Influence of active fillers in elastomers on the anisotropic Mullins effect

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Summary
The first uniaxial extension of an elastomer causes stress softening (the Mullins effect) not only in this loading direction but in any other direction of subsequent extension. However, the Mullins effect is less pronounced after a change of loading direction than in the direction of the initial loading. As a function of the material’s deformation history, its mechanical behaviour is distinctly anisotropic. In the interests of providing a more comprehensive evaluation of the anisotropic Mullins effect, the role of the active fillers carbon black and silica was investigated. In particular, the influence of carbon black properties, such as specific surface area and structure, and of the amount of carbon black incorporated, was determined experimentally. Comparing carbon black- and silica-filled elastomers as well as different rubbers provided more insights into the anisotropic material behaviour of filled elastomers.

Introduction
Active fillers, such as carbon black or silica, are essential blend components of engineering elastomers and enable the material’s mechanical properties to be adapted as required to suit a particular technical application. Although the reinforcement of rubbers with active fillers is a phenomenon that has been known for a long time, the reinforcement mechanism in filled elastomers has not yet been satisfactorily explained [1]. The term “reinforcement” means, in principle, a marked increase in tensile strength, tear propagation resistance and abrasion resistance. An increase in stiffness can also be observed, which goes far beyond the values that would be expected based on the Einstein-Guth-Gold theory [2].

Reinforcement depends to a large extent on the properties of the polymer and filler. Filler properties include particle size or specific surface area as well as the structure of the filler aggregates. Together with the amount of filler in the rubber blend, the specific surface area of the primary particles determines the effective contact area between polymer and filler. The so-called structure represents the degree of irregularity of the aggregates, which increases with larger numbers of primary particles per aggregate and with greater degrees of branching.

With filler aggregates that are more highly structured, the number of possible conformations of the polymer chains under macroscopic deformation is lower than for less structured filler aggregates. The increase in stiffness caused by fillers is composed of the effect of the hydrodynamic reinforcement of the unfilled polymer network, the filler-polymer interaction, which contains both physical (van der Waals interactions) and chemical bonds, and the filler-filler interaction (filler network) [3, 4].

Over 50 years ago, Mullins found that the increase in stiffness in reinforced elastomers is accompanied initially by significantly different stress-strain curves in the first loading-unloading cycles under quasi-static loading conditions [5]. In subsequent cycles with a constant strain level, this process stabilises until the material behaviour reaches a steady state. This deformation-induced stress softening, also known as the Mullins effect, is caused primarily by changes in the filler-filler interaction. The extent of this softening phenomenon is also determined to a significant degree by the strain level and the stress...
conditions in the material’s deformation history. Apart from stress softening, i.e. loss of stiffness, the Mullins effect also includes the residual strain occurring in the direction of loading. Recent studies have focused explicitly on accounting for residual strain in phenomenological material models [6, 7].

The authors’ own investigations [8] have shown that the Mullins effect is a much more complex phenomenon than was previously assumed. Upon closer examination, it can be seen that deformation-induced stress softening entails significant anisotropy. This anisotropy was demonstrated experimentally by Mullins and has been confirmed by other authors [9-14]. However, existing material models are generally based on the assumption of isotropic softening, i.e. that deformation-induced stress softening causes identical material behaviour in all spatial directions [15], although experiments showed long ago that this assumption was incorrect. The few papers concerned with modelling the anisotropic Mullins effect refer to the lack of experimental material data [16-18].

In this study, therefore, appropriate quasi-static tensile tests were performed to investigate experimentally the direction-dependent behaviour exhibited by a material as a function of its particular deformation history. To validate the directional dependence and generate a certain breadth of experimental data, various vulcanisates were investigated in this programme, making it possible to identify the influence of the amount and type of filler used (carbon black, silica) and of the different rubber polymers on deformation-induced anisotropy.

