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Melt compounded epoxidized natural rubber/layered silicate nanocomposites: structure-properties relationships

S. Varghese, J. Karger-Kocsis*, K.G. Gatos

Department of Materials Science, Institute for Composite Materials, Kaiserslautern University of Technology, Erwin-Schroedinger-Str. 58, D-67663 Kaiserslautern, Germany

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Abstract

Epoxidized natural rubber (ENR)-layered silicate composites were produced by melt compounding and sulfur curing. Pristine (sodium bentonite and sodium fluorohectorite) and organophilic modified silicates (organoclays with primary amine and quaternary ammonium modifications) were introduced in 10 parts per hundred rubber (phr) in the recipes and their effect on the curing and (thermo)mechanical properties determined. The dispersion state of the silicates was studied by X-ray diffraction and transmission electron microscopy. Fastest curing and best mechanical properties were found for the ENR containing the organoclay with primary amine modification. This organoclay was partly exfoliated, partly intercalated and partly confined (reaggregated). Due to the high shearing during compounding the pristine fluorohectorite was also intercalated by ENR. The complex dispersion state of the layered silicates was well reflected in the glass transition relaxation, which showed multiple peaks. Intercalation/exfoliation of the silicates were best displayed in stiffness- and strength-related mechanical parameters.

Keywords: Epoxidized natural rubber (ENR); Layered silicates; Curing

1. Introduction

The concept of ‘nano-reinforcement’ with layered silicates, credited to researchers at Toyota Central Research Laboratories (Japan), became very popular in the past decade as well reviewed in Refs. [1,2]. The ongoing interest is mostly due the unexpected high reinforcing effectiveness of the silicates when dispersed in nanometer instead of micrometer scale. However, to achieve nano-reinforcement, the layers of the silicate have to be completely separated from one another (termed delamination or exfoliation) in the matrix polymer. Major driving force of the latter is of thermodynamical origin [3]. Exploiting the cation exchange capacity of natural (clay) and synthetic layered silicates by suitable intercalants the initial interlayer distance of <1 nm can be increased by $>50\%$ [4]. This is usually enough for partial (intercalation) or full delamination (exfoliation) governed by terms of the Gibb’s equation, $\Delta H - T\Delta S < 0$, where H, T and S denote the enthalpy, temperature and entropy. Entropy gain (more probable) is usually attributed to the enhanced mobility of the intercalating compound (usually amine-containing compounds) caused by the interdiffused matrix polymer chains. Enthalpy reduction (less probable), can be achieved via special interactions with the matrix molecules (H-bonding, chemical reactions). On the other hand, the layered structure of silicates can be broken up upon high acting shear forces [5,6]. The effect of the latter is obviously the better the higher the molecular weight of the polymer and the lower the mixing temperature are. Considering the above conditions (i.e. production of organophilic silicates by amine intercalants and need for high shear stresses) rubbers should be preferred matrices among polymers. Note that amine-compounds are widely used in sulfur curing rubber recipes as accelerators [7]. As a consequence, via the amine-compound some beneficial effect may be expected in respect with the enthalpy (ΔH) and/or entropy (ΔS) terms. Further, rubbers are very high molecular weight materials showing extremely high viscosities during ‘melt’ compounding. Due to the latter high shear stresses accommodate locally which

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* Corresponding author. Tel.: +49-631-201-7203; fax: +49-631-201-7198.

E-mail address: karger@ivw.uni-kl.de (J. Karger-Kocsis).

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Table 1
Formulation of the mixes

Material	Parts
ENR (epoxide content 50 mol%)	100
Filler (various)	10
ZnO	5
Stearic acid	2
Sodium carbonate	0.3
Sulfur	1.5
Retarder, (*N*-cyclohexylthio-phthalimide)	0.2
CBS (*N*-cyclohexylbenzothiazole-2-sulfenamide)	1.5
Antioxidant-HS (2,2,4-trimethyl-1,2-dihydroquinoline in polymerized form)	1.5

support the peel-off, and thus the delamination of the silicate layers. This layer peel-off may work probably also in the case of pristine (i.e. non-organophilic) clays and silicates. Albeit some reports were published on solution blending [8–10], latex-compounding [11,12] with layered silicates, less works were devoted to the melt compounding route [13–15] which is, on the other hand, of high practical relevance. Therefore, major aim of this work was to study the effects of pristine and organophilic clays (of natural origin) and layered silicates (of synthetic origin) on the sulfur curing, morphology and mechanical properties of a highly epoxidized natural rubber (ENR) formulation. ENR was selected due to its high polarity which should be beneficial when compounding with polar fillers, such as layered silicates.

