Correlating mechanical rubber properties with moving die rheometer vulcanization curves under consideration of the material composition

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ABSTRACT

In this work mathematical models are presented, calculated from moving die rheometer vulcanization curves of natural rubber based materials (storage torque and loss angle after vulcanization), correlated with mechanical relevant properties like shore A hardness and rebound resilience values with respect to rubber composition. The tested rubber materials are used for various dampening solutions in the field of agriculture, transportation and for general mechanical engineering applications. The presented calculation models allow for the prediction of shore A hardness and rebound resilience with an error of less than 5% by just measuring a standard vulcanization curve.

INTRODUCTION

Investigating the vulcanization process of a rubber material measured in oscillation rheometry (so-called moving die rheometer or simply curemeter) under constant temperature and frequency conditions is a standard procedure to test for processability in quality assurance of rubber manufacturing and incoming goods inspection acc. to DIN 53529-3[1] and ISO 6502-2[2]. This test method is well suited to estimate the right processing parameters and vulcanization properties as well as the date of expiry of rubber material. Furthermore, it is possible to calculate shear modulus and damping factor from the complex torque. Nevertheless, to have an accurate prediction of the final mechanical properties and dynamic performance of the vulcanized rubber parts more time-consuming measurements are required[3] like shore A hardness (acc. to DIN ISO 7619[4]) and rebound resilience testing (acc. to DIN 53512[5]). But these further testing procedures require the production of a vulcanised sample plate taking at least additional 30 minutes in comparison to only 10 minutes for a classical oscillatory rheology investigation of the vulcanisation properties. The scope of this work is to present correlation models of moving die rheometer vulcanization curves (storage torque and loss angle after the vulcanization) with mechanically relevant properties like shore A hardness and rebound resilience values taking into account the rubber composition.

METHODS

The moving die rheometer curves of the BHC incoming goods inspection were tested with an MDR 2000[6] curemeter (alpha Technologies). All incoming material batches are tested with the BHC incoming goods inspection standard testing procedure acc. to ISO 6502. The oscillatory rheology measurements are performed at an amplitude of +/- 0,5° at 1.667 Hz in a bi-conical die[6] heated to 170°C. The bi-cone angle of the dies is $\alpha = 0.1251$ rad[7], Fig 1. In order to avoid slipping on the specimen surface and having a better introduction of torque both conical plates have additional sharp, radial grooves in their surfaces, Fig 2.
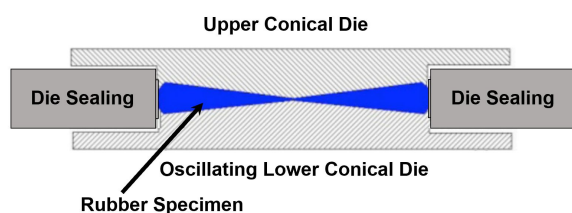
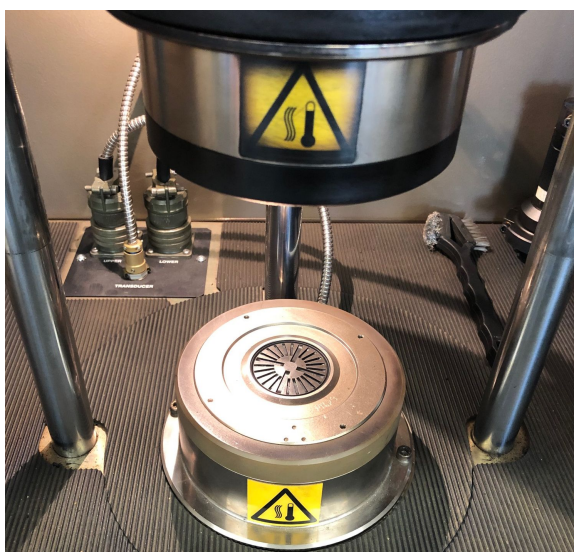Figure 1. Schematic measuring setup of MDR 2000 bi-conical moving die rheometer for rubber curing[6].

Figure 2. Test chamber of the MDR 2000 bi-conical moving die rheometer (top); rubber specimen after curing (bottom).

MATERIALS

In this study the moving die rheometer curing curves of the BHC Gummi-Metall GmbH incoming goods inspections of all material batches delivered in 2019 (varying between 1 to 7 batches) of 17 different rubber types are evaluated. The rubber types vary in polymer composition and filler/ softener content resulting in significant hardness variations, Table 1.

Table 1. Rubber types tested in this study.

