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Effects of primary and quaternary amine intercalants on the organoclay dispersion in a sulfur-cured EPDM rubber

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Abstract

The effects of primary and quaternary amine modified montmorillonite (MMT) on the nanocomposite formation in an ethylene/propylene/diene rubber (EPDM) were studied. The organoclay was introduced in 10 parts per 100 rubber (phr) amount in the related recipes. X-ray diffraction spectra (XRD) were recorded in various stages of their processing in order to get information about the intercalation process. The curatives found to play a crucial role, as they promote the intercalation/exfoliation phenomena. Incorporation of MMT modified with octadecylamine (MMT-PRIM) in the EPDM and its more polar version (contains maleic anhydride grafted EPDM, EPDM-MA) resulted in intercalated and exfoliated structures, respectively. Deintercalation of the clay (collapse of the layers), generated in both EPDM and EPDM-MA during vulcanization, was attributed to the reactivity of the PRIM and to its ability to participate in complex formation with the curatives (vulcanization intermediates). This explanation was supported by the non-collapse of the MMT layers when the less reactive modifier, viz. octadecyltrimethylamine served as MMT intercalant (MMT-QUAT). In the latter case the corresponding nanocomposite contained mostly intercalated clay layers based on XRD and transmission electron microscopic (TEM) results.

Keywords: EPDM; Intercalant type; Rubber nanocomposite

1. Introduction

Exploiting the 'nanoreinforcement' effect of layered silicates (clays), property improvement can be achieved even by adding small amount of organoclay [1–5]. Key aspect of the 'nano-concept' is to intercalate and exfoliate the layers of the silicate [6]. For that purpose, the inherent 'incompatibility' between the polymer and the clay has to be circumvented. In order to facilitate, the penetration of the chains in between the galleries and thus to form a nanocomposite, different strategies were followed. They include the modification of the surface of the clay layers and/or the polymeric chains [7–11]. Further important factors were the length of the organophilic intercalant [12] and its number of alkyl tails [13], the molecular mass of the polymer matrix [14] and its polarity [15,16], as well as, the type of the layered silicate [17,18]. Although also systems with intercalated structures are termed as nanocomposites, the ultimate goal is to reach full exfoliation of the clay. Parameters assisting to exfoliated/delaminated structures are the processing conditions [19,20] and the energetically favored interactions between the organoclay and the polymer molecules [13,21–23]. The development of 'reactive' organoclays, the intercalants of which participate in the polymer building/crosslinking reactions [4,23], is a recent strategy to facilitate the nanocomposite formation.

Considering the high molecular mass of rubbers along with the chemical reactions that are taking place during vulcanization [24], rubber can be considered as an ideal matrix for nanocomposites [25]. Note that high molecular mass is beneficial in respect to shearing, which supports the peel apart of the clay layers [14,20].

In the current paper, we report on the action of primary (PRIM) and quaternary (QUAT) amine intercalated montmorillonite (MMT) on the clay dispersion in a sulfur-cured ethylene/propylene/diene rubber (EPDM) as a function of processing (compounding and curing). Their effects on the

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clay dispersion were recorded in each processing step of the mixtures and possible reactions between the rubber curatives are discussed. Furthermore, the effect of an EPDM grafted with polar maleic anhydride (MA) was investigated to shed light on effects of matrix polarity.

2. Experimental

2.1. Materials

Montmorillonite modified by octadecylamine (MMT-PRIM; Nanomer® I.30P) and by octadecyltrimethylamine (MMT-QUAT; Nanomer® I.28E), were obtained by Nanocor Inc., Arlington Heights, USA. The initial basal spacing of these organoclays was 2.10 and 2.50 nm, respectively. EPDM (Buna® AP 451) with 50% ethylene and 8.6% ethylidene norbornene content having a Mooney viscosity of ML (1+4) at 125 °C=59 was supplied by Bayer AG, Leverkusen, Germany. EPDM grafted by maleic anhydride (EPDM-*g*-MA; Royaltuf 465A) with an ethylene/propylene ratio of 55/45 and MA content of 1 wt%, was supplied by Uniroyal Chemical, Louisiana, USA. This EPDM-*g*-MA showed a Mooney viscosity of ML (1+4) 125 °C=60. The vulcanization curatives: zinc diethyldithiocarbamate (ZDEC; Vulkacit® LDA), stearic acid, zinc oxide and sulfur were also donated by Bayer AG, Leverkusen, Germany. The mixing recipe used was as follows (in parts), rubber: 100, organoclay: various, ZnO: 5, stearic acid: 1, ZDEC: 1 and S: 2.

