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Nanoalloy Based on Clays: Intercalated-Exfoliated Layered Silicate in High Performance Elastomer

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A novel method is described for the preparation of nanocomposites comprising a high performance rubber for tire application and layered silicates clay. In this work nanocomposites of solution-styrene butadiene rubber (S-SBR) with montmorillonite layered silicate were prepared with carboxylated nitrile rubber (XNBR), a polar rubber, as a compatibilizer. A sufficient amount of organomodified layered silicate was loaded in carboxylated nitrile rubber (XNBR) and this compound was blended as a master batch in the S-SBR. Mixed intercalated/exfoliated morphologies in the nanocomposite are evinced by X-ray diffraction measurements and transmission electron microscopy. Dynamic mechanical analysis also supports the compatibility of the composites. A good dispersion of the layered silicate in the S-SBR matrix was reflected from the physical properties of the nanocomposites, especially in terms of tensile strength and high elongation properties.

Keywords: carboxylated nitrile rubber; solution-styrene butadiene rubber; organoclay; reinforcement; XRD

1 Introduction

Reinforcing fillers such as carbon black and silica are added to the rubber compounds to improve their mechanical, as well as dynamical, properties for different diversified applications. The reinforcing effect of the fillers depends strongly on their particle size and their structure, as well as on the existence of functional groups on the filler surface. Increasing attention has been paid to the use of precipitated silica as a reinforcing filler for the green tire tread formulations (1) to produce high performance tires, showing improved rolling resistance and wet grip behavior. Here the development of advanced coupling silanes provides a better compatibility between rubber and silica resulting in reduced rolling resistance and improved fuel economy. Recently, clay based polymer nanocomposites have become commercially viable technological materials due to the ability of organoclays to improve physical properties with only small amounts of filler in the polymer matrix (2). To use the complete reinforcement potential of organoclays, it is necessary to intercalate, as well as to exfoliate the single layers. However, intercalated/exfoliated structures are not easy to achieve in the rubber matrix due to the presence of strong adhesion forces between two layers in the silicate structure, which remain as staged agglomerates in the rubber matrix.

For this reason, organomodified montmorillonite is now extensively used in rubber research, assuming that organic molecules adsorbed in the layered clay gallery may help to intercalate the different layers and improve the compatibility between inorganic clay and organic polymer. Therefore, the organic modification of the clay surface seems to facilitate the penetration of rubber macromolecules into the interlayer spaces and, ultimately, intercalated/exfoliated rubber nanocomposites can be expected. Nevertheless, for a nanometer range dispersion of the inorganic layers, the strong adhesion forces between two layers of silicate have to be overcome by rubber molecules. Here, the surface energies of non-polar rubbers like SBR, BR, NR, EPDM etc. are too low. In the literature, various procedures can be found to prepare clay-rubber composites claiming layered structures in the nano-scale dispersion, including melt intercalation (3, 4), reactive mixing (5), latex coagulation (6, 7) or solution methods (8). However, there is no report about nanocomposites made of layered silicate and solution-styrene butadiene rubber. This high performance elastomer is widely used nowadays as a tire tread compound especially in tires of

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passenger cars where low rolling resistance and high wet grip are the challenging properties. Some literature (9–13) has been found concerning emulsion styrene butadiene rubber, but the obtained mechanical properties are too poor to consider these systems as a potential candidate for practical applications. Ma et al. (8) reported a preparation method by latex compounding without stating any mechanical properties. Mousa and Karger-Kocsis (13) describe nanocomposites of SBR and organoclay mixed by two-roll mill, showing a tensile strength of more than 12 MPa at 10 phr silicate content, but without any direct evidence of formation of a nanocomposite like X-ray diffraction or TEM studies.

In the present study, the highly polar carboxylated nitrile rubber (XNBR) was used as a vector to transfer layered silicate into S-SBR. A large amount of organomodified clay was blended into a XNBR matrix at high temperatures (160°C) by an internal mixer and subsequently, the obtained product was used as a master batch and mixed into the S-SBR. In this way, attempts were made to get a good degree of exfoliated clay in the non-polar S-SBR matrix. This process was described as a new preparation method to prepare S-SBR/clay nanocomposite by a melt compounding route (14).

