Mechanics of filled rubbers from a molecular point of view

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CHAPTER 1: INTRODUCTION

1.1 Overview

This dissertation presents my results, and associated background information, from my PhD research on polymer nanocomposites. My PhD project focused on explaining – from a molecular scale view – linear and nonlinear viscoelastic properties of polymer – and more specifically elastomer – based nanocomposites. A detailed outline of my thesis is provided below.

- **Chapter 1** provides a theoretical background of the work. First, basic principles of elastomers and elastomer-based nanocomposites are introduced. Then, the importance of studying the molecular-scale properties of nanocomposites to understand their macroscopic mechanical properties and practical uses is discussed. This chapter is closed by explaining viscoelasticity and polymer state-of-order in nanocomposites.

- **Chapter 2** starts with providing information about the polymer materials used in this thesis. This is followed by an explanation of the microscopic and spectroscopic instruments used in this work. Finally, a discussion of the different statistical tests used for deriving useful conclusions from noisy experimental results is included.

- **Chapter 3** focuses on how we generated a universal scaling parameter for explaining the linear viscoelastic properties (reinforcement) of polymer composite systems. Our work shows how the reinforcement of elastomers by various sized (micro and nano) inorganic fillers can be predicted based on filler size and volume fraction.

- **Chapter 4** focuses on the effect of rubber end group functionality on filler dispersion measured on multiple length scales in nanocomposite systems. The nature of interfacial interactions and molecular structure of rubber molecules on silica surfaces are determined by different surface-sensitive spectroscopic methods.

- **Chapter 5** focuses on the coupled behavior of nonlinear strain hardening and molecular orientation in typical nanocomposites. A potential reason
explaining increased nonlinear strain-hardening and increased polymer chain alignment with increasing filler content is presented with polarized Raman spectroscopy and simple scaling arguments describing chain alignment.

- **Chapter 6** is the future directions part of the thesis where I will present my preliminary results about the hardening behavior of nanocomposites under cyclic forces. I will end this chapter by including the next experimental ideas that I believe will contribute substantially to understand the strain-hardening properties of the nanocomposites under cyclic forces.

In this thesis, I have included the major subjects of my PhD research: spectroscopy and mechanics of rubber nanocomposite materials. In addition to the work shown here, I also took part in various side projects: (1) Understanding how fracture of nanocomposite materials is related to filler volume and size [1], (2) Raman imaging of graphene on silica to determine the intrinsic doping in the context of explaining photoconductivity of doped samples [2], (3) Supervision of a Diploma student, Christian Malm (now PhD student at the Max Planck Institute for Polymer Research) in his work focused on spectroscopic and rheological properties of simplified, bottom-up, and non-vulcanized nanocomposites.
1.2 Basics of elastomer based nanocomposites

1.2.1 Structure of elastomers

Literally, “poly” and “mer” mean “many” and “parts”, respectively. Looking deeper into the etymology, numerous groups of atoms form a “part” of a polymer called a monomer. A polymer macromolecule is generally accepted to consist of more than ten covalently bonded (repeating) monomers. In Figure 1-1, different configurations of repeating units of polybutadiene are shown. Letters n, k, and p indicate the average number of different monomers in a polybutadiene macromolecule. Even if the number and type of atoms are the same for each of these monomer units, it is very important to identify the number and position of these monomers along the chain. For example, a chain with different ratios of monomers (n,k,p) but the same molecular weight can have very different chain 3D spatial arrangement, or conformation. Similarly, the positioning of the n, k, and p subunits along the chain – whether random or in so-called “blocks” – also drastically affects chain conformation. Chain confirmation ultimately affects mechanical properties (e.g., softening or hardening) of polymers in networks. For instance, a large number of possible conformations (or a floppy polymer) makes the polymer more flexible compared to a chain with less confirmations.

