

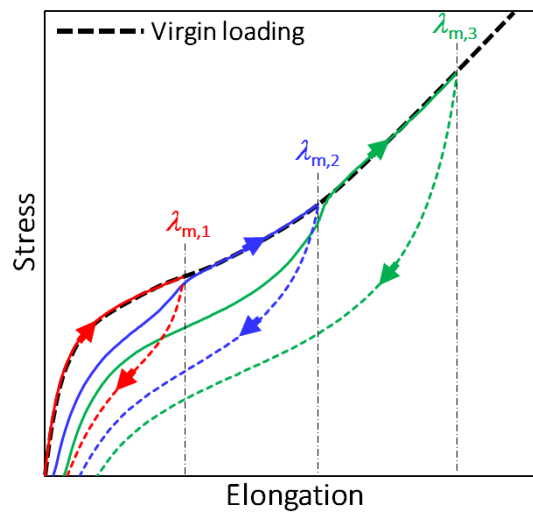
# Chapter I

## General Introduction

### 1. Background of the Mullins Effect

#### 1.1. What is the Mullins Effect?

Filler-reinforced elastomers are widely employed in industrial products such as tires. The introduction of a filler significantly enhances the mechanical performance of elastomers, including the elastic modulus, fracture stress, and toughness.<sup>1-3</sup> An important and intriguing characteristic of the mechanical properties of filled elastomers is that the loading-unloading cycles cause considerable mechanical softening, commonly known as the stress-softening or Mullins effect.<sup>4-7</sup>



**Figure 1.1.** Schematic of stress-elongation relation in the loading-unloading cycles for the Mullins effect. The solid and dashed curves are the loading and unloading processes, respectively. The maximum elongation in each stretching cycle is denoted by  $\lambda_{m,i}$  ( $i = 1, 2,$  and  $3$ ).

The stress-softening was observed firstly in unfilled as well as filled rubbers by Bouasse et al. (1903),<sup>8</sup> Shedd et al. (1904),<sup>9</sup> and Holt (1931)<sup>10</sup> using the simple extension (uniaxial extension). Afterward, this property has been investigated thoroughly by Mullins and his coworker to reveal some important factors of the stress-softening in filled elastomers on the basis of uniaxial stretching measurement.<sup>5</sup> The Mullins effect has the following general features (Figure 1.1):<sup>4,5</sup> (1) The softening degree is more pronounced for the filled elastomers than that for the unfilled elastomers, which initially contain crystallites like thermoelastic rubbers, or which crystallize during stretching. The softening degree also depends on a filler content and the interaction between fillers and polymer chains; (2) the softening occurs mainly in the second loading or unloading process, and further softening was very small after the second loading unless the stretching exceeds the previous maximum stretch; (3) the softening is obtained mainly at the strain which is lower or equal to the previous maximum stretch, and the stress-strain curve follows the path of the first extension when the strain exceeds the previous maximum stretch; (4) the softening increases with an increase in previous maximum extension; (5) the softening recovery is usually slow and incomplete in the testing temperature but it may be accelerated and reached to more complete by an increase in temperature, or by swelling in the suitable solvent. The residual strain and the difference in the stress-elongation curves between the loading and unloading processes caused by the inelastic effects, i.e., permanent set and viscoelasticity of elastomers, are observed commonly in filled and unfilled elastomer (Figure 1.1).<sup>5,6</sup> The residual strain increases with an increase in the degree of elongation and filler content;<sup>4</sup> and finally, (6) the softening has a strong direction-dependence known as an *anisotropic Mullins effect*, the details of which will be described in Section 1.3 in this chapter.

Interestingly, the emergence of such stress-softening is not limited to filled (or unfilled) elastomers, and the similar phenomena including cyclic hardening are broadly observed for polymer composites,<sup>4</sup> biopolymer hydrogels<sup>11,12</sup> or tissues,<sup>13,14</sup> and hard materials, such as shape-memory alloys.<sup>15,16</sup> For instance, the filled elastomers and double network hydrogels show apparently similar stress-strain softening behavior,<sup>4,12</sup> although they are different in the microscopic origin of the structural damage. A main origin of the

softening of filled elastomer is the destruction of the interfaces of filler and polymer chains,<sup>4</sup> whereas that of double network hydrogels is the chain-breaking.<sup>12,17</sup> Thus Mullins effect is a key mechanical property of many soft elastic materials.

