performed during cure in a compression mould at 160 °C. To achieve a fixed sample thickness, a ring made from brass with a height of 1 mm was placed in the mould. A defined amount of the compound was inserted in the middle of the ring and compressed during mould closure.

4. Results and discussion

The results of the measurements with the curemeter are shown in Fig. 2. In contrast to the recommendations of ISO 6502, the time is given in seconds and not in minutes to enhance the comparability with the ultrasonic measurements.

The storage part of the measured torque decreases slightly at the beginning due to the softening of the material by temperature increase and reaches a minimum after 40 s. In parallel, the loss part of the torque also decreases but much faster. Then, the storage torque starts to increase slowly. After 80 s, 2% of the total torque increase is reached. This time is used as the scorch time defined above. After the scorch time is reached, the increase in the storage part of the torque becomes much steeper and the loss part of the torque continues to decrease. The highest increase rates of the storage part are observed at 120 s. After 145 s, the t_{50}–value is reached and the loss part has attained a value of 0.8 dNm. The slope of the decrease levels off and the slope of the storage part of the torque decreases. t_{90} is reached after 290 s. The maximum torque of 22.7 dNm is reached after 550 s. Afterwards, the storage part slightly decreases due to what is generally called reversion and is rather typical for sulphur cured natural rubber compounds [23]. Reversion is generally understood as the degradation of already formed sulphur bridges.

Table 1
Material properties of the investigated NR-compound.

Properties	Value
Density	117 g/cm^3
Hardness	65 Shore A
Tensile strength	197 MPa
Ultimate elongation	390%

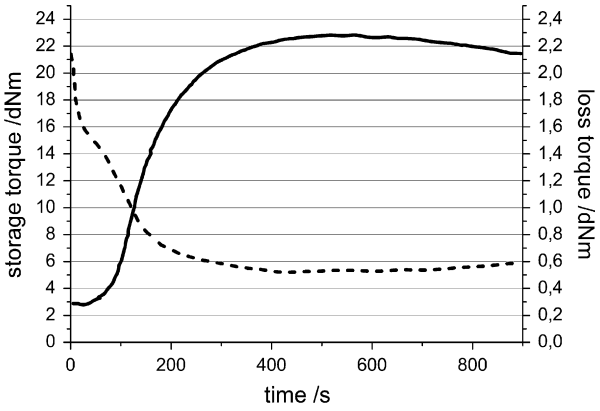

Fig. 2. Torque over time curves at 160 °C measured with the curemeter (solid line: storage torque, dashed line: loss torque).

The results of the corresponding measurement with ultrasound in a compression mould are given in Fig. 3.

At the beginning of the measurement, acoustic contact between the emitter and receiver is achieved. The temperature of the material increases which leads to softening of the material and a corresponding decrease of the sound velocity. After 90 s, a minimum in sound velocity is reached. Afterwards, the sound velocity starts to increase due to the crosslinking reaction. The total increase is finished after 500 s and the change in sound velocity is approximately 10 m/s.

The sound velocity data show some fluctuations that are due to slight changes of the pressure within the hydraulic press.

The overall shape of the sound velocity curve has high similarity to the torque curve of the curemeter. The minimum in sound velocity correlates very well with the scorch time when the closing time for the press which takes 10–15 s is considered.

In Fig. 4, the change in sound velocity relative to the maximum value after cure is compared with the storage

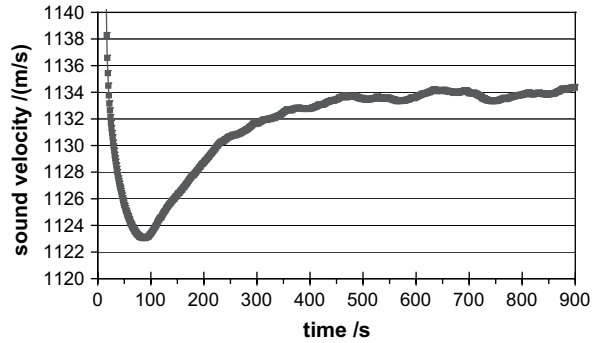

Fig. 3. Sound velocity over time curve measured at 160 °C.

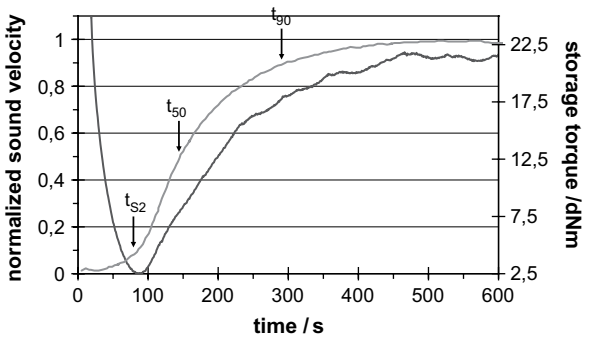

Fig. 4. Normalized sound velocity (black line) and the storage part of the torque (grey line) over time of cure.

part of the torque during cure. For better comparability, the characteristic times t_{S2}, t_{50} and t_{90} are highlighted in the curemeter-curve by small arrows.

The comparison of the curemeter-data with the normalized sound velocity shows that the scorch time correlates very well with the increase in sound velocity. At t_{50} the sound velocity has increased by 30% and at t_{90} the increase is roughly 75%.

As both techniques use a mechanical excitation and measure a quantity that is related to the shear modulus, the similarity is reasonable. The obtained sound velocity is an average value for the whole material between the emitter and the receiver, which could explain a certain time lag between the curemeter results and the ones obtained by ultrasound. The major effect that is detected by a curemeter, that uses in general a cone–cone sample geometry, is the crosslinking of the outermost part of the sample. The torque scales with the distance from the rotational axis by a power of 3. Therefore, the torque measured in a curemeter describes mainly the crosslinking of the outer parts of the sample that are in good thermal contact with the hot die wall. In contrast, the ultrasonic method measures an average effect of the crosslinking throughout the sample thickness. The measured sound velocity is the average of the sound velocities within the sample that correlates with the degree of cure. As the vulcanization takes place from the hot outside to the inside of the sample, the fraction of fully cured material increases with time. This enables the ultrasonic measurement to show also the effect of cure of the centre of the sample where, due to the rather slow heat transfer within polymers, the cure takes place much later.

5. Conclusions

The aim of this investigation was to compare the results of the ultrasonic online control US-Plus with the standard measurement of a curemeter according to ISO 6502. This was performed by investigating a natural rubber compound with a conventional sulphur crosslinking system.

It was shown that the ultrasonic online control is sensitive to the changes of the material properties of the elastomer caused by vulcanization. The obtained results are very similar to the results of the curemeter.

The main advantages of the ultrasonic measurement are that the measurement is non-destructive and requires no special sample geometry and can, therefore, be performed in-situ directly during the production process without the necessity of an off-line measurement, as is necessary for the investigations with the curemeter. The ultrasonic technique can, therefore, be applied as a curemeter which can be integrated into a production tool.

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