Ф₁ and Ф₂ in Figure 1-1 indicate the terminal (end) groups. Independent of the conformational structure, polybutadiene is classified as a homopolymer since all the repeating units belongs to a single type of monomer. For instance, if we call one repeating unit – butadiene – as A, the final homopolymer has a structure of A – A – A – A – A – A and it is presented as [A]ₙ. However, many polymeric structures in nature and synthetic chemistry include more than one different type of monomer, and they are called copolymers. In this thesis, polymeric structures generally include two different kinds of monomers (e.g. A and B) distributed along the polymer chains randomly (statistical copolymers): A – B – A – A – B – B.
In addition to chain conformation, multi-chain organization in networks strongly determines mechanical properties of polymer materials. Chain mobility can be tuned with temperature, giving polymer materials so-called thermomechanical properties. In different polymer systems, mechanical changes due to heating or cooling take place at two material specific thermal transition temperatures that are called the melt transition ($T_m$) and glass transition ($T_g$) temperature. In general, polymers are divided into three groups depending on their thermomechanical properties: (i) thermoplastics, (ii) thermosets and (iii) elastomers. (i) Polymers that get soft and fluid-like when they are heated over their $T_m$ or $T_g$ are called thermoplastics, and they are considered rigid when sufficiently cooled below their $T_g$. The structure of the polymers in thermoplastics can be either fully amorphous (Figure 1-2a) or partly (semi) crystalline (Figure 1-2b) depending on their macromolecular chain structure, regularity and interactions.[3] When fully amorphous polymers (which have only a $T_g$) and even some crystalline polymer liquids (which potentially have $T_g$ and $T_m$) are cooled quickly, both form amorphous “glassy” materials because the crystalline polymer molecules do not have enough time to form crystalline domains. Importantly, these materials can be reversibly heated into a molten state and molded. (ii) Polymers that get more rigid with increasing temperature, by increasing the number of cross-links, are thermosets. In thermosets, once the monomers are cross-linked (Figure 1-2d) at higher temperatures, they cannot be liquefied (or made molten) upon heating anymore. (iii) Polymers that have a $T_g$ below room temperature, are also cross-linked, and exhibit genuine elasticity are called elastomers as illustrated in Figure

![Molecular structure of polybutadiene](image)

**Figure 1-1.** Molecular structure of polybutadiene.
1-2c. Elastomeric structures also have cross-links but with lower density compared to the thermosets since cross-linking only takes place between the polymer chains not monomers. Due to the low density cross-links and the network like structure (similar to a spider web), elastomers can be elastically deformed to elongations up to approximately ten times the original dimensions. Because of the cross-links, elastomers do not flow under stress easily, and the material can assume its original shape after the stress release in all dimensions, assuming no plastic deformation. [3,4] It is these types of materials that form the basis of all the work presented in Chapters 3, 4, 5, and 6 of this thesis.

Figure 1-2. Illustration of macromolecular structure of (a) amorphous (b) semi-crystalline thermoplastics, (c) elastomers and (d) thermosets. All the structures are sketched by using green balls representing single monomers. Red balls represent chemical nodes in elastomer structure as the result of vulcanization (cross-linking).

Throughout this thesis and in the field of polymer science, one often hears the term “rubber-like” when referring to elastomers. The word rubber is a traditional way of referring to elastomeric materials, and these terms have often been used interchangeably. While rubbers and elastomers are very similar, an elastomer is rubber-like if it has the following three traditional properties which were first time proposed by L. R. G. Treloar in 1949:[4]

1. long polymer chains consisting of freely rotating (jointed) links,
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(2) cross-links (e.g., chemical via vulcanization or physical via van der Waals contacts) between polymeric molecules,

(3) forms a three-dimensional network as shown in Figure 1-2c.

Elastomeric molecules generally have high mobility (liquid like) under external forces (mechanical stress) in room temperature conditions (RT) thanks to their long polymer chains (and low $T_g$). Having the first condition alone without the other two requirements, materials behave like a liquid – they flow under constant stress. In order to control the motion of the polymer chains, the second and the third requirements are needed. Cross interactions between polymeric molecules partly impede liquid-like motion. Physical cross-linking in rubber usually originates from complex, geometrically entangled polymer chains and is stabilized by van der Waals forces. In addition to such physical cross-linking, chemical cross-links can also be introduced to rubber systems by process called vulcanization, which was discovered by Charles Goodyear in 1839.[4] During vulcanization, sulfur atom(s) chemically react at the active sides (e.g., C=C bonds along the polybutadiene molecule, see Figure 1-1) of the polymer molecules, and they build covalent nodes (red dots in Figure 1-2) in rubber network.[4] It is important to have sufficiently organized cross-links (nodes), as is illustrated in Figure 1-2c, to produce an elastomeric network where all the chains contribute to the total rubber elasticity.[4] When these three requirements are fulfilled the material is no longer a liquid, and it behaves like an elastic rubber.

