Mechanics of filled rubbers from a molecular point of view

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CHAPTER 2: MATERIALS & FUNDAMENTALS OF METHODS

2.1 Materials

The nanocomposites used in this work are classified in two main groups: (i) full nanocomposites and (ii) simplified nanocomposites. Chemical formulation details of the full nanocomposites will be explained to the extent that is possible while respecting the intellectual property of our industrial collaborators who produced these samples. Full nanocomposites are further classified by their polymeric matrix types which are styrene – butadiene rubber (SBR) and acrylo-nitrile-butadiene rubber (NBR). Simplified nanocomposites were produced only with SBR materials. In the following, a brief description of the different composites is presented.

Styrene – Butadiene Rubber (SBR) /silica full nanocomposites

SBR ($M_w = 1.5 - 1.6 \cdot 10^5$ g/mol, $T_g = -32 \text{ °C}$) / precipitated silica (Zeosil 1165 MP, primary particle size, $R_p \approx 12$ nm, surface area $\sim 160 \text{ m}^2 / \text{g}$, from Rhodia®) full nanocomposites and neat SBR without fillers inside were synthesized in Michelin® laboratories. [47] Due to presence of end-group functionality, SBR rubber was divided into two classes. As shown in the Figure 2-1, SBR carrying the silanol (Si-OH) end functional group is called functionalized SBR (F-SBR), and SBR without any functional group is called bare SBR (B-SBR). The functionalized end-group of F-SBR is chemically written as SBR−SiMe$_2$−OH (Figure 2-1b). The functional group fraction in one end of all F-SBR chains has previously been reported to be greater than 98% according to the results from 1H and 29Si NMR. [47] In the same study, the composition of both F-SBR and B-SBR were shown to be similar to each other due to their identical polymerization steps (anionic polymerization).[47] Both types of SBR were statistical copolymers consisting of 26 wt % of styrene and 74 wt % of butadiene units (41 wt % of 1,2-butadiene and 59 wt % of 1,4- butadiene units). The structures in Figure 2-1(a) and (b) denote the number of each subunit using the letters m, n, k and p for styrene, 1,2-butadiene, trans-1,4-butadiene and cis-1,4-butadiene monomers, respectively. The ratio of trans-1,4-butadiene to cis-1,4-butadiene ratio is not known, and it is not crucial for the content of this thesis as it is the same for B-SBR and F-SBR. Gel permeation chromatography (GPC) of the
polymer showed the $M_n$ and polydispersity index (PDI) of both stock polymer solutions in THF ($M_n \sim 150-160$ kDa, PDI $\sim 1.08-1.11$) to be very similar to each other, and very close to values previously reported for identical SBR polymers. [47]

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**Figure 2-1.** Molecular structure of (a) B-SBR, (b) F-SBR and NBR. Letters next to the brackets indicate the number of repeating units in each rubber.

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To produce full composites from these SBR polymers, the polymers were mixed with many other components in the melt state. A mixing chamber was heated to $160 \pm 5$ °C, and the rotor speed in the chamber was kept between 95 and 105 rpm to blend the composites into a uniform mix. The components were added to this chamber in the following way: 1) lamellas of SBR polymer were cut into small pieces and then added to the chamber and 2) after $\sim 1$ min, a mixture including silica fillers with different amounts (see Table 2-1), catalyzer for vulcanization of SBR (diphenyl guanidine (DPG), 2 wt % with respect to the silica), coating agent (octyltriethoxysilane (octeo), 4 wt % with respect to silica) and coupling agent (bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT or Si69), 4 wt % with respect to silica) was added to the chamber and mixed for an additional 4 min. The hot sample was taken out of the reaction chamber and quickly cooled and
laminated by rolling the samples 10 times through a 1 mm gap between rotating cylinders (two roll mill). The laminated mixture was then vulcanized (cross-linked) as a final step of the production.

Table 2-1. Type, amount of the ingredients and possible interfacial interactions in all the nanocomposites used in this thesis

<table>
<thead>
<tr>
<th>Synthetic parameters</th>
<th>Filler radius : surface area per weight</th>
<th>Filler amount (vol %)</th>
<th>Interfacial interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of rubber</td>
<td>Fillers radius</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>F-SBR</td>
<td>12 nm : 160 m²/g</td>
<td>3.5 6 16 21 24</td>
</tr>
<tr>
<td></td>
<td>B-SBR</td>
<td>12 nm : 160 m²/g</td>
<td>3.5 6 16 21 24</td>
</tr>
<tr>
<td></td>
<td>NBR</td>
<td>28 nm : 55 m²/g</td>
<td>3 8 14 22.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 nm : 130 m²/g</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15 nm : 180 m²/g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>F-SBR</td>
<td>6 nm : 200 m²/g</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>B-SBR</td>
<td>6 nm : 200 m²/g</td>
<td>16</td>
</tr>
</tbody>
</table>

