

**COMPARATIVE STUDY OF VARIOUS INTERCALANT MODIFIED CLAY/RUBBER NANOCOMPOSITES PREPARED BY MELT-COMPOUNDING****Magdalena Lipińska\***

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**Keywords:** rubber/clay nanocomposites, organic modified montmorillonites, ageing resistance.**Abstract**

Rubbers are commonly compounded with different fillers in order to achieve the optimum of final properties. In studies layered silicates, montmorillonites, in natural and organically modified form were applied as reinforcing fillers for two rubbers differ in polarity, ethylene-propylene copolymer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR. The clay/rubber composites were prepared by melt-compounding method using various mixing conditions to obtain an optimal level of intercalated and exfoliated montmorillonite structures in peroxide cured rubber composites. The aim of this paper is to compare the influence of various types of montmorillonites on the rubber curing, crosslink density and mechanical properties of vulcanizates. Additionally, the effect of montmorillonites on weathering and UV ageing resistance of EPM rubber was determined.

**Introduction**

In rubber technology silica and carbon black are commonly used as reinforcing fillers able to improve the mechanical properties of final cured rubber material. Lately nanoparticles have been widely studied as fillers with high potential to enhance various properties of rubber composites comparing to conventional ones. The application of nanofillers such as cationic layered silicates have become of great interest in rubber industry due to their unique particles structure and morphology. Montmorillonites (MMT) belong to phyllosilicate clays of the 2:1 type structure [1]. This naturally abundant smectite clays characterize a lamellar structure which is composed of two tetrahedron sheets with an edge-bridged octahedral sheet and counter metal ions such as:  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $Li^+$  [1]. The montmorillonite particles (MMT) characterize high particles aspect ratio (L/D ratio) and their chemical capacity to be modified through cation exchange reactions with organic species such as organic alkyl quaternary ammonium salts [2]. The modification of montmorillonites by cation exchange reactions with organic salts of alkyl ammonium ( $R_4N^+X^-$ ) and alkyl phosphonium ( $R_4P^+X^-$ ) leads to enlargement of the interlayer spacing (d-spacing) [1]. The exfoliated layered structures of montmorillonite have an average thickness of 1 nm what gives an interesting opportunity for the design of nanocomposites based on these fillers and various polymeric matrices [3-4]. The dispersion of montmorillonites in nanometric exfoliated scale in rubber is a challenge because of rubber higher viscosity comparing to thermoplastic materials. The most common techniques using for clay/rubber composites preparation are melt intercalation method [5-9] and a latex methods [10-11]. In the melt intercalation method the layered silicate is mixed with polymer or elastomer in the molten state using various shear mixing, under these condition the polymer chains can crawl into interlayer space of clay galleries and generate the intercalated or exfoliated structures. Natural rubber-montmorillonite nanocomposites prepared by blending on a two-roll mill were investigated [5-7]. Authors reported that for this type of mixing the properties of final material strongly depended on the concentration of clay, type of clay, type of intercalant used and vulcanizing system. The effect of montmorillonite loading and intercalant structure on the curing characteristics and cure parameters of natural rubber [8] and ethylene-propylene-diene rubber [12] was observed. It was found [13] that higher concentration of octadecylamine intercalant (1.5 times the CEC of Na-MMT) influenced on the speed of curing reaction of natural rubber/clay composites and thus led to increase of rubber crosslink density. The montmorillonite intercalants with various alkyl chain length ( $C_{12}$ - $C_{18}$ ) were investigated [14], authors reported that the modifying agents with longer alkyl chain lengths were more effective in intercalating the interlayer spacing of clay, furthermore they led to better filler dispersion in natural rubber causing the improvement of mechanical properties and the thermal stability of natural rubber. Montmorillonite modified with dimethyl di(hydrogenated talloyl) ammonium was estimated as a filler able to improve the properties of silica filled natural



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rubber/poly(styrene-co-butadiene) blends, the application of montmorillonite together with silica led to better stability of elastic modulus with temperature and enhancement of stresses at all elongation [15]. The simultaneous effect of organic modified montmorillonite and nano-calcium carbonate on the enhancement of tensile strength in natural rubber vulcanizates was also observed [16]. Organically modified montmorillonites at different ratios were applied as reinforcing and compatibilizing filler for butadiene-acrylonitrile/butadiene-styrene rubber blends, a remarkable decrease in optimum cure time with increasing clay content was observed [17]. From the literature it follows that by the application of these naturally occurring ecologically clays as various rubber fillers and by the suitable organic modification it is possible to achieve the significant enhancement in rubber properties such as: tensile strength of natural rubber, ethylene propylene diene rubber, acrylonitrile-butadiene rubber, polychloroprene rubber [18], styrene-butadiene rubber [19], silicon rubber [20]; the abrasion resistance of natural rubber [21], damping performance at elevated temperature of carboxylated styrene-butadiene rubber [22] and natural rubber [23], stress relaxation behavior of natural rubber/nitrile rubber blends [24], flame retardance and thermal stability of ethylene-propylene-diene rubber [25]. Several additional procedures as previous ball milling of clay [26] or the oil solution supported intercalation process [27] are reported to improve the level of montmorillonite delamination and intercalation and thus the properties of montmorillonite filled rubber. As confirmed by XRD studies the ball milling increased the delamination of pure and organic modified montmorillonite before the mastication with rubber [26]. The solvent supported method although it allows the preparation of exfoliated composites with improved thermal and mechanical properties it is more complicated method comparing with melt mixing, in which the additional step, the evaporation of solvent is needed. My investigations was aimed at adjusting and optimizing the properties of ethylene-propylene copolymer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR using commercially available organically modified montmorillonites. The reinforcing effect of montmorillonite considering various mixing conditions for the peroxide cured rubber mixtures was studied. Additionally organically modified montmorillonites reinforced ethylene-propylene copolymer EPM vulcanizates were subjected to accelerated heat, weathering and UV ageing to estimate its ageing stability and influence of various clay intercalants on changes in technical properties such as tensile strength, modulus and elongation of break.

## Experimental

### Materials

Two elastomers differ in polarity were used to prepare elastomer composites:

- hydrogenated acrylonitrile-butadiene rubber HNBR (Therban 3407, Arlanxeo) containing 34±1.0 wt.% acrylonitrile (ISO 24698-1) and ≤0.9% of residual double bonds after hydrogenation obtained from Arlanxeo,
- ethylene-propylene copolymer EPM (Dutral CO 054) containing 41 wt.% of propylene produced by Versalis Sp.A..