2.2. Rubber compounding

An internal mixer type Brabender plasticorder PL 2000 (Brabender®, Duisburg, Germany) operating at 60 rpm and at 100 °C was used for the mixing of the rubber with the organoclay. Mixing occurred for 10 min. In the mixes, designated as EPDM-MA compounds, EPDM-*g*-MA was added to the EPDM at 50/50 ratio by weight. Accordingly, the EPDM-MA mixtures had 0.5% overall MA content.

Incorporation of the curatives and other ingredients took place on a two roll mixing mill, LRM-150/3E (Labtech, Bangkok, Thailand) with a nip clearance of 1 mm and friction ratio 1.3 (22/17 rpm). Mixing was performed at room temperature for 5 to 10 min. The specimens were cured at 160 °C in an electrically heated hydraulic press for the respective curing times (t_{90}) derived from measurements on a Monsanto oscillating disc rheometer (ODR 2000).

2.3. Nanocomposite characterization

X-ray diffraction (XRD) spectra were collected in reflection mode using Ni-filtered Cu Kα radiation (λ= 0.1542 nm) by a D500 difractometer (Siemens, Munich, Germany). The samples were scanned in step mode (5 s/step, step=0.05°) in the range of 2θ up to 12°.

TEM images were taken in LEO 912 Omega microscope (Oberkochen, Germany) with an accelerator voltage of 120 kV. Thin sections (ca. 100 nm) of the specimens were cryo-cut with a diamond knife at ca. −120 °C and used without staining.

The tensile tests were performed on a Zwick 1445 (Ulm, Germany) universal testing machine at a cross-head speed of 100 mm/min using small specimens (DIN 53504).

Dynamic-mechanical thermal analysis (DMTA) spectra were recorded on rectangular specimens (length × width × thickness = $50\times10\times1.2$ mm^3) in tensile mode at a frequency of 10 Hz using an Eplexor 150 N device of Gabo Qualimeter, Ahlden, Germany. DMTA spectra, viz. storage modulus and mechanical loss factor (tan δ) were measured in the temperature range from −100 to 120 °C at a heating rate of 2 °C/min.

3. Results and discussion

3.1. Clay dispersion

Rubber compounding involves several steps in which various ingredients are added in the rubber matrix. Considering the kinetics of the macromolecular chains during melt processing [26] and the preferred break-up of the organoclay agglomerates in an internal mixer instead of an open mill [27], EPDM was compounded with organoclay in a kneader (internal mixer). As presented in Fig. 1, the basal spacing of the initial MMT-PRIM slightly increased during mixing of the EPDM with the organoclay (10 phr). This limited penetration of the EPDM into the clay galleries was observed also for other non-polar polymers like polypropylene (PP) [10,28].

After the second stage of compounding, i.e.

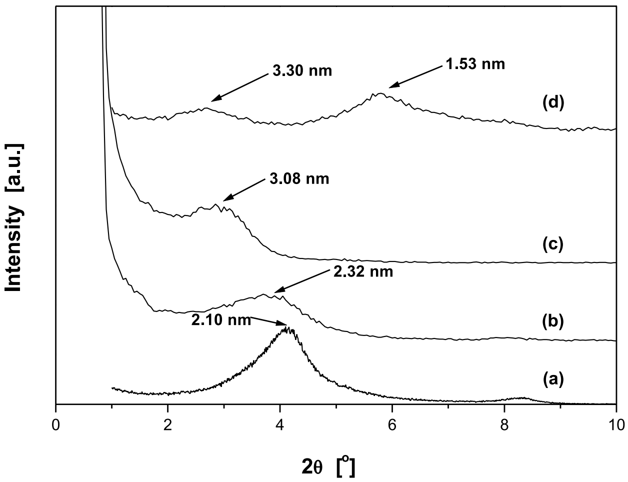

Fig. 1. XRD patterns of (a) the MMT-PRIM and (b)–(d) the EPDM/MMT-PRIM (10 phr) nanocomposite at the different stages of processing: (a) MMT-PRIM powder, (b) mixing of the EPDM and the MMT-PRIM (10 phr) in the internal mixer, (c) after addition of the curatives on the open mill and (d) after vulcanization at 160 °C.