1.2.2 Effect of fillers

Often, polymer-based materials are not composed of a single polymer component, and contain additives to modify and tune their mechanical properties. Materials made from more than one component that contain more than one phase – the polymer and e.g. inorganic particles – are called composite materials. In general, composite materials are divided into three groups: (1) particulate-filled composites including a discontinuous “filler” phase inside the continuous (polymer) matrix phase, (2) fiber filled composites, consisting of elongated or randomly distributed fibers inside of continuous matrix (such as carbon fiber), and (3) skeletal or interpenetrating network composites, which are a mixture of two continuous (percolated) phases. With these different formulations, it is possible to modify e.g., stiffness, strength, dimensional stability (especially in fiber-filled systems), toughness, mechanical damping, heat distortion temperature, gas and liquid
permeability, and even electrical conductivity and magnetic permeability of the polymeric matrices.

The work presented in this thesis focuses on particulate – filled composites, and the size of these fillers are in nanometer range. The general name of these nano-size (dimensions from 1 nm to 100 nm) inorganic filler loaded systems is nanocomposites. Thanks to their extremely high surface-to-volume ratio, very small amounts of these nanofillers are sufficient to tailor many of the characteristic properties of the continuous polymer matrix. The fabrication history of nanocomposites starts at the end of the 1980s by the researchers at Toyota who dispersed nano-sized clay platelets in nylon-6 polymer. They observed almost a 2-fold increase in tensile modulus and tensile strength of nanocomposite compared to that in nylon-6 alone. [5]

Many theories have been proposed to understand the basic physical origin of the macroscale properties of nanocomposites, but this remains an unresolved issue. This is mainly due to the structural complexity of nanocomposites, despite a wealth of experimental data on their mechanical properties. Previous studies have often focused on a single parameter e.g. $T_g$ or elasticity but have not always related this with the underlying structure of the nanocomposite. In addition, flexible polymer physics theory, while well-suited to explain homogenous networks, is not sufficient to explain the physical principles of highly heterogeneous nanocomposites.

One important way to understand macroscale changes of nanocomposites due to nano-filler presence is to study the effect of the fillers on $T_g$ of the continuous matrix. In nanocomposites, many theoretical[6,7] and experimental works[8,9] have shown that significant attractive and repulsive interactions at filler-matrix interphase makes the $T_g$ of the nanocomposite higher and lower, respectively.[6–8,10] This finding has been explained in terms of the difference of polymer dynamics at the surface of the fillers compared to the bulk polymer not near any filler surface. In nanocomposites having attractive interfacial interaction, polymer chains at the filler surface form a stable and low-mobility “layer” that has higher $T_g$ compared to the $T_g$ of the bulk polymer. This trend is reversed for systems having repulsive interaction between fillers and matrix. One might ask: Why is $T_g$ particularly important on nanofilled systems but not in the microfilled composites? The answer lies in the relative size difference of an average polymer chain and the filler as shown in Figure 1-3.
Figure 1-3. (a) Illustration of relative size of 10 polymer chains ($R_g = 35$ nm) together between two micro particles with diameter of 1 µm. (b) Single polymer chain ($R_g = 35$ nm) between two nanofillers having 12 nm diameter. For both illustrations perfect distribution of 3.5 vol % fillers is sketched and the average distance between the centers of micro and nano fillers are about 3 particle diameters.

For nanoscale fillers, the contact area between fillers is much larger than for microscale fillers. Thus, the “layer” effect on $T_g$ of the final microfiller composite is negligible compared to the nanocomposite.[10,11] The cartoon presenting the micro- and nanocomposites in Figure 1-3 shows the size of the polymer “layer” on a filler (green colored area in Figure 1-3b), which is ca. 10 nm – seemingly independent of the molecular mass, size and the amount of filler.[12] While Figure 1-3 shows a perfectly distributed filler population within the matrix, this is (almost) never the case – either for micro- or nanocomposites. Work shown in Chapter 3 and Chapter 5 will clearly demonstrate this point, and optimizing the filler distribution in the matrix is a very active research area.
Chapter 1

1.3 Molecular picture of nanocomposites

In this section, I will introduce certain molecular scale properties of nanocomposites based on two different kinds of elastomers: (1) acrylonitrile-butadiene rubber (NBR) and (ii) styrene-butadiene rubber (SBR). Fumed silica (SiO$_2$) nanofillers are used in these formulations with a wide range of primary size (from 12 nm to 30 nm). Importantly, $T_g$ of both rubbers and their composites are significantly lower than RT (ca. -30 °C).