Acrylonitrile – Butadiene Rubber (NBR) / Silica full nanocomposites
Precipitated silica (Evonik®, Essen, Germany) / Acrylonitrile Butadiene Rubber (NBR, \( M_w = 2.5 \cdot 10^5 \) g/mol, glass transition temperature, \( T_g \approx -36 ^\circ C \)) full nanocomposites were produced at SKF® Elgin, USA. NBR rubber was synthesized as nitrile elastomers via emulsion polymerization of 1,3-butadiene and acrylonitrile (ACN) with the monomer ratio of 28:72. In NBR nanocomposites, the primary size of the
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Filler particles were changed in different composites. Sizes, surface areas, and amounts of the three different size fillers are listed in Table 2-1. Similar to the SBR nanocomposites, NBR systems were also produced in melt in a mixing chamber; however, for reasons of confidentiality further production details cannot be provided. In general, NBR rubber (100 parts per hundred rubber (PHR)) was included with various amounts of silica (see Table 2-1) for different nanocomposites. The amount of stearic acid (1 PHR), zinc oxide (ZnO, 9 PHR), rubber activator (2.5 PHR), sulfur (1.2 PHR) and accelerator for curing agent (2.5 PHR) were kept constant for all the formulations, and their amounts were not scaled with respect to the filler amount as was done for SBR formulations. Mixtures out of the reaction chamber were then vulcanized as a final step.

**SBR / silica simplified nanocomposites**

Non-vulcanized (dissolvable) F-SBR and B-SBR bulk slabs were dissolved in Tetrahydrofuran (THF, Sigma-Aldrich) and prepared as polymer stock solutions (40 mg/mL). These stock solutions were used after keeping them in a fridge (4 °C) for at least 4 days until a uniform and clear rubber solution (as seen by eye) was obtained. Fumed silica nanofillers (Aerosil 200, Evonik®, $R_p \approx 6$ nm) were used as received to prepare filler stock solutions (15.2 mg/mL in THF). After adding the fillers inside of THF, the solution was sonicated on ice with a probe-type sonicator (Branson Sonifier W450 digital, 1/2 inch diameter, 10 s, 60% amplitude) to promote dispersion of the fillers. To form the final simplified composite, a mixture of both filler and rubber stock solutions was prepared and mixed using the ultrasonic tip for 10 sec, 60% amplitude while keeping the mixture in an ice-bath. The final mixture was placed in a rotary evaporator (Rotavapor R-200, Buechi, Essen) at RT under 20 mbar for 30 min in order to remove THF. After retrieving the mixtures from the rotary evaporator, complete removal of THF was done by keeping the simplified nanocomposite mixture inside a vacuum oven (< 1 mbar) for 24h at 80 °C. In order to avoid any possible condensation reaction between the end-groups of F-SBR and the glassware, plastic ware was used for simplified nanocomposite production.
Chapter 2

2.2 Experimental Methods

2.2.1 Tensile testing and rheology

**Tensile testing and calculation of strain-hardening modulus**

Uniaxial tensile testing of full nanocomposites was done using an Instron Universal Testing Machine (Instron 6022, Darmstadt). Slabs of nanocomposites samples with uniform thickness (ca. 0.2 cm) were cut into the small dumbbell shapes (length ≈ 1 cm, thickness ≈ 0.2 cm, width ≈ 0.18 cm). Cut samples were clamped to the tensile testing device by applying 5 bar of clamping pressure. No pre-strain was used and strain rate was kept 100 mm/sec for each measurement. Mechanical tests were terminated manually after the fracture of the composites. Three different tests were performed on each nanocomposite sample. Engineering stress (σ\textsubscript{Eng}) and engineering strain (ε\textsubscript{Eng}) were obtained from the tests and subsequently converted to true-stress (σ\textsubscript{True}) and true-strain (ε\textsubscript{True}), following the equations presented in section 1.4.2. The nature of the viscoelasticity of polymers is generally obtained by analyzing the tensile test response in the context of mechanical elements such as ideal springs as the perfect elastic (Hookean) element and dashpots as the perfect viscous element as presented in Figure 2-2a. The combination of ideal and nonlinear dashpots and springs shown in Figure 2-2a was proposed by Haward and Thackray [86] in order to replicate the tensile test response and explain the rubber elasticity in a tangible framework.[4] In order to apply this model to experimental tensile test results at large strain levels (far above the linear regime of the stress-strain curves), the following assumptions were made: 1) that the extension is dominated by strain from the non-linear deformation portion (ε\textsubscript{p}) rather than linear (Hookean, ε\textsubscript{H}) deformation and 2) that the material was incompressible, meaning that the Poisson’s ratio was 0.5. In many stress-strain curves of rubber-based nanocomposites, the linear deformation region is usually impossible to detect as it only appears for very small strains. Therefore, we assumed the output of the tensile tests ε\textsubscript{Eng} ~ ε\textsubscript{p} to calculate the extension ratio, \( \lambda \), as shown below,

\[
\lambda = \frac{\text{extended length}}{\text{original length}} \sim 1 + \varepsilon_p \sim 1 + \varepsilon_{Eng}
\]  