incorporation of the curatives and further ingredients on an open mill, a shift in the XRD peak towards lower 2*θ* values occurred. This indicates further opening of the clay galleries. But what can be reason for this 0.76 nm gallery expansion that is observed between the first and second stage? Considering the fact that EPDM alone does not favor intercalation, as it was proved during the first step, further compounding (i.e. on the open mill) should not contribute to a better intercalation. The parameter that changed during the second step was the addition of the curatives, i.e. ZnO, ZDEC, stearic acid and sulfur. Nanoparticles of ZnO was found by Németh et al. [29] to intercalate in kaolinite and montmorillonite layers. Note that ZDEC is quite polar and stearic acid is also a polar low molecular mass compound. Sulfur is rather inactive in its original form (ring of eight atoms) at room temperature. Conclusively, the observed layer expansion of the organoclay might be related, indeed, with the 'adsorption' of the curatives in the clay galleries. Adsorption of such agents has been reported on silica particles surfaces [30]. The further layer separation between the first and the second processing step has been observed recently by Usuki et al. [31] and Zheng et al. [32] for EPDM mixed with MMT-PRIM and MMT-QUAT, respectively. Both authors attributed this phenomenon to the prolongation of the compounding.

After vulcanization, as presented in Fig. 1—trace d, apart from a peak that can be attributed to the nanocomposite formation (3.30 nm) another one at higher 2*θ* appeared (1.53 nm). This may suggest some deintercalation of the clay galleries.

To check the role of the polar MA group during the stages of compounding the same procedure as above was followed for the EPDM-MA. As shown in Fig. 2, the beneficial action of the polar chains appears already in first stage (i.e. mixing in the internal mixer). After this step, an increase up to 3.15 nm interlayer spacing is observed (cf. Fig. 2—trace b). Adding the curatives (trace c) did not change practically the degree of intercalation. Trace d in Fig. 2 reflects the effect of vulcanization. There the only XRD peak at higher 2*θ* corresponds to a basal spacing of 1.31 nm. This is markedly lower than the initial interlayer spacing of the MMT-PRIM.

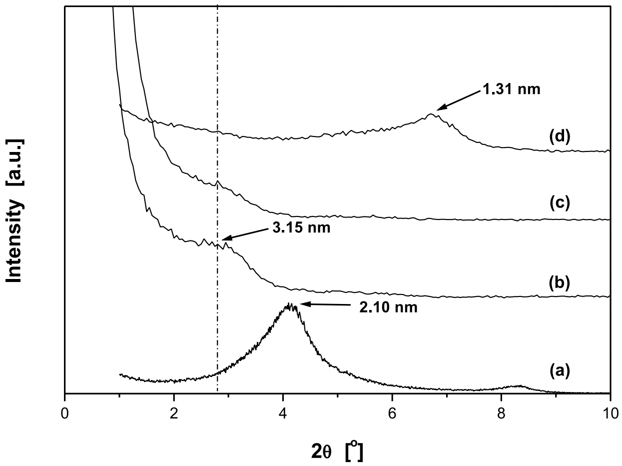

Fig. 2. XRD patterns of (a) the MMT-PRIM and (b)–(d) the EPDM-MA/MMT-PRIM (10 phr) nanocomposite at the different stages of processing: (a) MMT-PRIM powder, (b) mixing of the EPDM-MA and the MMT-PRIM (10 phr) in the internal mixer, (c) after addition of the curatives on the open mill and (d) after vulcanization at 160 °C.

In order to get a better insight in the clay dispersion, transmission electron microscopy (TEM) images where taken from these EPDM and EPDM-MA nanocomposites (Fig. 3). As can be seen in Fig. 3, apart from well dispersed silicate layers confined ones (stacks of layers) are also present. Comparison of Fig. 3(a) and (b) suggests that the clay dispersion in EPDM-MA is finer (i.e. better exfoliated) than in the EPDM. So, the question rises: Where the clay confinement comes from?

