



Evaluation of the suitability of different methods for determination of the crosslink density in highly filled EPDM compounds

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Abstract

The crosslink density of elastomers is the essential property that determines many other but especially the mechanical product properties. Different raw materials, especially recycled and bio-based materials, influence the vulcanization and may change the crosslink density when they are used as a substitute to conventional raw materials. Aim of this study is to develop a procedure that allows the reliable determination of the crosslink density in highly filled EPDM compounds as basis for future investigations focussed on substitution with sustainable materials in this compound. Unfortunately, experiences with other rubber compounds like tire treads cannot be directly applied here because of the use of other filler types and amounts as well as the differences in the polymer with regard to active sites (available double bonds). Equilibrium swelling, Flory-stress-strain-measurements, freezing point depression and temperature-scanning-stress-relaxation are applied to a model EPDM compound with high filler and softener amount as typically used for sealings. For sensitivity investigation the amount of the crosslink agent sulfur was varied. Furthermore, the influence of different accelerators was investigated. All methods are able to determine the crosslink density but with different standard deviations due to measurement errors. Partially, they can be optimized for this use case. Based on the results a combination of Flory-stress-strain-measurements and freezing point depression was chosen to be used in the future.

Keywords Crosslink density · EPDM · Equilibrium swelling · Freezing point depression · Flory-stress-strain-measurements · Temperature-scanning-stress-relaxation

Introduction

EPDM (Ethylene-Propylene-Diene-Rubber) seals are widely used in the automotive industry. They are found for example as body seals in the visible area and must meet high requirements in terms of their mechanical properties and appearance. In most cases, these seals are of complex geometry. Which leads to the fact that they are vulcanized to different degrees at different points during the manufacturing process. Here, the crosslink density plays an essential role. In addition to the polymer, fillers and additives, the crosslink density is also a major influencing factor with regard to the mechanical properties. In order to increase the sustainability,

the use of bio based and recycled raw materials instead of crude oil based raw materials is a focus in the rubber industry. In the most cases these sustainable materials cannot be replaced equally and influence the vulcanization and thus the crosslink density. For example, petrochemical softener could be replaced with vegetable oils, but these have a negative influence on the crosslink density as they are mostly unsaturated [1]. To develop more sustainable rubber compounds, the influences of new raw materials on the crosslink density and therefore on the processing especially the continuous vulcanization and the product properties need to be determined. A suitable methodology for measuring the crosslink density must be developed for these materials.

In contrast to other properties, the determination of crosslink density is so far only possible indirectly. Experiences with other elastomer products cannot be directly transferred [2–10]. Most equations determine the crosslink density assuming unfilled compounds which do not meet reality, but are used frequently for filled compounds [7–10]. Existing adaptations of those equations are proposed by

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different authors, mostly regarding carbon black as filler [8, 11–13]. Blume et al. investigated different methods to determine the crosslink density of a tire tread compound which contains a silica system. While all investigated methods were suitable to determine the crosslink density, the determination of mono-, di- and polysulfidic crosslinks with the thiol-amine-method was not applicable because silica and silane interact with the chemicals that should cleave the crosslinks. Silica and silane build chemical bonds with the polymer through silanization [8]. Vennemann et al. developed the temperature-scanning-stress-relaxation method which can determine the crosslink density based on the thermomechanical properties [13–16]. Carbon black bonds physically with the polymers by adsorption. An adaptation to determine the crosslink density of carbon black filled compounds was proposed, but only for filler fractions below the percolation threshold. Above the percolation threshold carbon black forms a network which hinders the thermoelastic stress increase in this method which is used to determine the crosslink density [13, 16]. The compounds in this study are crosslinked with sulfur and contain high filler fractions of carbon black and calcium carbonate. In contrast to the active fillers, calcium carbonate does not form bonds with the polymer. Therefore, an investigation of the methods to determine the crosslink density is necessary with regard to their suitability for this type of compounds.

The influence of sulfur and hence the crosslink density on compound properties is well known. Therefore, sulfur content was varied for the validation of the methods. The influence of the different accelerators on the crosslink density is not known yet for these compounds.

Different mechanical properties depend on the crosslink density and can be considered as a non-direct indicator for it. The vulcanization was measured via curing tests. The difference between measured minimum and maximum torque correlates with crosslink density. The higher the torque change, the higher the crosslink density. Hardness increases with increasing crosslink density. Tensile strength shows a maximum with increasing crosslink density. Compression set of elastomers is very important for sealing applications. Higher crosslink density leads to more elasticity and lower residual deformation [17].