(2.1)
Figure 2-2. (a) Spring – dashpot model explaining the large strain deformation of ductile polymers. The system consists of one elastic (Hookean) spring connected in series to another spring and a viscous dashpot which are connected to each other in parallel. $E$, $\varepsilon_H$, $\sigma_{Eng}$, $\sigma_{Eng(sp)}$, $\sigma_p$ represent Young’s modulus, strain for Hookean spring, engineering stress applied to the system, engineering stress at spring parallel to the dashpot, strain at the dashpot and second spring together, respectively. (b) Illustration of polymer chain distortion under stretching explained in terms of Langevin and Gaussian equations. The Langevin equation is used when a polymer chain approaches the maximum extension between entanglements (straight line between two crosses). Gaussian deformation applies if the polymer chain behaves like a statistical coil and cannot fully extent under deformation (illustrated in red box). Extension ratio, $\lambda$ of the coil is calculated by the formula shown as inset. In the formula, length difference between extended and original presented by $\Delta L$. (c) Example of volume-conserved deformation of a polymeric material. The polymeric sample with initial dimensions of $x_0$, $y_0$, $z_0$ and after the deformation it takes on dimensions $x$, $y$, $z$. 
The Haward and Thackray model can be applied in two ways, depending on the polymer chain extensibility at high strain levels (Figure 2-2b): (i) using Langevin equations by assuming the polymer chain can be extended until it becomes nearly straight at maximum elongation [87] or (ii) using Gaussian approximation by assuming that the polymer chains cannot be fully stretched at the highest strain level as illustrated in Figure 2-2b. Similar to what has been mentioned in the rubber literature, we do not expect a random crosslinked and very high molecular weight rubber molecule to stretch fully.[4] Hence, we employed the Gaussian modeling and used this model to find the so-called strain-hardening modulus ($G_p$) of our nanocomposites as,

$$\sigma_{\text{True}} = \lambda \sigma_{\text{Eng}} = G_p \left( \lambda^2 - \frac{1}{\lambda} \right)$$

(2.2)

The derivation of equation (2.2), which invokes the entropic elasticity of individual chains, has been discussed elsewhere[3,4] and is based on the following fundamental assumptions:

1- Chain segments between two successive crosslink points of cross-linked network are envisaged as independent chains. The complete rubber network, which is subjected to a deformation, is made up with the same number of chains per unit volume.

2- Network is constructed by freely joined chains which follow Gaussian statistics.[3] Therefore, sum of the individual chain (single) entropies gives us the total entropy of the network.

3- Extension ratio of each chain during stretching is equal to the extension of the bulk network. In other words, network sustains an affine deformation.

4- Material does not change its volume during the deformation (Figure 2-2c).

### 2.2.2 Dynamic-Mechanical analysis: Rheology

Dynamic mechanical measurements were performed at University of Amsterdam – The Netherlands (UvA) by M.R.B. Mermet-Guyennet in Prof. Daniel Bonn’s laboratory. An oscillatory rheometer (Anton Paar MCR 300) was used with different radii plate-plate geometries. For full nanocomposite samples, a superglue – Loctite 421 type – was used to improve the adhesion between the plates and the composite. During the rheology measurements, a sinusoidal shear strain was applied to the sample (strain-controlled measurements), which produces a stress response with similar frequency when the deformation is linear (Figure 2-3). The linear strain and stress response curves of rubber (or general viscoelastic materials)
are shown in Figure 2-3c. During the oscillatory measurement of the rubber, a fraction of the energy is stored elastically and the rest of it is dissipated as heat. The sinusoidal applied shear strain ($\gamma(t)$) is characterized by an amplitude ($\gamma_0$) and angular frequency ($\omega$) as:

$$\gamma(t) = \gamma_0 \sin(\omega t)$$  \hspace{1cm} (2.3)

Due to the viscoelastic nature of the rubber, the stress response of the rubber induced by the applied oscillatory strain has a phase shift ($\delta$) and it can be described as follows:

$$\sigma = \sigma_0 \sin(\omega t + \delta) = \gamma_0 [G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)]$$  \hspace{1cm} (2.4)

where $G'$ (called storage modulus) is the storage of the elastic energy, and $G''$ (loss modulus) quantifies the dissipated energy during the deformation. In perfectly elastic materials (Figure 2-3a), $G''$ is zero since energy is not dissipated and
completely stored by the material ($\delta = 0^\circ$). At the same time, for perfectly viscous material (Figure 2-3 b), $G'$ is zero since the stress and strain curves are perfectly out-of-phase ($\delta = 90^\circ$). However, in viscoelastic materials $G'$ and $G''$ are non-vanishing since the material has a stress response of both viscous and elastic origin. Thus, the phase shifts ($\delta$) of the viscoelastic materials always lie between $0^\circ$ and $90^\circ$ (Figure 2-3c).

2.2.3 Filler aggregate size determination

Measuring aggregate size

Nanofillers in nanocomposites often aggregate into large amorphous masses during the formulation process. These aggregates are usually ~ 2-10 fold larger than the size of a primary filler particle but can extend to be 100-fold larger in certain cases (as we will see in SBR full composites). This corresponds to ~ 20 – 100 nm in most cases and ~ 1 µm in extreme cases. Furthermore, because the agglomeration process almost certainly takes place out of equilibrium, aggregates often exhibit an extremely high polydispersity. Optical microscopy cannot provide accurate images of nanocomposite aggregates due to diffraction-limited spatial resolution of visible light (Figure 2-4a). Higher resolution images showing dispersed fillers in the matrix – from the primary filler to giant agglomerates – can in principle be obtained using electron microscopy. In electron microscopy, the deBroglie wavelength of an electron is at most ~ nm and typically much lower (depending on the acceleration voltage varying from tens to hundreds of kilo-electron volts (keV)), which is why this technique is able to resolve nanoscale aggregates.