## **1.2. Current Status of Physical Interpretations and Modelling of the Mullins Effect**

The Mullins effect has been studied for more than seven decades, but much still remains unknown about the physical mechanisms behind the Mullins effect during cyclic loading.<sup>4,16</sup> In general, the microscopic origin of the Mullins effect has been attributed to the destruction of the rubber-filler interface,<sup>18–24</sup> chain slippage,<sup>25–27</sup> and breakage of the filler cluster,<sup>21,28,29</sup> as well as other causes.<sup>4</sup> Filler network rupture (Payne effect) in the sample of carbon black-filled natural rubber occurred at very small deformation (< 5%) have been early reported by Payne (1962)<sup>30,31</sup> using the sinusoidal strain dynamic tester. So far, the mechanism of Mullins effect has not been unambiguously identified; the difficulty originates mainly from the limitation of visualization of the relevant microscopic structures during deformation,<sup>16</sup> although some recent studies reported the alternation in filler structure detected by the electrical conductivity<sup>32,33</sup> and the small angle x-ray scattering.<sup>34–38</sup> The generation of nanocavitation and the scission of the covalent bonds in the stretched states were revealed by real-time small angle x-ray scattering<sup>39,40</sup> and through the strain-induced light emission using cross-linker molecules with the mechanoluminescent ability,<sup>41</sup> respectively. Therefore, it is very important to correlate the mechanical responses in the application of various types of stretching with the microscopic structural changing of materials during deformation.

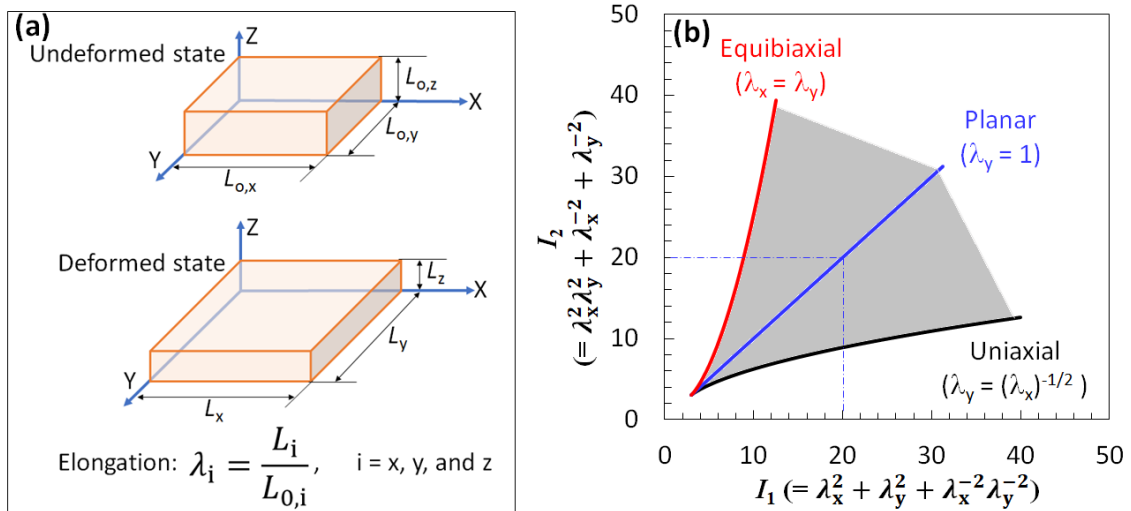
For accounting the Mullins effect, much effort has also been devoted to modeling the stress-softening behavior by phenomenological<sup>7,42–46</sup> and molecular<sup>28,47–50</sup> approaches. In phenomenological models, the early concept of two-phase system, i.e., hard and soft rubber, has been proposed by Mullins and Tobin (1957).<sup>7</sup> On the basis of uniaxially stretching data, they noticed that most of the deformation takes place in the soft regions, and the hard regions cannot deform much but they may be softened to become soft phase during the application of deformation. This means that the fraction of soft phase increases with an increase in the degree of deformation, while the fraction of

hard phase decreases during stretching. Afterward, some other phenomenological models, following the concept of Mullins and Tobin, have been developed to describe the stress-softening behavior, e.g., Qi et al. (2004),<sup>46,51</sup> Beatty et al. (2000),<sup>44</sup> and De Tomasi et al (2006).<sup>52</sup> In the other way, Simo (1987)<sup>43</sup> defined the damage parameter ( $\mathbf{d}$ ) which represents the generally physical phenomena of the softening, i.e., chain-breaking, structural damage, and generation of micro-void etc. The relation of  $\mathbf{d}$  and the elastic strain energy densities,  $W(\mathbf{F})$ , was defined as  $W(\mathbf{F}) = (1 - \mathbf{d})W_0(\mathbf{F})$ . Where  $W(\mathbf{F})$  and  $W_0(\mathbf{F})$  are the elastic strain energy density in pre-stretched and virgin states, respectively, as a function of the deformation gradient  $\mathbf{F}$ . As this definition, the reduction of  $W_0(\mathbf{F})$  during stretching is governed by  $(1 - \mathbf{d})$ . Various forms of  $\mathbf{d}$  have been proposed by some research groups<sup>42,53–56</sup> to describe the damage law, expressing the change of  $\mathbf{d}$ , of the Mullins effect. A famous example of phenomenon model was developed by Ogden et al. (1999)<sup>42</sup>. The authors showed a pseudo-elastic model for the Mullins effect in filled rubber including the permanent set, but the unrestricted using of parameters leads to an ambiguous understanding of softening origin. In addition, some phenomenological models can fit well the stress-softening behavior of filled or unfilled elastomers, especially for the uniaxial data, but their parameters miss having the meaning of physical interpretation.

