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Analysis of HNBR-Montmorillonite Nanocomposites
Morphology, Orientation and Macroscopic Properties

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Summary

Morphologies and dynamic mechanical properties of hydrogenated acrylonitrile butadiene rubber (HNBR) filled with organophilic layered silicates (OLS) were investigated. The results from transmission electron microscopy (TEM), small angle X-ray scattering (SAXS, especially X-ray diffraction on larger structures) and dynamic mechanical analysis (DMA) favor the notion of local filler-filler network-like clusters consisting of exfoliated silicate layers. Especially, processing under high shear forces leads to an anisotropic structure of the network. Due to the orientation of the clusters the aspect ratio (at small deformations) increases. This is in accord with the large reinforcing effect observed for these materials. For example, the stress at 50 % elongation from tensile test can be increased at 33 % with 5 phr OLS compared to the unfilled reference. We estimate the activation energy of the immobilized polymer layer around the filler structures and show that the values depend on the spatial direction (the values are between 3.4 kJ/mol and 4 kJ/mol). As a result, the DMA–analysis could be used as a supporting method to evaluate orientation effects of the filler structures.

Furthermore, from SAXS experiments, measured in the three directions in space, and from TEM analysis one could conclude that small amounts of intercalated structures are still present. These structures are orientated, too.

The results make evident that the orientation of intercalated structures should be taken into account, especially if SAXS is used to estimate the degree of exfoliation.

Introduction

Nanocomposites based on thermoplastics and OLS have been of fundamental interest for industrial and scientific applications, due to the property improvement: high reinforcement combined with high toughness, increased heat distortion temperatures, improved flame resistance and oxygen permeability are examples for these high performance materials and the first commercial applications [1] are introduced to the market [2-11].

The most commonly used clay material is modified montmorillonite (MMT) [8] where the interlayer cations were replaced by quaternary ammonium cations. The interlayer widening depends on the type of the intercalant. In the present work the modification with distearyldimethyl ammonium chloride causes an increase of the

interlayer distance from 1.98 nm to 2.80 nm [12]. Due to the reduced interlayer interaction and the reduced polarity of the filler–surface, nanoscaled materials with intercalated and exfoliated morphologies could be prepared *in situ* by mixing polar elastomers and the filler in an open mill or internal mixer.

Several developments and investigations were performed for elastomer-clay systems (see, for example [13, 14]). In polar elastomers like hydrogenated acrylonitrile butadiene rubber (HNBR) high reinforcement was observed, if dimethyldistearyl ammonium salts were used to modify the MMT. Important factors which influence the degree of exfoliation are the length of the alkyl chain of the quaternary ammonium salt, the polarity of the compound and the amount of shear forces during the processing [15-17].

Gatos et al. observed for HNBR nanocomposites a strong reinforcing effect, caused by a strong matrix–filler interaction and they conclude a formation of a rubber shell in the vicinity of the silicate platelets [18].

The comparison of ethylene-propylene-diene rubber (EPDM) and maleic anhydride grafted EPDM (MAH-g-EPDM) underlines the importance of the polarity of the polymer to prepare nanoscaled materials [9, 19, 20]. These results fit with the *in situ* formation of intercalated composites based on millable polyurethane rubbers [21].

In vulcanisation systems containing zinc (Zn(II)) and primary amines (PRIM), a reaggregation was observed [19]. Due to the fact that the reaggregation does not occur if the modifier is changed from a primary to a quaternary amine (QUAT), it was concluded that the reaggregation is caused by a Zn–complex with the modifier [19]. Analyzing the morphology of MAH-g-EPDM/QUAT with transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS, strictly speaking X-ray diffraction, XRD, at small angles) in these materials intercalated (with increasing interlayer spacing from 2.3 to 4.7 nm) and exfoliated structures were found. In the system MAH-g-EPDM/PRIM the SAXS pattern show reaggregation due to the complexation and stacked layers with a reduced interlayer spacing from 2.1 to 1.3 nm. In the dynamic mechanical analysis (DMA), a larger increase of the storage modulus G´ was observed for the MAH-g-EPDM/QUAT in comparison to the MAH-g-EPDM/PRIM system. Comparing tensile strength and elongation at break at low filler–contents the results were comparable, but at higher amounts (10 phr) due to agglomeration both, tensile strength at break and the ultimate elongation were reduced [19].