The two main electron microscopy techniques are transmission electron microscopy (TEM) and scanning electron microscopy (SEM). In terms of the typical spatial resolution limits presented in Figure 2-4a, SEM lies between optical microscope and TEM. In Figure 2-4b, the basic mechanisms of SEM and TEM are explained by showing how the incident electrons interact with the sample. Prior to TEM imaging (JEOL JEM 1400, Eching), bulk nanocomposite samples were cut to 50 nm thick slices by ultracryotome (LEICA EM UC6, Wetzlar) and these slices were placed on top of copper grids. Ultracryotome was performed at -60 C° in order to cool the samples considerably lower than their $T_g$, which makes them highly brittle. TEM electron path (1) in Figure 2-4b shows electron beam transmitted through the thin sample lying on the top of a copper, which is the basic principle of TEM imaging. Electron transmission is not equal over the entire imaged area of the sample, providing the contrast difference between filler and matrix in TEM images.
Silica nanoparticles appear dark due to their high density and high electron scattering from their surfaces (electron path (2) in Figure 2-4b). Due to very low atomic density in polymeric matrices compared to inorganic fillers, incident electrons scatter less in the matrix phase. Therefore, as it is shown in the TEM image in Figure 2-4c, more electrons pass through the matrix compared to the regions of fillers, and thus high numbers of electrons are collected by detector (ED in the electron path (1) in Figure 2-4b). In Figure 2-4c, crystalline ZnO particles have the darkest contrast because they have the most electron-dense atomic structure.

The basic principle of SEM is represented by electron path (3). In SEM, specimen surface is scanned with the focused electron beam and some of the electrons can go through the specimen (if the specimen is thin) while others are reflected from the surface of the specimen and are detected (ED on the electron path (3) in Figure 2-4b). As a consequence of the energy exchange between the focused electrons and the sample, reflected electrons can be grouped as secondary and backscattered electrons when the scattering is elastic and inelastic, respectively. The intensity of the reflected electrons changes due to the focused electron energy, the atomic (Z) number and density of the material at the focal point. Resulting SEM images show the distribution of the scattered electron intensity from the scanned area of the sample.[88] In both TEM and SEM, incident electron beam scatters some characteristic X-rays (path number (4) in Figure 2-4b) and such X-Rays can be detected by using additional X-Ray detectors (XD in Figure 2-4b). These scattered X-rays can be further analyzed to perform elemental analysis of the imaged surface in a technique called energy-dispersed X-Ray spectroscopy (EDX).

One advantage of SEM over TEM, is that the former does not require ultra-thin slice as a sample (see appendix of Chapter 5). However, TEM results in higher resolution micrographs, showing better the contrast between inorganic fillers and organic polymeric matrix in nanocomposites (Figure 2-4c). Nevertheless, TEM still lacks resolution for providing structural information from a single filler particle, especially in highly loaded nanocomposite samples due to imperfect contrast between matrix and filler. Because of these inherent limitations, the most accurate method to characterize aggregate size for nanocomposites is small angle X-ray scattering (SAXS).
Figure 2-4. (a) Polymeric sub-structures of different sizes and resolution limits of different microscopic techniques and small angle X-ray scattering method (SAXS) for observing these sub structures. Image is adapted from [88]. (b) Illustration showing the principles of TEM and SEM. Positions of the electron (ED) and X-Ray (XD) detectors are shown as labelled red boxes on the way of corresponding electron paths. (c) TEM and SEM images of silica (1.59 vol %) / NBR nanocomposite taken at the same magnification. Scale bars are 500 nm.
In a typical SAXS measurement, a rectangular cut of a nanocomposite sample (ca. 30 mm*8 mm, thickness of ca. 2mm) is illuminated by a collimated monochromatic X-ray beam with the wavelength of ~ 1.1 Å (12.46 keV), and the intensity of the scattered X-rays is recorded by a 2-dimensional X-ray detector. The distance between sample and the 2D detector is often variable. Larger features scatter over smaller angles while smaller features scatter over larger angles. Since scattering from silica nanofillers is much stronger than those from rubber, the signal from the fillers is easily obtained. By applying the right model, which is critical, SAXS can give structure of silica distribution in our nanocomposites starting from a single particle.[38] The technical details of the SAXS measurements and the model applied for data interpretation can be found elsewhere.[38] SAXS measurements on the full nanocomposite systems studied in this thesis were done at the ERSF in Grenoble at the (ID 26) beam line by our collaborators in UvA (M.R.B. Mermet-Guyennet and J. de Castro). Using their data, and additional published data, we verified the robustness of our TEM based aggregate size determination explained below.

As a final word, it must be pointed out that the main purpose of electron microscopy in this work was to quantify the nanofiller distribution in polymeric matrix. The biggest motivation to use electron microscopy was because of experimental accessibility and flexibility. ID26 is a user facility where it is difficult to check many samples on-demand. Moreover, the presence of zinc oxide (ZnO) particles (dark black particle in the micrograph presented in Figure 2-4c) in our NBR nanocomposite formulations strongly disturbed the SAXS measurements. TEM provides the best combination of structural information of filler aggregate/agglomerates and elemental specificity (via EDX). Owing to the aforementioned challenges in TEM, we developed a robust image analysis protocol to quantify aggregate size in our composite samples.

Image analysis of TEM images for aggregate size determination
Aggregate size determination of nanocomposite systems was done by using an open-source image processing software called ImageJ®. The TEM imaging parameters and ImageJ software parameters used for image processing are indicated in the methods section of each following chapter. Herein, I will explain the physical meaning of the parameters used for the image processing. The basic process is to use thresholding as an image operation to separate the image into two phases: foreground and background. By choosing the proper thresholding
options in ImageJ®, we can set the aggregates of fillers as foreground and polymeric matrix as background. The steps for this process are stated below.