VULCANISATES INVESTIGATED

Rubber blends

The following experimental investigations into the directional dependence of the Mullins effect were initially limited to the non-functionalised solution SBR (S-SBR) BUNA VSL 5025-2, a product of Lanxess Deutschland GmbH, Leverkusen, Germany, with a 46 wt% vinyl and 25 wt% styrene content (based on oil-free rubber). The oil-extended BUNA VSL 5025-2 with an oil content of 37.5 phr is used in highly reinforced, abrasion-resistant mouldings, particularly in tyre treads, in which good wet grip performance and particularly low rolling resistance are required. As well as the standard carbon black grades N220, N330 and N550, Ecorax S247 carbon black developed by Orion Engineered Carbons GmbH, Cologne, Germany, was also investigated as a reinforcing filler. Ecorax S247 is a nanostructure black and is used particularly in truck tyres. It has a moderate specific surface area with a very high structure of the aggregates, leading to improved filler-polymer interaction and thus to reduced internal friction (hysteresis) [19]. In addition, the influence of Ultrasil 7000GR silica from Evonik Industries AG, Wesseling, Germany, on deformation-induced anisotropy was determined for the above rubber polymer and compared with the carbon black-filled rubber vulcanisates. This investigation included experimental identification of the influence of different silanes on silica reinforcement, and also used varying filler contents from 20 to 80 phr. All the details of the formulations are compiled in Table 1.

Table 1. Blend formulations of the S-SBR vulcanisates investigated

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-SBR (solution styrene-butadiene rubber)</td>
<td>100</td>
</tr>
<tr>
<td>Oil extension</td>
<td>37.5</td>
</tr>
<tr>
<td>Carbon black</td>
<td></td>
</tr>
<tr>
<td>N220, N330, N550, S247</td>
<td>20-80</td>
</tr>
<tr>
<td>Silica</td>
<td></td>
</tr>
<tr>
<td>Ultrasil 7000 GR</td>
<td>80</td>
</tr>
<tr>
<td>Silane</td>
<td></td>
</tr>
<tr>
<td>Si69 (TESPT)</td>
<td>6.4</td>
</tr>
<tr>
<td>VP Si363</td>
<td>9.0</td>
</tr>
<tr>
<td>Vulcanox 4020</td>
<td>2</td>
</tr>
<tr>
<td>Protektor G 310B</td>
<td>2</td>
</tr>
<tr>
<td>Viveatec 500</td>
<td>8.75</td>
</tr>
<tr>
<td>ZnO</td>
<td>2</td>
</tr>
<tr>
<td>DPG</td>
<td>2</td>
</tr>
<tr>
<td>Vulcanox HS/LG</td>
<td>1</td>
</tr>
<tr>
<td>Aktiplast ST</td>
<td>3.5</td>
</tr>
<tr>
<td>CBS</td>
<td>1.5</td>
</tr>
<tr>
<td>TBzTD</td>
<td>0.2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2</td>
</tr>
</tbody>
</table>

Test apparatus

The uniaxial, quasi-static tensile tests were performed using a Z-010-type, spindle-driven, twin-column universal tensile tester from Zwick/Roell, Ulm, Germany, with 1 kN force transducers. Pneumatic sample grips with a constant clamping force of max. 6 kN ensure that samples do not slip out of the clamps, permitting the experimental investigations to be carried out accurately and reproducibly. In all of the test results described below, the samples were stretched with a constant strain rate of 10% per minute. The strain was measured by non-contact means using the Aramis optical deformation measurement system from GOM, Braunschweig, Germany, which determines the strain online with an accuracy of 0.01%, based on grey-scale correlation, and controls the tensile deformation.
MEASUREMENT OF THE ANISOTROPIC MULLINS EFFECT