2 Experimental

Solution-styrene butadiene rubber S-SBR, (CE 3418-01) was obtained from Continental AG Hannover, Germany. Carboxylated nitrile rubber (XNBR Krynac X 740) was received from Lanxess, Germany. Organomodified montmorillonite, (Na-MMT) was supplied by Süd-Chemie AG, Germany. This clay contains quaternary ammonium salt as an organic modifier and the basal spacing of this organoclay is 2.98 nm. The rubber composites were prepared by a two-step method. In the first step, organomodified clay was mixed in an internal mixer (HAAKE PolyLab-System, Thermo Electron, Karlsruhe, Germany) at 160°C with a rotor speed of 50 rpm during 10 min. In the second step, this obtained master batch was mixed with S-SBR in an open two-roll mixing mill and subsequently, the additives like zinc oxide, stearic acid, organic accelerators and sulfur were added. The rubber compound was cured in a hydraulic press at 160°C during the corresponding optimum curing time. The curing behavior of the nanocomposite samples was investigated by a moving die rheometer (Scarabaeus SIS – V50, Langgöns, Germany) at 160°C with a frequency of 1.67 Hz and a strain amplitude of 0.5°.

Mechanical tests have been done using a tensile tester (Zwick 1456, Z010, Ulm Germany) with a cross head speed of 200 mm/min (ISO 527). Dynamic-mechanical analysis were performed using an ARES Rheometrics device (strain amplitude 0.5%, frequency 1 Hz) with a heating rate of 1K/min. For XRD-measurements, a Philips XRD-6000 wide-angle X-ray instrument (WAXD) with Cu K_α-radiation (30 kV and 40 mA) and a wavelength of 1.542 Å was used. The scanning 2θ-angle ranged between 1° and 15° with a step scanning rate of 2 deg/min. TEM pictures were obtained using the Transmission-Electron-Microscope LIBRA 120 by Zeiss.

Table 1. Preparation of the XNBR master batch

Master batch	XNBR (g)	Organoclay (g)
M-30	100	30
M-40	100	40
M-50	100	50
M-60	100	60

3 Results and Discussion

3.1 Preparation and Cure Characteristics

The contents of the master batch are presented in Table 1. The torque and temperature behavior against time recorded during the mixing process is shown in Figures 1 and 2. The temperature during the mixing process increased up to 180°C. For loadings up to 30 phr organoclay, the torque during mixing of XNBR and organoclay remained constant. In contrast for higher loadings, the torque increased significantly. This effect might be an indication of the intercalation process.

The formulations and cure characteristics for the mixing of the master batch with S-SBR are given in Table 2. The curing additives were chosen according to silica filled green tire formulations. In the samples SB-00 to SB-14, different loadings of master batches were used in various combinations. The samples SB-15 and SB-16 were formulated to obtain the effect of an unfilled XNBR in the composite. Concerning the XNBR content these mixes are equivalent to SB-12 and SB-14, respectively. It is evident from the table that samples of pure S-SBR and XNBR (SB-00 and XN-00) have higher

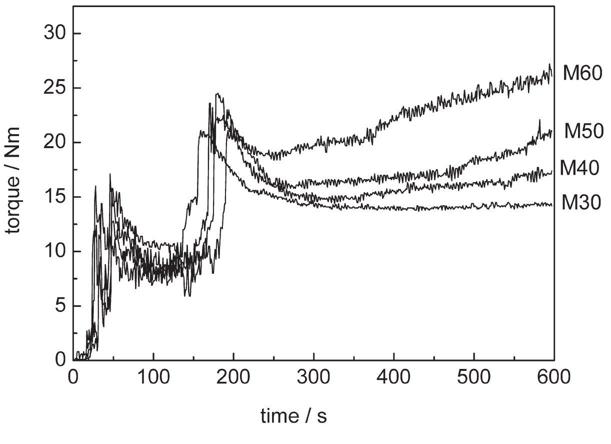

Fig. 1. Time torque curves for master batch preparations with XNBR and organoclay in the internal mixture at 160°C and 50 rpm rotor speed.