Composites were crosslinked with 3 phr of **(bis(1-methyl-1-phenylethyl) peroxide)**, dicumyl peroxide DCP (Sigma-Aldrich).

The following montmorillonites were applied as elastomers fillers:

- Na-montmorillonite AB134225 (ABCR GmbH, Germany),
- Na-montmorillonite AB210662 (ABCR GmbH, Germany),
- Nanomer PGV hydrophilic bentonite nanoclay (Nanocor Inc.),
- Nanomer I.30E, clay surface modified with 25-30wt.% octadecylamine (Nanocor Inc.),
- Nanomer I.31PS clay surface modified with 15-35 wt% octadecylamine and 0.5-5wt% aminopropyltriethoxysilane (Nanocor Inc.),
- Nanomer I.34TCN clay surface modified with 25-30 wt. % methyl dihydroxyethyl hydrogenated tallow ammonium (Nanocor Inc.),
- Nanomer I.28E clay surface modified with 25-30 wt.% trimethyl stearyl ammonium (Nanocor Inc.),
- Nanomer I.44P clay surface modified with 35-45 wt.% dimethyl dialkyl (C14-C18) amine (Nanocor Inc.).

**Preparation and characterization of EPM and HNBR composites**

The rubber mixtures were prepared using: a laboratory two-roll mill (friction ratio 1:1.2, dimension of rolls – diameter 200 mm, length 450 mm) in the temperature 40°C during 30 minutes. Additionally two-step method melt compounding method was applied. First fillers were mixed with rubber using an internal mixer Brabender at various mixing speed and temperature during 15 minutes. Subsequently, the compounded rubbers were homogenized with peroxide curing system in a laboratory two-roll mill (15 minutes).

**Techniques*****Fillers aggregates size***

The size of the fillers (montmorillonite) aggregates in a water dispersion was determined using a Zeta Sizer Nano Series S90 (Malvern Instruments). The measurements were based on the DLS (Dynamic Light Scattering) method. The concentration of the dispersion was 0.2 g/L. To estimate the tendency of the particles to agglomerate in the elastomer, the size of their agglomerates in paraffin oil (higher viscosity model of elastomer matrix) was determined. Before the measurements the dispersions were stabilized upon ultrasonic treatment (Bandelin Sonorex DT 255) during 15 minutes.

***Oil absorption measurement***

The oil absorption parameter OAP of fillers was measured according to ASTM D2414 using Absorptometer C equipment connected with Brabender station. The process parameters were: sample weight 20g, titration rate 4.0 mL/min. The oil used in this study was dibutyl phthalate (DBP).

***X-ray diffraction analysis (XRD)***

Room-temperature powder X-ray diffraction patterns were collected using a DRON 2EJ apparatus with (CuK $\alpha$ ) radiation. Data were collected in the 2 $\theta$  range of 1-21° with 0.05° step and 5 s exposition per step. The d-spacing within clay galleries was calculated according to Bragg equation ( $n\lambda=2d\sin\theta$ ).

***Analysis of filler particles morphology***

The morphology of filler particles was evaluated by scanning electron microscopy (SEM) using an LEO 1530 Gemini equipment (Zeiss/Leo, Germany). Samples with a graphite coated structure were used in these investigations.

***Curing studies, cross-link density and mechanical properties of composites***

The MDR rheometer RPA 3000 MonTech with the lower die of the chamber oscillated sinusoidally at a fixed angle 7° and frequency 1.67 Hz was used to characterize curing of EPM, HNBR composites. The curing studies were done at 160°C according to ASTM D5289. The parameters: the optimum cure time ( $\tau_{90}$ ) were calculated based on the curing curves. The compounded blends were molded and vulcanized using electrically heated hydraulic press under a pressure of 5 MPa at their optimum curing time. Cured sheets were conditioned before testing (24 h maturation at room temperature). The network structure was analyzed according to ASTM D 6814-02 standard. Weighed rubber samples were swollen at room temperature (25°C) in solvent (reagent grade purity toluene) for the time necessary to achieve weight balance of swelled samples (48h). The solvent were replaced with fresh toluene from time to time. After swelling the excess liquid was removed from the surface of the specimens with a soft paper towel and the samples were weighted. In the next step, the specimens were dried at 50°C in a forced-ventilating air oven for 24 h until constant mass. The dried samples were cooled down to room temperature (25°C) using a desiccator and weighted again

***Mechanical properties***

Stress-strain behavior was characterized using Zwick 1435 tensile machine. The moduli at 100%, tensile strength (TS) and elongation at break ( $E_B$ ) were measured at 25°C with crosshead speed of 500 mm/min for testing type 1 dumb-bell specimens prepared according to ISO-37-2005 standard. Five different specimens were tested and the average value for each formulation was reported.

***Accelerated ageing studies***



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Weathering aging studies were carried out using Atlas Weather Ometer Ci 4000 equipment, in 100 h using selected day and night panels with parameters such as: day panel (time 240 min, energy of radiation  $0.7\text{W/m}^2$ , temperature  $60^\circ\text{C}$ , humidity 60%, duration 8h), night panel (time 120 min., humidity 50%) Accelerated UV aging studies were carried out for rubber vulcanisates using UV2000 Atlas solar simulation chamber (Linsengericht, Germany) (UV-A,  $\lambda=342\text{ nm}$ ). Sample aging lasted for 120 h during which alternating day (radiation intensity  $0.7\text{ W/m}^2$ , temperature  $60^\circ\text{C}$ , duration 8 h) and night (without UV radiation, temperature  $50^\circ\text{C}$ , duration 4 h) segments were repeated. The retained percentage values of tensile strength, elongation at break were measured before and after the aging studies.

## Results and discussion

### Characteristics of applied layered silicate fillers

The particles size and the diameter of formed aggregates can be the key factor to achieve the meaningful improvement of mechanical properties for layered filler/rubber composites. The presence of isolated large agglomerates acting as center initiating breaking during deformation can lead to deterioration of tensile strength. Opposite the presence of nanostructures with high surface area even at low concentration caused stronger interphase contact between solid surface and elastomer matrix and thus generated stronger reinforcing effect. Eight commercially available for rubber industry montmorillonites able to intercalate and exfoliate were applied as fillers for two elastomers differ in polarity, ethylene-propylene copolymer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR. XRD analysis of various modified montmorillonite structures revealed different basal reflections corresponding to a Bragg diffraction peaks. Calculated values of d-spacing are compiled in table 1.