(i) All images were converted to 8-bit, grayscale images. In an 8-bit greyscale image, there are 256 \(2^8\) different intensity values which can be assigned to each pixel. Pixel with zero intensity looks black and white pixel has an intensity of 256.

(ii) In order to see the distribution of the intensities in the entire TEM image, we monitor the histogram of the image. The difference between the mean and standard deviation of the intensity histogram was used to obtain the critical threshold value. By calculating the critical thresholding value in this way, the threshold value was intrinsically consistent for all the analyzed TEM images, independent of changes in image contrast.

(iii) Apply threshold to the image.

(iv) Automated routines in ImageJ were used to analyze the resulting binary image for particles. We set the parameters to start counting from an area of a single particle to infinity. Since the shapes of the aggregates are completely random, we kept the circularity range between two maxima 0 and 1. 1 means a perfect circle. Each counted particle (aggregate) is numbered, and we could quickly scan the results and remove large, dark ZnO inclusions (see Figure 2-4c) from data set.

2.2.4 Surface-sensitive molecular spectroscopy

As mentioned before, many functions and applications in polymer-based nanocomposites are controlled by interfacial properties. Particularly, in order to explain the origin of filler dispersion and material property changes due to rubber functionality (F-SBR) in SBR nanocomposites, it was paramount to quantitatively analyze interfacial interactions e.g. between the silanol (Si-OH) functional groups of F-SBR on silica surface. Therefore, we used a mix of both ultrahigh vacuum (UHV) and in situ vibrational spectroscopy techniques. The two UHV surface sensitive emission spectroscopic methods used were X-Ray photoelectron spectroscopy (XPS) and Near edge X-ray absorption fine structure spectroscopy (NEXAFS). We used surface sensitive scattering spectroscopy Sum Frequency Generation Spectroscopy (SFG) for in situ interfacial spectroscopy.
X-Ray photoelectron spectroscopy (XPS)

XPS was used for determining the chemical composition of surfaces and can be classified as a surface sensitive since electrons cannot escape longer distances than a few Å.[89] During the XPS measurement, the sample is bombarded by incident X-Ray beam with a fixed energy \((h\nu)\), and due to the photoelectric effect, electrons are emitted with a specific kinetic energy. The energy of the incoming photons must be high enough in order to overcome the binding energy \((E_B)\) of the electrons and work function \((\Phi)\) of the measured material. In basic terms, the minimum energy required to remove one electron from the material is called work function of the material. In order to get an XPS signal, a potential barrier must be exceeded to remove an electron from its Fermi level to the vacuum level. When this electron leaves the material, it moves with a finite kinetic energy \((E_K)\) and can be detected by an analyzer. \(E_K\) is expressed as:

\[
E_K = h\nu - E_B - \Phi
\]  

Importantly, XPS is intrinsically quantitative and provides results of elemental analysis in atomic percentages. The final electron photoemission (PE) spectrum comes from an intrinsic interaction. It is free of an extrinsic background, which originates from a photo excited electron due to the interaction with other electrons (inelastic scattering electrons or secondary electrons) during its travel to the surface and it has no effect on the intrinsic data (peak areas, peak positions and the peak widths) after proper subtraction. Because XPS is intrinsic, intensities from different core levels (of different atoms) can be used as a means to identify atoms and therefore calculate the atomic abundance (%) of particular atoms in a sample. In addition to its quantitative nature and chemical sensitivity at the surface, using Argon cluster sputtering, one can obtain chemical composition data from different sample depths in the system. This is essentially a layer-by-layer measurement, where one obtains a XPS spectrum and sputters with the Ar cluster in an alternating manner. Further measurement, instrumentation and data analysis details of the XPS performed for understanding the nature of F-SBR end functional group interaction on silica surface, will be discussed in Chapter 4.
Figure 2-5. An example of polarization dependent NEXAFS spectra of benzene (C$_6$H$_6$) lying on Ag (110) surface. (a) unoccupied orbitals of σ and π symmetry aligned in and perpendicular (out-of-plane) to the ring plane, respectively, and the photon energies to excite these groups are illustrated. (b – c) Polarization dependence of the benzene groups on Ag surface are shown in two different NEXAFS spectra taken at different angle between surface normal and the incident polarized X-ray (polarization direction is shown by black line with arrows at both ends). Image is adapted from ref [52].

Near edge X-ray absorption fine structure spectroscopy (NEXAFS)
Differently from XPS, in NEXAFS the energy of the incident X-ray is not fixed. It is scanned, and the absorbed X-ray intensity, which is a consequence of excitation of an electron from a core orbital to an unoccupied molecular orbital is measured. Absorption-based NEXAFS requires thin samples (~ μm) because of the large absorption coefficients of X-rays in most materials, but it is not explicitly surface sensitive. As a result of X-ray absorption, decay of the core hole states results in emission of Auger electrons from valence molecular orbitals or so-called X-ray (Auger) fluorescence. Measuring the emission of electrons or fluorescence produces an Auger or electron yield NEXAFS spectrum.

Auger electron NEXAFS is surface sensitive mainly due to the low kinetic energy of electrons and their very short mean free path in a solid film, which is less
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than 1 nm for the energy range from 250 eV to 600eV. Because the excitation X-ray is absorbed throughout a sample, Auger fluorescence, can emerge from deeper depths within the sample. The photons can arise from the top ca. 200 nm of the sample because the photons have significantly higher energy compared to the kinetic energy of electrons and they scatter less during their travel along the sample thickness (large mean free path).[90] Both Auger electrons and fluorescence provide us data for determining the photoabsorption of the film sample on a substrate from different depths.