To step forward with the investigation the role of the curatives between the first and the second processing stage should be examined. Do they indeed interfere with the intercalation process or just the prolonged compounding on the open mill is the key aspect action? Are the curatives present in the gallery environment before vulcanization as it was speculated at the beginning of this study?

In order to get better understanding, samples were prepared similarly as before, but changing the compounding in the first stage. So, instead of compounding the rubber and the MMT-PRIM (10 phr) in the internal mixer for 10 min, their mixing was performed on the open mill for the same time. As can be seen in Fig. 4—traces a and c, just by working on the open mill does not support the intercalation because after 10 min of processing, both EPDM and EPDM-MA produce identical results. This result was expected for the EPDM compound, as this rubber does not favor intercalation due to its apolarity (compare Fig. 1—trace b with Fig. 4—trace a). On the other hand, in case of EPDM-MA the results are in contrast to those achieved in the internal mixer (compare Fig. 2—trace b with Fig. 4—trace c). It is now interesting to observe that just by adding the vulcanization curatives, Fig. 4—traces b and d, the XRD peak shifts to lower 2*θ* for both EPDM and EPDM-MA. Note that the addition of the vulcanization curatives took place on the open mill at room temperature (typical procedure) and lasted between 5 and 10 min. This evidences the decisive role of the curatives and makes clear their presence in the clay galleries. Proceeding further with the vulcanization of these samples, the related XRD spectra (not shown here) were similar to those presented as d traces in Figs. 1 and 2.

It is known that the sulfur-vulcanization of rubber proceeds in three stages [24]. The first regime is the induction (scorch) period during which an accelerator complex forms. The second period is that of the cure in which the crosslinked network is formed, and the third one is the overcure regime. Nieuwenhuizen and co-workers have presented the role of zinc accelerator complexes in sulfur-vulcanized systems [33,34] underlining the action of