**Table 1: Basal refraction peaks and values of d-spacing calculated from Bragg's equation.**

|                 | $2\theta$ ( $^\circ$ ) | d-spacing, (nm) |
|-----------------|------------------------|-----------------|
| Na-MMT AB134225 | 6.76                   | 1,31            |
| Na-MMT AB210662 | 7.15                   | 1,24            |
| Nanomer PGV     | 6.80                   | 1,30            |
| Nanomer I.30E   | 4.00                   | 2,21            |
| Nanomer I.31PS  | 4.10                   | 2,16            |
| Nanomer I.34TCN | 4.45                   | 1,99            |
| Nanomer I.28E   | 3.75                   | 2.36            |
| Nanomer I.44P   | 3.40                   | 2.60            |

The XRD curves for unmodified montmorillonites PGV, AB134225 and AB210662 are shown at Figure 1

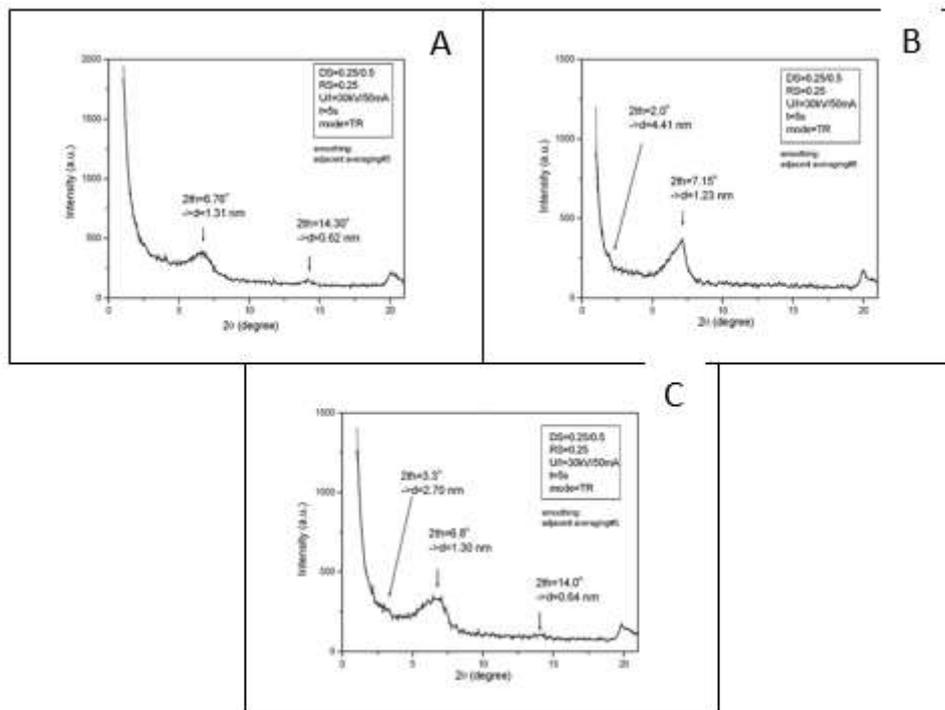


Figure 1: X-ray diffraction patterns of unmodified montmorillonites: A - Na-MMT AB134225, B - Na-MMT AB210662, C - Nanomer PGV.

The lower amount of water present in interlayer area of Na-MMT AB210662 comparing to Na-MMT AB134225 and Nanomer PGV caused slightly lower distance (d-spacing) between clay galleries (Table 1, Figure 1). The XRD studies of modified montmorillonites (Table 1) indicated that montmorillonites characterize various arrangement of organic cations in interlayer space, with different orientation of alkyl chains what resulted in changes of basal d-spacing in range 1.99 nm for Nanomer I.34TCN intercalated by methyl dihydroxyethyl hydrogenated tallow ammonium up to 2.60 nm for Nanomer I.44P intercalated by dimethyl dialkyl (C14-C18) amine.

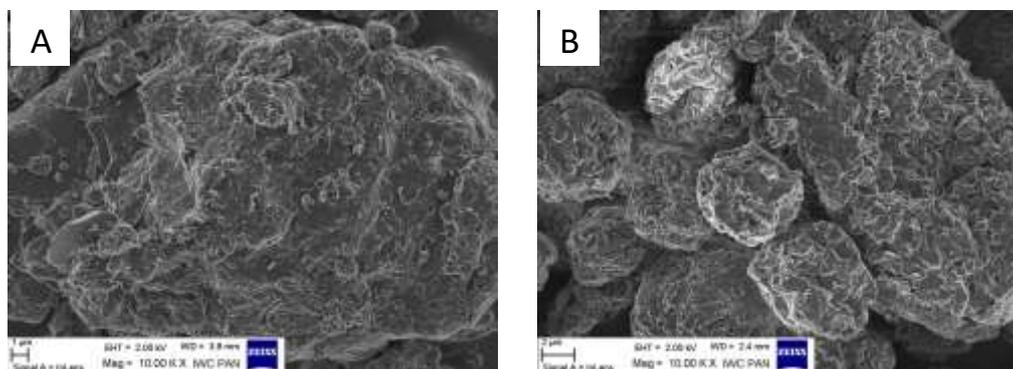
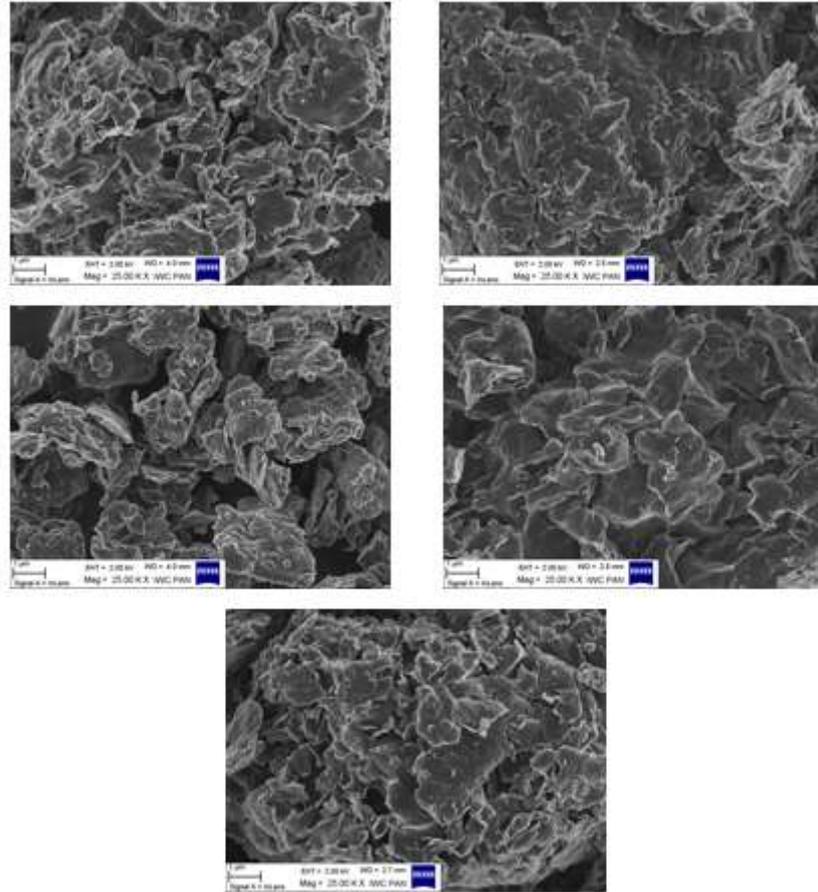


Figure 2: SEM pictures of unmodified montmorillonites: A: Na-MMT AB134225, B- Nanomer PGV.