Equilibrium swelling

Due to their crosslinking, elastomers cannot be dissolved, but only swollen. Depending on the combination of medium and polymer, the intensity of swelling varies. To determine the crosslink density, a suitable solvent is selected. The sample is placed in the solvent. The solvent migrates into the sample and extractable components such as plasticizers migrate into the solvent. The used solvent is

replaced with pure solvent and the sample is swollen until a constant weight is reached. The Flory-Rehner equation can then be used to determine the crosslink density [18].

$$\nu = \frac{\ln(1 - \nu_r) + \nu_r + X \cdot \nu_r^2}{V_0(\nu_r^{1/3} - 0.5\nu_r)} \quad (1)$$

$$\nu_r = \frac{1}{1 + \frac{\rho_P \cdot Q}{\rho_S}} \quad (2)$$

$$Q = \frac{m_1 - m_2}{m_2} \quad (3)$$

With

ν = crosslink density [mol cm⁻³].

ν_r = volume fraction of polymer in swollen gel.

X = Huggins interaction parameter (2.683 for EPDM/cyclohexane [19])

V_0 = molar volume of the solvent [cm³ mol⁻¹].

ρ_P = density polymer.

ρ_S = density solvent.

Q = swelling ratio.

m_1 = mass swollen specimen.

m_2 = mass unswollen specimen.

This applies to unfilled elastomers. However, most elastomer products contain fillers such as carbon black. These have an influence on the calculation of the crosslink density. Carbon black prevents the polymer chains bound to it from swelling [12]. Different existing adjustments using new variables and constants can reduce the influence of carbon black on the measured crosslink density [11, 12, 20]. Inactive fillers such as calcium carbonate, that are typically used in EPDM sealing compounds, also have an influence on the measured crosslink density. In contrast to active fillers, the polymer chains are not bound to the inactive fillers. By swelling the specimen vacuoles around the filler particles are formed and thus, not all of the solvent inside the specimen participates in the network swelling [21].

With the assumption that fillers do not swell, crosslink density can be calculated by using the value of equilibrium swelling ratio of the rubber alone [11]:

$$Q_{Rubber} = \frac{Q - \varphi}{1 - \varphi} \quad (4)$$

$$\Phi = (CTAB \cdot \rho_{CB} \cdot \Phi_{CB} \cdot \delta) + \Phi_{CB} \quad (5)$$

With

CTAB = CTAB (Cetyltrimethylammonium Bromide) Surface Area.

ρ_{CB} = density of carbon black.

δ = layer thickness of bound polymer chains.

Φ_{CB} = volume fraction of carbon black.

Flory-stress-strain-measurements

The crosslink density can be calculated on the basis of the stress-strain curves. The results are then plotted as stress versus $\rho(\lambda-\lambda^{-2})$. The slope of the linear regression line corresponds to the Flory-equation [19]:

$$A = \frac{R \cdot T}{M_c} \quad (6)$$

$$\nu = \frac{\rho}{M_c} \quad (7)$$

With

A = slope.

ρ = density rubber compound [g cm^{-3}].

λ = length ratio of loaded to unloaded specimen L/L_0 .

R = ideal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$].

T = temperature [K].

M_c = average molar mass of the molecule chain between crosslinks [g mol^{-1}].

ν = crosslink density [mol cm^{-3}].

This equation applies to unfilled elastomers. In order to reduce the influence of the filler, the filler network gets destroyed by stretching the specimen several times until no further stress softening can be detected. The stress-strain curve for calculation of crosslink density is recorded directly afterwards. Considering that the filler particles still exhibit reinforcing effects, the length ratio λ can be replaced by Λ which contains the reinforcing factor x [8]:

$$\Lambda = \epsilon \cdot x + 1 \quad (8)$$

$$x = 1 + 2,5\Phi + 14,1\Phi^2 \quad (9)$$

With

ϵ = relative strain.

The volume fraction of carbon black needs to be extended. A fraction of the polymer chains does not participate in the deformation and therefore acts like a filler - the bound polymer chains as well as the occluded polymer within the structure of carbon black. The effective, apparent volume fraction $\Phi'_{F,\text{eff}}$ is defined by [13]:

$$\Phi'_{F,\text{eff}} = F \cdot \left(\frac{OAN - 50}{100} \cdot \rho_{CB} \cdot \Phi_{CB} \right) + (1 - F) \cdot (CTAB \cdot \rho_{CB} \cdot \Phi_{CB} \cdot \delta) + \Phi_{CB} \quad (10)$$

With

F = effectiveness factor (0.5 for ideal isotropic fillers and uniaxial deformation), indicates the fraction of polymer chains which is shielded from deformation.

OAN = Oil Absorption Number (structure).

Freezing point depression

Solvents inside a solid material have a lower freezing point than free solvents. The freezing point shifts to lower temperatures the smaller the free volume in the solid becomes. In terms of elastomers, this means that the higher the crosslink density, the lower is the freezing point of the solvent in the sample. The temperature difference between the two freezing points can be used to determine the distance between the crosslinks. Following equation applies to cyclohexane as solvent [22]:

$$d_c = \frac{86}{\Delta T} \quad (11)$$

with

d_c = average distance between crosslinks [nm].

ΔT = temperature difference of the freezing points.