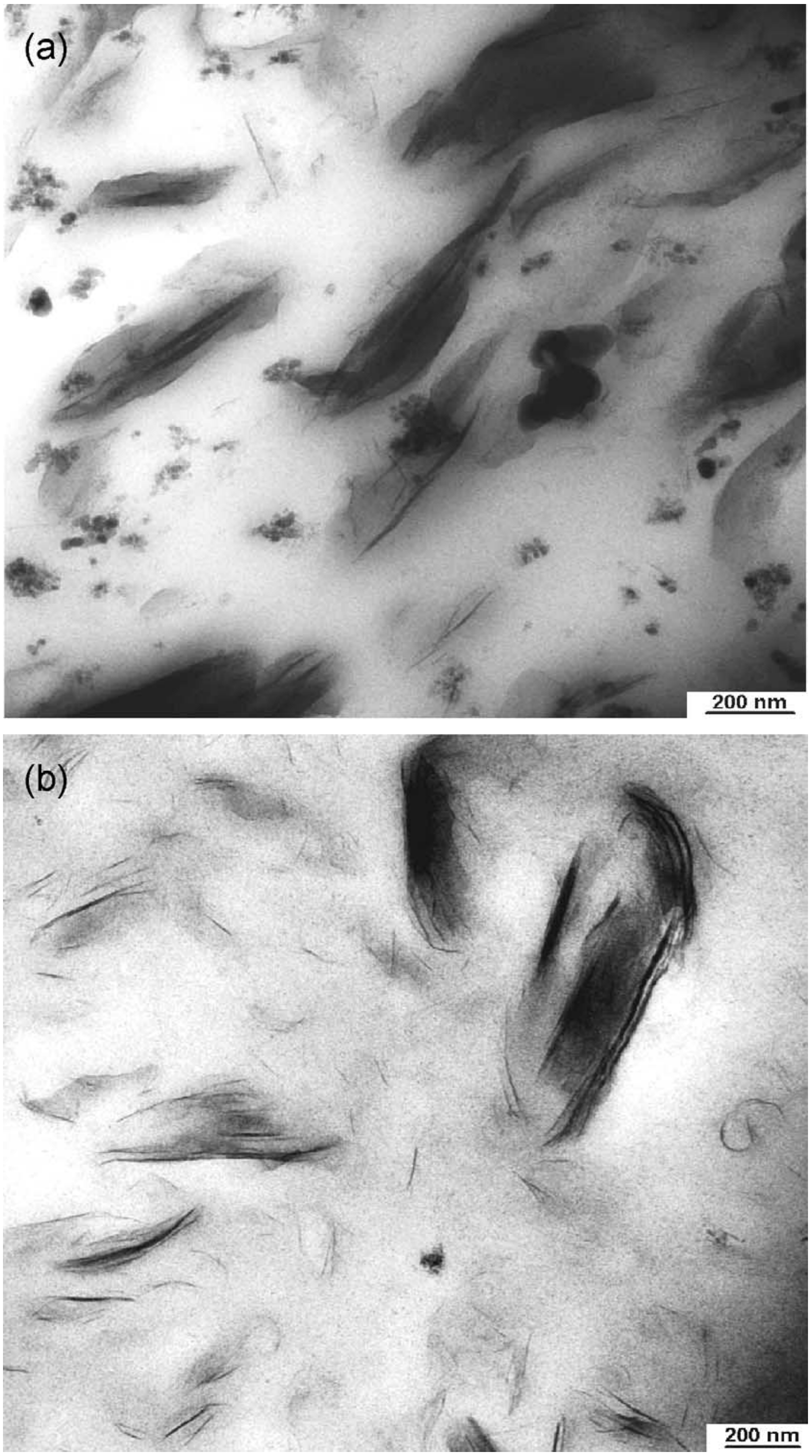

Fig. 3. TEM images of vulcanized films (a) EPDM/MMT-PRIM and (b) EPDM-MA/MMT-PRIM, both in 10 phr clay loading.

amines. They refer a mechanism where a nucleophilic attack of an amine on the carbon atom of the thiocarboxy group of a bis(dialkyldithiocarbamato)zinc(II) (ZDAC) yields an amine-dithiocarbamic intermediate from which, in the case of primary amines, thiourea products are obtained [35]. Tertiary amines were found not to react with ZDACs. In our system, primary amines can be found only inside the clay galleries (i.e. ODA intercalant). The presence of the curatives either inside or at the edges of the silicate layers could generate such complexes. By this way, the tethered ODA chain will leave the clay surface in order to participate in the vulcanization intermediate. This occurs either by migrating into the rubber matrix (resulting in confinement of the galleries-deintercalation) or causing rubber crosslinking

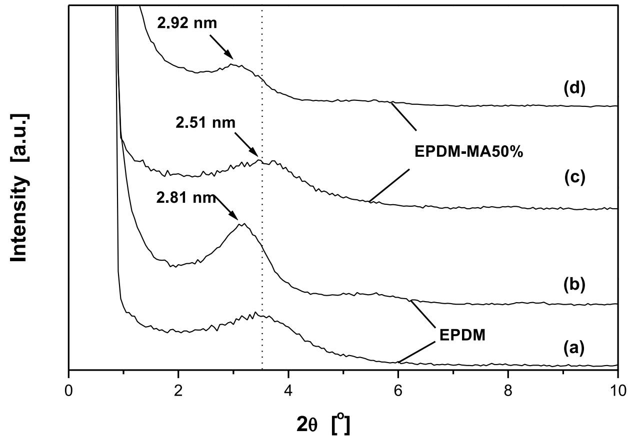

Fig. 4. XRD patterns of (a) the EPDM mixed with MMT-PRIM (10 phr) for 10 min on the open mill, (b) its further addition of the curatives, (c) the EPDM-MA mixed with MMT-PRIM (10 phr) for 10 min on the open mill and (d) its further addition of the curatives.

inside the galleries (inducing better clay dispersion via layers separation or delamination/exfoliation). If the above scenario holds, then by using a quaternary amine as modifier, creation of such type of complexes and thus confinement/deintercalation should not appear.

As shown in Fig. 5, when MMT-QUAT in 10 phr clay loading is used as organoclay (following the basic compounding procedure, i.e. internal mixer followed by open mill) the XRD spectra of the vulcanized EPDM rubbers strongly differ from those produced with MMT-PRIM. The spectra in Fig. 5 indicate intercalated nanocomposite structures presenting *d*-spacing (i.e. *d*(001)) of 4.20 and 4.69 nm for EPDM and EPDM-MA, respectively. At the same time, peaks at $2\theta = 4.4$ and 6.6° were observed. We speculate that the additional peaks in Fig. 5(b) and (c) are related on both reflections at higher order (especially for EPDM/QUAT; Fig. 5(b)) and some deintercalation phenomena due to the high sulfur content (especially for EPDM-MA/QUAT; Fig. 5(c)). Note that the right positions (calculated) of the reflections at higher order are indicated in Fig. 5. The TEM image of the EPDM-MA/MMT-QUAT (Fig. 6) presents a nanocomposite containing also exfoliated clay layers.