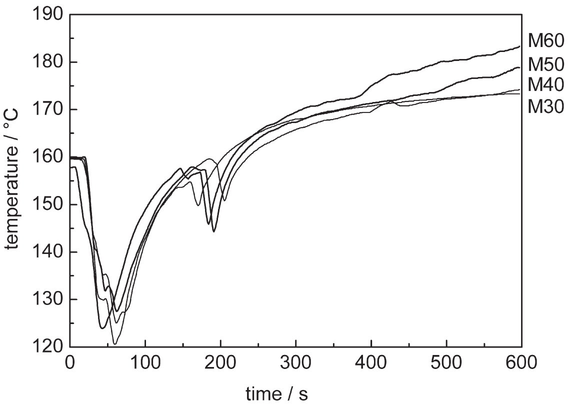

Fig. 2. Time temperature curves for master batch preparations with XNBR and organoclay in the internal mixture at 160°C and 50 rpm rotor speed.

'maximum rheometric torque' (R_∞) as the XNBR containing SBR samples. However, for every single master batch system the torque is decreasing with the increasing amount of master batch. Evidently, the presence of two different kinds of rubber with different polarity provides less torque than expected. The scorch safety seems to be independent of master batch content as well as filler loading. The cure-time listed in the last column of Table 2 is decreasing for the XNBR/S-SBR blend compared to the pure rubber samples SB-00 and XN-00. For every single master batch system, the cure-time increases with the amount of master batch due to the increasing XNBR to S-SBR ratio. For different master batches, the cure-time decreases with the amount of organoclay in the master batch except the M-60 containing samples, here the cure-time is higher than expected. It is also worth to mention that without organoclay, the cure-time of an XNBR/S-SBR blend is lower. The results are not quite understood, probably different acceleration effects are taking place due to the well known interaction of Zn-ions with carboxylic groups and the presence of ammoniums salts and organoclay.

3.2 Dynamic Mechanical and Thermal Analysis (DMTA)

Figures 3 and 4 display the storage modulus G′ and the mechanical loss factor tan δ as a function of temperature for the samples which contain the M-60 master batch. The sample with 5 phr master batch (SB-10) and the unfilled S-SBR sample SB-00 show no significant difference in G′ at room temperature. In contrast, the samples with higher loadings show strong reinforcement effects resulting in higher G′ values. For example, in the case of SB-11 (10 phr master batch) the increment was 1.65 times compared with S-SBR gum.

Additionally, it is interesting to discuss the effect of XNBR on the dynamic mechanical performance of the SBR vulcanizates. The vulcanizate containing 9.37 phr XNBR (SB-15) without filler, equivalent to SB-12 concerning the amount of XNBR, shows a smaller G′ value at room temperature indicating a lack of compatibility between the two different rubbers. Therefore, it can be stated that organophilic layered silicates not only reinforce the rubber matrix, but also act as a compatibilizer between the different phases. Figure 4 shows the tan δ plot of the nanocomposites.

Table 2. Recipes of the SBR vulcanizates

Mix number[a]	SBR (g)	M-30 (g)	M-40 (g)	M-50 (g)	M-60 (g)	XNBR (g)	Maximum rheometric torque (R_∞) dNm	Scorch time (t_2) min	Optimum cure time (t_{90}) min
SB-00	100	—	—	—	—	—	7.05	1.72	9.59
SB-01	100	5	—	—	—	—	6.40	1.09	8.83
SB-02	100	10	—	—	—	—	6.28	1.24	8.99
SB-03	100	15	—	—	—	—	5.87	1.67	9.00
SB-04	100	—	5	—	—	—	6.45	1.24	8.50
SB-05	100	—	10		—	—	6.40	1.27	9.20
SB-06	100	—	15	—	—	—	6.18	1.27	10.17
SB-07	100	—	—	5	—	—	6.66	1.18	7.61
SB-08	100	—	—	10	—	—	6.37	1.26	8.51
SB-09	100	—	—	15	—	—	6.22	1.25	9.29
SB-10	100	—	—	—	5	—	6.91	1.15	9.14
SB-11	100	—	—	—	10	—	6.78	1.30	9.60
SB-12	100	—	—	—	15	—	6.40	1.28	11.44
SB-13	100	—	—	—	20	—	5.48	1.31	11.59
SB-14	100	—	—	—	30	—	5.49	1.34	14.72
SB-15	100	—	—	—	—	9.37	5.87	1.49	8.11
SB-16	100	—	—	—	—	18.75	4.99	1.53	10.21
XN-00	—	—	—	—	—	100	8.53	1.12	16.47

[a] All the mixes were vulcanized at 160°C with 3 phr ZnO, 2 phr stearic acid, 1.4 phr sulfur, 1.7 phr CBS and 2 phr DPG.