Experimental procedure

For the experimental measurement of the anisotropic Mullins effect, the standard uniaxial tests have to be extended since directional dependence can only be detected by multi-stage, quasi-static tests in which the loading direction is changed. In connection with this, a number of studies have already proposed various procedures and specimen shapes. Besdo and Ihlemann [20], for example, were able to establish anisotropy in shear tests in which cylindrical specimens were subjected to positive and negative shear deformations in one plane. Pawelski [12] carried out investigations on a cross-shaped specimen in which the elastomer was first stretched several times in one direction and then again after rotating by 90° relative to the previous direction. Mullins [9] and later Diani [21] repeatedly stretched and unloaded a relatively large sample to a defined strain level in a first step. A smaller specimen was then taken from this sample at a defined angle to the previous loading direction, so that the material could be stretched in a new loading direction in the second step.

Based on Mullins' work, a large, rectangular sample (dimensions excluding clamping area: 140 x 40 x 2.0 mm³) was first cyclically stretched to a defined uniaxial strain level in the longitudinal direction (Figure 1). After five to ten uniaxial loading and unloading cycles, the Mullins effect is fully applied in this direction and a steady state is reached for the material behaviour. This is referred to below as the primary loading. A smaller S3A specimen (dumbbell specimen according to DIN 53504) was then stamped out of this rectangular sample in various positions, so that uniaxial deformation could take place in a new loading direction (secondary loading). The smaller S3A specimen was always central within the larger rectangular sample. This area of the sample had experienced virtually pure uniaxial deformation in the primary loading phase. For each S3A sample that was investigated, a rectangular sample had been subjected to previous uniaxial damage, on the one hand to ensure that every S3A sample had uniaxial damage in its deformation history prior to the secondary loading phase and on the other hand to enable the reclamping period of 10 minutes between primary and secondary loading to be reproduced, as shown in Figure 1.

The primary loading therefore produces a material that has been subjected to previous damage in the longitudinal direction of the rectangular sample. This deformation history which now exists has provided the previously isotropic elastomer with anisotropic mechanical properties. The actual measurement and characterisation of the deformation-induced anisotropy then come from the secondary loading. The test design and set-up illustrated in Figure 1 indicate that the primary residual strain relaxes during the reclamping period. This will be discussed in more detail below. The need to account for the remaining residual strain in terms of directional dependence is associated with its direct relationship with anisotropic stress softening [22]. The axis of strain therefore relates to the reference strain measure, so the secondary loading in the 90° direction (sixth cycle) begins in the negative strain range. This means that deformation work first has to be performed in order to recreate the initial shape of the virgin specimen. Precise explanations will be given in this section.

To illustrate the test method, the stress-strain diagram for a carbon black-filled S-SBR is shown in Figure 2, with the secondary loading direction orthogonal to the primary direction. N330 carbon black was chosen as an example here, in a content of 80 phr, but in principle the behaviour is similar for all carbon black grades. The diagram only shows the first, fifth (primary), sixth and tenth (secondary) loading and unloading cycles. The first loading curve in the 90° direction (secondary loading) shows significantly different stress-strain behaviour compared with the stress-softened loading curve in the primary loading phase. This shows that the uniaxial stress softening in the first loading direction results in the occurrence of the Mullins effect in each subsequent loading direction. However, with extension after a change in the loading direction, the Mullins effect is not as pronounced as in the case of secondary loading applied in the same direction as the primary direction of damage. Because of its previous damage following the primary loading, therefore, the elastomeric material is distinctly anisotropic [23].

Figure 1. Test methodology for measuring the anisotropic Mullins effect
Accounting for residual strain

The stress-strain curves in Figure 2 are shown in two different strain measures; on the one hand the current strain measure as determined by the testing machine and on the other hand the reference strain measure (in the 90° direction in Figure 2), which relates to the virgin material. It is necessary to differentiate between these strain measures so that the direction-dependent strain levels are comparable in the secondary loading phase and therefore the deformation work of any secondary loading direction can also be compared with the deformation work of the primary loading phase. The above strain measures differ in principle through different stress-free states and strain levels, which are assigned to the secondary loading applied in each case. The current strain measure does not account for the elastomer sample’s deformation history and only reflects the strain values that can be determined by measurement. This means that its stress-free state is assigned to the strain ε = 0, i.e. the measurement origin, which is redefined by the reclamping between the primary and secondary loading phases.