No.	Name	Polymer type: NR natural rubber, BR butadiene rubber, SBR styrene butadiene rubber	Mean Shore A Hardness (No. of tested batches)
1.	41-NRSBR	NR, SBR	41.0 (1)
2.	42-NRBR	NR, BR	41.8 (4)
3.	45-NR	NR	45.2 (7)
4.	47-NRBR	NR, BR	47.2 (7)
5.	50-NRBR	NR, BR	49.5 (6)
6.	52-NRBR	NR, BR	52.2 (4)
7.	53-NR	NR	52.5 (2)
8.	54-NRBR	NR, BR	53.8 (7)
9.	57-NRBR	NR, BR	57.1 (7)
10.	58-NRSBR	NR, SBR	58.4 (5)
11.	63-NRBR	NR, BR	63.2 (7)
12.	67-NRBR	NR, BR	66.8 (6)
13.	68-NRBR	NR, BR	68.3 (7)
14.	68-NRSBR	NR, SBR	68.3 (6)
15.	73-NRBR	NR, BR	72.5 (4)
16.	75-NRBR	NR, BR	74.8 (3)
17.	80-NRSBR	NR, SBR	80.0 (1)

RESULTS

Fig. 3 shows the max. storage torque during vulcanisation of the moving die rheometer measurement correlated with the shore A hardness values provided by the 3.1. test certificates of the rubber supplier. The results are plotted separately with respect to specimen types containing natural rubber blended with butadiene rubber (NR/BR plotted as circles) and specimen types containing only natural rubber as well as a blend of natural rubber with styrene-butadiene rubber (NR resp. NR/SBR plotted as triangles). The scattering of different material batch measurements of the same rubber type delivered within 2019 is indicated horizontally for the max. storage torque and vertically for the shore A hardness.
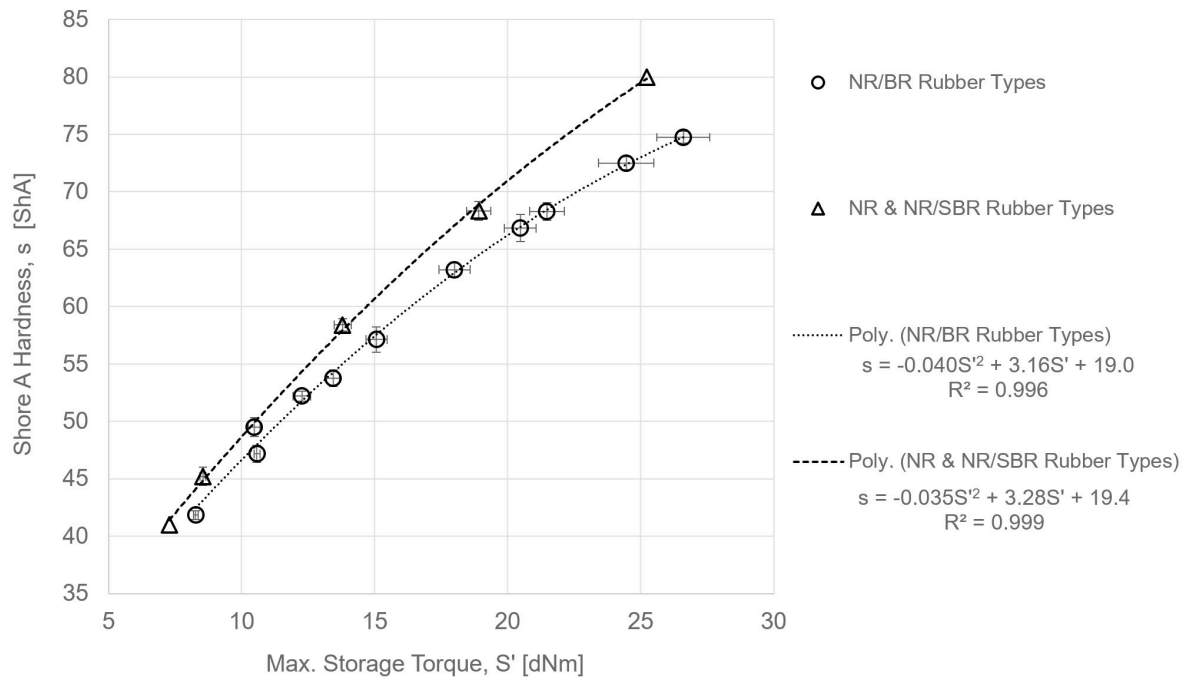
Figure 3. Shore A rubber hardness s acc. to 3.1 test certificate provided by the material supplier plotted over the max. storage torque S' measured with moving die rheometer.
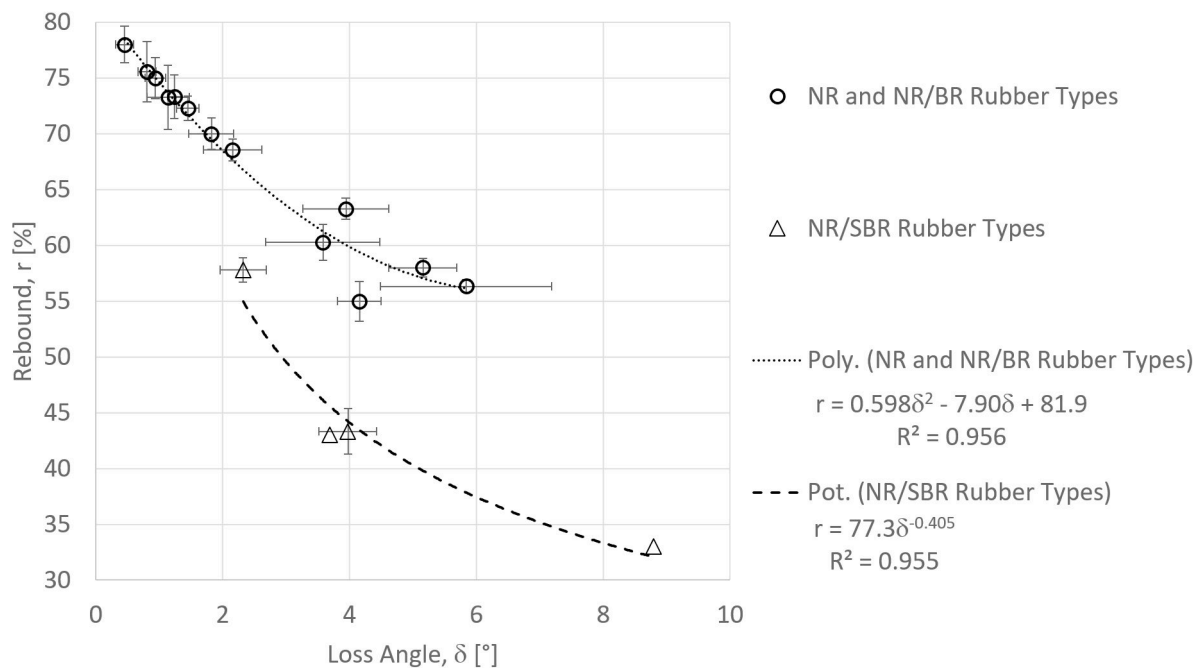