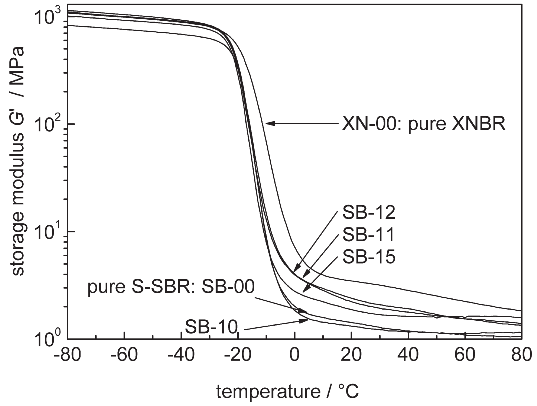

Fig. 3. Temperature dependence of G′ of the organoclay filled rubber composite.

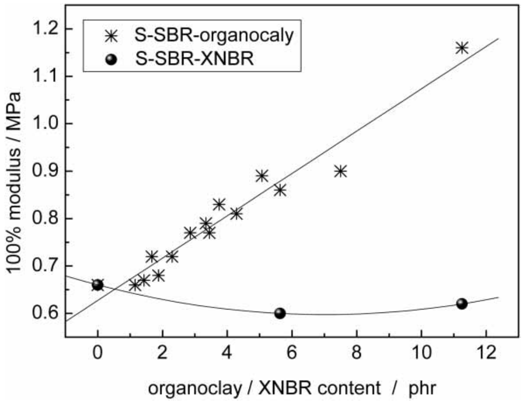

Fig. 5. Variation 100% modulus values with the organoclay and XNBR amount.

Usually, the tan δ peak indicates the compatibility of two polymers in a rubber blend for all nanocomposites. Here, the small amount of XNBR in the samples does not contribute enough thermal relaxation to show a peak broadening due to heterogeneity, hence, a single tan δ peak is obtained. For pure XNBR (XN-00) a second broad tan δ peak appears at higher temperatures (40–80°C). In the cure recipe, zinc oxide was used which can establish a metallic carboxylate linkage by ionic crosslinking in the rubber matrix. Consequently, these ionic rubber chain segments form ionic cluster as discussed with the multiple cluster model (15). The mobility of the rubber chain is restricted in the vicinity of these associated multiples, and this type of ionic force or Columbic attraction force opposes the polymer chain mobility. Therefore, a secondary transition appears at higher temperatures.

It is also interesting to compare the height of the tan δ peak of the composites. It is noteworthy that the smaller the tan δ peak, the higher the reinforcing efficiency of the related filler. Accordingly, for the sample with 5 phr master batch (SB-10) no reinforcement effects can be detected in contrast to the vulcanizates containing higher loadings of organoclay. Here, a sharp decrease in height of the tan δ peak was observed for SB-11 and SB-12 composites. Especially for SB-11, the peak height was decreased to 32%. The peak height for the sample containing S-SBR and XNBR without organoclay is only slightly decreased confirming the results in G′.

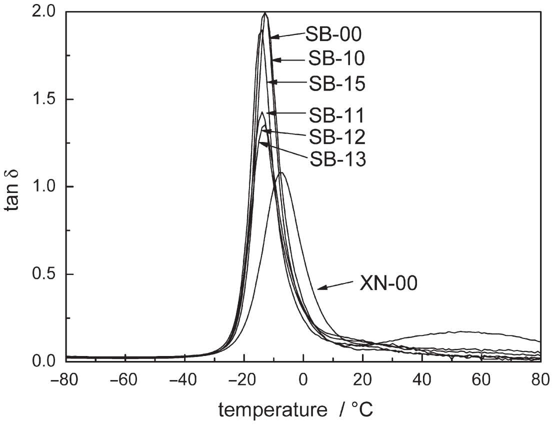

Fig. 4. Temperature dependence of tan δ of the organoclay filled rubber composite.