Therefore, it is necessary to develop macromolecular models for describing the microscopic mechanism of the softening. Govindjee and Simo (1991)<sup>47</sup> proposed the micro-mechanical model based on the destruction of filler-polymer bonds as defined by Bueche (1960).<sup>23</sup> They showed the construction of the first-order average free energy density of filled elastomer (composite) combined a nonlinear hyperelastic damaging material and filler particles. In other approaches, Killian et al (1994),<sup>49</sup> Klüppel et al. (2000),<sup>28</sup> and Marckmann et al (2002)<sup>50</sup> defined the softening models on the basis of irreversible chain slippage, filler cluster breakdown, and the rupture of the network polymer, respectively. Most of the macromolecular models mentioned above have remained some limitations, e.g., using too many parameters for fitting, depending on the phenomenological parameters although they have been deduced from the microscopic

origin of the Mullins effect, and the fit quality of models was assessed mainly by the uniaxially stretching data or by a specific type of deformation.

In fact, the phenomenological and molecular models are required to describe the stress-strain behavior under general loading conditions; i.e., not limited to uniaxial loading. Uniaxial tension is only a particular deformation among all accessible deformations of an elastomer (Figure 1.2), and the data relying on uniaxial tension offer a limited basis for the assessment of the models. Most of the experimental studies of the Mullins effect, however, have used uniaxial tension exclusively,<sup>4</sup> and only a few studies have employed deformations other than uniaxial tension for the characterization.<sup>44,45,57–59</sup> An experimental survey of the Mullins effect using various types of deformation is very important, not only for the assessment of models but also for the full characterization of stress-softening phenomena. For instance, commercial products of filled elastomers are usually subjected to variously complicated deformations during their use.<sup>60</sup>



**Figure 1.2.** (a) Schematic of general deformation and (b) the map of invariants ( $I_1$ – $I_2$  relation) of the deformation tensor for an incompressible material,  $I_3 = \lambda_x\lambda_y\lambda_z = 1$ . All types of the physically assessible deformation must occur in the shaded region enclosed by the uniaxial and equibiaxial extensions.

Some research efforts have employed the balloon inflation or bulge test<sup>57,58,61</sup> for the characterization of the Mullins effect. These deformations are substantially identical to an

equibiaxial extension, but various types of strain field are obtained, and the strain field inevitably becomes inhomogeneous.<sup>62</sup> Machado et al. (2010)<sup>58</sup> used the planar extension, where the materials are uniaxially stretched while the dimension in one direction is kept unchanged, in addition to a bulge test. They discussed the dependence of strain energy ratio (second loading / primary path) on several parameters, including the first and second strain invariants, maximum stretch and stress, and strain-energy density. The range of maximum stretch ( $\lambda_m$ ), however, remained modest ( $\lambda_m < 1.7$ ) in their biaxial tests. Pancheri et al. (2012)<sup>63</sup> investigated the stress-softening by general biaxial strain and explored a constitutive model to reproduce their data, but it was unclear how  $\lambda_m$  influenced the stress-softening due to the measurement using only a single value of  $\lambda_m$ .

### **1.3. Induced Anisotropy by Mullins Effect**

As is discussed above, extensive efforts have been made to model the Mullins effect from phenomenological and molecular aspects. In the early models, the isotropy for the damage caused by loading, i.e., identical damage in all directions, has been assumed. Some isotropic models apparently describe the stress-softening by uniaxial cyclic loading,<sup>4</sup> but most of them usually fail to describe the data of cyclic loading under other types of deformation. The presence of a finite *direction-dependence* of the damage has long been recognized,<sup>5</sup> and this anisotropic Mullins effect has considerable diversity and complexity in both the experimental and theoretical investigations.<sup>64</sup> Anisotropy in Mullins effect generally means that the softening in the direction of larger pre-strain is higher than those in the other direction in the case of anisotropic pre-stretching.<sup>65</sup>