The reference strain measure, on the other hand, "remembers" the previous loading (in this case the primary loading) experienced by the material and accounts for the resulting, primary residual strain. Consequently, the current strain measure, with its reference to the previously damaged elongated elastomer, results in lower deformations than those described by the reference strain measure (virgin elastomer without elongation). Accordingly, as a result of converting the current strain values determined by measurement into reference strains, the measured stress-strain curve is stretched further in the secondary loading phase.

The reverse situation can be seen in the 90° direction, as illustrated by the example in Figure 2. When the S3A sample is taken in the transverse direction from the previously damaged rectangular sample, a residual compression (transverse contraction) occurs as a result of the primary loading. The starting length used in the secondary loading phase is therefore shorter than the starting length of the virgin sample. In order to calculate back to the reference strain measure and thus to relate the deformation of the secondary loading to the virgin material prior to the primary loading, the relevant stress-strain curve is distorted into the compression range (Figure 2).

The reference strain axis in Figure 2 shows that, in contrast to the current strain measure, a uniaxial deformation of only ε = 91.3% is achieved and therefore the S3A sample has experienced less stretching than desired in the secondary loading direction. Consequently, in the test method used here, the primary residual strain is factored in analytically, as a function of direction, to the strain level to be applied and the tensile tester is controlled accordingly (Figure 1).

Similarly to the starting length and the associated differentiation between the current strain measure and the reference strain measure, the primary residual strain has an impact on the effective area, requiring correction. However, the effect of residual strain on
measured stresses is significantly lower and is therefore not shown in Figure 2 but is taken into account in the test results. This procedure enables the same strain levels to be applied to the elastomeric material in all of the secondary loading directions, based on the reference strain measure, so that the deformation work (per unit volume) in the secondary loading phase is comparable.

For a secondary loading direction other than the 0° and the 90° direction, the primary residual strain can only be factored in using the theory of continuum mechanical modelling. The direction-dependent determination of the primary residual strain or residual stretch \( \lambda_{res} = 1 + \varepsilon_{res} \) results from Equations 1 to 3. The line element \( dX \) in the initial non-deformed configuration is converted to the current (deformed) configuration \( dx = F \cdot dX \) using the deformation gradient \( F \). The length of \( dx \) is thus obtained as:

\[
\|dx\|^2 = dx \cdot dx = Fdx \cdot Fdx = F^T F dX = dX C dX
\]

where \( C = F^T F \) represents the right Cauchy-Green tensor. In the event of uniaxial strain, \( F \) can be represented as a matrix which only has entries on the main diagonal. These entries correspond to the strains in the respective eigendirection. The line element \( dX \) is now defined as a function of the angle \( \alpha \) between the first and the current loading direction (Figure 1) as:

\[
dX = [\cos(\alpha), \sin(\alpha), 0]^T
\]

where \( \lambda_{res} \) is the residual stretch in the direction of damage [24].

\[\lambda_{res}(\alpha) = \sqrt{\lambda^2_{res}(\alpha) \cos^2(\alpha) + \frac{1}{\lambda_{res}} \sin^2(\alpha)} \]

Recovery effects

Despite the low rates of deformation used for these quasi-static investigations, viscoelastic effects cannot be avoided in the measured stress-strain curves. On the one hand, this is made clear by the hysteresis loops that occur during the loading and unloading process, the area of which represents a measure of the dissipated energy. On the other hand, relaxation of the residual strain can be observed in the stress-free state. Since the primary residual strain is very important in the procedure being applied here and has a significant influence on the secondary loading, the residual strain continues to be measured in the stress-free state after the 5th cycle. This is necessary in order to reproduce the relaxation of residual strain during the reclamping period between the large and small samples, as illustrated in diagrammatic form in Figure 1, and to transfer the primary residual strain to the secondary loading without any viscous elements. The test results show that the residual strain undergoes only negligible change after a holding time of around 10 minutes in a stress-free state.