3.3 Mechanical Properties

Results of tensile tests are shown in Figures 5–8 and 10. In Figures 5–7, the stress values at 100%, 200%, and 300% elongation are plotted against the amount of clay and compared to the samples without clay, which are plotted against the amount of XNBR. Although the clay is always accompanied by XNBR we do not display its amount for better understanding.

It is evident from these figures that with an increase of filler amount, the modulus is increasing with a linear tendency. In contrast, in the unfilled samples containing S-SBR and XNBR the corresponding physical values are very low. These observations prove that the obtained higher rigidity of the rubber

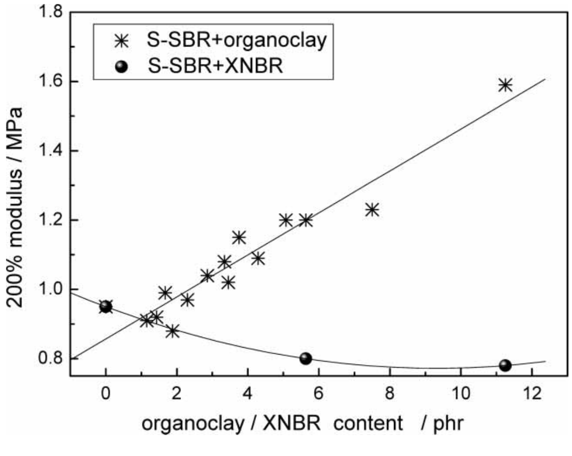

Fig. 6. Variation 200% modulus values with the organoclay and XNBR amount.

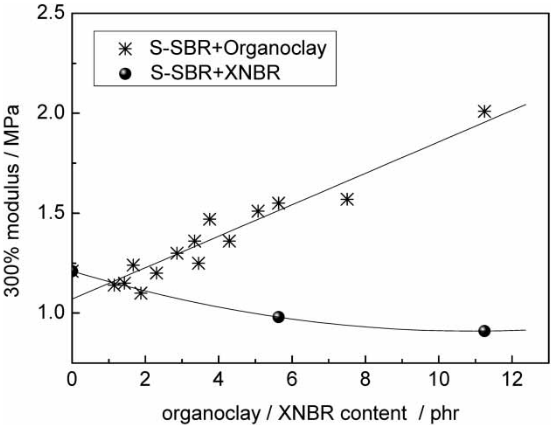

Fig. 7. Variation 300% modulus values with the organoclay and XNBR amount.

matrix is not caused by the XNBR part and support the suggestion of reinforcement caused by the organoclay.

Concerning tensile strength, the above mentioned fact is also reflected in Figure 8. For the samples with around 5 phr loading seven times higher values in tensile strength are obtained compared to the gum. It is also found from the polynomial fit curve in Figure 8 that there is a maximum of tensile strength at around 5 to 8 phr organoclay. At higher loading, the clay particles aggregate and obviously do not contribute to the ultimate strength of the composite. Stress-strain plots are shown in Figure 9 for some composites. In these stress-strain curves, a remarkable effect due to organoclay is observed. The mechanical properties of the nanocomposites become enhanced at higher elongations due to the presence of a small amount of organoclay (4.6 phr) in the rubber matrix. In contrast, an equivalent amount of XNBR without any filler deteriorates the corresponding mechanical properties of the composites. Therefore, it can be stated that the organomodified nanoclay not only provides excellent reinforcement effects on the rubber matrix, but also acts as a compatibilizer between polar and non-polar rubber as

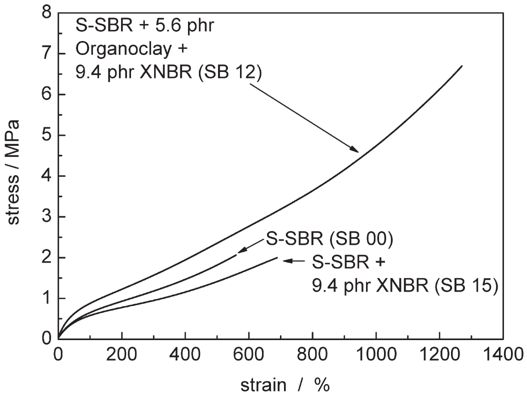

Fig. 9. Stress-strain diagram of the organoclay rubber composite.

mentioned before. The investigated types of rubber nanocomposites also show very high elongation at break values as presented in Figure 10. High elongation at break values are otherwise found in silica filled rubber compounds (16) with a direct chemical bonding between polymer and silica. In the rubber nanocomposites made of XNBR, S-SBR, and organoclay it can be assumed that the surface silanol groups of the layered silicates react with the carboxyl groups of the XNBR and thus direct rubber filler bonds are formed. In this way, the high elongation properties can be explained.