1.3.1 Nanofiller dispersion

As indicated in the previous section, the interface between nanofiller and polymeric matrix has a direct effect on the mobility of the polymer molecules close to the filler surface, and this is a critical property for varying linear and non-linear viscoelastic properties of the nanocomposites.[13–16] Beside mechanics, filler dispersion and the interfacial interaction between filler and matrix also changes optical,[17,18] electrical,[19–21] biological properties[22,23] of the nanocomposites. Given this importance, we should ask ourselves the following questions: 1) how can we control the dispersion of the fillers, and 2) how can the dispersion be quantified?

Silica and carbon black are the most common used nanofillers in elastomer-based nanocomposite formulations in industry due to their low cost and good processability. In early filled elastomer technologies, particularly the car tire industry, carbon black had been used for many years as reinforcing agent. However, starting from the early 1990s, significant car tire performance improvements in terms of wet grip and rolling resistance have been detected by replacing carbon black with silica nanofillers.[24–26] Compared to carbon black, the biggest drawback of silica nanofillers is that they have numerous silanol groups on their surfaces which make them highly polar and hydrophillic. Therefore, silica nanofillers tend to gather – aggregate – when they are mixed inside of hydrophobic polymeric matrices. In what follows below, I will introduce different methods to quantify nanocomposite microstructure and specifically filler dispersion. Two fundamental methods, (i) electron microscopy[27–31] and (ii) x-ray scattering methods.[17,32–37] have the appropriate spatial resolution, penetration, and provide sufficient contrast between fillers and the matrix. Even though transmission-electron microscopy (TEM) is most widely used since it is relatively
1.3. Chemical methods to control filler dispersion

With methods in place to quantify the nano-filler distribution in the polymeric matrix, now it is possible to address the second question: how can we control the dispersion of hydrophilic inorganic fillers inside of hydrophobic matrix? Two primary methods are used in elastomer-based nanocomposite systems to control the dispersion of the silica nanofillers. The first method is covalent coupling.
between the silica surfaces and active groups on the polymers. This, in turn, can be achieved in the two ways shown in Figure 1-4: 1) via silanes attached to the silica, which then couple to the polymer, and 2) direct attachment via end or side functionalized silanol (Si-OH) groups on the elastomer chain. [30,40] The second strategy to control the dispersion is by changing the surface polarity of the fillers.[41,42] These different strategies, as related to the materials in this thesis, are illustrated in the Figure 1-4.

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**Figure 1-4.** Illustration of a single silica particle with possible surface treatments in order to improve the filler dispersion inside of the polymeric matrix. Curved arrows and numbers next to them in (c) and (d) represent the sequence of the treatment steps. R is the initiator used for grafting on polymerization which takes place on the filler surface.

In Figure 1-4a chemical bridge between filler and polymer is mediated by the multifunctional silane, bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT). This method is a popular method for improving the filler dispersion in the nanocomposite industry, e.g. in car tires. The major drawback of this method is the
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high cost of TESPT molecules. [40] Therefore, especially in the tire industry, research has focused on finding other methods, including changing the surface polarity of hydrophilic fillers by using different short hydrocarbons and silanes (Figure 1-4b), [41–44], polymerizing molecules by initiating them on the filler surface [45] (Figure 1-4d), or by modifying the end group of the elastomer chains for direct coupling to the filler surface (Figure 1-4c).

Among all these strategies, modified – functionalized – groups at the end or side groups of the polymer chains is gaining interest by industrial producers. [38,39,46] In recent works, it has been reported that the size of silica nanofiller aggregates could be controlled in SBR by changing the ratio of chains with functional groups to those without functional groups. [38,39] These works have shown that even a low concentration of chains with functional groups (25% of the total end groups of SBR molecules) was sufficient to tune the filler distribution and thus the non-linear viscoelasticity of complex SBR based nanocomposite systems. [47] However, an unambiguous picture of the chemistry at the polymer-filler interface (such as that illustrated in Figure 1-4c) is not easy to obtain.