2. Experimental

2.1. Rubber recipe and its curing

ENR with 50 mol% epoxidation (ENR-50) showing a Mooney viscosity of ML $(1+4)100\,^\circ\mathrm{C} = 140$ was obtained from the company Kumpulan Guthrie, Malaysia. The recipe used is indicated in Table 1. As pristine layered clay and silicate sodium-bentonite (EXM 757, Süd-Chemie, Germany; interlayer distance: 1.24 nm) and sodium-fluorohectorite (Somasif ME-100, Coop Chemicals, Japan; interlayer distance: 0.94 nm) were used and denoted furtheron as B and F, respectively. Note that the aspect ratio of F is ca. twofold of B [16]. The organoclays were montmorillonite-based ones intercalated by octadecylamine (MMT–ODA; Nanomer® I.30P of Nanocor Inc., USA; interlayer distance: 2.10 nm) and methyl-tallow-bis-2-hydroxyethyl quaternary ammonium salt (MMT–MTH; Cloisite® 30B of Southern Clay Inc., USA; interlayer distance: 1.85 nm). For comparison purpose compounds with amorphous silica (Ultrasil-VNZ GR of Degussa, Germany) were also made. The rubber mixes were prepared on a laboratory two roll mixing mill (LRM-150/3E of Labtech, Thailand). The samples were then cured at 150 °C in an electrically heated hydraulic press to their respective cure times, t_{90}. The t_{90} values were derived from Monsanto oscillating disc rheometer (MDR 2000) measurements.

2.2. Testing

Cure characteristics were determined by the MDR 2000 rheometer under the following conditions: 8–10 g of the compound was feeded in the chamber of the rheometer operated at a frequency of 1.66 Hz and 0.5° arc.

The dynamic-mechanical thermal analysis (DMTA) spectra were recorded on rectangular specimens (length × width × thickness $= 6 \times 1 \times 0.25\ \mathrm{cm}^3$) in tensile mode at a frequency of 10 Hz using a Eplexor 150N device of Gabo Qualimeter, Germany. DMTA spectra, viz. storage and loss moduli and mechanical loss factor (tan δ) were recorded in the temperature range from -120 to 100 °C at a heating rate of 2 °C/min.

Tensile and tear tests were performed on dumbbell and crescent shaped specimens according to the ASTM standards D 412 and D 624 on a Zwick 1485 universal testing machine at a cross-head speed of 50 cm/min. Five specimens were tested and the average of the values was taken. Hardness and resilience were tested according to the respective ASTM standards (D 2240 and D 1054, respectively).

The dispersion of the silicates was studied by transmission electron microscopy (TEM) and wide angle X-ray scattering (XRD). TEM pictures were taken in a LEO 912 Omega transmission electron microscope with an acceleration voltage of 120 keV. The specimens were prepared using a Ultracut E cryo-microtome. Thin sections of about 100 nm were cut with a diamond knife at -120 °C.

X-ray diffractograms (XRD) were obtained, using Ni-filtered Cu Kα radiation ($\lambda = 0.1542$ nm) by a D500 diffractometer (Siemens, Germany) at 40 kV and 35 mA. The samples were scanned in step mode by 1.5°/min scan rate in the range of $2\theta < 12°$.

3. Results and discussion

3.1. Cure characteristics

Table 2 lists the cure parameters derived from the Monsanto measurements. The cure time (t_{90}) values indicate that both pristine (B, F) and organophilic clays (MMT–ODA, MMT–MTH) accelerate the vulcanization. In case of the organophilic clays this effect, observed also for other rubbers [13,15], is likely linked a transition metal complexing in which sulfur and amine-groups of the intercalants participate [16]. This aspect, however, has not been studied yet. The reason behind the t_{90} reduction for B and F fillers when

