**The Effect of Boundary Conditions on the Failure Behavior of Rubber Vulcanizates under Tensile Deformation**

**Introduction**

The estimation and the prediction of the mechanical properties and failure behavior of a rubber product depend on boundary conditions. They are depending on the shape of the rubber product and the manner how external stress is applied under operating conditions. In spite of the industrial as well as academic importance of this problem, the origin of these boundary conditions and their impact is not completely understood.

Generally, for elastic bodies tensile deformation regimes can be distinguished into two types of elongation: simple and pure elongation. In Figure 1 the deformation principles of both types are shown schematically. Simple elongation (Figure 1a) is plane stress deformation with volume consistency due to low degree of transversal constraints, e.g. uniaxial stretching of a dog-bone tensile specimen. The dimensions \( (x, y, z) \) of such a specimen change under elongation as

\[
x \rightarrow x \cdot k^{-1}, \quad y \rightarrow y \cdot k^2, \quad z \rightarrow z \cdot k^{-1}.
\]

\( k^2 \) represents the strain ratio leading to an elongation of the specimen in \( y \)-direction. Due to the assumption of volume consistency for uniaxial tension the dimensions in \( x \)- and \( z \)-direction are reduced by \( k^1 \).

Contrary, pure elongation (Figure 1b) is dominated by a multiaxial stress state with constraint transversal strain accompanied by the possibility of dilatation, e.g. stretching of a disk-shaped pancake specimen. In this case the dimensions of a specimen \( (x, y, z) \) become

\[
x \rightarrow x, \quad y \rightarrow y \cdot k, \quad z \rightarrow z.
\]

For rubber vulcanizates, an elementary experimental testing method with a low degree of strain constraint is the conventional uniaxial tensile test. Due to the Poisson effect, rubber can freely compress in directions perpendicular to the axis of tension for this type of deformation. It is well known that there are two independent moduli representing the elasticity of solid, isotropic materials: One is the shear modulus (G), which represents the resistance of deformation without any change of volume. The other one is the bulk modulus (K), which represents the resistance against volume deformation. The Young’s modulus (elastic modulus under simple elongation, \( E_s \)) can be expressed as follows

\[
E_s = \frac{3G}{1 + \frac{G}{5K}}
\]

where \( G \) and \( K \) represent shear and bulk modulus, respectively. Furthermore, \( K \) can be expressed as follows using the Young’s modulus \( E_s \) and the Poisson ratio \( \nu \).

\[
K = \frac{E_s}{3 \cdot (1 - 2\nu)}
\]

For unfilled rubber vulcanizates the Poisson ratio is assumed to be approximately 0.5. In that case, \( K \) becomes infinite and the elastic deformation under plane stress is dominated by shear behavior.

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In contrast, the deformation under pure elongation is characterized by constraint strain. Thus, multiaxial stress is caused in rubber vulcanizates if the deformation in directions perpendicular to the axis of tension is entirely suppressed. Under such conditions a large amount of volume change can be observed and is attributed to the evolution of structural changes. For example so-called pancake specimens are used to generate high strain constraints. A.N. Gent and C. Wang, P.A. Kakavas as well as N.A. Hocine et al. [1-3] have studied experimentally the deformation of rubber vulcanizates under pure elongation using pancake specimens. However, it is generally confirmed that it is practically difficult to perform this test method, because the specimens tend to fail at the interfaces between the rubber sample and the rigid plates due to the high strength of rubber compared to the limited adhesion strength at the interface.

The elastic modulus at pure elongation ($E_p$) can be expressed using Lindsley’s approach [4] with the following equation.

$$ E_p = \frac{E_s \cdot (1 - \nu)}{(1 - 2\nu) \cdot (1 + \nu)} $$  

In general, $E_p$ is higher than $E_s$. Particularly, for rubber vulcanizates the value of $E_s$ becomes extremely high. This means that the contribution of $K$ is strong during the tensile deformation of pancake specimens.