**Figure 3: SEM pictures of modified montmorillonites.**

The SEM pictures for unmodified montmorillonites AB134225 and PGV, figure 2 showed that the particles formed grain structures with the diameters in micrometric scale. The tendency to form dense and cohesive agglomerates was stronger for AB134225 montmorillonite comparing to PGV. The layered plate-like morphology of particles was observed for organic modified montmorillonites (Figure 3). The particles formed well-spaced grains, single flaky-like particles with diameter less than 1  $\mu\text{m}$  were presents. It is worth noted, that the changes in agglomerates morphology and more aggregated grain structures are observed in case of montmorillonite modified by octadecylamine and additionally by aminopropyltriethoxysilane Nanomer I.31PS comparing to montmorillonite modified only by octadecylamine Nanomer I.30E.



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**Table 2: Values of oil absorption parameters (OAP) and size of filler agglomerates measured in paraffin oil (concentration of the dispersion 5g filler/100 ml paraffin oil).**

|                 | OAP, gDBP/100g | Range of agglomerate size in paraffin oil, $\mu\text{m}$ | Size of the most numerous fraction, $\mu\text{m}$ | Number percentage of the most numerous fraction, % |
|-----------------|----------------|--|---|--|
| Na-MMT AB134225 | 51,51          | 3.1÷4.8  | 4.2   | 47.0   |
| Na-MMT AB210662 | 55,27          | 2.3 ÷3.6   | 3.1   | 37.9   |
| Nanomer PGV     | 51,79          | 0.8÷1.3  | 1.1   | 39.5   |
| Nanomer I.30E   | 49,56          | 2.0÷3.1  | 2.3   | 46.0   |
| Nanomer I.31PS  | 69,42          | 2.7÷4.8  | 3.6   | 48.8   |
| Nanomer I.34TCN | 58,21          | 1.3÷2.0  | 1.5   | 45.2   |
| Nanomer I.28E   | 69,88          | 2.3 ÷3.6   | 2.7   | 45.9   |
| Nanomer I.44P   | 47,8           | 1.1÷2.0  | 1.3   | 24.8   |

The nature of surrounding medium influences on the formation of aggregated structures, therefore the size of the agglomerated structures was studied in paraffin oil, non-polar medium which could be considered as a low viscosity model of non-polar elastomers. The smallest size of formed agglomerates, less than  $2\mu\text{m}$ , as measured in paraffin oil, was indicated for the unmodified montmorillonite PGV, modified with dihydroxyethyl tallow ammonium Nanomer I.34TCN and modified with dimethyl dialkyl (C14-C18) amine Nanomer I.44P (Table 2). Both modified montmorillonites characterized also the smallest diameters of formed grain structures as indicated by SEM images (Figure 3). Oil adsorption parameter is one of the filler characteristics attributed to the tendency to create “filler particles structure” as a result of particle/particle interactions. Fillers able to create “structure” inside the elastomer matrix enhance the mechanical properties of vulcanizates. This phenomenon is strongly contributed to the reinforcing effect caused by active fillers such as silica and carbon black. Base on the volume of dibutyl phthalate adsorbed on particles surface and in the empty space (void volume) between linked together through physical interactions agglomerates by the given amount of filler (g DBP/100g filler) it is easy to estimate the ability of particles to create network structure. Comparing the values of oil absorption parameters (OAP) for the silica Aerosil 380 particles (OAP = 515,3 gDBP/100g), the filler with high ability to create the particles/particles network structure via –OH groups present on the filler surface, with the OAP values measured for montmorillonites (Table 2) we indicated that all applied montmorillonites characterized low tendency to create “filler particles structure” as a result of particle/particle interactions. The differences in OAP values were caused by different porosity and aggregates size of the montmorillonites.

### Mechanical properties, crosslink density and resistance to ageing of ethylene-propylene vulcanizates containing various MMT

In our work the rubber premixtures containing various montmorillonites (10 phr, parts per hundred of rubber) were prepared using laboratory Brabender mixer. Various shear rate, two different mixing speed 50 rpm, 100 rpm and temperature  $40^\circ\text{C}$  were applied in order to improve the dispersion ratio of nanoparticles and facilitate the intercalation of montmorillonite layers in elastomer matrix. After the preparation of filler/elastomer composition the peroxide curing substance was added using laboratory two-roll mill. Crosslinking of elastomers with peroxide become more popular because of enhanced aging resistance of final cured rubber product. Commercially used are peroxide such as: dicumyl peroxide, which upon heating generate free radicals able to abstract an H-atom from elastomer backbone. The rheometric studies indicated that the addition of montmorillonites did not influenced the optimum cure time  $\tau_{90}$ . The values of the optimum cure time  $\tau_{90}$  for unfilled EPM rubber and filled vulcanizates containing 10 phr of various montmorillonites and cured by 3 phr of dicumyl peroxide were in range 20-21 minutes. The addition of montmorillonites did not influenced the optimum cure time  $\tau_{90}$ . The crosslink density of cured elastomer was determined from swelling measurements. The Flory-Rehner's equation [29] was used to determine the crosslink density according to equation:

$$v_T = - \frac{\ln(1-v_p) + v_p + \chi v_p^2}{v_s(v_p^{\frac{1}{3}} - \frac{v_p}{2})} \quad (1),$$