3.4 XRD Measurements

Figure 11 shows the X-ray diffraction patterns for the rubber compounds of S-SBR with organomodified layered silicate. The 2θ-values along the x-axis can be converted to layer spacing values d by the Bragg relationship ($\lambda = 2d \sin\theta$, where λ is the wavelength of the radiation). A broad peak appears for unmodified clay at about 1.32 nm, for organomodified clay, this peak is shifted to 2.98 nm. For SB-10, SB-11, and SB-12 the corresponding values are 4.43 nm, 4.01 nm, and 3.82 nm, respectively. The diffraction peak of organoclay is obviously shifted towards the low angle direction

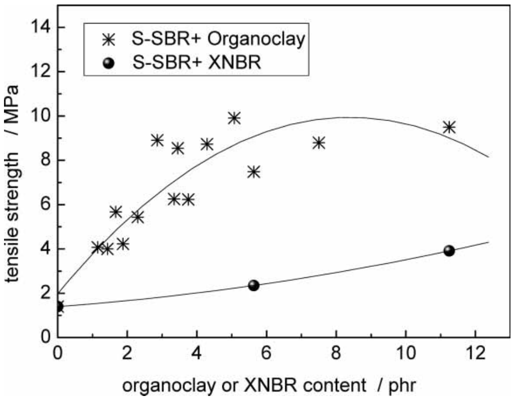

Fig. 8. Variation of tensile strength values with organoclay and XNBR amount.

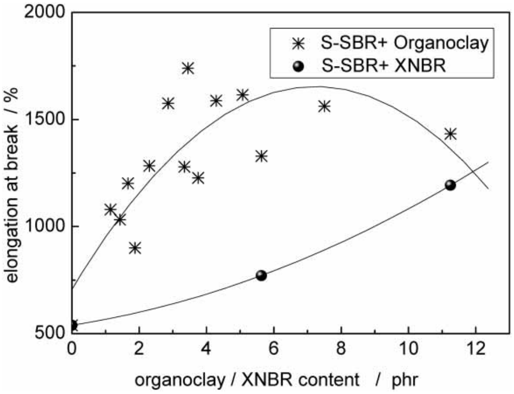

Fig. 10. Plots of elongation at break values with amount of organoclay and XNBR.

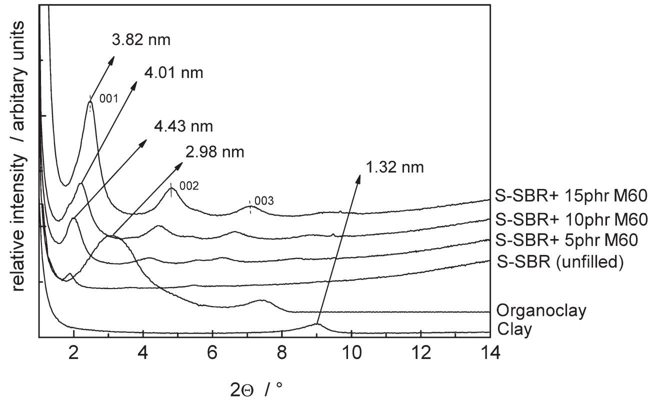

Fig. 11. XRD spectra of S-SBR reinforced with organically modified montmorillonite.
Notes: the spectra of the related clays and organoclay were also shown. The position of the (001), (002), and (003) reflexes is indicated by dotted line.