Furthermore, it is also known from the literature [5] that high strain constraints occur close to a notch or a crack tip. Results from stress analysis by fracture mechanics show, that even if macroscopically applied strain is small constraint strain is occurs. Due to the generation of multiaxial stress the nucleation and the growth of nanoscopic cavities and subsequently the formation of cracks is initiated. This has already been confirmed for some non-rubber polymeric materials [6-8]. However, from the mechanical point of view, the understanding of failure behavior of rubber vulcanizates is still insufficient. To improve the durability of rubber parts, it is essential to understand rubber failure processes comprehensively by investigating both, simple elongation dominated by plane stress deformation and pure elongation characterized by multiaxial stress. The focus of this study is the investigation of the mechanical and the failure behavior of unfilled and carbon black filled styrene-butadiene-rubber vulcanizates under pure elongation. The results will be discussed with respect to the mechanical and failure behavior of rubber vulcanizates applied to simple elongation. For experimental investigations of the dilatation of pancake specimens under tensile deformation dilatometry and computed tomography will be synchronized with tensile tests under static as well as cyclic loading.

**Experimental**

**Materials**

The unfilled and carbon black (CB) filled rubber vulcanizates were prepared using styrene-butadiene-rubber (SBR) Nipol 1502 (ZEON Co., Japan). The mixing process consisted of two steps: (i) 100 parts per hundred rubber (phr) of SBR were mixed with 2.0 phr of zinc oxide and 3.0 phr of stearic acid and 1.5 phr of sulfur and 1.0 phr of two kinds of accelerator (N-tert-butyl-2-benzothiazolesulfenamide and 1,3-Diphenylguanidine) by a two roll mixing mill at 80°C. The obtained green rubber compounds were mixed with 1.5 phr of sulfur and 1.0 phr of two kinds of accelerator (N-tert-butyl-2-benzothiazolesulfenamide and 1,3-Diphenylguanidine) by a two roll mixing mill at 80°C. The obtained green rubber compounds were vulcanized to sample sheets with a thickness of 1 mm using a heating press at 170°C. The vulcanization time (t90) was determined from the results of “Curelastmeter” (JSR Trading Co., Japan) at 170°C. t90 for the filled and unfilled samples were 12 and 14 minutes, respectively. To prepare the pancake specimens, the upper and bottom surfaces of the rubber sample were fixed between two highly rigid polycarbonate sample holders using Loctite 406 (Henkel, Germany) as superglue. The pancake specimen geometry has a diameter $D = 20$ mm, thickness $h = 1$ mm and resulting shape factor $S = 5.0$. For rubber pancake specimens the shape factor was introduced by A.N. Gent [9] to quantify the degree of strain constraints as follows

$$ S = \frac{D}{4h} $$

**Measurements of cavity formation by dilatometry**

Using a customized dilatometer cell as a testing device, the volume change of a pancake specimen during tensile loading was measured. Details of the dilatometer cell and the testing procedure are described elsewhere [10]. Generally, the pancake specimen was fixed in a glass vessel filled with a liquid. The volume change during deformation was estimated by the displacement of the liquid column in a calibrated glass capillary, using a video camera system. In this work, the relative volume change, which is the absolute volume change divided by the initial volume, is termed as apparent volumetric strain.

**Measurements of cavity formation by computed tomography**

To characterize cavity formation and growth in rubber vulcanizates during tensile loading, in-situ computed tomography (in-situ CT) measurements were performed at elevated loading steps. Measurements were done at a X-ray CT device from FineTec (FCTS 160 – IS) with 100 kV/100 µA, combined with a 4 column tensile machine 2250 (Zwick, Germany). The scan time was 15 min (1440 radiographs over a 360° rotation, exposure time 640 ms), the spatial resolution 1 Voxel = 15 µm.
Results