Temperature-scanning-stress-relaxation

One of the latest methods for determining crosslink density is the temperature-scanning-stress-relaxation (TSSR). A standard S2 dumbbell is clamped and pre-stretched. First, the sample is relaxed for two hours at room temperature to reach an equilibrium state. Then the chamber is heated and the applied force on the specimen at the constant strain is measured during heating. A normalized force curve and a relaxation spectrum versus temperature are obtained. Using the change κ in relaxation spectrum, the crosslink density can be calculated by following equation [15]:

$$\nu = \frac{\kappa}{R \cdot (\lambda - \lambda^{-2})} \quad (12)$$

This method was applied only on rubber compounds without fillers or with maximum contents of 65 phr (parts per hundred rubber) of active fillers [13–16]. The equation also can be extended to consider filler fraction like for the Flory-stress-strain-measurements before by replacing λ with Λ [8].

Materials

A model EPDM compound was used as reference (Tables 1 and 2). The master batch of 380 phr in total consists of high molecular weight high ENB (Ethylidenenorbornene) EPDM

Table 1 Recipe of the masterbatch without curing system

Material	phr
Vistalon 9600	100
Purex HS 25	107
Calcium carbonate	47
Paraffinic oil	105
Zinc oxide active	4
Stearic acid	0.5
Polyethyleneglycole PEG 4000	2
Calcium oxide	9
Struktol WB 16	2

grade, ultra clean high structure carbon black and calcium carbonate as fillers, paraffinic mineral oil as a softener, zinc oxide, stearic acid and polyethyleneglycole as activators, calcium oxide as desiccant. The curing system contains sulfur and several accelerators. This masterbatch is used as a reference compound and based on this, compounds with -0.5 phr and $+0.5$ of sulfur, compounds with -1 , -0.5 , $+0.5$ and $+1$ phr of the primary accelerator 2-mercapto-benzothiazole (MBT), compounds with -0.5 and $+0.5$ phr of the secondary accelerator zinc-dibenzyl-dithiocarbamate (ZBEC) and compounds with -0.4 and $+0.4$ phr of the secondary accelerator tetra-isobutyl-thiuram-disulfide (TiBTD) were prepared.

The test specimens were prepared either from 2 or 6.3 mm test slabs cured for 8 min or respectively 10 min at $180\text{ }^{\circ}\text{C}$ in a compression mold. The vulcanization times were chosen according to the industrial processes.

Experimental

For all equations adjusted filler volume fractions were considered. Assuming that only carbon black as an active filler bounds polymer and exhibits a structure within polymer

chains can be occluded, Eqs. (5) and (10) were extended to include the contribution of calcium carbonate:

For equilibrium swelling:

$$\Phi = (CTAB * \rho_{CB} * \Phi_{CB} * \delta) + \Phi_{CB} + \Phi_{\text{Calcium carbonate}} \quad (13)$$

For Flory and TSSR:

$$\begin{aligned} \Phi'_{F,eff} = & F * \left(\frac{OAN - 50}{100} * \rho_{CB} * \Phi_{CB} \right) \\ & + (1 - F) * (CTAB * \rho_{CB} * \Phi_{CB} * \delta) \\ & + \Phi_{CB} + \Phi_{\text{Calcium carbonate}} \end{aligned} \quad (14)$$

The minor contribution of adsorbed polymer chains on carbon black is neglected for now. As all compounds contain the same type and amounts of fillers, the error made by this is not significant. In future studies the contribution of the adsorbed polymer will be considered.

Equilibrium swelling

In this study five samples of each compound were placed in cyclohexane. The solvent was changed in between and the samples were swollen to constant weight. After weighing in the swollen state, the samples were dried and weighed again. The crosslink density was calculated by Eqs. (1), (4) and (13).

Flory-stress-strain-measurements

Five S2 dumbbells were die-cut from the sheets. These were clamped in the 10 kN universal testing machine Allround Table Top from Zwick Roell and stretched several times to 200% until the stress-strain curves no longer changed (Mullins effect). The maximum of 200% was chosen according to the general tensile properties of the samples. Equations (6), (8) and (14) were used to determine the crosslink density.

Table 2 Reference curing system and changes of sulfur and accelerator amounts to reference curing system

	Sulfur [phr]	MBT [phr]	ZBEC [phr]	TiBTD [phr]	ZDTP* [phr]
Reference	1.5	2.0	1.0	0.8	1.4
-0.5 phr Sulfur	-0.5				
+0.5 phr Sulfur	+0.5				
-1 phr MBT		-1			
-0.5 phr MBT		-0.5			
+0.5 phr MBT		+0.5			
+1 phr MBT		+1			
-0.5 phr ZBEC			-0.5		
+0.5 phr ZBEC			+0.5		
-0.4 phr TiBTD				-0.4	
+0.4 phr TiBTD				+0.4	

*ZDTP Zinc dialkyldithiophosphate

Freezing point depression

Three samples each were treated by Soxhlet extraction with cyclohexane for 16 h. Subsequently, samples were stored in fresh solvent. The freezing points of the cyclohexane inside and outside the samples were measured by differential scanning calorimetry on the DSC 200 PC from Netzsch with a cooling rate of 5 K min^{-1} . Assuming that the distance between crosslinks calculated by Eq. (11) can be seen as the diameter of a sphere and a room of 1 m^3 is filled with the densest sphere packing, the crosslink density is calculated by:

$$\nu = \frac{0,74048}{\frac{4}{3} * \pi * \left(\frac{d_c}{2}\right)^3 * N_A} \quad (15)$$

With

N_A = Avogadro Constant.