In the prevailing work the development of new OLS-modified hydrogenated acrylonitrile butadiene rubber (HNBR) compounds with improved properties for several technical applications is described and characterized. The explanation of the structure-properties-relationships based on the underlying morphology and the filler structure is the major aspect of this work. Established techniques like transmission electron microscopy (TEM) reach their limits. According to Sinha Ray [10] too little can be said about the spatial distribution of the silicate layers, although SAXS offers a convenient method to determine the interlayer spacing (within nm-scale). TEM is an extensive method and allows a qualitative understanding of the internal structure and the spatial distribution. With SAXS only intercalated structures are detectable. To evaluate orientation effects of the local filler-filler network we analyzed the materials in the different direction in space with DMA. Classical methods like SAXS and TEM-analysis support the results of the DMA-analysis. The main advantages of the DMA-analysis are easy handling and sample preparation. Further more quantitative measurement categories can be achieved.

Experimental

Preparation of Samples, Materials and Sample Designation

HNBR (Therban C3446; ACN-content: 33-35 %; degree of hydrogenation: 95-97 %) was purchased from Lanxess, Germany. Carbon black N339 (CB; Degussa AG, Germany) and organically modified silicates on the base of montmorillonite (MMT; Nanofil 15) from Süd-Chemie, Moosburg/Germany have been used as fillers. MMT was modified with C18 chains (distearyldimethyl ammonium chloride). The layer distance of this organoclay is 2.8 nm. For comparison a Sodium-Bentonite (Nanofil 757, Süd-Chemie, Moosburg/Germany) with a layer distance of 1.2 nm was used. All investigated nanocomposites were produced with HNBR as matrix polymer und organophilic layered silicates (OLS) as filler. The clay concentration was kept constantly at 5 phr or varied to 15 phr as example. OLS and HNBR were compounded in two steps: for the first step an internal mixer was used (5 min at 80 to 130°C with approximately 50 rpm; all ingredients excepting peroxide). In the second step, after the composition rested at least 12 hours, the peroxide was added on a roll mill. Due to the degree of hydrogenation of the used HNBR and the mixing conditions degradation during melt blending was excluded [21]. The rubber samples were vulcanized for 20 min at 180°C. Table 1 shows the list of chemicals, nature and grade of the rubber and their suppliers. Table 2 and 3 show the formulation of various compounds (in phr).

Table 1. Details of the materials and their suppliers

Material	Supplier/manufacturer
HNBR (Therban C3446)	Lanxess, Germany
Coactivator (Saret 634 C)	Sartomer, Stratford/USA
Carbon Black (N339)	Degussa AG, Germany
Plasticizer (Edenol W 310 S)	Lanxess, Germany
ZnO	Lanxess, Germany
Ageing protection (Vulkanox HS/LG)	Lanxess, Germany
Ageing protection (Vulkanox ZMB2/C5)	Lanxess, Germany
organoclay	Südchemie, Moosburg/Germany
Peroxide	Lanxess, Germany

Table 2. Recipes of compounds A-D

Ingredients	A	B	C	D
Rubber (HNBR; Therban C3446)	100	100	100	100
Coactivator (Saret 634 C)	25	25	25	25
Carbon Black (N339)	15	15	15	15
Plasticizer (Edenol W 310 S)	5	5	5	5
ZnO	10	10	10	10
Ageing protection (Vulkanox HS/LG)	1	1	1	1
Ageing protection (Vulkanox ZMB2/C5)	1	1	1	1
Unmodified organoclay (Nanofil 757)		5		
Modified organoclay (Nanofil 15)			5	15
Peroxide	5	5	5	5