Mechanical behavior under static pure elongation

Figure 2 shows the nominal stress and the corresponding apparent volumetric strain as a function of apparent strain for both unfilled and 48 phr CB filled SBR under pure elongation. The mechanical behavior can be separated into four stages: (i) When the applied strain is low, stress increases linearly with increasing strain. The high stiffness is due to the strong contribution of the bulk modulus caused by strain constraints. (ii) Once stress exceeds a certain threshold, stress ceases to increase, as though a critical stress value comparable to the yield point of thermoplastics has been reached. (iii) As the applied strain increases beyond the threshold of elastic volumetric deformation, stable deformation occurs under almost constant stress. (iv) For filled rubber, failure occurs at a critical strain level after stress begins to increase once again due to orientation hardening. This effect is ascribed to molecular orientation in the rubber-filler network that is characterized by strain concentration between adjacent CB particles. For pure elongation, the stress-strain curve of filled rubber is similar to stress-strain curves of thermoplastic polymers that plastically deform due to yield. For unfilled rubber, failure occurs when the stress decreases stronger at a critical strain level, here no orientation hardening occurs. For both materials, apparent volumetric strain is present when tensile loading passes the threshold of elastic volumetric deformation (ii). This threshold can be determined: For unfilled rubber the value is below 0.20 of strain; for filled rubber it is below 0.05 of strain. In stage (iii), apparent volumetric strain increases in a linear fashion. Since the apparent volumetric strain is controlled by constraint of strain, it is expected that the difference in apparent volumetric strain between unfilled and CB filled rubber is not significant. In the final stage the values of apparent volumetric strain is smaller for filled rubber than that of unfilled rubber. This could be explained by the contribution of bulk modulus of CB particles.

Figure 3 shows typical CT results for tensile deformation of an unfilled SBR under static pure elongation. The middle slices are reconstructions of the 3D object perpendicular to the loading direction. The CT images show the cavity population at different apparent strain values (8% to 35% of strain). In general, when strain reaches the threshold of elastic deformation, regions of lower density arise. These regions, in which density decreases, become more prominent and distributed throughout the entire rubber specimen with increasing strain. At the same time, the density in some of these regions decreases even further, leading to the formation of spatial regions that can be considered as cavities (Figure 3). The size and number of these regions of significantly lower density expands in conjunction with further increasing strain. Finally, the regions with lowered density will join together leading to coalescence of cavities (not shown here). The connected cavities further expand leading to the internal destruction of the specimen due to increased local stress exceeding the tensile strength of the rubber vulcanizates.

Mechanical behavior under cyclic pure elongation

Figure 4 shows the nominal stress and the corresponding apparent volumetric strain of 48 phr CB filled SBR as a function of apparent strain under cyclic pure elongation. When the maximum applied strain is lower than the threshold of elastic deformation, the stress-strain curve of the rubber specimen behaves like those of an elastic body. As a consequence, the amount of energy loss, as determined from the hysteresis loops, is negligible. The same tendency can also be seen in the apparent volumetric strain curves. As the amplitude of strain increases, the hysteresis becomes higher, and consequently, the amount of energy loss increases. When the amplitude of stress reaches the critical threshold, the amount of energy loss begins to increase rapidly. The hysteresis loops of apparent volumetric strain increase simultaneously. It is worth to note, that the amount of apparent volumetric strain remains large in the unloading phase compared to corresponding strain values during loading. This indicates that the SBR pancake specimen cannot recover as readily from damage that has been formed inside. Even after the maximum cyclic loading strain, residual apparent volumetric strain remaining from the application of larger loads can be detected. The effect becomes predominant with increasing strain. However, apparent volumetric
strain decreases during unloading due to relaxation.

In Figure 5 typical fracture surfaces of unfilled and 48 phr CB filled SBR pancake specimens are shown. For both materials, interfacial failure can be excluded, since the fracture plane is almost in the middle of the specimen’s thickness. Furthermore, a homogeneous distribution of spherical cavities is clearly visible for unfilled and CB filled SBR. It was observed, that the previously discussed rupture process is initiated by the failure of the remaining rubber in the regions between the expanded cavities.