This method is not yet capable of distinguishing crosslinks from filler particles which both limit the migration of solvent into the specimen.

Temperature-scanning-stress-relaxation

Five S2 dumbbells per material were measured in the Brabender TSSR-Meter. Short time relaxation of the specimens was eliminated by applying an initial strain of 50% for two

hours at room temperature. The specimens reach an equilibrium state and are then heated with a heating rate of 2 K min^{-1} up to $200 \text{ }^\circ\text{C}$. The crosslink density was calculated by Eqs. (8), (12) and (14).

Other tests

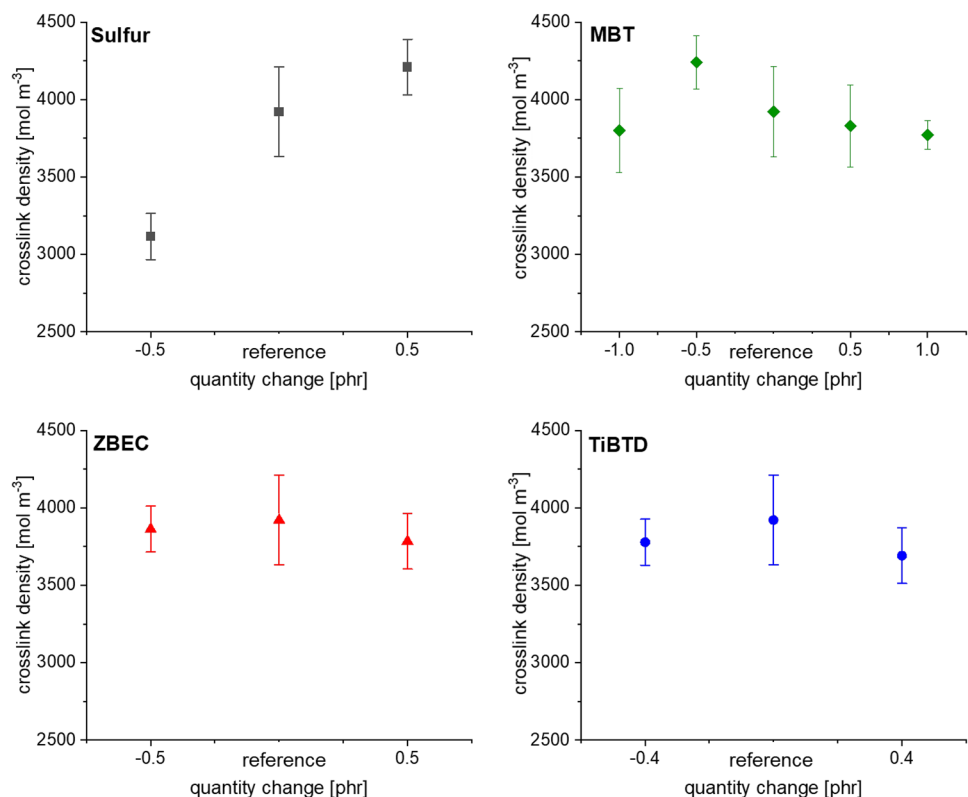
Other properties that depend on the crosslink density were also measured for plausibility and correlation to the crosslink density results from the different methods. Curing tests were performed with Göttfert Elastograph at $180 \text{ }^\circ\text{C}$ for 6 min. Shore A hardness was measured according to DIN 53505 with the Bareiss U72 hardness tester. Standard S2 dumb-bells were tested with the 10 kN universal testing machine Retro Line from Zwick Roell according to DIN 53504 with a strain rate of 200 mm min^{-1} . Compression set was examined according to ISO 815-1 method B for 22 h, heated to $100 \text{ }^\circ\text{C}$ in the oven Elastocon EB 12-II.

Results and discussion

Equilibrium swelling

Swelling does not show a linear increase in crosslink density for increasing amounts of sulfur (see Fig. 1).