Auger electron yielding of low Z elements (C, N, O etc.) are way stronger compared to their yield of fluorescence[52] and as mentioned before, Auger electron results are more surface sensitive compared to those from Auger fluorescence. Thus, in this thesis, we measure ordering of SBR films – which include aromatic groups – on silica surfaces by monitoring the so-called partial electron yield (PEY), which measures the Auger electrons.

NEXAFS measurements are useful for detecting the orientation of specific orbitals of carbon bonds (e.g., C-C in benzene rings (C₆H₆) in SBR). Particularly the transition matrix elements for instance π* orbital, have a polarization dependence with respect to the electric field vector (E) of the polarized incident X-Rays. A benzene molecule lying on Ag (110) surface is a popular example for showing the polarization dependence property of the NEXAFS (Figure 2-5).[52] Benzene includes unoccupied orbitals of σ and π symmetry and they are oriented parallel and perpendicular to the benzene ring plane, respectively (Figure 2-5a). A simple example of the power of NEXAFS was determining the orientation of benzene rings on the Ag surface. This was done by shining incident polarized X-Rays at the chemisorbed benzene on Ag (110) surface at two different angles. When the direction of E was parallel to the surface normal, peaks from the out-of-plane π orbitals became more dominant (Figure 2-5b). When the E was perpendicular to the surface normal, as shown in Figure 2-5c, in-plane σ orbital peaks became more intense. This experiment proves the benzene rings lies flat on the Ag (110) surface as it is shown in the insets of Figure 2-5(b) and (c). We performed similar experiments in order to monitor the ordering ability of the silanol end functional groups of F-SBR on silica surface, which will be discussed in details in Chapter 4.

Sum Frequency Generation Spectroscopy (SFG).

Sum Frequency Generation (SFG) spectroscopy, is a nonlinear optical spectroscopy that can provide surface specific vibrational spectra of sub-monolayer organization
Being a second order nonlinear process, the coherent SFG signal cannot be detected in centrosymmetric media. The macroscopic SFG polarization can be expressed as,

\[ P^{(2)}(\omega_{SFG}) = \chi^{(2)}(\omega_{SFG})E_{VIS}(\omega_{VIS})E_{IR}(\omega_{IR}) \]  

(2.6)

Where \( \chi^{(2)} \) represents the second-order nonlinear susceptibility of the material. \( E_{VIS} \) and \( E_{IR} \) are the electric field of incident visible and infrared beams, respectively.

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**Figure 2-6.** (a) Schematic illustration of SFG measurement at sample – air interface and the general energy diagram of SFG. (b) Energy (photon) diagrams explaining IR, spontaneous Raman processes. In the both energy diagrams shown in (a) and (b), incoming photons leading to an excitation of matter are presented by upward arrows. Emitted photons as a result of relaxation of matter are presented by downward arrows.
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Experimentally, SFG is performed by overlapping a broadband IR and narrowband visible beam in space and time at an interface, and consequently an SFG photon is eventually generated and its frequency is written as,

$$\omega_{SFG} = \omega_{IR} + \omega_{VIS}$$  \hspace{1cm} (2.7)

While the broadband IR allows simultaneous detection of different IR modes, the narrowband visible beam provides spectral resolution down to 10cm^{-1}. The SFG signal is spectrally resolved and measured with a CCD camera. In our work, the SFG measurements were performed to obtain the interfacial signature of the SBR polymer at polymer – silica interface (Figure 2-6a). This was done to see quantify the effect of silanol end functional groups on F-SBR-filler interaction (Chapter 4).

2.2.5 Polymer anisotropy measurements

Polarized vibrational spectroscopy

Fourier Transform Infrared Spectroscopy (FT-IR)) and Polarized Raman spectroscopy are two popular techniques for measuring polymer chain anisotropy. Basic physics of these methods are illustrated in Figure 2-6b. When IR light (\(\omega_{IR}\)) interacts with matter, the IR gets absorbed at certain frequencies if they match the energy gap between (or, are resonant with) the vibrational (real) energy states in a sample as shown in Figure 2-6b. In physical terms, these different vibrational states correspond to different molecular oscillations of bonded nuclei with, each having different transition dipole moments \(\mu\). The strength of the absorption is proportional magnitude of \(\mu\) associated with a particular vibration.

In spontaneous Raman spectroscopy, matter interacts with visible light (\(\omega_p\)). A large portion of the illuminating light reflects, elastically (Rayleigh) scatters and/or transmits, thereby not changing the frequency (energy) of the incident radiation. A (very) small fraction (~1 in \(10^7\)) of the illuminating light changes its energy as a result of inelastic, or Raman, scattering (Figure 2-6b)[92] The energy change can be traced to a particular vibrational mode present in the matter. Unlike IR absorption, Raman scattering is proportional to the variation of polarizability, \(\alpha\), during interaction with the light. Raman scattering can result in two different outcomes,

$$\omega_{Raman} = \omega_p - \Delta\omega$$ for Stokes Raman scattering

or

$$\omega_{Raman} = \omega_p + \Delta\omega$$ for Anti-Stokes Raman scattering

(2.8)
\[ \omega_{\text{Raman}} = \omega_p + \Delta \omega \text{ for anti-Stokes Raman scattering} \]

During Stokes Raman scattering, molecules or atoms are polarized by incident light energy and scatter photons having less energy than those of the illuminating light. In anti-Stokes scattering, the scattered light has more energy than the incident illuminating light because the atom or molecule was initially in a vibrationally excited state.