Upon closer examination, it is found that the viscous elements in the elastomeric material have not yet subsided completely several days after a deformation (Figure 3). To illustrate this phenomenon, a large sample was first pre-damaged up to 90% of its ultimate elongation. A circular sample was then taken from the pre-damaged material immediately after this stretching. The subsiding of the viscoelastic effects and the associated development of the circular sample into an elliptical shape were observed over a prolonged period. Viscoelasticity is wholly responsible for this reversible element of residual strain.

However, this recovery cannot be observed in the induced stress softening. Bueche [25] found that no healing of the elastomer takes place without external energy input. These investigations also provided experimental confirmation of the fact that the Mullins effect is an irreversible phenomenon and is retained in the material after a long stress-free period.

\[\text{Figure 3. Relaxation of residual strain after loading, illustrated with a circular sample}\]
Quantifying the Anisotropic Mullins Effect

To quantify the deformation-induced anisotropy of the Mullins effect, the deformation work was determined for the first, fifth (primary), sixth and tenth (secondary) loading cycles. The ratio of these areas is used here as a measure of anisotropic stress softening (Equations 4-6, Figure 4). The relative reductions in deformation work are defined as follows in the form of energy losses [23]:

Uniaxial energy loss (Mullins effect) = 1 - \(\frac{W_{5\text{th cycle}}}{W_{1\text{st cycle}}}\)  (4)

Anisotropic (primary) energy loss = 1 - \(\frac{W_{6\text{th cycle}}}{W_{1\text{st cycle}}}\)  (5)

Secondary energy loss (Mullins effect) = 1 - \(\frac{W_{10\text{th cycle}}}{W_{6\text{th cycle}}}\)  (6)

with,

\(W_{1\text{st cycle}}\) \(\rightarrow\) deformation work (per unit volume) for the virgin material loading

\(W_{5\text{th cycle}}\) \(\rightarrow\) deformation work (per unit volume) for the stress-softened material, primary loading

\(W_{6\text{th cycle}}\) \(\rightarrow\) deformation work (per unit volume) for the first secondary loading

\(W_{10\text{th cycle}}\) \(\rightarrow\) deformation work (per unit volume) for the stress-softened material, secondary loading.

The uniaxial energy loss (Mullins effect) represents the stress softening observed in standard uniaxial tensile tests (Figure 4b). As with the uniaxial energy loss, the anisotropic (primary) energy loss or anisotropic (primary) Mullins effect also relates to the first loading of the virgin material in the primary loading phase (Figure 4c). Thus, ignoring viscoelastic effects during the reclamping process, the uniaxial energy loss simultaneously describes the anisotropic energy loss in the 0° direction. In contrast to the previous measures, the secondary energy loss (Mullins effect) relates to the first extension in the secondary loading phase and thus represents the additionally occurring Mullins effect (Figure 4d) [23, 26].

DEFORMATION-INDUCED ANISOTROPY IN FILLED S-SBR

Variation of carbon black content and grade

The test results presented in Figure 5 for the deformation-induced anisotropy of the Mullins effect relate to carbon black-filled S-SBR, making it possible to identify the influence of the carbon black content (Figure 5a) and carbon black grade (Figure 5b) on direction-dependent stress softening.

The direction-dependent Mullins effect is illustrated using a comparison of the values for deformation work from Equations 4 to 6. At the same time, the strain measures (current and reference strain measures) introduced in the previous section are compared to illustrate their influence on the test results. Since the current strain measure in the primary loading phase corresponds to the reference strain measure, there are no differences for uniaxial energy loss (Mullins effect) in the illustration of the results, since the secondary loading phase is not taken into account here.