Table 2
Rheometric properties of the ENR mixes containing 10 phr fillers

Parameters	Silica (S)	Fluorohectorite (F)	Bentonite (B)	MMT−ODA	MMT−MTH
Minimum torque (dNm)	0.25	0.27	0.33	0.48	0.52
Maximum torque (dNm)	9.41	8.16	8.46	9.18	9.39
Max−min torque (dNm)	7.9	18.19	8.85	8.93	8.87
Scorch time t_2 (min)	9.20	4.38	4.09	2.00	2.29
Cure time t_{90} (min)	12.10	7.08	6.65	3.85	4.94
Cure rate $t_{90}-t_2$ (min)	2.9	2.7	2.56	1.85	2.65

compared to S may be similar, i.e. of complexing nature. The cure rate, as defined ($t_{90}-t_2$) is not affected by the silicates except the MMT−ODA. The increase in maximum and minimum torques, as well as, in their difference compared to the silica filled stock already suggest some reinforcement for both pristine and organophilic layered silicates. Note that this is possible only if the silicates are intercalated and/or exfoliated. As the effect of reinforcement is well reflected by the DMTA response, next this behavior will be considered.

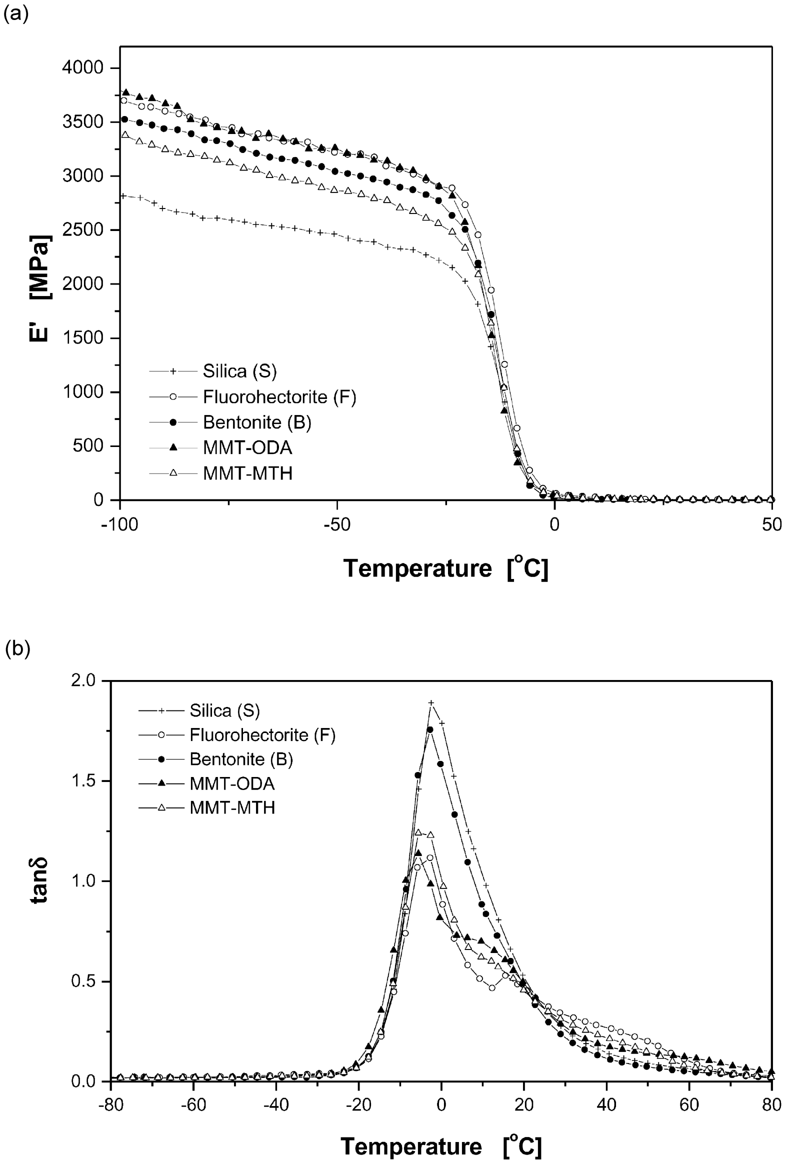


Fig. 1. (a) Storage modulus (E'-graph) and (b) mechanical loss factor (tan δ-graph) as a function of temperature for the ENR stocks containing various fillers in 10 phr.