Table 3. Recipes of compounds 1-3

Ingredients	1	2	3
Rubber (HNBR; Therban C3446)	100	100	100
Coactivator (Saret 634 C)	25	25	25
Carbon Black (N339)		5	
Modified organoclay (Nanofil 15)			5
Peroxide	5	5	5

Tensile and tear tests were performed on a Zwick 1446 (Ulm, Germany) universal testing machine at a cross-head speed of 100 and 200 mm/min. The specimen were tested according to DIN 53504 (tensile test) and DIN 53507 (tear resistance). The mechanical measurements were implemented at a DMA861^e from the company Mettler-Toledo. The temperature sweeps were measured in the shear mode on samples with a thickness of 1-2 mm. The temperature sweeps were taken over a temperature range from -80°C to 200°C in steps of 2 K/min with a frequency of 10 Hz and maximum force rate of 1 N and maximum distance amplitude of 10 µm.

The state of dispersion of the OLS-particles in the HNBR-matrix was investigated by transmission electron microscopy (TEM) micrographs of clay particles from ultrathin sections of nanocomposites, using a Zeiss TEM with an acceleration voltage of 80 kV.

The layer distances of the organoclays in the rubber matrix and the layer orientation, respectively, were implemented with X-ray scattering investigations in transmission mode by using Ni-filtered Cu K_α-radiation (λ = 0.154 nm) with a KRATKY-camera (Anton Paar, Graz, Austria). The scattering curves were only transformed into Lorentz-corrected intensity data (no desmearing procedures).

Results and Discussion

Mechanical Properties

If carbon black is substituted with OLS, improved mechanical properties can be found (see Table 4).

The behavior of unmodified MMT (Ref.I+5MMT (B)) sample is comparable to the unfilled sample (Table 4). With OLS the characteristic behavior for polymer-OLS nanocomposite materials is observed. Compared to the corresponding conventional rubber-clay composite (Ref.I+5MMT (B)) containing the equivalent amount of clay (5 phr), all of the nanocomposites (Ref.I+5OLS (C), Ref.I+15OLS (D)) exhibit substantially higher tensile moduli, shore A hardness and tear strength. The stress at 50 % elongation from tensile test increases with increasing OLS content at 33 % with 5 phr filler and at 110 % with 15 phr OLS. The largely increased reinforcement and the tear resistance of the nanocomposites should be ascribed to the dispersed structure of clay at the nano level, the high aspect ratio and the planar orientation of the silicate layers [23]. All results from physical tests are shown in Table 4.

The tensile test results of the investigated HNBR/OLS-nanocomposite (Ref.II+5OLS (3)) compared to the references without OLS (Ref.II (1)) and the conventional nanofiller carbon black (Ref.II+5CB (2)) are shown in Figures 1 and 2.