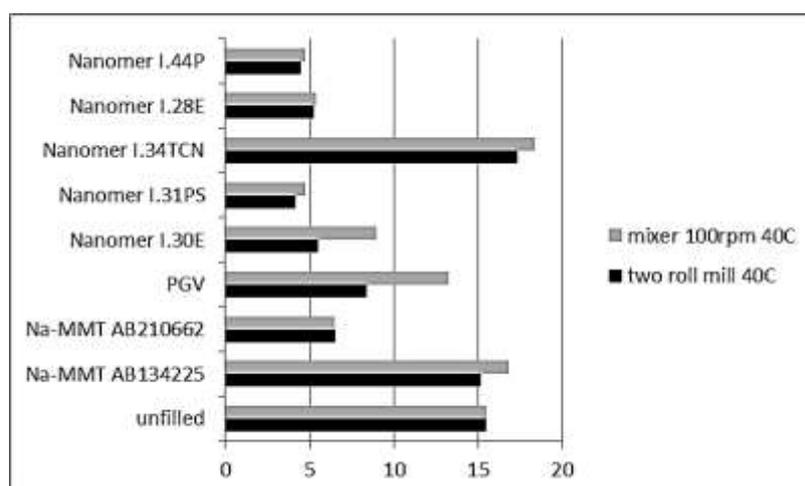


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where  $\nu_T$  is crosslink density,  $V_p$  is the volume fraction of elastomer in the swollen gel,  $V_s$  is the molar volume of solvent ( $\text{mole}/\text{cm}^3$ ). The Huggins parameter ( $\chi$ ) for elastomer-solvent interaction are given by following equations:

$$\chi = 0.425 + 0.34 V_p \quad (2) \quad [30]$$

In Figure 4 are presented calculated values of crosslink density  $\nu_T \cdot 10^5$  ( $\text{mole}/\text{cm}^3$ ) for EPM vulcanizates containing 10 phr of various montmorillonites.



**Figure 4: Crosslink density  $\nu_T \cdot 10^5$  ( $\text{mole}/\text{cm}^3$ ) for EPM vulcanizates containing 10 phr of various montmorillonites. Rubber mixtures were prepared at similar temperature  $40^\circ\text{C}$  using two-roll mill and Brabender mixer at speed 100 rpm.**

The incorporation of montmorillonites into EPM elastomer caused decrease of crosslink density values  $\nu_T$  for vulcanizates prepared using two-roll mill. It is known that many fillers including some clays can interfere with peroxide and lead to ionic peroxide decomposition. According to literature [31] effect strongly occurs for ethylene-propylene elastomer thus the decrease of the crosslink density should be compensate by the optimization of the amount of curing substance used or by the passivation of the clay surface. The preparation of rubber mixtures using Brabender mixer at 100 rpm speed led to improving of filler dispersion in rubber matrix. The facilitated dispersion caused the higher filler/matrix contact and filler/matrix interphase interactions resulting in the higher amount of permanently bounded and occluded rubber chains on filler surface. This bounded and occluded rubber prevented swelling increasing the values of crosslink density for vulcanizates prepared by Brabender mixer comparing with these prepared by two-roll mill. The increase of crosslink density  $\nu_T$  was observed for EPM vulcanizates containing Nanomer I.34TCN, the surface characteristic of this type of montmorillonite, the hydrophobicity of the filler surface led to better dispersion in non-polar ethylene-propylene rubber increasing amount of bounded rubber on filler surface, also the application of methyl dihydroxyethyl hydrogenated tallow ammonium led to passivation of clay surface reducing the influence on the peroxide curing. Having established the influence of montmorillonites on crosslink density we then examined their mechanical properties, results are compiled in table 3. As a parameter estimating the reinforcing effect of various fillers can be used the reinforcing index RI proposed by Kohija and Ikeda [32] and calculated according to equation:

$$RI = \frac{N}{N_0} * \frac{m_F}{100} \quad (3),$$

where  $N$ ,  $N_0$  are the values of selected mechanical parameters for vulcanizates filled and without filler adequately,  $m_F$  is mass of filler added. Reinforcing fillers characterize different tendency to create filler/filler network and different strength of filler/polymer interphase interactions. Occurrence and strength of reinforcing phenomenon is determined by the filler characteristics (surface area, particles size, activity of surface) as well as nature of surrounded matrix thus RI parameter allows to compare the reinforcing effect of various fillers in selected elastomer.



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Table 3: Mechanical properties, tensile strength  $TS$ , modulus at 100% elongation  $SE_{100}$ , elongation at break  $E_B$  and  $RI_{TS}$  parameters for EPM vulcanizates containing unmodified montmorillonites. Rubber mixtures were prepared using two-roll mill (\*), and using Brabender mixer (\*\*).

| EPM vulcanizates          | mixing   | Speed, rpm | $SE_{100}$ MPa | $TS$ , MPa  | $E_B$ %    | $RI_{TS}$  |
|---------------------------|----------|------------|----------------|-------------|------------|------------|
| <b>without filler</b>     | <b>*</b> | <b>---</b> | <b>1.13</b>    | <b>2.18</b> | <b>373</b> | <b>---</b> |
| Na-MMT AB134225<br>10 phr | *        | ---        | 0.99           | 2.12        | 363        | 0.10       |
|                           | **       | 50         | 1.23           | 3.58        | 440        | 0.16       |
|                           |          | 100        | 1.13           | 3.12        | 437        | 0.14       |
| Na-MMT AB210662<br>10 phr | *        | ---        | 0.93           | 3.24        | 798        | 0.15       |
|                           | **       | 50         | 1.22           | 8.09        | 720        | 0.37       |
|                           |          | 100        | 1.19           | 7.56        | 607        | 0.35       |
| PGV<br>5 phr              | *        | ---        | 0.75           | 1.97        | 771        | 0,04       |
|                           | **       | 50         | 0.92           | 2.01        | 539        | 0,05       |
|                           |          | 100        | 0.95           | 3.24        | 537        | 0,07       |
| PGV<br>10 phr             | *        | ---        | 0.92           | 4.63        | 586        | 0,21       |
|                           | **       | 50         | 0.93           | 10.5        | 702        | 0,48       |
|                           |          | 100        | 0.83           | 9.62        | 637        | 0,44       |

The incorporation of both montmorillonites NA-MMT AB134225 and Na-MMT AB210662 led to improvement of mechanical properties of EPM vulcanizates, values of tensile strength  $TS$  increased, filled vulcanizates characterized higher values of elongation at break  $E_B$ . The increase of elongation at break  $E_B$  and decrease of the modulus at 100% of elongation is caused by the lower crosslink density of vulcanizates comparing to unfilled EPM rubber. The strengthening effect of fillers were stronger for the vulcanizates prepared by Brabender mixer at higher mixing speed, higher values of  $RI_{TS}$  indexes. Unmodified montmorillonite PGV influenced the mechanical properties of EPM increasing the tensile strength  $TS$  of vulcanizates, effect was stronger for higher concentration of filler, 10 phr, although even for the concentration of 5 phr was possible to improve the mechanical properties of PGV-EPM vulcanizates using Brabender mixer at higher speed of mixing. As we expected the incorporation of 5 phr of various modified montmorillonites using Brabender mixer at higher 100 rpm mixing speed also led to obtaining nanocomposites with higher amount of intercalated structures and better mechanical properties, higher values of tensile strength  $TS$  were observed (Figure 5).