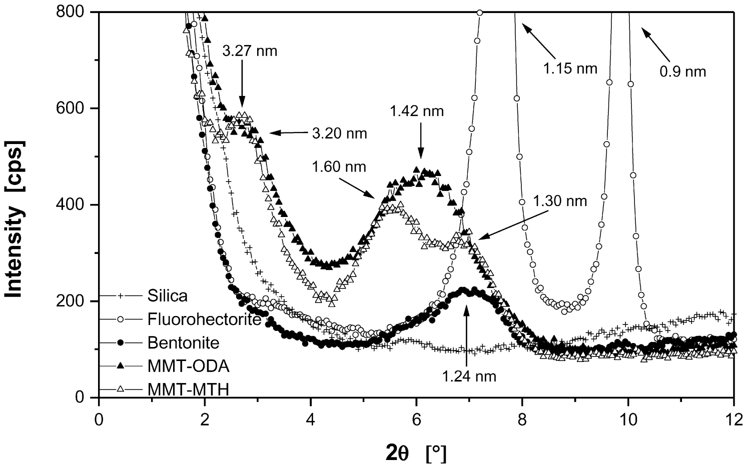


Fig. 2. XRD spectra of the ENR nanocomposites studied.

3.2. DMTA response

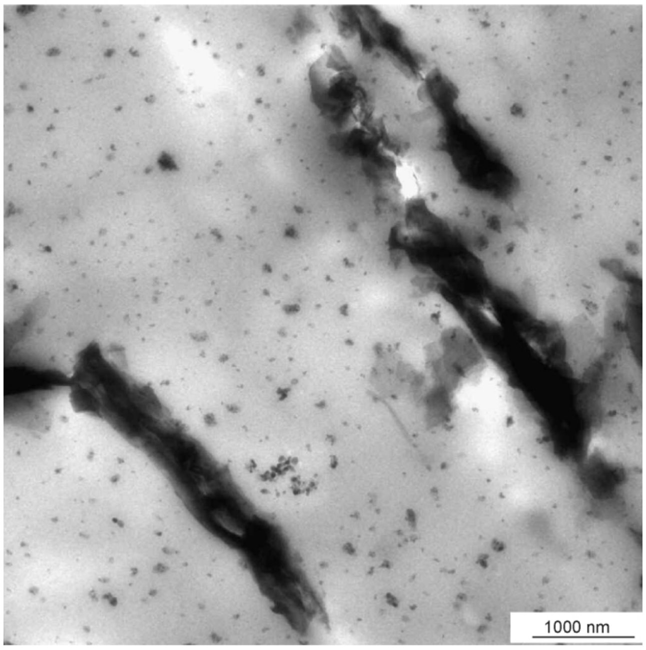
Fig. 1(a) and (b) display the course of the storage (E') and mechanical loss factor (tan δ) as a function of temperature (T). The ranking of the fillers in respect with the stiffness in the temperature range below the glass transition temperature (T_g) of the ENR is: S < MMT–MTH < B < MMT–ODA ≈ F.

More interesting is the information one can derive from the tan δ–T traces in the T_g region. It is noteworthy that the smaller the T_g peak, the higher the reinforcing efficiency of the related filler is. Accordingly, high reinforcement effect can be predicted for fluorohectorite (F) and for the organoclays (MMT–ODA, MMT–MTH). The more or less pronounced doubling and tripling of the T_g peak (as additional peak and/or shoulder on the main peak) suggest that at least a part of the ENR molecules is less mobile. Reduced chain mobility owing to physical adsorption of the ENR molecules on the filler surface causes a height reduction of T_g peak. The multiplication of the T_g peak (that could be explicitely shown by deconvolution techniques) hints for several ENR populations with different chain mobilities. It is intuitive that this behavior should be a product of the silicate intercalation/exfoliation by ENR. If it is so then the tan δ–T traces may deliver further insight in the intercalation/exfoliation stage of the silicates. Albeit this has been suggested in previous works [12,14], not yet addressed by studies in detail. In order to shed light on this issue the dispersion state of the silicates has to be characterized first.