In our work, IR and polarized Raman spectroscopies are used for monitoring the alignment of rubber molecules in different nanocomposites under tensile stretching. Drawing the nanocomposite slices (ca. 20 µm thick) was done with a home-built stretching device including a motorized actuator (Thorlabs Z825B, New Jersey) which has a minimum achievable incremental movement of 50 nm. During our Raman measurements, in order to avoid complicated depolarization ratio calculations, we did not place any polarizer in front of the detector, and thus we could detect all the scattered Raman light. Therefore, below mentioned theory of dichroism for detecting polymer chain orientation could be applied both to the results from our FTIR and polarized Raman measurements.

**Calculating polymer anisotropy**

The measured sample has a coordinate system \((w, u, v)\) as shown in Figure 2-7, where \(w, u,\) and \(v\) represents the stretching, transverse and thickness directions, respectively, and coincide with the laboratory coordinate axes directions. An IR or Raman absorption in \((w, u, v)\) coordinate system \(A_{uvw}\) is calculated from the interaction between the incident electric field vector \(\vec{E}\) and the transition dipole moment of a particular molecular vibration vector \(\vec{M}\). \(A_{uvw}\) is expressed by an inner product of \(\vec{E}\) and \(\vec{M}\): \(A \propto (\vec{M} \cdot \vec{E})^2\). [83]

In the simplest scenario, one assumes that the polymer chains are perfectly aligned parallel to the stretching direction, all the dipole moments of the absorbing groups in the polymer chain lie within a cone with a semi angle \(\Psi\) to the stretching (and chain axis) direction. In this scenario, the IR or Raman absorptions when the incident light is parallel \((A_{\parallel})\) and perpendicular \((A_{\perp})\) to the stretching direction of the sample are defined as,[83]

\[
A_{\parallel} = A_{uvw}(90^\circ, 0^\circ) = \kappa \cos^2 \Psi \\
A_{\perp} = A_{uvw}(0^\circ, 90^\circ) = \frac{1}{2} \kappa \sin^2 \Psi
\]

(2.9)
where $\kappa$ is a constant. The dichroic ratio $R$ is a classical two-dimensional factor for defining the uniaxial orientation of the molecules to the axis of stretching. It is defined as $\frac{A_w}{A_u} = \frac{A_\parallel}{A_\perp}$. The dichroic ratio, $R_0$, calculated from chains aligned perfectly along the stretching direction is then found as,

$$R_0 = 2 \cot^2 \Psi$$

(2.10)

Figure 2-7. Transition moment distributions in an oriented polymer with respect to the stretching direction as a model which is used for our FTIR and Raman data interpretations.

In “real” conditions molecules will never be fully and perfectly aligned to the drawing direction. Therefore, a more realistic orientation of the chain molecules to the stretching direction is defined by a factor $f$, described by assuming a certain fraction, $f$ of molecule (polymer) is uniaxially (perfectly) aligned and remaining fraction $(1 - f)$ is randomly distributed.[83] Therefore, dichroic ratio, $R$ is expressed in terms of orientation fraction as,[93]
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\[
R = \frac{f \cos^2 \Psi + (1/3)(1 - f)}{(1/2)f \sin^2 \Psi + (1/3)(1 - f)}
\]

(2.11)

Eq. 2. 11 can be rewritten as eq. 2. 12 in order to find the orientation factor as a function of the dichroic ratio,

\[
f = \frac{(R - 1)(R_0 + 2)}{(R + 2)(R_0 - 1)}
\]

(2.12)

where \(R\) represents the measured dichroic ratio of a molecular vibration in the “real” system and \(R_0\) is expressed as in eq. 2. 10. In such “real” systems, it is also considered that polymer chains are on average separated from the stretching direction by a semi-angle \(\vartheta\) as it is shown in Figure 2-7. Therefore, the dichroism, \(R\) (eq. 2.11), in this imperfect orientation is re-expressed by using the \(\Psi\) and \(\vartheta\) together as,[93]

\[
R = \frac{2 \cot^2 \Psi \cos^2 \vartheta + \sin^2 \vartheta}{\cot^2 \Psi \sin^2 \vartheta + (1 + \cos^2 \vartheta)/2}
\]

(2.13)

From eq. 2. 13, average orientation of the polymer with respect to the draw direction can be easily found if the angle between the dipole moment direction of the absorbed group and the polymer chain backbone (axis) is known. Furthermore, one can express the orientation function, \(f\), more generally as shown below.[94–96]

\[
f = \frac{3 < \cos^2 \vartheta > - 1}{2}
\]

(2.14)

where \( < \cos^2 \vartheta > \) is the orientational average of all groups calculated as shown below,[83]

\[
< \cos^2 \vartheta > = \frac{\int_{\vartheta=0}^{\pi} F(\vartheta) \cos^2 \vartheta \sin \vartheta \, d\vartheta}{\int_{\vartheta=0}^{\pi} F(\vartheta) \sin \vartheta \, d\vartheta}
\]

(2.15)