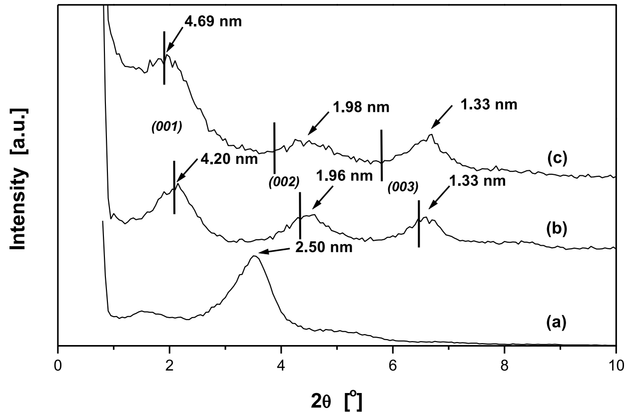

Fig. 5. XRD patterns of (a) the MMT-QUAT, (b) the EPDM/MMT-QUAT after vulcanization and (d) the EPDM-MA/MMT-QUAT after vulcanisation (clay loading in 10 phr).

It is believed that the primary amine of MMT-PRIM created a complex with the vulcanization curatives during the curing. This may yield deintercalation of the clay galleries or their delamination. It should be mentioned that deintercalation of the organoclay was recently reported for epoxidized natural rubber (ENR) [36] and poly(methylmethacrylate) systems [37]. In the current investigation the basal spacing of 1.31 nm after curing (Fig. 2—trace d) is close to the value of pristine sodium montmorillonite [38–40]. Furthermore, the related XRD peak has an asymmetric shape suggesting that the surface coverage of the clay has been altered [41]. This may be attributed to the formation of a monolayer ODA arrangement in between the clay galleries [42].

Verification of the above-mentioned speculations about the different role of the PRIM and the QUAT intercalants took place recently on a hydrogenated nitrile rubber (HNBR) nanocomposite [43]. For this polar rubber, addition of MMT-PRIM produced a combination of intercalated/deintercalated structures, whereas for MMT-QUAT perfectly intercalated organoclay structures were obtained.

It is the right place to emphasize again the important role of the MA group on the nanocomposite formation. In EPDM/MMT-PRIM intercalated and deintercalated (cf. XRD spectra), as well as, exfoliated structures (cf. TEM images) were generated. On the contrary, for the EPDM-MA/MMT-PRIM only exfoliated and deintercalated structures (cf. XRD spectra and TEM images) were obtained. The increased polarity of the EPDM alone does not support the exfoliation, as it was shown for EPDM grafted with

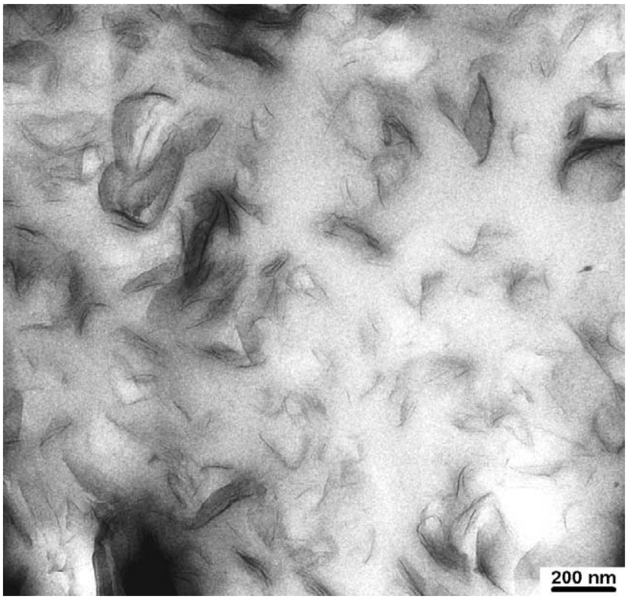

Fig. 6. TEM image on a EPDM-MA/MMT-QUAT (10 phr) vulcanizate.

glycidyl methacrylate, where mostly clay intercalation was achieved [44]. It can be assumed that the MA ring opened and affected by this way the complex formation. It is well known that the maleic anhydride reacts with the primary and secondary amine groups of polymers [45]. In this reaction the MMT-PRIM may also be involved [11].