Fig. 1 Equilibrium swelling: Crosslink density at different amounts of sulfur, MBT, ZBEC and TiBTD



The crosslink density is rising between approximately $3,100 \text{ mol m}^{-3}$ and $4,250 \text{ mol m}^{-3}$. Changing the amount of MBT seems to have no influence on crosslink density with one exception at -0.5 phr , which shows a maximum with 300 mol m^{-3} higher crosslink density (see Fig. 1). As the deviations are high and no other measuring method shows this trend the results are not clear. Various influences like inhomogeneity and quite high measurement errors in swelling experiments can lead to such results. No difference in the crosslinking density can be seen for the different compounds with varying ZBEC amount (see Fig. 1). With 0.5 phr more ZBEC, the average value is slightly below the others, but within the standard deviation. So, it is not a significant change here. The crosslink density is around $3,800 \text{ mol m}^{-3}$. Since ZBEC serves exclusively as an accelerator in vulcanization and does not donate sulfur, this result is reasonable [23]. Varying amounts of TiBTD show no significant change in crosslink density as well (see Fig. 1). In addition to acceleration TiBTD serves as a sulfur donor in sulfurless or low-sulfur vulcanization systems [24]. As the curing systems of these compounds contain more sulfur than typical efficient or sulfurless systems, it is possible that TiBTD does not act as sulfur-donor and therefore has no influence on crosslink density [17]. The distribution of crosslink types can give more information about the crosslinking and the influence of the accelerators. This will be considered in future studies.

Flory-stress-strain-measurements

The determination of the crosslink density according to Flory shows a linear increase of the crosslink density with increasing amount of sulfur (see Fig. 2). The standard deviation is relatively small. The crosslink densities are about 35 mol m^{-3} for the compound with the lowest sulfur content, about 40 mol m^{-3} for the reference and about 46 mol m^{-3} for the compound with the highest sulfur content. Different amounts of MBT show changes within a range of only $\pm 0,5 \text{ mol m}^{-3}$ (see Fig. 2), with a low standard deviation for all results. However, there is no dependence of the crosslink density for the different MBT concentrations found. A crosslink density about 41 mol m^{-3} for all compounds with varying ZBEC content is recognized. The values for TiBTD variations show nearly the same crosslink densities than the reference (see Fig. 2).

Freezing point depression

The freezing point depression shows a reduction of the distance between the crosslinks and therefore an increase in crosslink density with increasing amount of sulfur. The sample with less sulfur shows a crosslink density of about 5 mol m^{-3} the reference of about 8 mol m^{-3} . The highest crosslink density with 15 mol m^{-3} show high deviations but still a significant increase (see Fig. 3). This may be due to

Fig. 2 Flory-stress-strain-measurements: Crosslink density at different amounts of sulfur, MBT, ZBEC and TiBTD

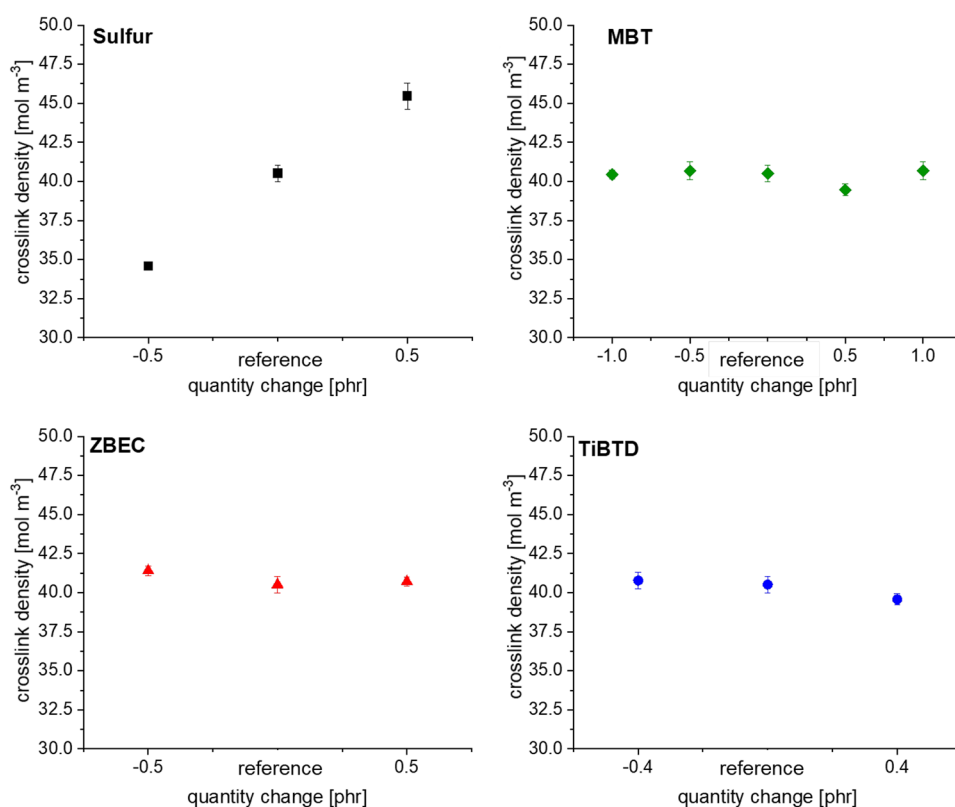
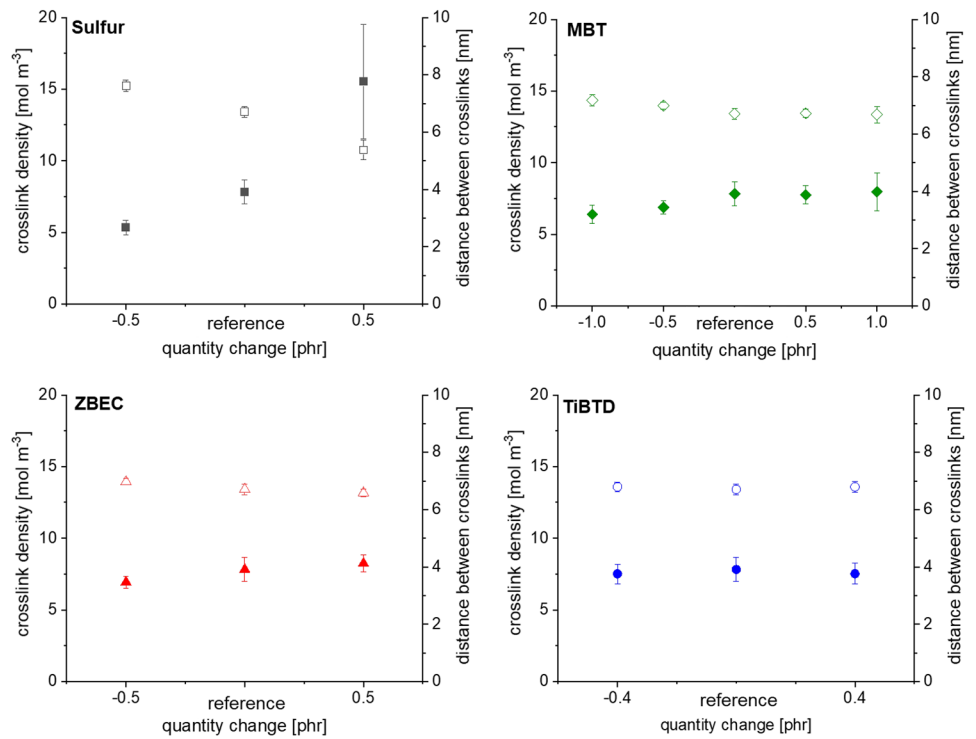


