Test Method

Monitoring the vulcanization of rubber with ultrasound: Influence of material thickness and temperature

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ABSTRACT

In consideration of the influence of the curing reaction on the material properties of elastomers, it is very important to control the vulcanization process properly.

As shown previously [1], the effects of the vulcanization reaction of an elastomer can be monitored by use of ultrasonic sound waves. This technique has to a certain degree a high similarity to the standard curemeter test according to ISO 6502 but can be applied also inside a production tool.

So far, the method was only applied to the vulcanization of one compound at a given temperature and sample thickness. This is now complemented with measurements on another compound system at different temperatures and sample thicknesses.

The expected effects of temperature and thickness on the curing behaviour were found by use of the ultrasound online control.

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1. Introduction

The importance of elastomers is undisputed. For several applications their outstanding properties such as their high elasticity, good damping and sealing characteristics make elastomers the first choice in a material selection process.

However, it is well known that the end use properties of an elastomer depend on several factors, e.g. the raw materials, fillers, crosslinking system and the crosslinking process. In the course of the chemical crosslinking process an insoluble and shape persistent material is formed. As several properties change in the course of the crosslinking process, the measurement of the material properties over time according to ISO 6502 [2] is a suitable way to determine the vulcanization characteristics. The required curing time at a given temperature to reach a sufficient state of crosslinking is of high interest. Therefore, in general, curemeter measurements are performed to get an estimate of the required curing time. A drawback with respective limitations is that these measurements are performed in an additional instrument with a given sample geometry and have only a limited correlation to the processing conditions during production.

Direct cure monitoring is so far not commonly used for elastomers. For thermoset materials, two such direct measurement techniques, are available and for certain applications commonly employed. One is the dielectric cure control that measures the ion mobility in the form of the complex permittivity described in [3]. The other uses mechanical waves within the ultrasound range to measure the change in sound velocity that correlates to the modulus of the material and damping which correlates to the occurring losses. This technique has been described by several authors [4–7] in more detail. It was used as an online process control by Schmachtenberg et al. [8], Maffezzoli et al. [9] and Rath et al. [10]. Other researchers used ultrasound as a spectroscopy method, e.g. Eckert-Kastner et al. [11], Kroll et al. [12] and later Oprisoni et al. [13], to

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investigate the mechanical properties of elastomers or thermosets [14] at high frequencies.

Based on the multitude of publications concerning the cure control of polymeric systems, the high economical importance and our own experience with the ultrasound technique we decided to test it on elastomers. Recently we presented some results of a natural rubber compound with a conventional sulphur curing system [1]. These results showed the possibility of using the US-Plus system (http://www.isk-iserlohn.de/us-plus.htm) produced by Iserlohner Kunststoff-Technik GmbH (ISK) Germany, in combination with ultrasound sensors that are integrated into the production tool, to measure the crosslinking characteristics of elastomers during the production process.

In this work, the same analysis is applied to a different natural rubber compound with a Semi-Efficient-Vulcanization-system (Semi-EV) that is cured within a compression mould. In contrast to our former work, this is investigated not only at a single but at several temperatures and also for several thicknesses. The influence of temperature and material thickness on the sound velocity values are discussed with respect to the results of the curemeter.

2. Methods and equipment

A Monsanto Moving Die Rheometer (MDR2000) was used to measure the vulcanization isotherms. The design of the MDR2000 allows the lower half of the die to perform an oscillating rotation of $0.5°$. Due to this rotation, the sample is deformed and exerts a restoring force that is detected by a torque transducer. The shear stress (τ) within the sample material can be calculated by consideration of the sample geometry. The following equation relates the shear stress with the complex shear modulus (G^*) of the material under consideration of the applied strain (γ).

$$G^* = \frac{\tau^*}{\gamma^*} \qquad (1)$$

Due to the chemical crosslinking of the polymer chains, the shear modulus increases. Some characteristic points of a typical isotherm are T_L as the minimum torque that occurs before the start of the crosslinking due to the torque reduction during the heating of the material and T_H as the maximum torque that occurs during the measurement. If the torque curve shows a maxima, the drop after the maximum is called reversion and is related to an

degradation respectively rupture of formerly formed crosslink's [15]. Reversion is typical for natural rubber compounds with sulphur crosslinking systems and is related to the rupture of polysulfidic bonds.

For the interpretation and comparability of the measurement results, it is convenient to use a relative degree of cure x according to the following equation [16]:

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

With use of this parameter, several characteristic times are defined such as the scorch time (t_s) where 10% of the total torque increase is reached as a measure for the start of the crosslinking reaction, or t_{90} where 90% of cure is reached as the time of optimal crosslinking.