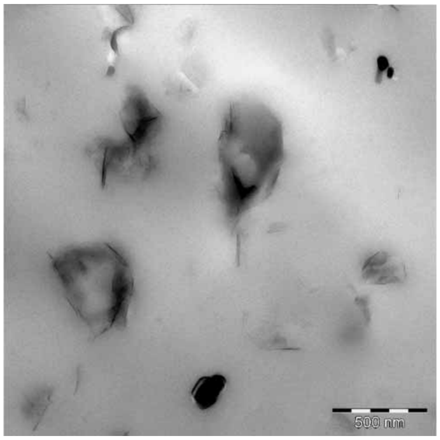

Fig. 13. TEM image of the organoclay filled rubber nanocomposite.

indicating the effective expansion of the interlayer distance of the clay. However, the interlayer spaces decrease with an increase of clay content. Possibly, with increasing filler loading, not enough space is available where the clay layers could occupy their positions without sacrificing the gallery gap.

3.5 TEM

Transmission electron microscopy delivers a direct visualization of the dispersion of the organoclay in the polymer matrix. TEM pictures have been taken from the SBR vulcanizates containing 5, 10, and 15 phr XNBR master batch (M-60). Figure 12 shows the TEM picture of SB-10 where 5 phr M-60 has been used. The actual organoclay concentration of the vulcanizate is 1.8 phr. It is observed from this figure that there are a lot of small dark lines preferably oriented in a north-south direction. Here, the organoclay is distributed evenly in the whole rubber matrix. Some small dark clusters are shown enlarged in Figure 13. These structures are formed due to the separation of the polar XNBR phase from the non-polar S-SBR matrix. Furthermore exfoliated layers of organoclay are visible in the interface between the two polymer phases which obviously promote a better compatibility between XNBR and S-SBR phases.

Figure 14 displays the TEM image of SB-11 where 10 phr master batch M-60 has been used which corresponds to an organoclay concentration of 3.7 phr. Obviously, layered silicate form local network-like structures remaining in the exfoliated and intercalated state. The rise of such network structures is also seen in the vulcanizate containing 15 phr master batch M-60 (Figure 15). No considerable amount of staged (tactoid) layered silicates is observed. Therefore, we conclude that most of the layered silicates are either exfoliated or intercalated and the rubber matrix is sufficiently reinforced.

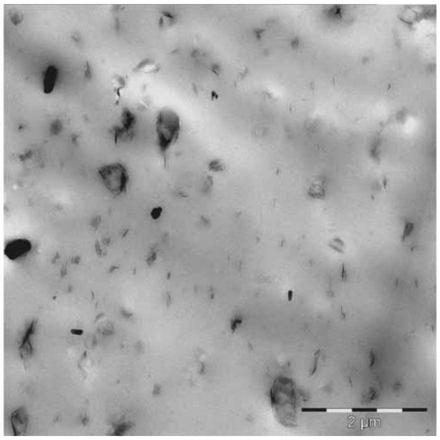

Fig. 12. TEM image of the organoclay filled rubber nanocomposite.

Fig. 14. TEM image of the organoclay filled rubber nanocomposite.

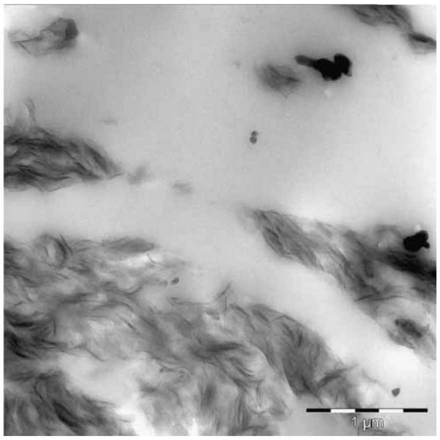

Fig. 15. TEM image of the organoclay filled rubber nanocomposite.

4 Conclusions

It was revealed that XNBR has a unique role of forming a synergistic pair with organoclay to facilitate the intercalation/exfoliation process of layered silicates in a S-SBR matrix. Excellent mechanical performance was achieved by the nanocomposite thus obtained. TEM pictures show that even at a higher amount of organoclay, a good degree of exfoliated structures was achieved by using XNBR as a vector. Further investigations pertaining to the effects of XNBR on intercalation/exfoliation processes and rubber-filler networks, as well as filler-filler networking and percolation point determination are necessary to implement this study to a relevant field. Finally, the realization that this study could be a guide to make a compatibilized rubber blend with different polarity by the help of a organomodified layered silicate as a compatibilizer.

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