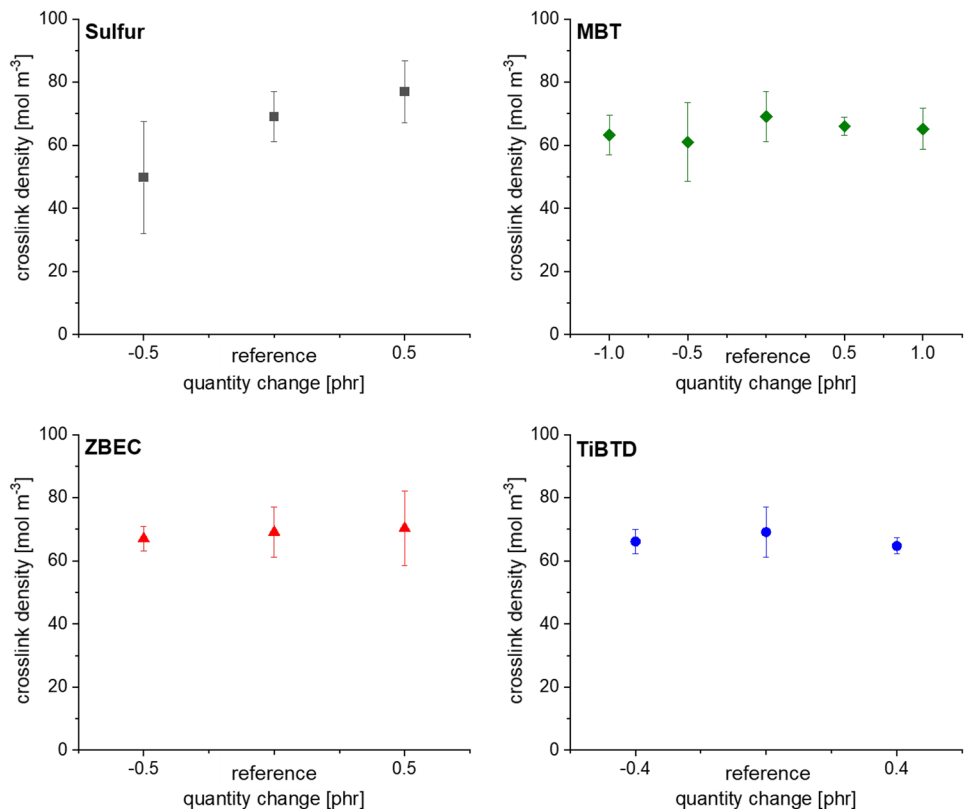
Fig. 3 Freezing point depression: Distance between crosslinks (unfilled points) and calculated crosslink density (filled points) at different amounts of sulfur, MBT, ZBEC and TiBTD



the fact, that the distance between crosslinks enters the equation with the third power and therefore also the deviations from the measurements. Further optimizations regarding this

will be implemented in future studies. The crosslink density slightly increases with increasing amount of MBT and reach a plateau at 8 mol m⁻³ (see Fig. 3). The measured crosslink