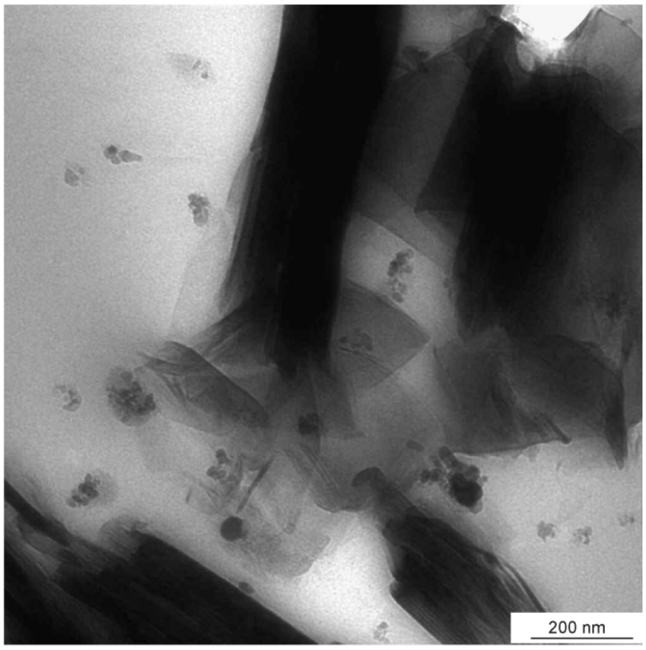
3.3. Dispersion of the layered silicates

The XRD spectra of the ENR mixes are shown in Fig. 2. As expected, the amorphous silica (S) does not show any crystallographic peak. The rather small peak of bentonite (B) did not change his position, so it is hardly intercalated by ENR (note that the interlayer distance agrees with that of the initial bentonite powder, = 1.24 nm). For the fluorohectorite filled ENR two peaks are discernible at ≈0.9 and 1.15 nm. The former one agrees with the initial layer distance of F, whereas the latter demonstrates the onset of some intercalation. MMT–MTH possesses three peaks at 1.30, 1.60 and 3.27 nm. Recall that that two of them are below the initial value of this organoclay (= 1.85 nm). So, here instead of exfoliation a confinement, reaggregation of the silicate layers took place. The shoulder at low 2θ value (= 3.27 nm), on the other hand, evidences pronounced intercalation with ENR. The XRD trace for the MMT–ODA filled ENR shows also two peaks, one at 1.42 nm, and the other at 3.20 nm interlayer distances. Recall that the former interlayer distance is far below the initial value of this organoclay (≈2.10 nm). Accordingly a part of the organoclay is reaggregated (a reduction of the layer distance is apparent). Based on the other peak, however, MMT–ODA was definitely intercalated by ENR. The above findings from the XRD measurements corroborate our speculations in respect with the tanδ–T traces (cf. Fig. 1(b)), viz. the more or less well discernible multiplication in the T_g relaxation reflects the difference in the mobility of the molecular chains in various confined regions.

It is of interest to check how the TEM technique can contribute to clarify the dispersion of those silicates which strongly imparted the T_g relaxation, i.e. F, MMT–MTH and MMT–ODA. Fig. 3(a) and (b) show characteristic TEM pictures of the F-filled ENR. Fig. 3 supports that fluorohectorite should exhibit a very high aspect ratio as the original particle length is between 1 and 2 nm. The image in Fig. 3(a) demonstrates further that no delamination of F took place. What Fig. 3(b) actually reveals is that the stacked silicate particles were partially peeled off due to the locally acting shear stress field. In between the peeled layers ENR molecules could penetrate the mobility of which became strongly hampered. Recall that the latter effect was seen in the DMTA response (Fig. 1(b)). The TEM picture in Fig. 4



(a)



(b)

Fig. 3. TEM images taken at low (a) and high magnifications (b) from the ENR mix containing sodium fluorohectorite (F). Note: the black spots visible on all TEM pictures are caused by the ingredient sodium carbonate.

taken from the ENR mix with MMT–MTH seems to be in concert with both DMTA and XRD results. Large silicate aggregates (laying edge-on) and intercalated/exfoliated platelets (laying flat-on in the related TEM pictures) are simultaneously present. The scenario is similar to the ENR nanocomposite with MMT–ODA (Fig. 5). In this system exfoliated, intercalated and aggregated organoclay platelets and particles can be found. This finding corroborates the above conclusions based on the DMTA and XRD measurements. Note that XRD does not deliver any experimental evidence for exfoliation as in this case no long range ordering of the silicate layers exists.