For the measurements with ultrasound, a transmission technique with a setup given in Fig. 1 was used. The setup incorporates two ultrasonic longitudinal wave transducers in a compression mould for discs of 60 mm diameter. To get a fixed sample thickness, different rings made from brass were put into the mould. One of the transducers is used as an emitter and the other as a receiver. The detected ultrasonic signal is amplified and analyzed by a special peak analysis software described by Doring et al. [17].

The design of the ultrasonic transducers distributed by ISK Germany allows use up to 200 °C and uses a middle frequency of 4 MHz. With a diameter of roughly 8 mm and a length of 40 mm, they are small enough to be incorporated in most production tools.

The tool was mounted in a Schwabenthan Polystat 200S laboratory press with individually controlled heating of the tool, the upper and the lower mounting plates.

With use of a reference signal, which was measured in direct contact of both sensors to get the delay caused only by the sensors, the US-Plus system corrects the measured transmission time t_m to get the time that was necessary for the ultrasound pulse to pass through the sample t_s.

$$t_s = t_m - t_r \qquad (3)$$

Considering the sample thickness (d), the sound velocity (v_L) can be calculated according to Eq. (4):

$$v_L = \frac{d}{t_s} \qquad (4)$$

The sound velocity is also a measure for the material properties of the passed material as it is correlated with the longitudinal modulus, which is described by the following equation:
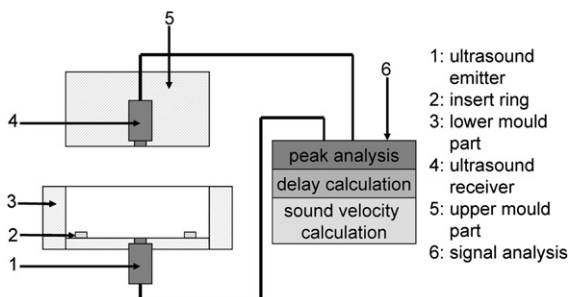
$$L^* = \frac{4}{3}K^* + G^* \qquad (5)$$

Fig. 1. Set up of the mould equipped with the ultrasonic online control.

1: ultrasound emitter
2: insert ring
3: lower mould part
4: ultrasound receiver
5: upper mould part
6: signal analysis

peak analysis
delay calculation
sound velocity calculation

Table 1
Material properties of the natural rubber compound with a Semi-EV-vulcanization-system.

Property	Value
Density	1.17 g/cm^3
Hardness	70 Shore A
Tensile strength	12.4 MPa
Ultimate elongation	195%

where K^* is the complex bulk modulus and G^* the complex shear modulus. The complex longitudinal modulus L^* is correlated with the sound velocity as given in Eq. (6)

$$L^* = \frac{\rho v_L^2}{1 - i(\alpha v_L/\omega)} \qquad (6)$$

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

As for any complex modulus, the longitudinal modulus can be expressed as the sum of a real and an imaginary part, where the real part describes the stored and the imaginary part the lost energy.

According to Alig et al. [18], the storage and the loss parts of the longitudinal modulus can be expressed, under the assumption that $\alpha v/\omega$ is much less than one, as follows:

$$L' = \rho v_L^2 \qquad (7)$$

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

Equations (7) and (8) show that a change in sound velocity is directly correlated to a change of the storage modulus.

As well known from the curemeter measurements, at least the shear modulus increases during the vulcanization of a rubber compound. Due to this increase in shear modulus the sound velocity also increases which was recently shown. According to DIN 6502, this change in material properties can be used to determine the vulcanization characteristics.

3. Material and processing conditions

A carbon black filled natural rubber compound with a Semi-Efficient-Vulcanization (Semi-EV) system was used for the measurements. As typical for an Semi-EV system, the accelerator concentration is increased and the sulphur concentration decreased in comparison to a conventional crosslinking system giving a comparable crosslinking density [15].
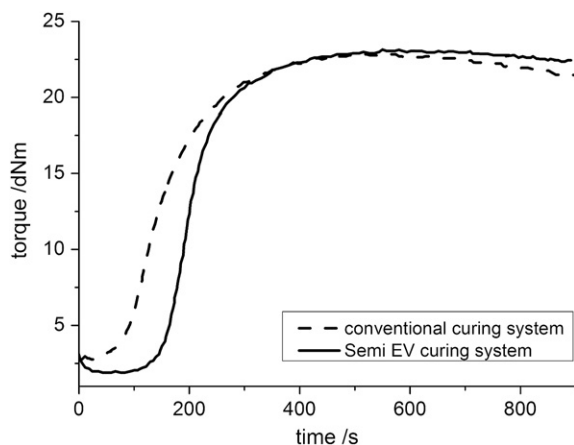
Table 2
Characteristic curing parameters of the NR-compound with a conventional and a Semi-EV-vulcanization-system.