1.3.3 Measuring interfacial chemistry between fillers and matrix

It is particularly challenging to quantitatively (or even qualitatively) describe the nature of the interaction between fillers and the matrix. Is the interaction between the intended partners covalent or non-covalent? Making drawings like those in Figure 1-4 is straightforward (known as “Powerpoint Science”), but actually proving these bonding interactions is not straightforward, especially in complex industrial composites. In my department at the Max Planck Institute interface-specific spectroscopic methods have been developed that can provide information on the interface between polymer and silica surface. Three techniques are discussed in this thesis: (i) Sum Frequency Generation (SFG) spectroscopy, (ii) near edge x-ray absorption fine structure (NEXAFS), and (iii) X-ray photoelectron spectroscopy (XPS). The latter two are ultra-high vacuum techniques whereas SFG is an ambient environment spectroscopic tool to determine interfacial molecular structure of materials. All of these methods are sensitive to (sub) monolayer quantities at the surface/interface. NEXAFS and SFG are also sensitive to the orientation of molecules at the interface/surface while SFG is exquisitely sensitive to the ordering of the functional groups at the interface. [48–52] XPS is a truly quantitative tool that provides chemical composition in atomic % and probes the upper few tens of
Angstroms [53–55] of an interface, and importantly for this thesis, it is possible to use depth profiling by using argon ions or clusters to drill into a material. The physical background of SFG, NEXAFS and XPS will be provided in Chapter 2. In Chapter 4, we will show how we studied a model system to clearly identify interfacial chemistry between functionalized SBR and fillers using these surface-sensitive spectroscopic methods.

Figure 1-5. Strain (ε) response of materials with ideal (a) elastic, (b) viscous and (c) Burgers viscoelastic behaviors under an instantaneous stress (σ₀) applied between times 0 and t’.

1.4 Resistance to deformation of nanocomposites

1.4.1 Viscoelasticity of polymers

The goal of creating nanocomposites is to improve their mechanical properties, often their resistance to deformation or applied loads. For a purely elastic material, such as an ideal spring, this property is called elasticity; however, polymers are not purely elastic, hence they are termed viscoelastic. To understand the term viscoelasticity, we first need to define the roots of this word, which are viscous and
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Viscous, elastic or viscoelastic response of the materials can be detected by creep tests, which measure the time-dependent strain in response to a (constant) step stress. A purely elastic, purely viscous and viscoelastic response of a material due to applied constant stress \( (\sigma_0) \) (between times, 0 and t’) are illustrated in Figure 1-5. Strain response of a purely elastic (Hookean) material increases instantaneously with force and stays constant till the force is removed \( (t=t’) \) (Figure 1-5a). For the ideal (Newtonian) viscous material, the strain increases linearly with increasing time as long as load is applied to the material. After removing the load from the system \( (t’) \), strain in purely viscous material remains constant unless a further load is applied (Figure 1-5b). Viscous deformation is called non-reversible (plastic) since there is no recovery. In viscoelastic materials, the material presents the strain response of both elastic and viscous material (Figure 1-5c). The curve in Figure 1-5c is called the Burgers model, which has been used to explain viscoelasticity of many thermoplastics.[56] More details of using spring and dashpots for understanding the elasticity of nanocomposites are explained in Chapter 2 (section 2.2).

Differently from many other polymers (glassy and semi-crystalline) having viscoelastic behavior, an “ideal (cross-linked) rubber” mechanical response is almost completely dominated by the elastic response. Long and freely rotating rubber molecules are highly entropic and thus under deformation rubber behaves elastically.[57] Moreover, rubber based composites used in this thesis are cross-linked (vulcanized, see Figure 1-2c) and cross-linked network structure further enhances the elastic behavior of the material since the rubber molecules cannot slide over each other easily during their deformation.

1.4.2 Deformation under static forces: tensile testing

**Static mechanical testing** methods are used for measuring the force response of material under stretching, compressing, or shearing at a constant rate. In this thesis, we routinely performed static mechanical tests of our samples using tensile tests, as well shear to a lesser extent. For a typical tensile test measurement, a material is cut in the form of a dog bone (or dumbbell), which is shown as inset in Figure 1-6a, and it is fixed at one end while the other end is pulled with a constant rate of elongation (strain rate) until the sample fractures. The measures of stress and strain are divided in two main groups as “engineering” and “true”. The engineering stress \( (\sigma_{Eng}) \) and engineering strain \( (\varepsilon_{Eng}) \) are calculated from the measured load \( (F) \), original (initial) cross-sectional area \( (A_0) \) of the center of the
specimen (black shaded area in the illustration of Figure 1-6a inset), original length ($L_0$) and displacement during stretching ($\Delta L$) of the specimen as,

$$\sigma_{Eng} = \frac{F}{A_0}, \epsilon_{Eng} = \frac{\Delta L}{L_0} \quad (1.1)$$

However, at high strain levels, the engineering stress-strain curve is not accurate since stress is not calculated using the actual cross-sectional area of the material (which changes during deformation). As a solution, the stress-strain response of the sample can also be reported in terms of true stress ($\sigma_{True}$) and true strain ($\epsilon_{True}$).

$$\sigma_{True} = \frac{P}{A}, \epsilon_{True} = \int_{L_0}^{L} \left( \frac{1}{l} \right) dl = \ln \left( \frac{L_0 + \Delta L}{L_0} \right) \quad (1.2)$$