Some studies have also been devoted to the modeling of the anisotropic Mullins effect induced by a specific pre-stretching, i.e., uniaxial extension,<sup>48,66,67</sup> balloon inflation (bulge test)<sup>68</sup> or general deformation.<sup>69–71</sup> The microsphere concept,<sup>72</sup> has been commonly employed to create the constitutive models of filled elastomers.<sup>48,68,70,73</sup> Accordingly, the total network structures of filled elastomers is divided basically into the crosslink-to-crosslink (CC, polymer matrix) and the particle-to-particle (PP, the chains interacted with particles),<sup>68,70,73</sup> The anisotropic damage phenomenon is embedded into the PP network based on the mechanism of filler-polymer rupture.<sup>23,43</sup> The elastic strain energy density

for each network (CC or PP) is defined independently. Recently, Khiêm et al. (2017)<sup>70</sup> showed an averaging deformation of three network components, i.e., CC, PP with irreversible, and reversible adsorptions, using the network decomposition<sup>74</sup> as a micromechanically based constitutive model. These models can generally describe the Mullins effect involved the anisotropy and permanent set with various types of deformation, but the assessments of such models have restricted only in the data of uniaxial stretching or a specific deformation. Therefore, full characterization of the anisotropic Mullins effect with various modes of deformation is a key to assess and develop the current models involving the anisotropic damage, as well as permanent set, and to elucidate the physical origin of the phenomena.

For investigating of the anisotropic softening, the earlier experimental studies on the anisotropic Mullins effects have commonly employed a sequence of two tensile measurements to characterize the degree of anisotropy:<sup>14,27,48,75–77</sup> the pre-stretched sheet specimens are cut into the rectangular subsamples at various angles relative to the stretching direction, and the directional damages are evaluated by comparing the uniaxial loading curves of the virgin specimens and the subsamples. Most of the corresponding studies employed uniaxial extension for pre-stretching. Recently, some researchers used a planar extension (pure shear),<sup>14</sup> balloon inflation (bulge test)<sup>65</sup> and some biaxial deformations for pre-stretching.<sup>45,78</sup> As is mentioned above, the inhomogeneous strain field in the bulge test impedes obtaining the subsamples with homogeneous strain-histories along meridional as well as circumferential direction, which complicates the analysis and interpretation of the data. Marckmann et al. (2016)<sup>78</sup> employed "modified biaxial" tensions in which the cross-shaped virgin sample was successively subjected to uniaxial stretching in the two orthogonal directions. They emphasized the difference in the strain-histories between the modified biaxial and simultaneous equibiaxial deformations. The complicated strain-histories in the modified biaxial extension, however, lead to the difficulties in the direct interpretation of the data. Dorfmann et al. (2012)<sup>45</sup> explored a constitutive model to describe their data using uniaxial and planar extensions for pre-stretching, but the effects of the magnitude of the imposed pre-

stretching on the anisotropic Mullins effect were unclear due to the experiment with only a single magnitude of pre-strain.

## **2. Silica-Filled Styrene-Butadiene Rubber**

The reinforcement of polymers by fillers has been studied more than six decades ago.<sup>1</sup> The term of reinforcement of polymers means that an increase drastically in the mechanical properties, i.e., tensile strength, tear resistance, abrasion resistance, and modulus, beyond the hydrodynamic effect.<sup>3,21,79</sup> It is important to notice that the ability of filler reinforcement is mainly governed by the distribution of fillers in the polymer matrix and filler-polymer interactions (interface), which relate directly the softening at the small strain (Payne effect)<sup>30</sup>, as well as large strain (Mullins effect).<sup>5</sup>

Various types of fillers, i.e., carbon blacks, silicas, clays, celluloses, carbon nanotubes etc., are used for the reinforcement of elastomers in the laboratory as well as industrial applications.<sup>1</sup> In particular, silica particles are a popular filler like carbon black. Silica is used in many rubber products, especially in tires, because silica filler has the advantage that it decreases the rolling resistance leading to low fuel consumption, and a hysteresis, which is of major interest to the automobile industry.<sup>1,60</sup> Furthermore, the use of silane-coupling agents (SCA), significantly improves the mechanical properties of silica-filled elastomers as a result of the enhanced interaction (generation of covalent bonds) between silica particles and rubber.<sup>1,2,80</sup> This chemical interaction also limits the adsorption of polymer chains on the filler surfaces due to a shielding effect.<sup>1</sup> In addition, the concentration of filler clusters and polymer chains mobility (around filler surface) will decrease with the aid of SCA. It is important to reveal the effect of SCA on the softening of filled elastomers because it is one of the basis for understanding the microscopic origin of Mullins effect as well as the performance of rubber products such as tires.