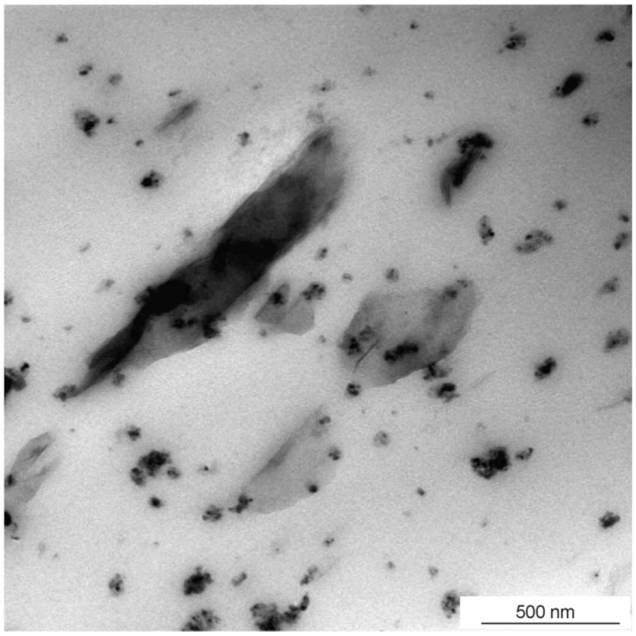
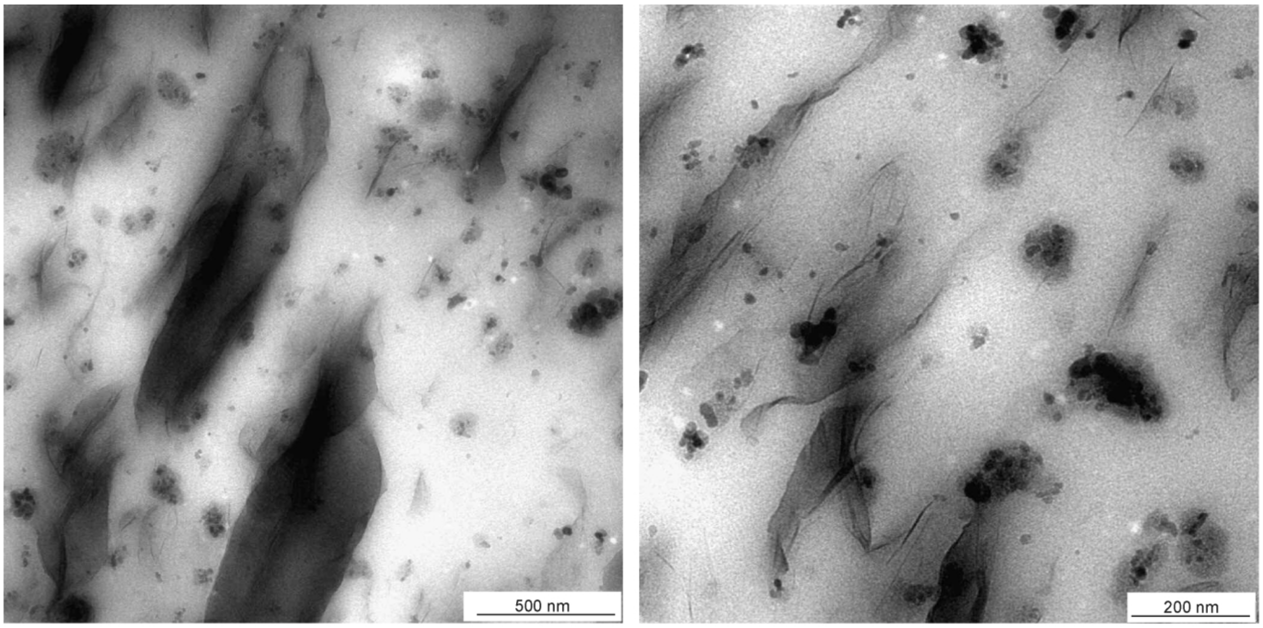


Fig. 4. TEM picture taken from the ENR mix containing MMT–MTH.