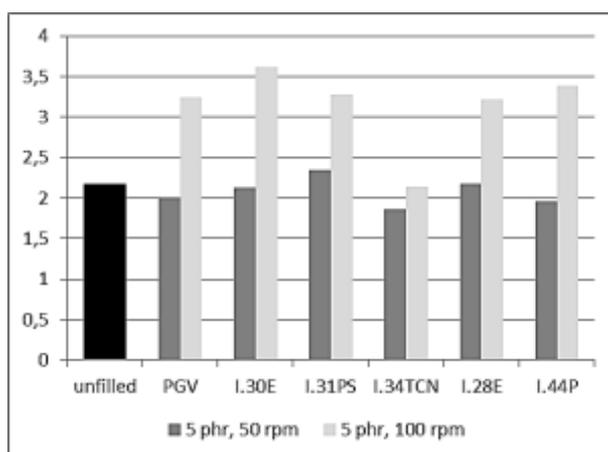


Figure 5: Values of tensile strength  $TS$ (MPa) for vulcanizates EPM containing 5 phr of various montmorillonites. Rubber mixtures were prepared using Brabender mixer at two speed of mixing (50 and 100 rpm).

Table 4 shows the mechanical properties for selected vulcanizates filled with 10 phr of modified montmorillonites prepared using different methods. From the values presented in table 4, it can be noted that Nanomer I.30E and Nanomer I.31 PS had a strong impact on the mechanical properties of EPM vulcanizates. The higher values of tensile strength  $TS$  and reinforcing indexes  $RI_{TS}$  were reported. The lower reinforcing effect was observed for Nanomer I.34 TCN. As we expected two-step method of rubber mixtures preparation, mixing the filler with



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elastomer in mixer at higher speed of mixing before the addition of curing agent caused better dispersion of filler in matrix and thus higher enhancement of mechanical properties comparing to vulcanizates prepared by two-roll mill.

Table 4: Mechanical properties, tensile strength TS, modulus at 100% elongation SE<sub>100</sub>, elongation at break E<sub>B</sub> and RI<sub>TS</sub> parameters for EPM vulcanizates containing modified montmorillonites. Rubber mixtures were prepared using two-roll mill (\*), and using Brabender mixer (\*\*).

| EPM vulcanizates           | mixing | Speed, rpm | SE <sub>100</sub> MPa | TS, MPa     | E <sub>B</sub> % | RI <sub>TS</sub> |
|----------------------------|--------|------------|-----------------------|-------------|------------------|------------------|
| <b>without filler</b>      | *      | ---        | <b>1.13</b>           | <b>2.18</b> | <b>373</b>       | ---              |
| Nanomer I.30 E<br>10 phr   | *      | ---        | 0.92                  | 8.28        | 736              | 0.38             |
|                            | **     | 50         | 1.03                  | 12.6        | 658              | 0.58             |
|                            |        | 100        | 1.07                  | 10.8        | 656              | 0.49             |
| Nanomer I.31 PS<br>10 phr  | *      | ---        | 1.01                  | 7.13        | 926              | 0.33             |
|                            | **     | 50         | 1.14                  | 9.52        | 712              | 0.44             |
|                            |        | 100        | 1.11                  | 9.45        | 802              | 0.43             |
| Nanomer I.34 TCN<br>10 phr | *      | ---        | 0.88                  | 2.69        | 332              | 0.12             |
|                            | **     | 50         | 1.09                  | 3.59        | 444              | 0.16             |
|                            |        | 100        | 1.09                  | 3.75        | 456              | 0.17             |

Furthermore it was found that the incorporation of montmorillonites had an impact on ageing properties of EPM vulcanizates. Elastomers can be sensitive to oxidation initiated by heat, ultraviolet (UV), radiation or gamma radiation, obviously elastomers containing saturated bonds such as ethylene-propylene rubber have more enhanced ageing stability than unsaturated as for example natural rubber. The exposure to UV radiation can initiate photo-oxidation which leads to deterioration of mechanical properties and therefore the lifetime of the product is limited in outdoor application. To estimate the effect of weathering and UV ageing on mechanical properties the ageing coefficients (K<sub>UV</sub>, K<sub>W</sub>) were calculated according to equation:

$$K_{UV,W} = \frac{(TS \cdot E_B)_{after\ UV,\ W\ ageing}}{(TS \cdot E_B)_{before\ UV,\ W\ ageing}} \quad (4),$$

where TS is tensile strength, E<sub>B</sub> is elongation at break measured for the vulcanizates before and after UV and weathering ageing. According to our studies the modification of montmorillonites with organic salts influence the ageing properties of vulcanizates (Figure 5).

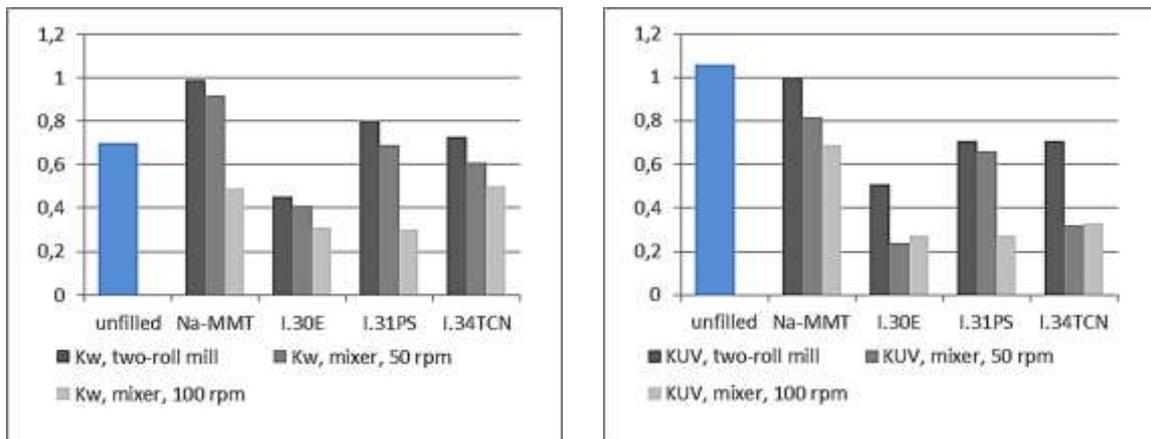


Figure 5: Values of weathering ageing K<sub>W</sub> and UV ageing K<sub>UV</sub> coefficients for EPM vulcanizates.