The true stress reports the measured load at each strain divided by the actual cross-sectional area, $A$, rather than the initial value $A_0$. Since the actual cross-sectional area decreases as the sample elongates, $\sigma_{True} > \sigma_{Eng}$. In elastomeric materials the volume of the sample is assumed to not change during deformation, and the $\sigma_{True}$ can be related to the $\sigma_{Eng}$ simply as,

$$\sigma_{True} = \sigma_{Eng} \left( \frac{L_0 + \Delta L}{L_0} \right) \quad (1.3)$$

An exemplary engineering stress-strain curve of a ductile material is shown in Figure 1-6b. In very short displacement range of $\sigma_{Eng}$-$\epsilon_{Eng}$ curve of many materials stress linearly increases with strain and type of deformation in this range is called elastic deformation (Figure 1-6b). In elastic deformation range, the material obeys Hooke’s law and the constant of proportionality is the modulus of elasticity or Young’s modulus $E$:

$$\sigma_{Eng} = E \epsilon_{Eng} \quad (1.4)$$

With the increasing strain, many materials diverge from this linear regime at a specific point, called the proportional limit. At higher strain beyond the proportional limit, the material shows a non-linear stress-strain relation, which is called non-linear elasticity. In many ductile materials, especially ductile polymers, it is very challenging to pinpoint the exact starting point of non-linear elasticity region in terms of stress. Therefore, the yield stress ($\sigma_Y$) has been defined as the accepted location where non-linear deformation starts in a material during tensile testing. $\sigma_Y$ is found by sketching a line from the strain axis at $\epsilon_{Eng} = 0.2 \%$ that has the same slope of that which defines the initial Young’s modulus. This is shown schematically in Figure 1-6b. The intersection of this line with the engineering stress-strain curve is defined as the yield and marks the $\sigma_Y$. In other sources, this offset value is $0.1 \%$. 
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In Figure 1-6, I summarize typical stress-strain curves of different types of polymers by their deformation behaviors in RT condition tensile tests. A stress-strain curve of brittle and hard polymers is presented by curve 1 in Figure 1-6a. Both amorphous and semi-crystalline polymers can show such a curve if their mechanical tests are performed at a temperature well below their T_g. These polymers have linear stress-strain behavior over nearly the full range of deformation, which eventually ends with a fracture prior to any plastic flow. Stress-strain characteristics of many engineering thermoplastics are presented by curves 2 and 3 in Figure 1-6a. In curve 2 and 3, at the initial part of the deformation, stress increases with increasing strain and after a certain strain level, stress begins decreasing with the increasing strain. The strain level for which the stress reaches its maximum value (i.e. where dσ/dε = 0) in both curves is called the ultimate tensile stress (UTS). After UTS, first the stress shows a drop (decrease) with further increasing strain, and this process is called strain softening. The minimum stress in this softening regime is called draw stress, and at this point, material either fractures (curve 2) or starts getting harder due to orientation hardening (curve 3).
immediately before the fracture. In general, during orientation hardening or strain hardening polymer chains are aligned to the direction of loading, and the system shows increasing resistance to further deformations (strain). Depending on the polymer type, it is possible to have permanent, non-catastrophic – plastic – deformation. In ductile polymers (but not in elastomers), such a process happens between the UTS and strain level where orientation hardening starts (point IV on curve 3 in Figure 1-6a), and the shape of the specimen changes. After UTS, the central width of the dog bone decreases in a process called necking (between points I and II on curve 3). After the neck formation, the sample extends along its length and the cross-section of the necking region gets smaller at the same time (between II and III of curve 3) and this process is called cold-drawing. For the samples showing orientation hardening before their fracture (between III and fracture points (IV) of curve 3), necking (decrease in the size of width) gets stabilized when the orientation hardening starts. During the orientation hardening, only the neck propagates from the center of the specimen along the gage distance outward until the sample fails.[5,3]

The stress-strain behavior of a typical elastomer rubber is shown by the curve 4. These rubbers have the smallest modulus but the highest extension ratio compared to the others systems in Figure 1-6a. Before the fracture of rubber, similar to other ductile polymers (curve 3), the cross-linked rubber molecules align to the loading direction, and the material shows the effect of strain hardening prior to fracture. In ductile and rubbery polymers, strain-hardening is a very crucial parameter for understanding the mechanical behavior of these materials in cyclic, high-stress environments and during extended periods of mechanical deformation.