Fig. 4 TSSR: Crosslink density at different amounts of sulfur, MBT, ZBEC and TiBTD



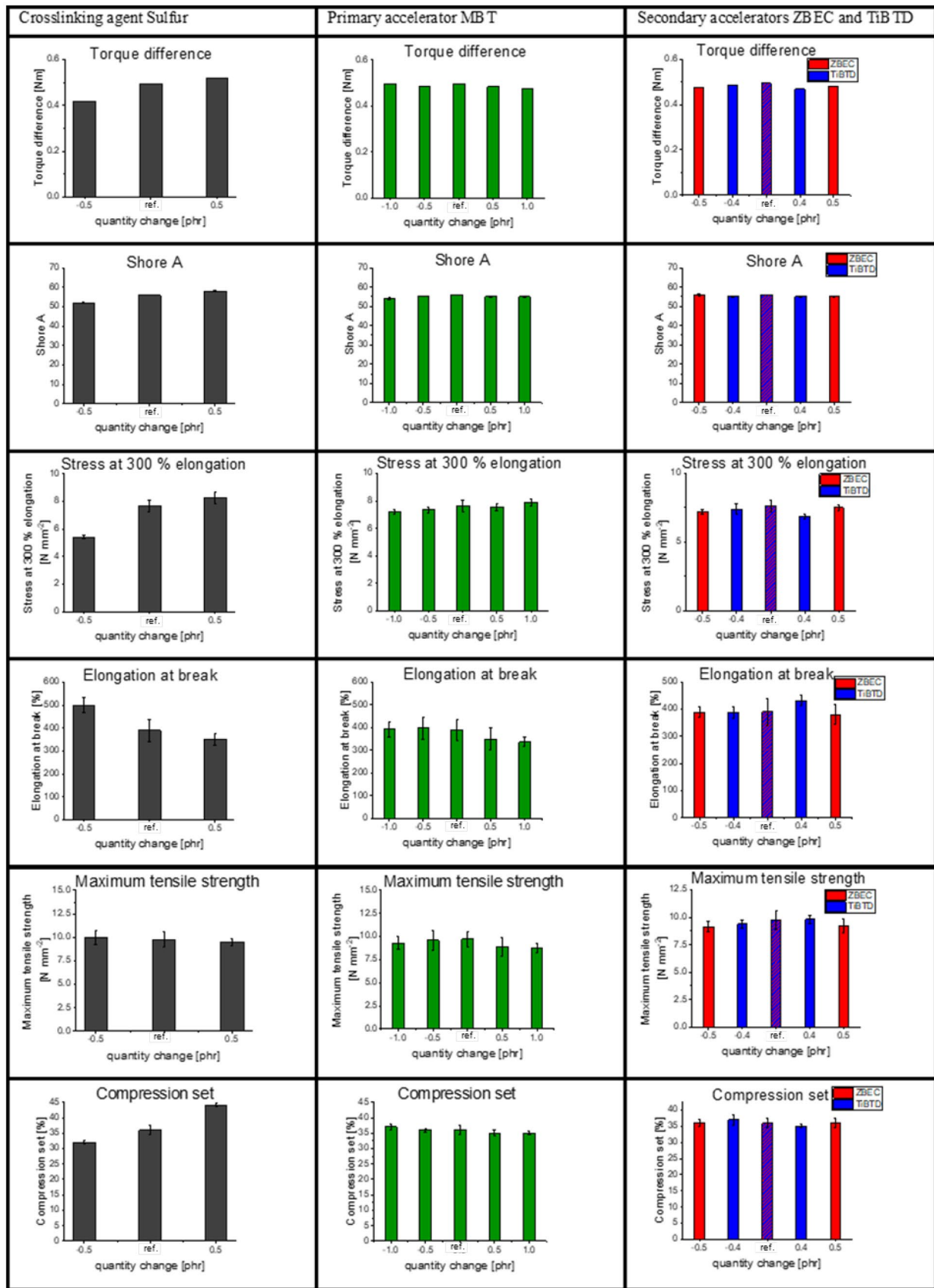


Fig. 5 Different mechanical properties at different amounts of sulfur, MBT, ZBEC and TiBTD

density also shows a slight increase with increasing ZBEC content from 7 to 8 mol m⁻³. The compounds with varying TiBTD content show no change in crosslink density within standard deviation. The high standard deviation of the compound with the highest TiBTD and sulfur amount may be due to sample preparation.