Based on obtained K<sub>W</sub> and K<sub>UV</sub> values (Figure 5), which correspond to the weathering and UV-stability. The unmodified montmorillonite filled vulcanizates characterized higher UV and weathering ageing stability. The



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modification of montmorillonites with ammonium salts led to deterioration of UV-stability. The influence of the preparation method on ageing stability was observed. The better modified montmorillonite dispersion, higher amount of intercalated structures achieved by the two-step method using high speed mixing caused higher diffusion of intercalant into matrix during ageing what influenced on ageing stability. Also the higher speed of mixing, the higher shear rate could cause the thermomechanical degradation of polymer material during mixtures preparation what resulted in lower values of ageing stability comparing to mixtures prepared using two-roll mill. The lowest UV and weathering protection (the lowest values of  $K_{UV}$  and  $K_W$  coefficients) was observed for vulcanizates containing Nanomer I.30E modified with octadecylamine. The application of silane as a second modifying agent for octadecylamine modified montmorillonite Nanomer I.31PS reduced the influence on ageing stability and increased the values of  $K_{UV}$  and  $K_W$  coefficients. The passivation of the clay surface with silane led to increase of ageing stability.

### Influence of modified montmorillonites on mechanical properties of hydrogenated butadiene-acrylonitrile rubber HNBR.

Goal of this part of investigation was to estimate the influence of Nanomer I.31PS montmorillonite on the mechanical properties of hydrogenated butadiene-acrylonitrile rubber HNBR. Nanomer I.31 PS montmorillonite is modified with octadecylamine, intercalant which increase the d-spacing between clay galleries, as we described above, and additionally the surface of this filler is covered by (aminopropyl)triethoxysilane. The additional surface passivation reduce the influence on peroxide curing. The silane modifier containing amine groups makes the montmorillonite particles more compatible with the HNBR polymer, thus it should facilitate the mixing during compounding and improve filler dispersion. The more compatible surface characteristics should lead to stronger filler/polymer interphase interactions and have significant impact on mechanical properties of filled HNBR rubber. As for the EPM rubber the rubber mixtures were prepared using Brabender mixer, various speed of mixing (50, 100, 150 rpm) and temperature of mixing (40°C, 60°C) were applied. In table 5 are compiled the results of mechanical properties measurements for vulcanizates of HNBR prepared using various parameters of mixing. Occurrence and strength of reinforcing phenomenon is estimated using reinforcing index  $RI_{TS}$  defined according to equation (3).

**Table 5: Mechanical properties, tensile strength TS, modulus at 100% elongation  $SE_{100}$ , elongation at break  $E_B$  and  $RI_{TS}$  parameters for HNBR vulcanizates containing 5 phr of montmorillonites. Rubber mixtures were prepared using two-roll mill (\*), and using Brabender mixer (\*\*) at temperature 40°C.**

| HNBR vulcanizates         | mixing | Speed, rpm | $SE_{100}$ MPa | TS, MPa     | $E_B$ %    | $RI_{TS}$ |
|---------------------------|--------|------------|----------------|-------------|------------|-----------|
| <b>without filler</b>     | *      | ---        | <b>0.74</b>    | <b>8.80</b> | <b>718</b> | ---       |
| Nanomer PGV<br>5 phr      | *      | ---        | 0.73           | 8.13        | 719        | 18.48     |
|                           | **     | 50         | 0.85           | 6.51        | 771        | 14.79     |
|                           |        | 100        | 0.87           | 6.64        | 776        | 15.09     |
| Nanomer I.31 PS<br>5 phr  | *      | ---        | 0.82           | 9.33        | 748        | 21.20     |
|                           | **     | 50         | 1.24           | 11.60       | 815        | 26.36     |
|                           |        | 100        | 1.42           | 20.31       | 702        | 46.16     |
| Nanomer I.31 PS<br>10 phr | *      | ---        | 0.87           | 11.60       | 740        | 13.18     |
|                           | **     | 50         | 1.88           | 16.50       | 771        | 18.75     |
|                           |        | 100        | 2.02           | 18.90       | 723        | 21.48     |

The incorporation of unmodified montmorillonite Nanomer PGV had no impact on mechanical properties of vulcanizates. The decrease of tensile strength TS was reported. The enhancement of mechanical properties, the higher values of modulus at 100% elongation  $SE_{100}$  and tensile strength TS were observed for HNBR vulcanizates filled with modified Nanomer I.31 PS (table 5). The higher reinforcing effect (higher values of  $RI_{TS}$  indexes) for Nanomer I.31 PS/HNBR vulcanizates indicating stronger filler/polymer interactions. As we described above, the additional modification with silane with amine group leads to changes in filler surface characteristics, facilitate the dispersion of filler in matrix and formation of bounded rubber on filler surface thus it improves the mechanical properties of HNBR rubber. The incorporation of higher amount 10 phr of Nanomer I.31 PS filler did not result in further increase of tensile strength values TS comparing to vulcanizates containing only 5 phr of filler. Dispersion of montmorillonite filler strongly depends on the amount of the filler used and the method of rubber



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mixtures preparation. In order to facilitate the dispersion of unmodified montmorillonite Nanomer PGV the higher temperature (60°C) and higher speed of mixing was applied (150 rpm) (Figure 6). The higher 150 rpm mixing speed at higher temperature of mixing (60°C) influenced the dispersion of the PGV montmorillonite and resulted in higher values of tensile strength, effect was observed for both concentration of filler, 5 phr and 10 phr. The higher temperature of mixing did not provide significant changes in mechanical properties of I.31 PS filled HNBR vulcanisates. Also the higher mixing speed 150 rpm instead of 100 rpm did not lead to improvement of tensile strength TS.