The anisotropic energy loss or anisotropic Mullins effect in the 90° direction in Figure 5a confirms the deformation-induced anisotropy that was already established in Figure 2. Thus, uniaxial stress softening also leads to softening of the elastomeric material orthogonal to the primary loading direction. When the material is stretched after changing the loading direction, the Mullins effect is less pronounced than in the case of secondary loading in the direction of damage. As with the uniaxial Mullins effect, increasing softening can be observed after a change in direction in highly filled vulcanisates. A comparison between the current and the reference strain measures shows...
a weaker influence of filler content on the anisotropic Mullins effect in the illustration with the reference strain measure (Figure 5a). Taking into account the primary residual strain (illustration with the reference strain measure), this can be attributed to the fact that the elastomer sample is loaded with higher deformation. Particularly in the case of the highly filled vulcanisates, which display high primary residual strain, the differences are more marked [14].

The reverse is the case with the secondary Mullins effect, which represents the additional stress softening in the secondary loading phase. The higher energy losses when the primary residual strain is taken into account are also caused by the higher deformations applied. Both strain measures reflect a higher secondary energy loss with increasing carbon black contents.

When the carbon black grades are compared in Figure 5b, in contrast to the uniaxial Mullins effect, differences in behaviour are identified for both the anisotropic and the secondary Mullins effect. While N220 carbon black experiences the highest energy loss and N330 the lowest in the case of the uniaxial Mullins effect, the highest anisotropic Mullins effect (current strain measure) occurs with N330 carbon black. The anisotropic (primary) Mullins effect in the reference strain measure, on the other hand, is greatest with N220 and N550 carbon blacks. These grades also display lower residual strains after loading, resulting in lower strain levels (based on the current strain measure) for the secondary loading in the 90° direction. This also explains why the highest secondary stress softening (reference strain measure) is observed with N330.

After the advantages and disadvantages of the two strain measures for the investigations into directional dependence in the 90° direction were considered, the need to relate the secondary loading to the reference strain measure is clearly shown in Figure 6. While the current strain measure reflects a lower anisotropic stress softening for small changes in direction, this effect is reversed for large changes in direction. This effect also reflects the reversal of the primary residual strain into a so-called residual compression as the change in direction increases for the secondary loading stage. In the depiction of the current strain measure, only the secondary Mullins effect correlates with the secondary loading direction, whereas the reference strain measure also clearly shows the deformation-induced anisotropy when the anisotropic Mullins effect is considered.

Deformation-induced anisotropy in silica-silane systems

Silica forms a significantly stronger filler-filler interaction than carbon black in rubber blends. Owing to the polar surface of silica particles, this filler cannot be adequately incorporated into non-polar rubber polymers in its original form. Hydrophobic treatment of the silica particles is necessary. To enable silica-filled rubber blends to be used in combination with SBR rubber in tyre treads, silanes have to be added. The addition of silanes modifies the surface
of the hydrophilic silica (hydrophobic treatment) and thus increases its compatibility with rubber. In the case of functional organosilanes, such as bis(triethoxysilylpropyl) tetrasulfide (TESPT, Si69), chemical bonds are also formed between the silica agglomerates and the polymer chains. The formation of filler-polymer bonds simultaneously reduces filler-filler bonds or the formation of a filler network. This material technology is crucial in reducing the rolling resistance of tyres.

The bifunctional organosilane VP Si363, developed by Evonik Industries AG, Wesseling, was developed from the known product Si69, which is used in silica-silane technology. The use of VP Si363 is associated with an 80% reduction in VOC (volatile organic compound) emissions during the manufacturing process and therefore meets stricter environmental requirements. In addition, rolling resistance can be reduced by a further 10% with the use of VP Si363 in tread blends [27, 28].