Curing system	t_s/s	t_{90}/s	T_L/d Nm	T_H/d Nm
Conventional	80	290	2.6	22.79
Semi-EV	155	313	2	23.19

The end use properties were determined on an additionally produced plate of 2 mm thickness. The curing conditions were 10 min at 160 °C. The properties are given in Table 1.

For the investigation, the processing conditions were varied between 150 and 170 °C and different sample heights were tested. For all measurements a brass ring was inserted into the mould to set the sample height to a fixed value. Depending on the sample height, a defined amount of compound was put into the mould and compressed during the closure of the mould.

4. Results and discussion

To make a comparison between the conventional natural rubber compound that was investigated previously [1] and the new compound with a Semi-efficient-vulcanization-system possible, the curemeter curves of the storage part of the torque for both materials are shown in Fig. 2.

As can be seen, the Semi-EV system has a higher scorch time but reacts faster as the torque increases more steeply. The minimal torque is also lower than for the compound with the conventional curing system. In Table 2, the characteristic curing times and the minimum and maximum torques are given.

The scorch time of the Semi-EV system is nearly twice as long as for the conventional system, whereas the t_{90} times are nearly the same. The minimal torque of the Semi-EV compound is lower but the maximal torque is higher than for the conventional system. The lower T_L can be explained by a more complete heating of the compound before the start of the crosslinking reaction, which reduces the viscosity of the compound. The conventional system shows, as expected, a higher tendency to reversion. It can
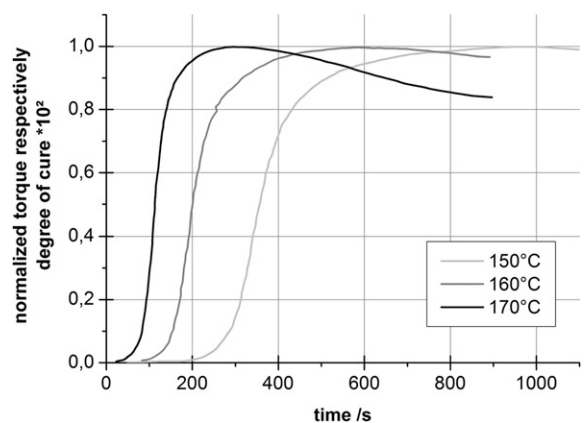

Fig. 2. Comparison of the storage part of the torque during cure at 160 °C of a natural rubber compound with a conventional and a Semi-EV system.

Fig. 3. Torque over time curves at 160 °C measured with the curemeter.

Table 3
Characteristic values of the curemeter curves of the natural rubber compound with a Semi-EV-vulcanization-system at different temperatures.

Temperature/°C	t_s/s	t_{90}/s	T_L/d Nm	T_H/d Nm
150	287	508	2.48	24.55
160	155	313	2	23.19
170	85	166	2	23.03

be concluded that the investigated natural rubber compound with a Semi-EV-vulcanization-system has, compared to the previously investigated compound with a conventional crosslinking system, a higher scorch time but shows a faster reaction process.

The further investigations were only concerned with the natural rubber compound with a Semi-EV-vulcanization-system.

4.1. Influence of temperature

First, the temperature dependence of the crosslinking reaction was investigated by the cure meter. In Fig. 3 the normalized storage torque curves at different temperatures over time are shown. If the storage torque is normalized to the total rise between T_L and T_H, it can also be understood as the degree of cure.

As can be seen, the rise in temperature has a large impact on the necessary curing time and the reversion. The characteristic values from the curemeter curves are given in Table 3.

An increase of the cure temperature by 10 °C leads to a reduction of t_s and t_{90} by more than 40% and a slight reduction in T_H. The slope of the torque curve increases with increasing temperature, and characterizes the acceleration of the crosslinking reaction.

The measurement of the sound velocity during the crosslinking within the compression mould was also performed at temperatures between 150 and 170 °C. The sample thickness was kept constant by insertion of a brass

ring of 1 mm height. Some representative results are shown in Fig. 4.