Temperature-scanning-stress-relaxation

The TSSR meter determined average crosslink densities between 50 and 80 mol m⁻³ for the compounds with varying sulfur content. However, a high standard deviation is noticed here for each measurement. The compounds with the variation in MBT show no reasonable change with increasing amounts (see Fig. 4). These changes lie within the standard deviation; therefore, no significant change is determined. For ZBEC and TiBTD the compounds exhibit approximately the same crosslink density as the reference. The standard deviations of most measurements are quite high (Fig. 4). In addition, the software could not evaluate all curves, so an own data evaluation to determine κ was needed. The graphs of the measurements showed artefacts that could not be explained yet. In fact, this method cannot be reliably applied on these compounds at the moment and needs further adjustments in the data processing. One possible reason is the high amount of different fillers and softener that has not been investigated yet.

Mechanical tests

The different methods to determine the crosslink density and distance between crosslinks, respectively, show plausibly that an increasing amount of sulfur increases crosslink density while changing the amount of the accelerators are not changing the crosslink density.

The torque difference increases with increasing amount of sulfur from 0.418 Nm to 0.519 Nm while changing the amounts of the accelerators has no significant influence on it (see Fig. 5). The same tendencies are seen with Shore A hardness. Hardness increases from 52 to 58 with more sulfur and does not change significantly with varying accelerator amounts from the reference value of 56 (see Fig. 5). The stress at 300% elongation is increased with increasing amounts of sulfur from 5.4 N mm⁻² to 8.3 N mm⁻² (see Fig. 5). Changing amounts of the different accelerators show approximately the same value as the reference compound. Maximum elongation at break with 500% is obtained with less sulfur, the compound with the highest sulfur content shows an elongation at break about 350% (see Fig. 5). The reference shows an elongation at break at 390%. An increasing amount of MBT leads to lower elongations from about 400–340%. As there are high deviations up to $\pm 50\%$, the results are not significant. Less and more ZBEC

result in the same elongations at break. TiBTD shows higher elongations with more phr at 430%, this change lies within the deviation (see Fig. 5). The maximum tensile strength of the reference is 9.7 N mm⁻² (see Fig. 5). The tensile strength is decreasing slightly with more sulfur. With varying content of ZBEC lower values of tensile strength are measured. Lower TiBTD content leads to a slightly lower tensile strength. The tensile strength for the compounds with less MBT shows the same value, with further increase the maximum tensile strength decreases to 8.7 N mm⁻². All changes of tensile strength are within the deviation and are not significant. The ultimate properties elongation at break as well as tensile strength show greater deviations than the stress at 300% elongation. This is due to random defects in the material leading to the break which have a greater influence on those properties than the crosslink density. Therefore, the stress at 300% is more sensitive to crosslink density than elongation at break and tensile strength.

The compression set of the reference and the compounds with varying accelerator contents have the same value of about 36% (see Fig. 5). With increasing amount of sulfur, the compression set increases from 32 to 44%. Normally a higher crosslink density leads to lower compression set. But adding more sulfur shifts the relation sulfur/accelerator more towards conventional curing system resulting in more thermally labile crosslinking. As the compression set is measured at higher temperature it is possible that polysulfide crosslinks cleave and rearrange. While the crosslinks of the original state tend to return in the uncompressed state, newly formed crosslinking sites tend to fix the polymer network in the compressed state [25]. This results in a higher compression set. In following studies, the type of sulfur bonds will be analyzed in addition before and after the compression set measurement to confirm this hypothesis. There are no changes of compression set with varying amounts of accelerators.

Conclusion

All investigated methods can be used to determine the crosslink density of the examined compounds. Although the values differ strongly from method to method, a tendency can be derived from them. No significant changes in the crosslink density were found for varying amounts of the primary and different secondary accelerators.

Equilibrium swelling and freezing point depression exhibit measurement errors due to evaporation of the solvent, these are higher for the equilibrium swelling and lead to relatively high standard deviations. The freezing point depression is also depending on the fillers, since these, in addition to the crosslinking sites, determine the swellable volume in the solid. There is a need for more investigations with regard to adjustments like in the other methods.

In many cases the TSSR measurement curves showed artefacts that could not be explained yet and led to high standard deviations. Further investigations and possible adjustments for this method are planned. Future studies will also include the adsorption layer of polymer chains on carbon black as part of apparent filler volume fraction measured via bound rubber content and the investigation of crosslinking types with the thiol-amine-method. [8] First measurements with nuclear magnetic resonance spectroscopy are promising and are also considered in future studies as this adds a third physical measurement principle.

For following studies focused on substitution of fossil derived with sustainable raw materials the Flory-stress-strain measurements and freezing point depression will be used. They will be used complementary along with the nuclear magnetic resonance spectroscopy, also because of the different underlying test principles in order to get more reliable results and to be able to make recipe and process adjustments to maintain the required mechanical properties.

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