The remaining question on the role of the organoclays is: what is the reason for the clay confinement (reaggregation) when parallel to that intercalation and even exfoliation occur. This should be relied on possible interactions between ENR, organophilic intercalant and sulfuric curatives. The epoxy groups of ENR can react, or at least form hydrogen bonds, with both amine (ODA) [17] and hydroxyl-groups (MTH) of the intercalants. This is likely favoring the exfoliation of the organoclay. The amine functionality of the intercalant when removed from the interlayer to participate in the formation of a Zn-based complex (along with sulfur) should result in close-up of the silicate galleries. Simultaneous intercalation and confinement were observed also for natural rubber (NR) stocks where reactions via the epoxide groups are excluded [16]. This suggests that for the confinement of the organoclay the possible reaction between the intercalant and the sulfuric curatives are responsible. If this assumption is correct then the recipe of sulfur curing, and thus in general the curing system, are crucial in view of the intercalation/exfoliation behavior. This aspect, to which a contribution was already made [18], has to be studied in the future.

3.4. Mechanical properties

The mechanical properties of the ENR (nano)composites are summarized in Table 3. The ultimate tensile



(a) (b)

Fig. 5. TEM pictures taken at various magnifications from the ENR mix containing MMT–ODA.

properties (strength, elongation) do not reflect the tendency expected by considering the dispersion of the silicates. Intercalation/exfoliation of the silicates should result in enhanced strength and reduced elongation as this is obvious for MMT–ODA. The ranking of the fillers according to the moduli at elongations 100, 200, 300% are fairly matched with that of the stiffness derived from DMTA for the sub-T_g region (cf. Fig. 1(a)). The tear strength, which proved to be also a useful indicator for clay dispersion [19], gives another ranking for the fillers, viz. $\mathrm{S} \approx \mathrm{B} \approx \mathrm{MMT{-}MTH} < \mathrm{F} < \mathrm{MMT{-}ODA}$. Based on the resilience and Shore A hardness values a further ranking can be deduced for the layered silicates. Nevertheless, the best mechanical response was achieved in most cases by MMT–ODA. Note that this silicate was present in exfoliated (TEM), intercalated (XRD) and confined-intercalated (XRD) forms, as well. In view of the above findings the octadecylamine (primary amine groups) modified clay (MMT–ODA) is far more efficient in ENR stocks than that of modified by a methyl-tallow-dihydroxyethyl ammonium compound (quaternary ammonium; MMT–MTH).

4. Conclusions

Based on this work addressed to study the effect of layered silicates with and without organophilic modification in sulfur cured ENR recipes, the following conclusions can be drawn:

- Fastest curing and best mechanical performance were

Table 3
Mechanical properties of the ENR mixes containing various fillers in 10 phr amount

Properties	Fillers				
	Silica (S)	Bentonite (B)	Flurohectorite (F)	Organoclays	
				MMT–ODA	MMT–MTH
Tensile strength (MPa)	16.7	20.6	17.0	21.2	18.4
Tensile modulus (MPa)					
100% Elongation	0.9	1.5	1.2	1.7	1.2
200% Elongation	1.4	2.0	1.9	3.1	1.9
300% Elongation	2.0	3.1	2.8	4.6	2.7
Elongation at break (%)	946	857	785	767	888
Tear strength (kN/m)	27.9	28.0	33.0	41.2	28.7
Resilience (%)	38.3	43.9	45.1	45.1	48.8
Hardness (Shore A)	34	40	40	44	40

found for the recipe containing organoclay with octadecylamine intecalant (MMT–ODA). This organoclay was partly exfoliated, partly intercalated and partly confined. The latter phenomenon, i.e. reduction of the interlayer distance, was argued to be a possible effect of sulfur curing (zinc–sulfur–amine complexation).

- ENR intercalation of the pristine sodium flurohectorite, resulting in good mechanical properties, was due to peeling of the layers. This was favored by high acting shear stresses owing to high viscosity of the ENR during compounding and high aspect ratio of the fluorohectorite.
- The dispersion state (exfoliation, intercalation, confinement) was best reflected in the T_g relaxation (DMTA) and stiffness-related data (E' from DMTA, moduli at various elongations during tensile test).

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