Table 4. Mechanical properties of HNBR and HNBR nanocomposites

Sample	Elongation at break [%]	Tensile modulus [MPa]			Shore A	Tearing resistance [N/mm]
		50 % elongation	100 % elongation	300 % elongation		
Ref.I (A)	507	2.0	3.1	14.9	68	43
Ref.I +5MMT (B)	476	2.0	3.3	8.3	68	40
Ref.I +5OLS (C)	491	2.7	4.2	16.1	72	40
Ref.I +15OLS (D)	469	4.2	6.2	16.4	84	35
Ref.II (1)	487	1.6	2.5	10.0	63	47
Ref.II +5CB (2)	510	1.7	2.7	11.3	66	44
Ref.II +5OLS (3)	485	2.6	3.9	10.6	72	44
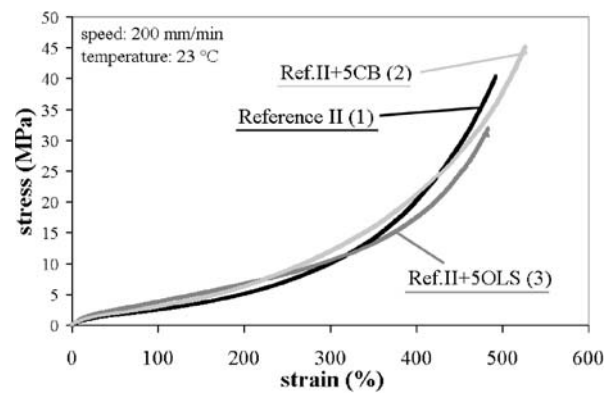
Figure 1. Stress strain curves of a reference HNBR sample (1), HNBR-sample with 5 phr organophilic layered silicate (3) and a HNBR sample with 5 phr carbon black (2)
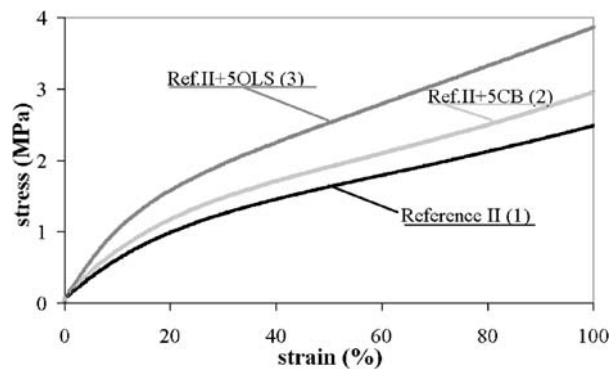
Figure 2. Cut-out of a stress strain curve of a reference HNBR sample (1), HNBR-sample with 5 phr organophilic layered silicate (3) and a HNBR sample with 5 phr carbon black (2)

For an elongation lower than 100 % the Ref.II+5OLS (3) material shows a strong reinforcing effect. For example the tensile stress at 100 % static elongation is increased about 56 % where the conventional nanofiller CB (sample 2) shows an improvement about 19 %. At higher elongations the stress is reduced compared to CB (cross over at ca. 240 % elongation), and as a consequence the tensile strength at break is decreased. Comparable results were discussed in literature [19]. Because of the elongation at break remains nearly constant, aggregation phenomena or a poor dispersion of the filler are excluded. Based on the investigations of the present work, the lower tensile stress at high elongation could be explained with the formation of a filler-filler-network. Following this hypothesis, the tensile stress at high elongation is reduced due to the deterioration of the filler-matrix interaction and of the filler-filler networks.

Dynamic Mechanical Analysis (DMA)

As shown in fig. 3 the storage (and loss) modulus of the samples with 5 phr OLS (Ref.II+5OLS(3); G´ = 4.3 MPa at room temperature) is 1.8 times larger than the modulus of the system without layered silicate (Ref.II (1)) and the composite with carbon black (Ref.II+5CB(2); G´ = 2.4 MPa at room temperature).
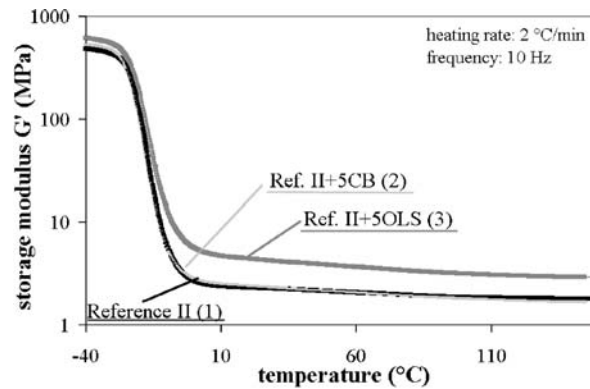

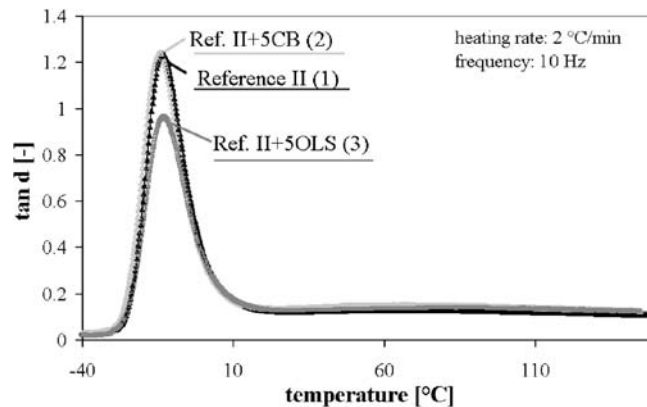**Figure 3.** Temperature dependence of the storage moduli of samples 1-3

Figure 4. Temperature dependence of the tan δ of samples 1-3

The tan δ curves for the different materials are shown in Figure 4. For the samples with 5 phr OLS (Ref.II+5OLS (3)) the intensity of the tan δ peak is reduced upon 67 %.