Styrene-butadiene rubber (SBR) known as a synthetic elastomer is the resulting from a copolymer of styrene and butadiene.<sup>81</sup> SBR is commonly considered to be a part of the tread composition due to the advantages of excellent abrasion resistance and crack resistance, which are important properties for the application in tire industries.<sup>60</sup> However, it is necessary to improve the strength of SBR by the reinforcement of fillers

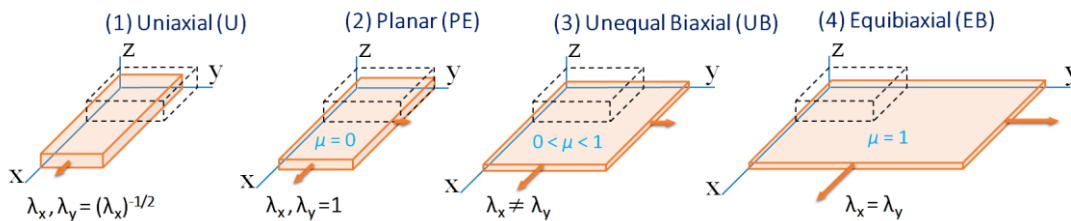


(carbon black, silica etc.) because the unfilled SBR is poor in the tensile and tear strengths as compared with other rubbers.<sup>1,3,21,81</sup>

### 3. Aim of Study

In this thesis, the Mullins effect and induced anisotropy by stress-softening in filled elastomers are characterized by the stretching measurements in various geometries. The present study reveals the effects of (1) *degree* and *type* of deformation, (2) *filler content*, (3) *filler-polymer interaction*, and (4) *crosshead speed* on the Mullins effect, and anisotropic Mullins based in energy dissipation, and directional energy dissipation, respectively.

The Mullins effect for silica filler-reinforced styrene-butadiene rubber (SBR) is investigated by three types of extension, i.e., uniaxial, planar and equibiaxial extensions (Figure 1.3), using a custom-built biaxial tester. The comprehensive data obtained under various types of extension for SBR with varying silica contents, and with or without silane-coupling agents, significantly contribute to a more comprehensive understanding of the Mullins effect, and they provide a definite basis to elucidate the origin of the stress-softening behavior. We correlate the characteristic dependence of energy dissipation on the degree of deformation, represented by the first strain invariant of deformation tensor, with the destruction processes of the inherent structures, including filler network and filler-polymer interface, and the friction between the fillers and the rubber matrix.



**Figure 1.3.** Schematics of several types of deformation: (1) uniaxial, (2) planar, (3) unequal biaxial, and (4) equibiaxial extensions.  $\mu$  denotes the ratio of the two nominal strains ( $\varepsilon_i = \lambda_i - 1$ ;  $i = x, y$ ).

The same materials of silica-filled SBR with various filler contents, and with and without SCA was employed to study the directional dependence of the Mullins effect. A sequence of two tensile experiments was conducted for the evaluation of the anisotropy: firstly the virgin specimens were pre-stretched by several modes, i.e., uniaxial, planar and equibiaxial extensions, and unequal biaxial extensions with a variety of the strain ratio in the two orthogonal directions (Figure 1.3); secondly, the small subsamples, which were cut out from the pre-stretched and relaxed specimens at various angles relative to the axis of the larger pre-strain (x-axis), were uniaxially stretched. The direction-dependence of the energy dissipation was examined on the basis of the comparison of the uniaxial loading curves of the subsamples and virgin samples. This comprehensive data under various types of pre-stretching with very different degrees of strain anisotropy enables us to elucidate unambiguously the effects of the anisotropy in the pre-strain field, including the cross-effect of strain, on the directional dependence of damage.

#### **4. Structure of Thesis**

In the present thesis, the Mullins effect and induced anisotropy by Mullins effect in filled elastomers are investigated by various modes of deformation. The basic introduction of the Mullins effect in filled elastomers, the material of silica-filled styrene-butadiene rubber, and the objective of this study are shown in Chapter I as general introductions.

In Chapter II, the features of materials and samples, and the methodologies used in this study are illustrated. Silica-filled styrene-butadiene rubbers (SBR-silica) with varying volume fractions of silica, and with or without silane coupling agent (SCA) are employed in the experiments. The details of the mechanism of the custom-built biaxial tester, and the experimental investigations of the Mullins effect, as well as anisotropic Mullins effect, using cyclic stretching with various types of deformation, are shown. In addition, the estimation of the energy dissipation ( $D$ ), and directional energy dissipation ( $D_{\theta}$ ) are also illustrated.