3.2. Mechanical properties

Investigating the mechanical performance of the rubber nanocomposites containing the MA group (yields better clay intercalation/exfoliation) the choice of 10 phr clay appears to be optimum. Note that the tensile strength of the nanocomposites reaches a maximum at about 10 phr organoclay content (Fig. 7(a)). It is interesting to observe the different trend of the curves for these two types of nanocomposites. The EPDM-MA/MMT-PRIM presents a plateau as a function of increasing organoclay content, whereas for the EPDM-MA/MMT-QUAT a deterioration in the ultimate strength occurs at high organoclay content. Pronounced are also the differences in the elongation at break vs. clay loading traces (Fig. 7(b)). The EPDM-MA/MMT-PRIM nanocomposite above 10 phr organoclay content has surprisingly high strain values. On the contrary, for the EPDM-MA/MMT-QUAT a decrease in the elongation at break can be found, which is likely related with agglomeration phenomena. This agglomeration results in premature failure, owing to which both ultimate stress and elongation at break are reduced. Similar stress–strain behavior has been reported for various rubber nanocomposites [46–55]. Usually, at favorable matrix/organoclay interactions and relatively low organoclay content, both tensile strength and elongation at break increase [46,50,54,55]. Further increase of the organoclay content produces a plateau (saturation) or a reduction in the ultimate stress and strain values [46,49,51,54,55]. This rather typical behavior was found for the EPDM-MA/MMT-QUAT nanocomposite (Fig. 7). It should be mentioned that intercalation/exfoliation of the organoclay take place just by the addition of a few phr of organoclay (1–3 phr), as these processes are mostly of thermodynamical origin. This ideal case can hardly be achieved by melt compounding but approached by solution compounding [25,49,55–59].

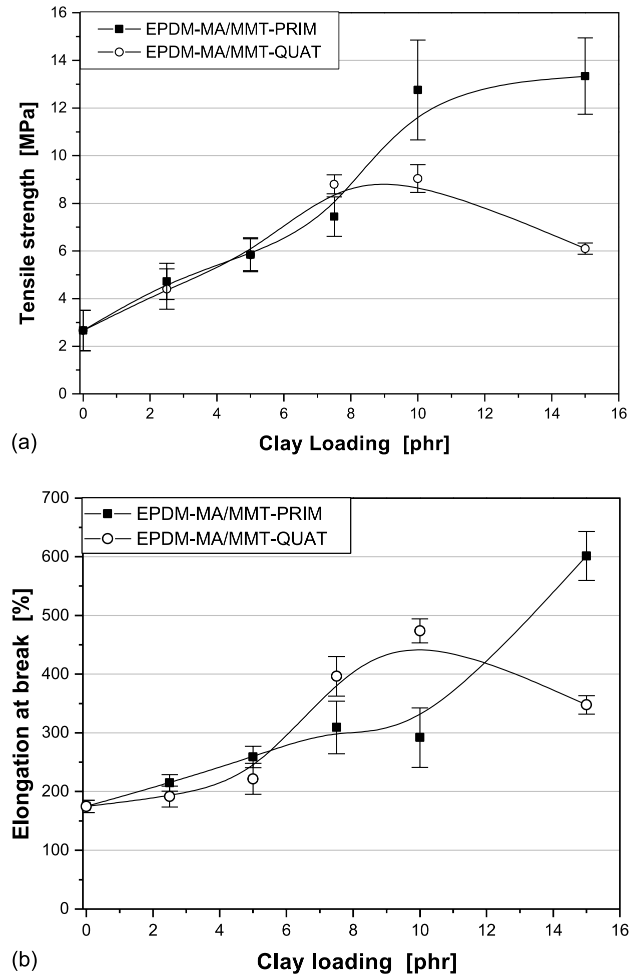

Fig. 7. (a) Tensile strength and (b) elongation at break vs. clay loading for the EPDM-MA/MMT-PRIM and EPDM-MA/MMT-QUAT nanocomposites.