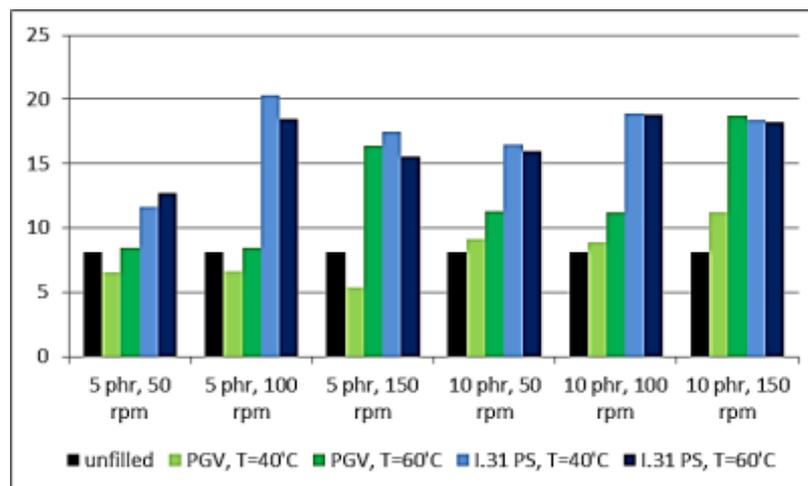


Figure 6: Values of tensile strength TS (MPa) for HNBR vulcanizates prepared using Brabender mixer at various mixing speed (50, 100, 150 rpm) and temperature (40,60°C).

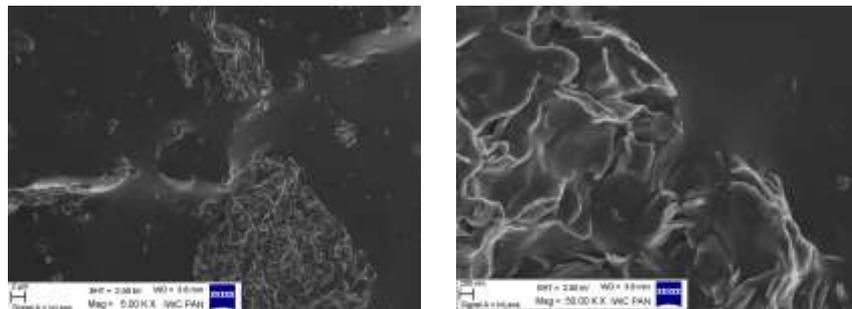
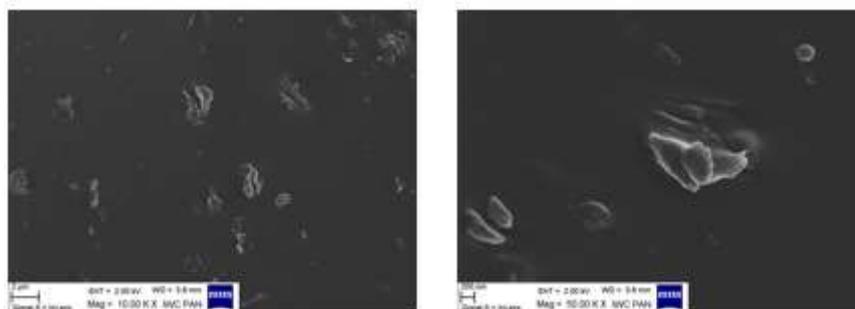


Figure 7: SEM images of HNBR vulcanizates containing 5 phr of montmorillonite Nanomer I.31 PS. Rubber mixtures were prepared using laboratory two-roll mill, temperature of processing 40°C.

To estimate the effect of various method of rubber mixtures preparation the SEM images of HNBR vulcanizates containing I.31 PS Nanomer were analyzed. As shown in Figures 7 the rubber mixtures prepared using two-roll mill characterized uneven distribution of filler in matrix, the large aggregates more than 5µm were present. The SEM images indicated good adhesion between aggregates and surrounded rubber, no empty voids between particles surface and matrix were present. Preparation of rubber mixtures using Brabender mixer using 100 rpm speed led to better dispersion of filler (Figure 8). The size of the largest filler agglomerates was up to 2µm. The nanometric structures with size less than 200 nm were present. The nanometric structures even at low concentration 5 phr are able to provide strong reinforcing effect resulting in higher values of tensile strength TS, double in value comparing to unfilled HNBR rubber (Table 5).



**Figure 8:** SEM images of HNBR vulcanizates containing 5 phr of montmorillonite Nanomer I.31 PS. Rubber mixtures were prepared using Brabender mixer, temperature of processing 40°C, speed of mixing 100 rpm.

## Conclusion

The XRD analysis of various modified montmorillonite structures revealed that montmorillonites intercalants with longer alkyl chain lengths were more effective in intercalating the interlayer spacing of clay, the octadecylamine Nanomer I.30E, trimethyl stearyl ammonium Nanomer I.28E and dimethyl dialkyl (C14-C18) amine Nanomer I.44P modified montmorillonites characterized the highest enlargement of the interlayer spacing (d-spacing). The layered plate-like morphology of particles was observed for organic modified montmorillonites

The type of intercalant influenced on the tendency to form more aggregated, grain structures as observed using SEM measurements. The smallest size of formed agglomerates was indicated for the unmodified montmorillonite PGV, modified with dihydroxyethyl tallow ammonium Nanomer I.34TCN and modified with dimethyl dialkyl (C14-C18) amine Nanomer I.44P. The addition of montmorillonites did not influenced the optimum cure time  $\tau_{90}$  of ethylene-propylene elastomer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR. Addition of clay caused decrease of crosslink density values  $\nu_T$  probably as a result of ionic peroxide decomposition. To prevent the decrease of the crosslink density the optimization of the amount of curing substance used or the passivation of the clay surface is recommended. The montmorillonites strongly influenced on the mechanical properties of EPM rubber. The strengthening effect of fillers were stronger for the vulcanizates prepared by Brabender mixer at higher mixing speed, higher values of  $RI_{TS}$  indexes were reported. The octadecylamine Nanomer I.30E, trimethyl stearyl ammonium Nanomer I.28E and dimethyl dialkyl (C14-C18) amine Nanomer I.44P modified montmorillonites, montmorillonites with the highest enlargement of the interlayer spacing (d-spacing) have the strongest influence on the tensile strength of vulcanizates. Using the two-step method of rubber mixtures preparation, and optimizing the speed of mixing for 10 phr of filler was possible to increase the tensile strength values six times for Nanomer I.30E (12.6 MPa) comparing to unfilled vulcanizate (2.18 MPa). It was found that the incorporation of montmorillonites had negative impact on ageing properties of EPM vulcanizates. The modification of montmorillonites with ammonium salts led to deterioration of UV-stability. The enhancement of mechanical properties, the higher values of modulus at 100% elongation  $SE_{100}$  and tensile strength TS were observed for HNBR vulcanizates filled with modified Nanomer I.31 PS. The presence of nanometric structures (up to 200 nm) influenced on mechanical properties was confirmed by SEM measurements.

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