In Chapter III, stretching experiments with various geometries are performed using a custom-built tensile tester to reveal the intriguing features of the mechanical softening

phenomena of filled elastomers in loading-unloading cycles. The dissipated energy ( $D$ ), residual strain ( $\epsilon^r$ ), and dissipation factor ( $\Delta$ ; the ratio of  $D$  to input strain energy) in the loading-unloading cycles are evaluated as a function of the maximum stretch in cyclic loading ( $\lambda_m$ ) using three types of extension, i.e., uniaxial, planar, and equibiaxial extension, for silica-filled elastomers with various filler contents, and with or without silane coupling agent. The characteristic dependence of  $\Delta$  on degree of deformation in each of the small and large deformation regimes is revealed, and the physical origin of the Mullins effect is discussed.

In Chapter IV, anisotropy induced by stress-softening phenomena in filled elastomers has been intensively investigated using various stretching modes for pre-stretching. A sequence of two tensile experiments is conducted for the evaluation of the anisotropy, i.e., pre-stretching of virgin samples by several modes, i.e., uniaxial, planar, unequal-biaxial and equibiaxial extensions, and the uniaxially stretching of the subsamples. The direction-dependence of the energy dissipation ( $D_0$ ) is examined on the basis of the comparison of the uniaxial loading curves of the subsamples and virgin samples. The effect of *type* and *degree of deformation*, *filler content*, *filler-polymer interaction*, and *crosshead speed* on the  $D_0$ , as well as the degree of dissipation anisotropy ( $f_0$ ), are discussed to understand the physical meaning of the directional dependence of softening in filled elastomers. The feature of the cross-effect of strains on the damage is also interpreted.

In Chapter V, the important results of present thesis are concisely summarized, and the future tendency for the study of stress-softening in soft matters revealed by biaxial deformation is described.

## References

- 1 J.-B. Donnet and E. Custodero, in *The Science and Technology of Rubber*, eds. J. E. Mark, B. Erman and M. Roland, Elsevier, Waltham, 4th edn., 2013, pp. 367–400.
- 2 M. Strankowski, in *Non-linear Viscoelasticity of Rubber Composites and Nanocomposites: Influence of Filler Geometry and Size in Different Length Scales*, eds. D. Ponnamma and S. Thomas, Springer International Publishing, Switzerland, 1st edn., 2014, pp. 59–83.
- 3 G. Heinrich, M. Klüppel and T. A. Vilgis, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 195–203.
- 4 J. Diani, B. Fayolle and P. Gilormini, *Eur. Polym. J.*, 2009, **45**, 601–612.
- 5 L. Mullins, *Rubber Chem. Technol.*, 1948, **21**, 281–300.
- 6 L. Mullins, *Rubber Chem. Technol.*, 1969, **42**, 339–362.
- 7 L. Mullins and N. R. Tobin, *Rubber Chem. Technol.*, 1957, **30**, 555–571.
- 8 H. Bouasse and Z. Carrière, *Ann. la Fac. des Sci. Toulouse Mathématiques*, 1903, **5**, 257–283.
- 9 J. C. Shedd and R. L. Ingersol, *Phys. Rev. (Series I)*, 1904, **19**, 107–116.
- 10 W. L. Holt, *Rubber Chem. Technol.*, 1932, **5**, 79–89.
- 11 J. P. Gong, *Soft Matter*, 2010, **6**, 2583.
- 12 R. E. Webber, C. Creton, H. R. Brown and J. P. Gong, *Macromolecules*, 2007, **40**, 2919–2927.
- 13 E. Maher, A. Creane, C. Lally and D. J. Kelly, *J. Mech. Behav. Biomed. Mater.*, 2012, **12**, 9–19.
- 14 M. Rebouah and G. Chagnon, *Acta Mech.*, 2014, **225**, 1685–1698.
- 15 M. TAHARA, H. Y. KIM, H. HOSODA and S. MIYAZAKI, *Funct. Mater. Lett.*, 2009, **2**, 79–82.
- 16 K. M. Schmoller and A. R. Bausch, *Nat Mater*, 2013, **12**, 278–281.
- 17 T. Nakajima, T. Kurokawa, S. Ahmed, W. Wu and J. P. Gong, *Soft Matter*, 2013, **9**, 1955–1966.
- 18 K. W. Stöckelhuber, A. S. Svistkov, A. G. Pelevin and G. Heinrich,