Discussion

In this work, the mechanical properties and the failure behavior of SBR vulcanizates have been investigated under pure elongation. In the following, these results are compared and discussed with respect to the behavior of rubber vulcanizates applied to simple elongation by conventional uniaxial tensile tests. Furthermore, potential mechanisms for damage formation in general and in the crack tip zone are described and discussed.

A literature review on static tensile deformation behavior: Simple elongation vs. pure elongation

Y. Merckel et al. [11] investigated SBR rubber vulcanizates considering stress-strain and apparent volumetric strain under simple elongation. It was pointed out that for unfilled rubbers no clear increase in apparent volumetric strain was observed. However, for filled SBR a critical strain range corresponding to the onset of dilatation was determined. Once the tensile strain exceeds that critical level, the Poisson ratio drops from 0.5 and the volume of the sample begins to increase. As the content of CB increases, this critical strain value decreases and the increase in apparent volumetric strain becomes more significant.

H. Zhang et al. [12] synchronized small angle X-ray scattering (SAXS) with standard tensile tests for vulcanized CB filled SBR. They pointed out, that the expansion of volume is derived from the formation of nano-cavities extending to a microscopic scale. Y. Merckel [11] as well as H. Zhang [12] found out, that the threshold of increasing apparent volumetric strain under simple elongation is in the range of apparent strain values beyond 2.00.

Contrary to this paper, Zhang et al. [13] pointed out, when strain is once again increased apparent volumetric strain does not begin to increase until strain reaches the same level as it had been at maximum. After that point apparent volumetric strain also begins to increase again. The authors of this paper assume a possible reason for this contrasting effect due to a viscoelastic effect due to a fluctuation of molecular chains and the orientation of filler agglomerates affected by the degree of constraints. Further investigations on this phenomenon will be performed in future.

Fig. 5: Fracture surfaces of pancake specimen for unfilled and 48 phr CB filled SBR.
such as uniaxial deformation. Since the Poisson ratio of vulcanized rubber is almost 0.5, the volume would be invariant during deformation. Thus, the Young’s modulus derived from entropy elasticity is reflected by \( G \) as shown in eq. (1). In this case, \( K \) is infinite although the Young’s modulus has a finite value.

The cohesion of the molecular chains between the crosslinks of unfilled rubber vulcanizates originates from very strong covalent bonds. In contrast, the energy of interaction between adjacent molecular chains is about two orders of magnitude smaller than that of covalent bonds. There is a distribution of density caused by the constitution of the rubber network. In unfilled rubber, unevenness in density is mainly affected by the crosslinking process. Density distribution of CB filled rubber vulcanizates is particularly influenced by the formation of a CB network structure due to affinity between CB and rubber [14, 15]. For instance, constraint strains always occur around CB particles and agglomerates or due to density unevenness. This greatly affects the stiffness and strength of rubber vulcanizates.

In the following part experimentally obtained mechanical properties of rubber vulcanizates are discussed with respect to potential damage mechanisms. Figure 6 shows an agglomeration state model for CB filled rubber, considering simple and pure elongation deformation. Primary particles of CB and CB agglomerates are distributed in the matrix of vulcanized rubber (Figure 6a). When pure elongation is applied transversal strain is suppressed and a multiaxial stress state is generated. Since the interaction of adjacent molecular chains between crosslinks of rubber is small, the stress easily introduces the expansion of volume. Additionally, breakage of molecular chains can be expected when local stress levels exceed the molecular strength. As a consequence, regions of lower density are formed and the nucleation of nano-cavities is initiated (Figure 6d).