VP Si363 has a molecular weight almost four times as high as that of TESPT (Si69), which requires a greater proportion of silane in a blend. If the high coupling yield (filler-polymer bonds) of VP Si363 is taken into account based on the content of mercapto groups, less than twice the amount of TESPT is needed [28].

The influence of the various silanisation mechanisms on quasi-static, direction-dependent material behaviour is shown in Figure 7, with the tests described below all shown in the reference strain measure. While the silica-silane systems react to high deformations in particular with significantly higher engineering stresses as a material response, vulcanisates with untreated silica display substantially softer material behaviour (Figure 7a-c). The higher deformation work in the vulcanisates with silane can therefore be attributed to the bound rubber. The stiffer material behaviour thus expresses a better filler-polymer interaction at high deformation. The high stress-strain gradient in low strain ranges and the marked stress softening with untreated silica indicate that silica-filled S-SBR without the addition of silanes tends to form a strong filler network (Figure 7a).

If a secondary loading phase follows after a 90° change in direction, it can be seen from Figures 7a-c that, for silica-filled elastomers too, the first loading in the new direction lies below the virgin material curve. As is the case for carbon black reinforcement, therefore, deformation-induced stress softening is also strongly anisotropic in silica-filled elastomers. The anisotropic Mullins effect (energy loss) is strongest in the S-SBR with untreated silica, in other words without the addition of silanes (Figure 7d), whereas the greatest additional induced energy loss is experienced by the vulcanisate with Si69. It should be added that this silica-silane system also requires the highest deformation work for the defined strain level (Figure 7b) [27].

Furthermore, the test results show that the modified silica also results in more pronounced anisotropy after previous loading compared with a standard carbon black (N330) (Figure 7d).

The influence of the primary residual strain on the secondary energy loss can be better explained by Figure 8. The high primary residual strain for the organosilane Si69 means that lower strain levels...
are reached for small changes in direction based on the current strain measure, and this effect is jointly responsible for the lower secondary energy loss. If the change in direction is increased, the secondary strain level increases most strongly for Si69 based on the current strain measure. With carbon black-filled S-SBR, on the other hand, the additional secondary Mullins effect (energy loss) shows less dependence on the secondary loading direction, which in turn can be attributed to the low level of primary residual strain (Figure 8b).

**Anisotropic Mullins effect in different elastomers with silica reinforcement**

Once the influence of the filler on the reinforcement mechanism and anisotropic Mullins effect had been characterised, the base polymer from the blend formulation in Table 1 was varied and its deformation-induced, anisotropic material behaviour was investigated (Table 2). S-SBR rubber molecules with functional groups distributed along the entire length of the carbon chain promote a more intensive interaction between filler and polymer. This gives rise to a vulcanisate with lower hysteresis, resulting in optimisation of the rubber blends used in tyre treads [29].

Further silica-silane systems were investigated based on natural rubber (NR) and NR blended with polybutadiene (BR). Silica-filled NR and NR/BR vulcanisates are of interest to the truck tyre industry and are a topic of current research. For a long time, the use of low-hysteresis silica blends in truck tyres was not considered feasible because of the high abrasion resistance required. However, it has been shown that precipitated silica with a high BET surface area is indeed suitable for use as a filler in NR blends, and therefore in commercial vehicle tyres. Even a blend of NR and BR, which increases the life of tyres, can incorporate silica-silane technology [30].

**Comparison between carbon black and silica**

Figure 10 compiles and compares both the uniaxial and the anisotropic Mullins effect (energy loss) of the carbon black- and silica-filled vulcanisates investigated within the framework of this study. In order to ensure that the
various vulcanisates with different types and amounts of filler can be compared with one another, the stress softening values are plotted over the deformation work for the virgin material (per unit volume) $W_{1\text{st cycle}}$.