- Macromolecules*, 2011, **44**, 4366–4381.
- 19 M. Klüppel, in *Filler-Reinforced Elastomers/Sanning Force Microscopy*, eds. A. Abe, K. Dušek and S. Kobayashi, Springer-Verlag Berlin Heidelberg, Heidelberg, 1st edn., 2003.
  - 20 L. Tadiello, M. D. Arienzo, B. Di Credico, T. Hanel, L. Matejka, M. Mauri, F. Morazzoni, R. Simonutti, M. Spirkova and R. Scotti, *Soft Matter*, 2015, **11**, 4022–4033.
  - 21 J. Fröhlich, W. Niedermeier and H.-D. Luginsland, *Compos. Part A Appl. Sci. Manuf.*, 2005, **36**, 449–460.
  - 22 Y. Bréchet, J.-Y. Cavallé, E. Chabert, L. Chazeau, R. Dendievel, L. Flandin and C. Gauthier, *Adv. Eng. Mater.*, 2001, **3**, 571–577.
  - 23 F. Bueche, *J. Appl. Polym. Sci.*, 1960, **4**, 107–114.
  - 24 A. S. Pavlov and P. G. Khalatur, *Soft Matter*, 2016, **12**, 5402–5419.
  - 25 R. Houwink, *Rubber Chem. Technol.*, 1956, **29**, 888–893.
  - 26 S. Cantournet, R. Desmorat and J. Besson, *Int. J. Solids Struct.*, 2009, **46**, 2255–2264.
  - 27 D. E. Hanson, M. Hawley, R. Houlton, K. Chitanvis, P. Rae, E. B. Orler and D. A. Wroblewski, *Polymer (Guildf.)*, 2005, **46**, 10989–10995.
  - 28 M. Klüppel and J. Schramm, *Macromol. Theory Simulations*, 2000, **9**, 742–754.
  - 29 G. Heinrich and M. Klüppel, in *Filled Elastomers Drug Delivery Systems*, Springer Berlin Heidelberg, Heidelberg, 1st edn., 2002, pp. 1–44.
  - 30 A. R. Payne, *J. Appl. Polym. Sci.*, 1962, **6**, 368–372.
  - 31 A. R. Payne, *J. Appl. Polym. Sci.*, 1965, **9**, 3245–3254.
  - 32 R. Diaz, J. Diani and P. Gilormini, *Polym. (United Kingdom)*, 2014, **55**, 4942–4947.
  - 33 L. Bokobza, *C*, 2017, **3**, 10.
  - 34 M. Takenaka, *Polym. J.*, 2013, **45**, 10–19.
  - 35 K. Brüning, K. Schneider and G. Heinrich, *J. Polym. Sci. Part B Polym. Phys.*, 2012, **50**, 1728–1732.
  - 36 Y. Shinohara, H. Kishimoto, K. Inoue, Y. Suzuki, A. Takeuchi, K. Uesugi, N. Yagi, K. Muraoka, T. Mizoguchi and Y. Amemiya, *J. Appl. Crystallogr.*, 2007,

- 40, 397–401.
- 37 J. Oberdisse, W. Pyckhout-Hintzen and E. Straube, in *Recent Advances in Polymer Nanocomposites*, eds. S. Thomas, G. Zaikov and Valsaraj, Taylor & Francis Group, Boston, 2009, pp. 397–438.
- 38 K. Hagita, T. Arai, H. Kishimoto, N. Umesaki, H. Suno, Y. Shinohara and Y. Amemiya, *Rheol. Acta*, 2008, **47**, 537–541.
- 39 H. Zhang, A. K. Scholz, F. Vion-Loisel, Y. Merckel, M. Brieu, H. Brown, S. Roux, E. J. Kramer and C. Creton, *Macromolecules*, 2013, **46**, 900–913.
- 40 H. Zhang, A. K. Scholz, J. De Crevoisier, F. Vion-Loisel, G. Besnard, A. Hexemer, H. R. Brown, E. J. Kramer and C. Creton, *Macromolecules*, 2012, **45**, 1529–1543.
- 41 J. M. Clough, C. Creton, S. L. Craig and R. P. Sijbesma, *Adv. Funct. Mater.*, 2016, **26**, 9063–9074.
- 42 R. W. Ogden and D. G. Roxburgh, *Proc. R. Soc. London. Ser. A Math. Phys. Eng. Sci.*, 1999, **455**, 2861–2877.
- 43 J. C. Simo, *Comput. Methods Appl. Mech. Eng.*, 1987, **60**, 153–173.
- 44 M. F. Beatty and S. Krishnaswamy, *J. Mech. Phys. Solids*, 2000, **48**, 1931–1965.
- 45 A. Dorfmann and F. Q. Pancheri, *Int. J. Non. Linear. Mech.*, 2012, **47**, 874–887.
- 46 M. C. Boyce and E. M. Arruda, *Rubber Chem. Technol.*, 2000, **73**, 504–523.
- 47 S. Govindjee and J. Simo, *J. Mech. Phys. Solids*, 1991, **39**, 87–112.
- 48 R. Dargazany and M. Itskov, *Phys. Rev. E*, DOI:10.1103/PhysRevE.88.012602.
- 49 H. G. Kilian, M. Strauss and W. Hamm, *Rubber Chem. Technol.*, 1994, **67**, 1–16.
- 50 G. Marckmann, E. Verron, L. Gornet, G. Chagnon, P. Charrierb and P. Fortb, *J. Mech. Phys. Solids*, 2002, **50**, 2011–2028.
- 51 H. J. Qi and M. C. Boyce, *Mech. Mater.*, 2004, 1–51.
- 52 D. De Tommasi, G. Puglisi and G. Saccomandi, *J. Rheol. (N. Y. N. Y.)*, 2006, **50**, 495–512.
- 53 A. Elías-Zúñiga, *Polymer (Guildf.)*, 2005, **46**, 3496–3506.
- 54 R. Kazakevičiūtė-Makovska, *Int. J. Solids Struct.*, 2007, **44**, 4145–4157.
- 55 M. Kaliske, L. Nasdala and H. Rothert, *Comput. Struct.*, 2001, **79**, 2133–2141.
- 56 C. Miehe and J. Keck, *J. Mech. Phys. Solids*, 2000, **48**, 323–365.