The general form of the sound velocity curve is fairly typical for a crosslinking polymer system that is introduced into a hot mould. The fast decrease in sound velocity at the beginning of the measurement is due to the fast heating of the relatively cold material to mould temperature. The sound velocity drops as does the shear modulus in curemeter measurements. After a certain time, the drop slows and a minimum is reached. After that, the sound velocity increases again due to the change in material properties caused by the crosslinking reaction. After some time, a plateau value is reached that represents nearly completed cure. The curves are, in general, a bit bumpy which is correlated to pressure fluctuations within the used setup.

It is obvious that the increase in temperature has a similar influence on the sound velocity curve of the curing reaction as on the torque curve. The final value of the sound velocity decreases with increasing temperature and the characteristic increase that describes the crosslinking reaction shifts to lower times.

To allow a better comparison between the results of the curemeter and the ultrasonic online control, the normalized results are shown together for every temperature in Fig. 5.

As can be seen, there is resemblance between the torque curve and the sound velocity curve. At higher temperatures, good agreement between the time of the start of rise in torque and the rise in sound velocity is observed. At 150 °C, the sound velocity starts to increase earlier than the torque. At the moment there is no explanation except possibly an undetected difference in temperature.

The heat transport into the sample should be much faster in the curemeter than in the compression mould as the sample thickness is lower and, due to the special die geometry, the outer surface higher. A slightly higher temperature for the ultrasonic measurements would explain the observed difference.
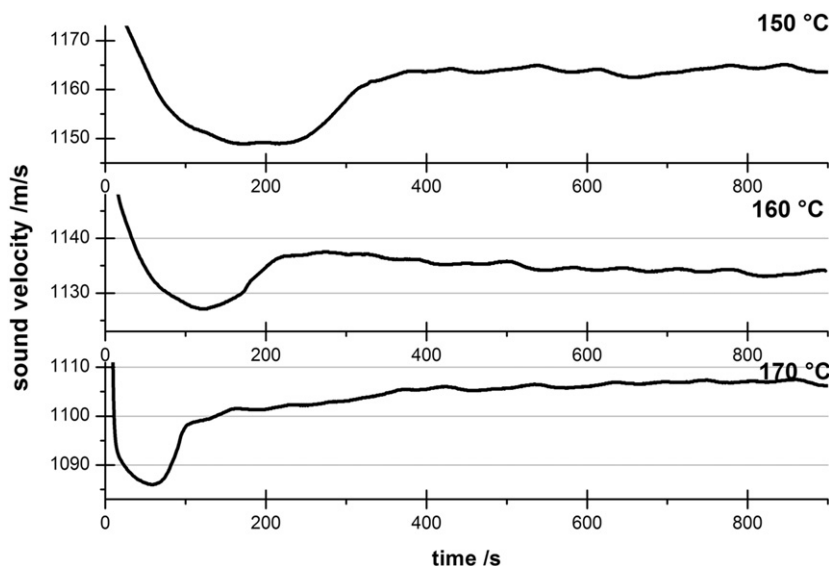
Fig. 4. Measurements of the sound velocity of the natural rubber compound over the curing time at different temperatures and a thickness of 1 mm.
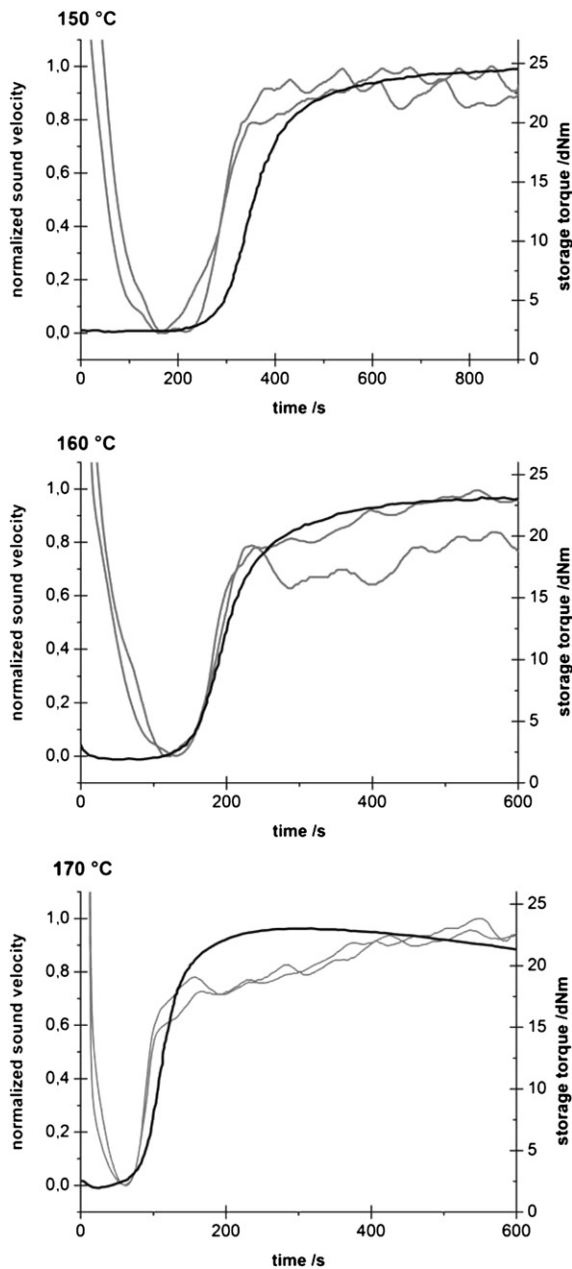
150 °C