For acrylonitrile butadiene rubber (NBR) with carbon black a decrease of the tan δ peak compared with the unfilled material was noted, too [24, 25]. Furthermore, Mishra [22] and coworkers observed comparable effects in rubbery polyurethane compounds with an intercalated morphology. The reduction of the tan δ is likely due to the increase in G' which indicates a strong bond between the nanoclay and HNBR.
The investigated carbon black filled material shows nearly the same amplitude of tan δ. This does not conflict with the interpretation mentioned above. Due to the low content of carbon black (5 vol.-%) and the different structure of the filler in the polymer matrix the surface/volume-fraction should be lower for the carbon black and the amount of filler–matrix interactions should be reduced compared to the exfoliated layers.
As shown later, in the materials of the present work dominates the exfoliated morphology. Therefore it is concluded that the strong polymer-filler interaction is caused by the polar polymer and the curing system.
In HNBR nanocomposites Gatos et al. conclude that the creation of a rubber shell in the vicinity of the silicate platelets [18] is responsible for the strong reinforcing effect. In compounds with traditional nanofillers like carbon black or silica the percolation of the particles lead to a filler–filler network. For the investigated compounds a comparable network of the exfoliated layers it is expected. Due to the high aspect ratio (> 100:1) anisotropic (ribbon structures) and isotropic networks (cardhouse structures) could be formed.

For the interpretation of the filler-filler network studies we used the "hinge–model" [26]. Because of the reduced mobility of the polymer chain near the filler particle (e.g. carbon black) a glassy-like polymer layer in the vicinity of the particles is formed. If the particles percolate to a network, the interface between the filler–particles consists of a polymer layer with reduced mobility. An essential part of the bound rubber around the filler particles consists of this layer of immobilized, glassy-like polymer. The temperature or frequency dependence of the shear storage modulus correlates with that of the glassy-like polymer. The temperature dependence of the storage modulus G' [26] should follow the law of Arrhenius:

$$G'(0,T) \sim G_0 \exp (E_a /RT) \qquad \textbf{(1)}$$

with: $\qquad$ $G'(0,T) \gg G'(\infty,T)$

$\qquad$ $G'(0,T)$: $\qquad$ small strain modulus
$\qquad$ $G'(\infty,T)$: $\qquad$ high strain modulus
$\qquad$ G_0: $\qquad$ storage modulus at reference temperature
$\qquad$ R: $\qquad$ gas constant
$\qquad$ T: $\qquad$ temperature
$\qquad$ E_a: $\qquad$ activation energy

From temperature sweeps with small amplitudes Arrhenius plots were constructed (the storage modulus G' was logarithmic plotted against the inverse temperature 1/T) and the activation energy of the immobilised polymer layer was calculated within

a temperature range of approximately 20°C to 100°C [26]. To investigate the orientation of the network, the measurement considered the directions in space (see Figure 5). An orientation of the exfoliated platelets in the direction of flow is expected, due to the processing conditions (rolling in x-direction).
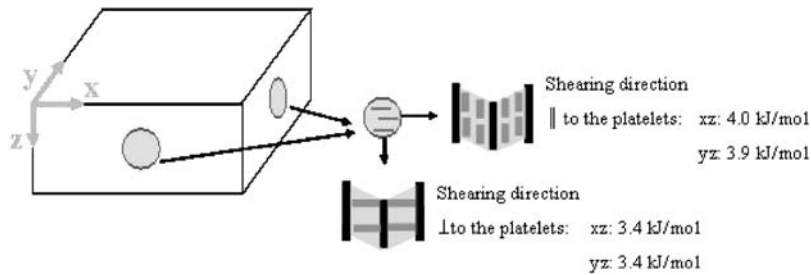