It is important the note that the preceding discussion and Figure 1.6 was in the context of pure polymer matrices and NOT in the context of composite materials. The effect of nanofillers on the elasticity strain-hardening characteristics of the rubbers will be discussed in Chapter 5. Additionally, further details of tensile test analysis, for instance Gaussian statistics of rubber molecules, and observation of the modulus of strain-hardening in ductile polymer and nanocomposite systems will be discussed in Chapter 2.

1.4.3 Reinforcement

As mentioned before, the main reason for including fillers (carbon black or silica) in rubber is for improving the mechanical properties of the rubber. For instance,
improving the lifetime of rubber used in car tires can be done by preventing the rupture failure due to fatigue, which occurs during the wear of the rolling tire. Increasing not only the fatigue resistance, but also modulus, rupture energy, tear strength, tensile strength, cracking resistance and abrasion resistance can be done by increasing the linear elastic (storage) modulus of the rubber, or its reinforcement, by including fillers among other ingredients. Reinforcement of a filled elastomer system can be observed from the linear portion of a storage modulus versus increasing shear amplitude graph, which is obtained from the dynamic mechanical tests (DMA) (Figure 1-7a). The theory of DMA is introduced in Chapter 2 (see section 2.2). Obtaining higher reinforcement (increasing the storage modulus in the linear deformation regime) is a very complex phenomenon depending on two main parameters: (i) arrangements of the fillers in the polymeric matrix and (ii) interaction between the fillers and the polymeric matrix. As explained in section 1.3, the complex interaction between fillers and polymer molecules influences the size, shape and aspect ratio of the filler aggregates and such changes in the filler nature have a direct impact on the composite reinforcement. For rubber-based composites filled with very low concentrations of fillers, in which there is no risk of having particle–particle interaction, it has been found that reinforcement linearly scales with the filler concentration. However, at higher filler concentrations the reinforcement gets more sensitive to the filler aggregate size. In systems containing a similar amount of fillers with different aggregate sizes and with the possibility of direct interaction between rubber molecules and fillers, a higher reinforcement is observed for the sample with smaller aggregates compared to that with larger aggregates. This is explained in terms of having stronger interaction between matrix and fillers in the better dispersed system owing to the larger surface area between the aggregates and matrix compared to that in the other sample with bigger aggregates. On the other hand, reinforcement gets more efficient when the fillers are in the shape of complex structures (e.g., branched or fractal) rather than being dispersed perfectly in the rubber. A precise and straightforward relation between filler dispersion and reinforcement involves many different criterions and is still not completely understood. This topic will be addressed further in Chapter 3.
Figure 1-7. (a) Example storage modulus of two different filled rubbers having different viscoelastic properties – reinforcement and nonlinear softening. The storage modulus is linear to the left of the red dashed line and non-linear (via the Payne effect) to the right. Typically ~ 10% shear strain is the critical shear deformation where the sample starts responding to the further deformation non-linearly. (b) Typical tensile stress-strain behavior of a filled elastomer until fracture. Non-linear elastic softening (Payne effect) and hardening are separated by red dashed line. Both in (a) and (c), the boxed “1” mark the regions in the illustrated data where the Payne effect is observed. (c) Example of the Mullins effect by showing tensile stress-strain curves of a rubber material in 2 cycles. The region where the Mullins effect is observed during the second stretching is shown in the borders of the shaded area (grey color).

1.4.4 Payne and Mullins effect

The non-linear softening response of rubber and rubber-based samples is called the Payne or Mullins effect, depending on its origin.[65,66] The Mullins effect is the stress softening of filled, and even some unfilled, rubbers in the stress-strain curves over multiple cycles as shown in Figure 1-7c. The Payne effect is stress softening observed at moderate strains. This is shown in Figure 1-7a for a DMA measurement and in Figure 1-7b for a tensile test. In literature, the following factors have been invoked for explaining such softening response of the materials: (i) disentanglement of the rubber molecules physically, (ii) reduced interactions between filler and the rubber molecules, (iii) breakdown of the filler network and (iv) chain scission in rubber molecules.[10] Because the both the Payne and Mullins effects are observed in tensile cyclic loading experiments (Figure 1-7c), it is not easy to define which effect is dominant. In order to avoid this confusion, the Payne
effect has been defined as *reversible* strain softening whereas the Mullins effect is defined as *irreversible* strain softening. [67] In contrast, the Payne effect is only observed in filled rubber systems and it gets more prominent with higher concentration of fillers. Furthermore, Payne effect is clearly observed under oscillating loads at very small strain amplitudes whereas the Mullins effect is observed at substantially higher strain levels (outside of the region number 1 in Figure 1-7b) in more than one cycle of tensile loadings. Both softening features are of significant importance in industrial nanocomposites such as car tires, with regards durability, grip, and rolling resistance.[68]