In the comparison of the uniaxial Mullins effect, it can be seen that all of the carbon black-filled elastomers in the representation selected in Figure 10a lie on an imaginary diagonal or exhibit a virtually constant ratio between the uniaxial Mullins effect and the deformation work of the virgin material. The silica-filled elastomers, on the other hand, deviate from this region. The vulcanisate without added silane, the silica-filled natural rubber and the NR/BR blend lie above this region. This indicates that the mechanical behaviour of these vulcanisates is “poorer” since, although no pronounced reinforcement is present, a high level of stress softening is caused by deformation. The opposite is the case for S-SBR containing silica silanised with Si69 or Si363. The associated values lie below this region and thus display a less pronounced Mullins effect in relation to the deformation work performed on the virgin material.

The behaviour observed in the anisotropic, primary Mullins effect in Figure 10b is similar to that found with the uniaxial Mullins effect. However, it must be pointed out that there is greater scattering with the anisotropic Mullins effect, which can be attributed to the influence of the primary residual strain. In summary, Figures 10a and b demonstrate that the elastomers in which low primary stress softening occurs also exhibit low deformation-induced anisotropy of the Mullins effect.

**DISCUSSION**

The maximum level of deformation applied in the deformation history of filled elastomers has a major influence on their quasi-static, mechanical material behaviour, which is characterised by the Mullins effect, i.e. the stress softening that occurs. In addition, the Mullins effect is substantially affected by the change in loading direction relative to the previously applied load. The elastomer therefore displays direction-dependent material behaviour as a result of its deformation history.

The deformation-induced anisotropy of the Mullins effect can only be identified by multi-stage tests in different loading directions. These experiments require a suitable specimen geometry and appropriate test methodology. The time and effort involved in the experimental detection of this phenomenon can certainly provide an explanation for the paucity of studies in this field.

**CONCLUSIONS**

The investigations presented in this paper provided experimental proof that, in a new loading direction, previous loading leads to material behaviour that differs significantly from the stress-strain behaviour of both the virgin material and of material that has been stress-softened in the same direction. This proves on the one hand that uniaxial stress softening in one loading direction entails the occurrence of the Mullins effect in every subsequent loading direction. On the other hand, it can also be observed that the Mullins effect is less pronounced after a change in loading direction than in the case of a secondary loading in the direction of damage. The material behaviour therefore depends substantially on the secondary loading direction. The experimental investigations also show that the first loading in the new direction induces a secondary, additional stress softening.

In order to demonstrate the deformation-induced anisotropy of the Mullins effect, the deformation work per unit volume was compared for the different loading cycles. This made it clear that the anisotropic energy loss or anisotropic Mullins effect decreases as the change in loading direction increases for the secondary loading phase. Conversely, the additionally induced Mullins
effect in the secondary loading phase becomes more pronounced as the angle between the loading directions is increased.

This approach requires the primary residual strain to be taken into account, although this can only be achieved mathematically and not experimentally. The primary residual strain has a major effect on the secondary strain levels and thus on the resulting deformation work. This study therefore differentiated between the current strain measure and the reference strain measure. The current strain measure expresses the measured deformations in the elastomer that has been stress-softened in the primary loading phase. The reference strain measure, on the other hand, processes the measured data, accounting for the primary residual strain in the secondary loading phase and thus referring to the virgin material.

The phenomenon of direction-dependent stress softening was successfully demonstrated in all of the elastomers investigated in this study. It was found that the extent of the anisotropic (primary) Mullins effect is substantially affected by the quantity and grade of filler, the reinforcing system (carbon black or silica) and the rubber polymer used. A correlation was also identified between the known uniaxial Mullins effect and the anisotropic Mullins effect. Elastomers in which a weak Mullins effect already occurs after previous loading also exhibit a weakly anisotropic material behaviour based on their deformation history. Similarly, it was found that, of the elastomers investigated here, the vulcanisates with a strong tendency towards stress softening also exhibit pronounced deformation-induced anisotropy of the Mullins effect.

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