160 °C

170 °C

Fig. 5. Normalized sound velocity curves (shown in grey) and storage torque curves (shown in black) of the curing reaction of the natural rubber compound at 150, 160 and 170 °C.

Additionally, the curemeter curves show a clear maximum whereas the sound velocity curves show after roughly the same time a change in the slope of the sound velocity increase. The increase in sound velocity becomes smaller but is still rising even after long times. This shows that the ultrasonic method is able to show the whole crosslinking process throughout the sample height. The measured sound velocity is an average of the whole sound velocity distribution within the sample. As the heat is transferred from the outside to the inside of the sample the crosslinking reaction, which is thermally activated, also
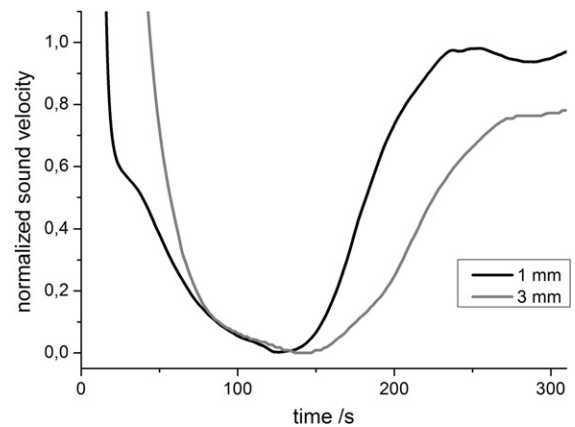

Fig. 6. Normalized sound velocity of the natural rubber compound over the curing time at 160 °C for samples with a thickness of 1 and 3 mm.

starts at the outside and progresses into the sample. The slight increase over time represents the effect of the final crosslinking reaction in the middle of the sample.

4.2. Influence of the sample thickness

To test whether the behaviour of thicker samples can also be shown with the ultrasonic method, samples with a thickness of 1 and 3 mm where measured. Some typical results at 160 °C are shown together in Fig. 6. The sample thickness shows a clear influence on the heating behaviour of the sample. The fast drop in sound velocity after closure of the mould tends to longer times with increasing sample thickness. The time to reach a sound velocity comparable to the final value after cure (a normalized value about 1) increases from roughly 15 s for a 1 mm thick sample to more than 45 s for a 3 mm thick sample. This simply shows that the heating of the thick sample takes longer. The normalized sound velocity curves over curing time show that the curing reaction of the thin sample starts earlier and finishes faster. This is also due to the faster increase of the bulk temperature within the thin sample that leads to higher reaction rates.

5. Conclusions

The aim of this paper was to show, based on the results of the former investigations [1], that the ultrasonic online control is applicable to other rubber compounds and delivers results comparable to the results of the curemeter according to ISO 6502. Additionally, the influence of the curing temperature and the sample thickness were investigated.

It was shown that the changes of the material properties in the natural rubber compound with a semi EV crosslinking system caused by vulcanization can be detected by the ultrasonic online control. An increase in curing temperature shows a clear accelerating effect on the curing reaction. This results in a shift of the curemeter curve to lower times and higher observed changes in degree of cure. The same behaviour is observed with the ultrasonic online control.

On the other hand, an increase in sample thickness that cannot be investigated with the curemeter as the sample geometry of this technique is fixed, is expected to lead to an increase in the required curing time. This can be shown by use of the ultrasonic online control.

Overall, the presented results show that the use of ultrasonic waves as a tool to get an insight into the curing reaction of a rubber compound during the production process delivers valuable information for the process control.

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