Figure 5. Sample preparation for dynamic mechanical analysis in the shearing mode and the measured activation energies for sample 3. The measured activation energies depend on the shearing directions and are independent from the preparation in the xz plane or yz plane

The activation energy E_a amounts 4 kJ/mol, which is in a common dimension for filler-filler networks. Furthermore, the amount of the E_a depends on the direction of the deformation. E_a in the direction perpendicular to the platelets ($\perp$) is about 15 % lower than the E_a in the direction parallel to the platelets ($\parallel$). Moreover the magnitude in the xy-plane is independent from the direction of the deformation and fits to the values of the $\parallel$ direction. Therefore we conclude that the exfoliated layers are orientated in the x-direction.

This formation could be explained by the processing conditions, because the direction of flow was the x-direction. Depending on the spatial deformation the storage moduli show different values, which fit with the observed activation energies (Figure 6 and 7). In $\parallel$ direction the modulus is increased compared to the $\perp$ direction. In comparison the moduli of the reference materials without OLS are significant lower and are independent from the direction of deformation. Therefore the stronger reinforcing effect in the direction $\parallel$ to the platelets could be explained by the ordination of the layers along the x-direction, which leads to an increase of the effective aspect ratio.
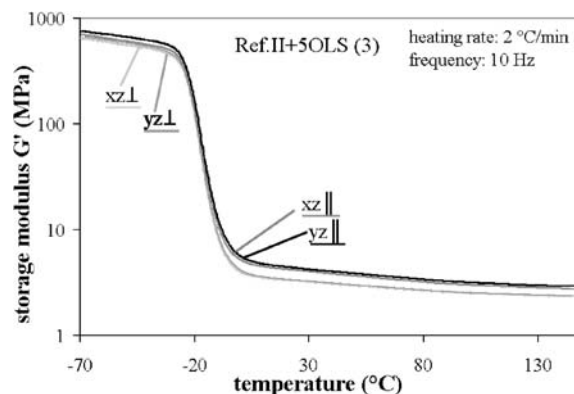

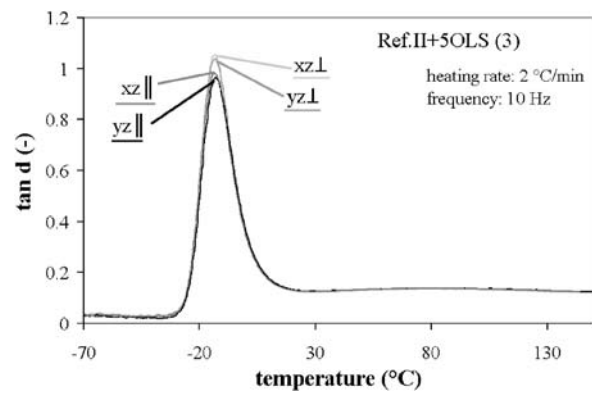**Figure 6.** Storage moduli of sample Ref.II+5OLS (3) measured in different directions

Figure 7. Tan δ of sample Ref.II+5OLS (3) measured in different directions

Comparable effects were observed in poly(butylene succinate) (PBS). The strong increase of G´ (compared to other nanocomposites having the same clay content) is explained by the formation of ribbon like structures [10]. This would be the simplest model that could explain the properties of the materials investigated in the present work. Furthermore, the results from TEM and SAXS support the observed orientation of the exfoliated clay. In the TEM micrographs (see Figures 8 and 9) a few intercalated
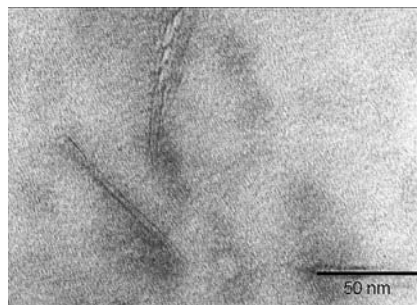
Figure 8. TEM-picture of HNBR-sample (Ref.I) with 5 phr organophilic layered silicate (C); scale: 50 nm
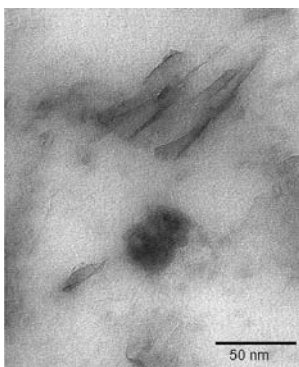