Figure 4. Rebound resilience r acc. to 3.1 test certificate provided by the material supplier plotted over the loss angle δ calculated from the moving die rheometer dynamic torque measurement.

Fig. 4 shows the loss angle calculated from the moving die rheometer dynamic torque measurements correlated with the rebound resilience values provided by the 3.1. test certificates of the rubber supplier. The results are plotted separately with respect to specimen types containing only natural rubber as well as natural rubber blended with butadiene rubber (NR resp. NR/BR plotted as circles) and specimen types containing a blend of natural rubber with styrene-butadiene rubber (NR/SBR plotted as triangles). The scattering of different material batch measurements of the same rubber type delivered within 2019 is indicated horizontally for the loss angle and vertically for the rebound resilience.

DISCUSSION

The correlation of the max. storage torque x with the shore A hardness y of the NR/BR rubber types (circles) depicted in Fig. 3 can be nicely fitted with a 2nd order polynomial having a coefficient of determination of R²=0.996, see Eq. 1. The analogue fitted correlation of the NR as well as NR/SBR rubber types (triangles) in Fig. 3 has an even better coefficient of determination of R²=0.999, see Eq. 2. This allows for the precise prediction of Shore A hardness values of every rubber batch tested in a moving die rheometer acc. to the incoming goods inspection standard procedure with an estimated error below +/-2ShA hardness. In case of setting up correction factors for each different rubber type shifting the mean values on the fitting curve the prediction accuracy could be increased further probably to an error below +/-1ShA.

Polynomial fitting for NR/BR rubber types:

$$y = -0.04x^2 + 3.16x + 19.0 \qquad (1)$$

Polynomial fitting for NR and NR/BR rubber types:

$$y = -0.035x^2 + 3.28x + 19.4 \qquad (2)$$

The correlation of the loss angle δ with the rebound resilience y of the NR as well as the NR/BR rubber types (circles) depicted in Fig. 4 can be fitted with a 2nd order polynomial having a coefficient of determination of R²=0.956, see Eq. 3. The fitted correlation with a power function of the NR/SBR rubber types (triangles) in Fig. 4 has a coefficient of determination of R²=0.955, see Eq. 4. This allows for the prediction of rebound resilience values of every rubber batch tested in a moving die rheometer acc. to the incoming goods inspection standard procedure with an estimated error below +/-3% for loss angles below 3° an +/-5% above. In case of setting up correction factors for each different rubber type shifting the mean values on the fitting curve the prediction accuracy could be increased further probably to an error below +/-2%.

Polynomial fitting for NR and NR/BR rubber types:

$$r = 0.598\delta^2 - 7.90\delta + 81.9 \qquad (3)$$

Exponential fitting for NR/SBR rubber types:

$$r = 77.3\delta^{-0.405} \qquad (4)$$

CONCLUSION

Important mechanic properties as shore A hardness and rebound resilience can be calculated by mathematical models from the incoming goods inspection standard testing procedure using dynamic measuring data of a moving die rheometer. This allows for the characterisation of important mechanical properties of every incoming rubber batch without further testing efforts. This data can either be used to be compared with 3.1 test certificate values from the rubber supplier as well as to evaluate changes in the mechanical application properties of certain rubber batches with respect to longer storage times prior to vulcanization.

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