It is suggested, that the expansion of nano-cavities is dominated by the constitutional relationship of pure rubber. If the local stress value increases and the accumulated elastic strain energy \( (U) \) satisfies equation 5, the size of the regions with low density begins to grow rapidly. Then nano-cavities are formed and expand to micro-cavities, as shown in figure 6d.

\[
\frac{\partial u}{\partial S} > \frac{\partial S}{\partial V} 
\]

In eq. (5), \( S \) represents the energy required to expand the cavities and \( V \) represents the volume of low density regions. For example, the macroscopic cavities observed in the CT images depicted in Figure 3 are presumed to be formed by merging of cavities, which are smaller than the resolution of CT.

Using the constitutive equation of a nonlinear elastic body, the conditions for rapid cavity expansion (eq. 5) have already been analyzed by J.M. Ball, S. Biwa as well as P.A. Kakavas and A.V. Perig [16-18]. These analyses explain the hydrostatic stress \( (\sigma) \) required for the nucleation of cavities following eq. (6)
where $G$ and $E_y$ represent the shear and the Young’s modulus, respectively. Eq. (6) was introduced by A.N. Gent [1].

In this study, the Young’s modulus of 48 phr CB filled SBR has been estimated by uniaxial tensile tests; $E_y = 2.9$ MPa. Using eq. (6), the analytically estimated onset of cavity formation is $\sigma_c = 2.4$ MPa, which fits in good approximation with the experimental data considering the yield point in Figure 4.

When regions with low density convert to nano- or micro-cavities, the amount of interaction between molecular chains naturally decreases. This leads to a reduction of the Poisson ratio. As a result, strain constraint is relieved, resulting in a reduction of the elastic modulus under pure elongation and an increase in the rate of stress. When the stress surpasses the threshold of elastic volumetric deformation (yield point in stress-strain curves) the constant strain level can be surmised to be the result of a similar mechanism (see figure 2).

Under pure elongation, the expansion of cavities leads to a decrease in the amount of stress required to expand the cavities. However, with increasing strain, the rate of orientation hardening in the regions surrounding the cavities accelerates. This conduces to increasing local stress values in the regions surrounding the cavities, which in turn suppresses the further expansion of the cavities. It can be surmised that, when stress is in the stable range of deformation, these two effects are counterbalancing each other.

For CB filled SBR, the stable volume increase within this range can be explained by suppressed unstable rapid expansion of cavities due to orientation hardening by molecular orientation in the rubber-filler network.

In contrast, under simple elongation, stress remains uniaxial and constant tensile deformation is predominant. This deformation changes the structure and distribution of CB agglomerates (see figure 6b). The aggregation of rigid CB particles leads to an increase of the shear modulus. But accompanied by shear sliding between the CB particles, the rubber network between the CB particles gets broken and the aggregation structure changes in a direction to relax $G$. Under simple elongation, the transversal distance ($r$) between CB agglomerates decreases during stretching due to the Poisson effect. Ultimately, these agglomerates come into contact with each other (Figure 6c). Because the CB particles are rigid segments and cannot be deformed, further transversal deformation is suppressed. A critical transversal distance ($r_c$) is reached. As a result, the stress state in the rubber phase between the agglomerates becomes multiaxial and increases due to constraint strain. At this point, the rubber phase undergoes a large deformation and it is assumed that the stress-strain curve is in a range that indicates a high degree of orientation hardening. It is thought, that the induced constraint strain generates similar conditions compared to that of pure elongation. Thus, the conditions of eq. (3) are fulfilled and formation of cavities is initiated. The volumetric expansion in rubber vulcanizates applied to simple elongation has been observed at high strain values (cf. [12]) and can be explained using this model.

Furthermore, the cavity formation under constraint strain can be generally explained by the breakage of molecular chains and/or crosslinks at multiaxial stress states. As discussed, a multiaxial stress state caused by particle orientation or due to constraint strain leads to high stresses at molecular chains and crosslinks. In the case of highly constrained conditions, the long-range thermal fluctuation of molecular chains is suppressed. As a consequence, the elasticity along the molecular chain changes from entropic to energetic due to covalent bonds. When the applied stress reaches the value of the bonding force, the molecular chains or crosslinks are destroyed and cavities can be formed. Figure 7 visualizes this damage mechanism schematically.