In this equation, \(F(\vartheta)\) is the probability distribution function for the reference axis and \(F(\vartheta) \sin \vartheta\) is the overall probability that chains lie along the reference
From the above equations we can observe that if the polymer groups align perfectly parallel to the reference axis ($\theta = 0^\circ$), $\langle S_{mol}(\cos \theta) \rangle = 1$ and for perfectly perpendicular alignment ($\theta = 90^\circ$) $\langle S_{mol}(\cos \theta) \rangle = -1/2$. For randomly oriented polymer chains, $< \cos^2 \theta > = 1/3$ and thus $f$ becomes vanishingly small. Then, for these systems the orientation factor equation (eq. 2.12) can be rewritten as,

$$f = \frac{(2 \cot^2 \Psi - 1) (R - 1)}{(2 \cot^2 \Psi + 2) (R + 2)}$$

(2.16)

For the NBR and SBR molecules investigated in this thesis, the exact transition moment angle, $\Psi$, between their chain axes and the vibrational units used for quantifying alignment are unknown. Therefore, the orientation of the rubbers have been quantified without calculating $R_0$, which is assumed to be a fixed value for a particular molecular bonding geometry and is not changed with strain. Hence, the anisotropy of the rubbers at increasing strain level are found by calculating the dichroic function, $S_{mol}$, using the experimental absorption data observed when the incident light is parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the stretching direction as shown below,

$$S_{mol} = \frac{R - 1}{R + 2} = \frac{A_{\parallel} - A_{\perp}}{2A_{\parallel} + A_{\perp}}$$

(2.17)

$S_{mol}$ can be conceptually interpreted as the orientational distribution ($f$) scaled by the (constant) dichroic function between the vibrational mode and the chain axis, $S_{mol,0}$ established by the chemical bonding.

### 2.3 Statistics

In the course of my doctoral work, suitable methods to validate the statistical significance of the measured data were necessary to quantify the accuracy and repeatability of my results. In particular, I have used different statistical approaches to test my hypotheses: t-tests (a test statistic that follows a Student t-distribution under the null hypotheses) and analysis of variance, known as ANOVA.

While a t-test can be used to determine the statistical difference between two data sets (with a certain level of significance), the ANOVA analysis extends
such an approach to many groups. The biggest drawback of the t-test is its inability to test the significance of more than two different groups at the same time. Thus, I used ANOVA for analyzing the variance among and within groups when there are more than two. Different types of ANOVA analyses exist, however we used only “one-way ANOVA” test which compares more than two populations by changing only one factor at a time (e.g. aggregate size of different silica / NBR nanocomposites at the same volume fraction). We performed all the ANOVA analyses using software called IgorPro (Wavemetrics, Portland). In general, during an ANOVA test, we first set up the null hypothesis, assuming there is no significant difference between the groups, and an alternative hypothesis, which assumes that there is a significant difference between the groups. To this direction, we used F-test in order to assess whether the expected values of a quantitative variable among several populations are statistically different from each other. ANOVA first calculates the F-ratio. F-ratio quantifies the variance between different populations in a group with respect to the variance within each population as,

\[
F \text{ - ratio} = \frac{\text{variance between the sample means}}{\text{variance within the samples}}
\]  

(2.18)

Details of the algorithm for calculating the between group variance and within group variance can be found in ref [97]. The typical F distribution used in an F-test is shown in Figure 2-8, from which one can determine if there is a significant difference between one or more populations. Generally speaking, if the null hypothesis is true, the within population variance is comparable to the between population variance, or in other terms, \(F \sim 1\). When the variability between population means becomes significantly larger than the variability within the populations, the F-ratio gets bigger. As shown in Figure 2-8, significant differences between the means in the group of samples during an ANOVA test is observed (rejection of the null hypothesis) if the F-ratio gets very high and exceeds the critical value which is corresponding to \(p < 0.05\) in this thesis. [97]

After knowing whether one or more group(s) are significantly different when compared to all groups, ANOVA helps us in a second step to identify exactly in which group(s) we observed this significant difference. To this direction, ANOVA includes some further tests, which are called post-hoc tests. In these tests, ANOVA mainly runs pairwise difference tests between pairs in the population and reports those pair(s) for which there are significant differences.
Figure 2-8. Example F distribution used for testing the null hypothesis in our ANOVA analysis showing the critical F-ratio at 5% (0.05).

This might prompt one to ask: why we do not just use multiple t-tests instead of using complicated ANOVA method with post-hoc test(s)? In multiple t-tests (comparing more than two groups together only as isolated pairs), the probability of making a Type I error (an error of rejecting a true null hypothesis) increases with increasing number of t-test. [98] Thus, after multiple t-tests in a population with more than two groups, the outcome is much more likely to show significant differences between certain pairs, even though no real (significant) difference exists.[99] The post-hoc tests are able to keep significance level ($p$) stable regardless of the number of groups being compared. Based on the particular research question, post-hoc tests give us different methods for group comparisons. For instance, with the help of post-hoc tests, we can compare one particular group against a combination of all remaining groups in a population, or against only some of the chosen control groups.

There are different kinds of post-hoc tests and along the thesis, we used Tukey and the Newman-Keuls tests as the two most common methods of post-hoc tests.[100] In this thesis, significant difference among certain group(s) is/are only accepted after observing the significant difference of the same pair(s) from the results of both Tukey and the Newman-Keuls tests. Using more than one pairwise comparison helps us to identify whether a statistical difference between certain group(s) is connected to the sampling error (size of the groups) or not.