The EPDM-MA/MMT-PRIM and EPDM-MA/MMT-QUAT compounds containing 10 phr of organoclay were tested also by dynamic mechanical thermal analysis (DMTA, Fig. 8). As presented in Fig. 8(a), below the glass transition temperature (T_g) there is slight increase in the storage modulus for both nanocomposites compared to the neat rubber. Above the T_g, the EPDM-MA/MMT-QUAT shows the highest modulus values compared to EPDM-MA/MMT-PRIM or the neat rubber. From the small change in the T_g relaxation (cf. Fig. 8(b)) hardly any information can be deduced in respect with the clay dispersion. The above DMTA behavior agrees with earlier results published on EPDM nanocomposites [46].

4. Conclusions

This work was devoted to check the effects of primary (PRIM) and quaternary (QUAT) amine intercalants on the organoclay (MMT-based) dispersion in EPDM rubbers of various polarities as a function of processing and curing. Based on the results of this work the following conclusions can be drawn:

- Increasing the polarity of the EPDM favors the intercalation/exfoliation of the organoclay irrespective to the type of its intercalant (PRIM, QUAT). Exfoliation is likely favored by the possible interaction of the maleic anhydride (grafted on the EPDM) with the PRIM. The 10 phr of clay loading appears as an optimum for enhanced modulus and tensile strength of the respective nanocomposites.
- The organoclay intercalation is governed by the curatives instead of the processing conditions often claimed.

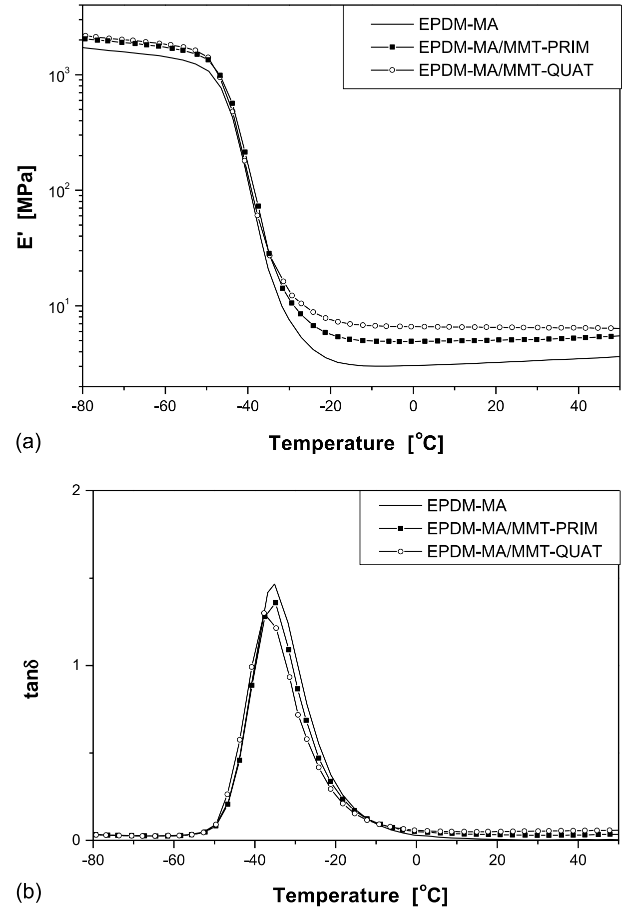

Fig. 8. (a) Storage modulus (E') and (b) mechanical loss factor (tan δ) as a function of temperature for the EPDM-MA/MMT-PRIM and EPDM-MA/MMT-QUAT (at 10 phr clay loading).

However, the processing conditions affect the organoclay dispersion and thus the final properties of the nanocomposite. It seems that the amine intercalant of MMT (more pronounced effect for PRIM) participate in the formation of a zinc coordination complex (even during compounding on the open mill) via which the gallery distance of MMT widens.

- During curing a prominent change occurs in the Zn-complex as the activated sulfur competes with the amines as possible ligand. This is the reason for the confinement (re-aggregation, de-intercalation) of the organoclay, which can be observed for MMT-PRIM. Exfoliated organoclay population was conducted for EPDM-MA mixed with MMT-PRIM and traced to additional chemical reactions between MA and PRIM in between the galleries.

Acknowledgements

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