**Damage formation mechanisms under static tensile deformation: Situation at a crack tip**

For rubber vulcanizates, regions of multiaxial stress occur for instance in the crack tip zone of a notched specimen. The fracture mechanics of rubber vulcanizates considering the crack propagation behavior has been investigated and discussed in the literature (e.g. [19]).

Since the formation of cavities due to breakage of molecular chains between the crosslinks release previously accumulated elastic strain energy, the strain rate at the crack tip is rapidly accelerated. When the strain rate near the crack tip is higher than the relaxation time of the breakage of interaction between adjacent molecular chains and crosslinks,
high stress concentration is maintained. As a result, unstable and rapid crack propagation can be observed, especially in unfilled rubber vulcanizates. A model describing this mechanism schematically is shown in Figure 8. If, in the case of the CB filled rubber, a large number of cavities is formed before breakage of crosslinks, the local stress concentration at the crack tip is relieved and unstable crack propagation is suppressed.

It is concluded that the release of constraint strain due to cavity formation and growth might improve the strength and elongation at break as well as the resistance against unstable crack propagation of CB filled rubber vulcanizates.

**Damage formation mechanisms under cyclic tensile deformation: General assumptions**

Similar to the mechanisms of cavity formation at static tensile loading, damage generation occurs under cyclic pure elongation. If the formed and expanded cavities contract reversibly during unloading, the stress will also decline through a path similar to the loading process. In fact, the unloading stress is less than the loading stress, and the corresponding apparent volumetric strain reduction is greater than the increase in the loading phase. The obtained experimental results confirm that the damage process can be separated into several stages: (i) When the amplitude of the repetitive load is smaller than a critical stress threshold, the hysteresis loss is small because no cavities have been formed or their contribution is small. (ii) In the region where the amplitude of the repetitive load is in the critical stress range, the energy loss due to the expansion of the cavity is added, so the hysteresis loss in stress-strain curves increases. (iii) Once the threshold of elastic deformation is passed a residual volume change consists even at the unloaded stage. Thus, the structural damage cannot be recovered completely even after the stress is completely removed.

Especially in the case of CB filled rubber, the agglomerated structure of CB, which has not experienced a load before, may possibly form a percolation structure which contributes to the constraint strain. The first load on the vulcanized rubber will destroy such percolation structure. Since the destroyed structure does not recover, it is suggested that the stress originating from the broken structure disappears at reloading. If the strain increases repeatedly until the agglomerates come into contact, the degree of constraint strain increases. With further increasing strain, the network structure of CB agglomerates is destroyed progressively due to shear sliding between the CB particles and agglomerates. Consequently, the structure and the distribution of the agglomerates have been changed. These changes do not recover during unloading, so the unloading stress path is lower than that of the loading one. As a result, it is suggested that energy loss due to cyclic loading increases with increasing strain as well as the formation of cavities, potentially related to the Payne effect.

**Conclusion**

The influence of the tensile deformation mode — simple or pure elongation — on the mechanical properties and the failure behavior of unfilled and filled SBR vulcanizates is significant. However, in dependency of the structural orientation processes during tensile deformation, constraint strain conditions will occur in any case. Tensile deformation under highly constrained conditions will lead to multiaxial stress states initiating the nucleation and the expansion of cavities. The cavitation process can be investigated experimentally using i.e. dilatometry or computed tomography.

For designing rubber products it is necessary to consider the significance of constraint strain and its influence on the mechanical properties and the lifetime. The results and discussion in this study will be the basement of further investigations of this working group. Particularly, investigations of the damage behavior of several industrial rubber materials, including carbon black and silica filled rubber systems, will be in the focus in future.

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