- 57 F. Beatty and S. Krishnaswamy, *Zeitschrift für Angew. Math. und Phys. ZAMP*, 2000, **51**, 984–1015.
- 58 G. Machado, G. Chagnon and D. Favier, *Mech. Mater.*, 2010, **42**, 841–851.
- 59 E. M. Arruda and M. C. Boyce, *J. Mech. Phys. Solids*, 1993, **41**, 389–412.
- 60 B. Rodgers and W. Waddell, in *The Science and Technology of Rubber*, eds. J. E. Mark, B. Erman and M. Roland, Elsevier, Waltham, 4th edn., 2013, pp. 653–695.
- 61 M. A. Johnson and M. F. Beatty, *Int. J. Eng. Sci.*, 1995, **33**, 223–245.
- 62 G. Machado, D. Favier and G. Chagnon, *Exp. Mech.*, 2012, **52**, 865–880.
- 63 F. Pancheri and L. Dorfmann, *Rubber Chem. Technol.*
- 64 Y. Xia, *Faraday Discuss.*, 2016, **191**, 597–604.
- 65 G. Machado, G. Chagnon and D. Favier, *Mech. Mater.*, 2012, **50**, 70–80.
- 66 M. Itskov, A. E. Ehret, R. Kazakevičiute-Makovska and G. W. Weinhold, *ZAMM Zeitschrift für Angew. Math. und Mech.*, 2010, **90**, 370–386.
- 67 Y. Merckel, J. Diani, M. Brieu and J. Caillard, *Mech. Mater.*, 2013, **57**, 30–41.
- 68 G. Machado, G. Chagnon and D. Favier, *J. Mech. Phys. Solids*, 2014, **63**, 29–39.
- 69 M. Rebouah, G. Chagnon and P. Heuillet, *Mech. Time-Dependent Mater.*, , DOI:10.1007/s11043-016-9324-x.
- 70 V. N. Khiêm and M. Itskov, *Int. J. Plast.*, 2017, **90**, 96–115.
- 71 Y. Merckel, M. Brieu, J. Diani and J. Caillard, *J. Mech. Phys. Solids*, 2012, **60**, 1257–1264.
- 72 H. Pawelski, *Const. Model. Rubber II*, 2001, 27–34.
- 73 S. Göktepe and C. Miehe, *J. Mech. Phys. Solids*, 2005, **53**, 2259–2283.
- 74 R. Dargazany, V. N. Khiêm and M. Itskov, *Int. J. Plast.*, 2014, **63**, 94–109.
- 75 M. Itskov, E. Haberstroh, A. E. Ehret and M. C. Vöhringer, *KGK Kautschuk Gummi Kunststoffe*, 2006, **59**, 93–96.
- 76 J. Diani, M. Brieu and J. M. Vacherand, *Eur. J. Mech. A/Solids*, 2006, **25**, 483–496.
- 77 R. Dargazany and M. Itskov, *Int. J. Solids Struct.*, 2009, **46**, 2967–2977.
- 78 G. Marckmann, G. Chagnon, M. Le Saux and P. Charrier, *Int. J. Solids Struct.*, 2016, **97–98**, 554–565.
- 79 R. Petrucci and L. Torre, in *Modification of Polymer Properties*, eds. C. F. Jasso-

- Gastinel and J. M. Kenny, Elsevier Inc., Cambridge, 2017, pp. 23–46.
- 80 L. Qu, G. Yu, X. Xie, L. Wang, J. Li and Q. Zhao, *Polym. Compos.*, 2013, **16**, 101–113.
- 81 R. P. Quirk and D. L. Pickel, *Polymerization: Elastomer Synthesis*, Elsevier Inc., Fourth Edi., 2013.