### 1.5 State of order in polymers and composites

Understanding the orientation of polymer molecules is a fundamental requirement for explaining various macro-scale properties of polymer materials and polymer based composites, most importantly their mechanical properties.[69] As previously mentioned, strain hardening of many polymeric materials under uniaxial stretching is correlated to the dynamic alignment mechanism of the polymer molecules along the loading direction. In cross-linked rubber materials at high strain level, it is important to connect their mechanical and/or swelling behaviors to their strain induced crystallization caused by molecular orientation. This helps explains their deformation mechanism particularly prior to their fracture (strain-hardening).[70] Moreover, in order to design new polymeric materials with superior physical properties (e.g. directional stiffness in composites), the relation between orientation behavior and the properties in polymer films or fibers has significant importance.[71] For nanocomposites, the presence of nanofillers in polymers certainly affects the macromolecular orientation of these polymers due to (i) their large surface area, (ii) interfacial interactions between fillers and polymer and (iii) impeding the motion of the polymer chains close to the filler surface (bound layer).[71–76].

Different methods to measure chain orientation *in situ* are NMR spectroscopy, x-ray diffraction, polarized fluorescence or optical birefringence, Raman and Fourier transform infrared (FTIR) spectrosopies.[77–79] Among these methods, optical birefringence is often preferred for measuring the orientation of polymers. However this method cannot discriminate the anisotropy of oriented molecules between crystalline or amorphous phases of a homogenous polymer or different phases in a heterogeneous polymer because there is no molecular
specificity. For instance, at a certain deformation of a semi-crystalline polymer, it is known that the deformation stages of different phases are different and it is important to understand the connection between total polymer deformation and the chain anisotropy of specific molecules in different phases. In the same way, x-ray scattering, while able to discriminate between crystalline and amorphous phases, is limited to observe the orientation in the amorphous phase unless there is strain-induced crystallinity and also has no molecular specificity. Polarized Raman spectroscopy and Fourier transform (FTIR) dichroism are the two most useful methods since they provide orientation data of specific molecular groups within chemically and/or conformationally different chain segments of polymers with or without fillers inside. Owing to the molecular level sensitivity of these vibrational techniques, certain deformation of polymeric samples under stretching can be explained in terms of molecular alignment.

Using x-ray scattering and IR dichroism methods, the direct relation between clay nanofiller content and chain orientation of various polymers like PS, polyamide 6 and polyurethane (PU) has been studied by monitoring the alignment of the polymer molecules via tensile deformation. However, these studies could not simultaneously measure polymer chain orientation during mechanical deformation. This limitation was because $T_g$ of PS and Polyamide 6 are higher than the RT, so the nanocomposites first were heated, stretched at high temperatures and then they were cooled down to room temperature to measure spectroscopic alignment measurements. In contrast, the PU had a lower $T_g$ than RT, so they could be stretched at RT while measuring chain alignment. However, the PU was not crosslinked and was therefore not stable at RT during deformation. The authors allowed 15 minutes of “stress-relaxation”, after stretching PU samples, before measuring chain alignment. Hence, there is a need to measure chain alignment under simultaneous deformation, especially in elastomeric systems.

Fortunately, vulcanized nanocomposite rubber systems such as SBR and NBR, which also have very low $T_g$ (ca. -30 °C), are stable under RT conditions (no flow) thanks to their cross-links (vulcanization). Therefore, they can be stretched at RT without the need for any additional procedures (heating or stress-relaxation). While these properties make elastomer materials attractive to investigate the mechano-chemical alignment, there are two major challenges compared to non-crosslinked thermoplastics: (i) Segments of chains in elastomeric networks are cross-linked to each other and are not as independent as non-crosslinked polymeric
chains. (ii) Random cross-linking causes some imperfections or defects in rubber macrostructure such as physical entanglements, looping (pinning of single chain to itself) and terminal chains.[3] Such imperfections make the elastomer alignment mechanism less uniform. In Chapter 5, the alignment of the elastomeric networks along the loading direction, and the effect of fillers on chain anisotropy was quantified with polarized Raman micro-spectroscopy and quantification of molecular order for particular vibrational modes. The technical details of deciding which vibrational modes to study, and the statistical strategies for showing the chain anisotropy will be presented in Chapters 2 and 5.