Figure 9. TEM-picture of HNBR-sample (Ref.II) with 5 phr organophilic layered silicate (3); scale: 50 nm
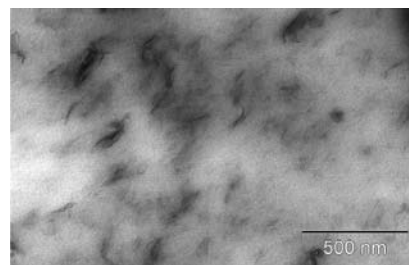

Figure 10. TEM-picture of HNBR-sample (Ref.II) with 5 phr organophilic layered silicate: scale: 500 nm

structures with increased interlayer distance are observed. Compared to the raw material, the number of the stacked layers is reduced from several hundreds to less than 10 layers. This supports an exfoliation of the modified clay material. Due to the small thickness of the layers (1 nm), we believe that only a fraction of the exfoliated layers is observable. The orientation of the nanoscaled structures is shown in Figure 10.

SAXS Investigations

SAXS experiments show the following result (as an example see Figure 11). The orientation of the layers is perpendicular to z-axis, i.e. in x-direction. The residues of intercalated structures are detectable in both the x and y dimension. Therefore it is concluded that the residues of the intercalated structures are orientated in the same direction. Furthermore, the interlayer distance is increased from 2.8 nm to 3.6 nm in comparison to the pure organoclay.
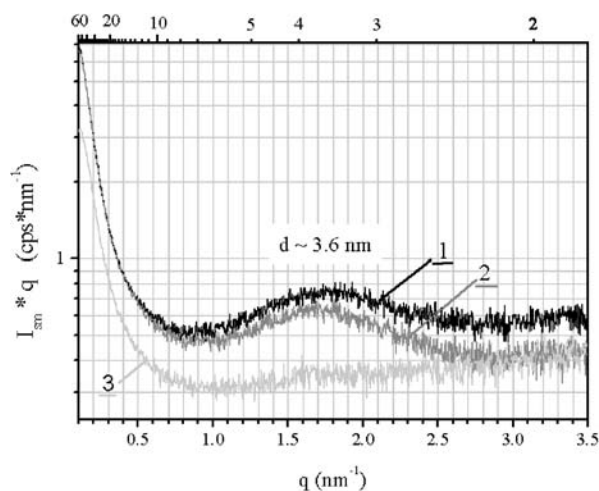

Figure 11. Representative SAXS-curves of sample Ref.II+5OLS (3) for different primary beam directions (transmission); 1: into x with scattering in z-direction (i.e. upon the xy-plane); 2: into y with scattering in x- and z-direction, respectively, as well as into x with scattering into y-direction; 3: into z with scattering in x-and y-direction, respectively

Conclusions

We report about new compounds based on hydrogenated acrylonitrile butadiene rubbers (HNBR) containing organophilic layered silicates (OLS = C18-modified montmorillonite). With a very low fraction of OLS, high reinforced materials with equal or even rising elongation at break and tearing resistance can be achieved. The presence of a strong matrix-filler interaction was verified with DMA measurements (high storage modulus G' and a decreasing tan δ peak for the nanocomposites). After vulcanization the nanocomposites show residues of the intercalated structures and a high amount of exfoliated platelets. The activation energy (E_a) from dynamic mechanically measurements were evaluated in different directions; the results depend on the spatial direction and correlate to the qualitative results of TEM and SAXS.

The observed mechanical properties of the materials could be explained by the formation of an anisotropic, orientated filler-filler network.

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