# Influence of POSS Addition on Properties of Ethylene-Propylene EPM and Hydrogenated Butadiene-Acrylonitrile HNBR Composites Containing Layered Silicate and Nanometric Silica

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*Abstract*—*Polyhedral oligomeric silsesquioxanes (POSS) with functional groups: octavinyl-POSS and octamethacrylate-POSS were applied as additives to ethylene-propylene copolymer (EPM) and hydrogenated butadiene rubber (HNBR). As reinforcing fillers nanometric silica Aerosil 380 and montmorillonite Nanomer I.31 PS were chosen. The POSS modified EPM and HNBR compositions were prepared using melt mixing and they were chemically peroxide crosslinked. Effect of octamethacrylate-POSS and octavinyl-POSS on curing characteristics and mechanical properties was investigated. The rheometric measurements indicated that octavinyl-POSS and octamethacrylate-POSS influenced the curing behavior of rubbers causing increase of crosslink density. The POSS moieties participated via functional groups in curing reactions and cured rubber network formations. Significant enhancement of tensile strength TS and modulus at 100% elongation $SE_{100}$ resulting from higher density of vulcanizates and nanometric reinforcement generated by grafted POSS particles was observed. The modified HNBR and EPM/HNBR vulcanizates containing methacrylate-POSS characterized higher UV-stability. Additionally the reinforcing effect of octamethacrylate-POSS on properties of EPM/HNBR blends was reported.*

*Keywords*— *Hydrogenated butadiene-acrylonitrile rubber, ethylene-propylene copolymer, curing, polyhedral oligomeric silsesquioxanes POSS.*

## I. INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSS) are unique nanomaterials which have received lately considerable attention because of their combined organic/inorganic properties. The inorganic cage of POSS molecules is built of silicone and oxygen. The POSS nanostructure empirical formulas are: $R(SiO_{1.5})_n$ where n is an even number, n>4 [1]. The POSS molecules can be easily functionalized with a wide variety of substituent groups R bonded to the corners of the silica cage. Recently, the preparation of polyhedral oligosilsesquioxanes (POSS)-based hybrid polymers is aim of studies among the academic community and industries because the POSS-based hybrid polymers can be designed and controlled at the molecular level [2]. POSS molecules differ from other conventional (silica, carbon black) and nanometric fillers (layered clay fillers, carbon nanotubes). POSS moieties can be dispersed in polymer matrix at the nanometric level, additionally functionalization of POSS cages creates opportunity for the POSS grafting to polymer chains or incorporation into the polymer network. It is well known that hybrid polymer-POSS systems can be obtained by methods such as: a physical incorporation or chemical approach, and both of them can lead to a nanometric distribution of POSS cages in polymer matrix resulting in the improvement of properties and performance of obtained material [1,2]. The hybrid polymeric materials were prepared based on the polyamide 6 (PA6) and styrene-maleic anhydride copolymers (PSMA) and Ti-containing polyhedral oligomeric silsesquioxanes Ti-POSS using various method of synthesis (in-situ polymerization, melt blending, grafting), the chemical and morphological analysis of the prepared hybrid systems has confirmed that it was possible to homogenously distribute Ti-POSS at a nanometric level within PA6 and PSMA matrices [3]. The grafting of various POSS particles provided opportunity for the enhancement of interfacial interactions with polyimide matrices and led to a significant improvement in the thermal, mechanical properties of polyimide/POSS composites [4]. The aromatic polyamide/POSS composites were prepared using amino-functionalized POSS, the modification of polymer structure with POSS moieties increased the storage modulus and Young's modulus of the polyamides and influenced on the glass transition temperatures and dielectric constants [5]. The various POSS filled thermoplastic materials such as polystyrene (PS) [6] composites and polypropylene (PP) [7] composites were prepared by melt-processing. The POSS with alkyl functional groups acted as plasticizers changing the rheological properties and processability of PS/POSS composites in melt [6]. The influence of POSS with methyl functional groups on rheology of polymer melt was also observed in case of POSS containing ethylene-propylene copolymer, presence of POSS molecules changed the rheological behavior above melting temperature from a melt-like (neat polymer) to a structured solid-like (POSS-composites) [8]. The POSS addition increased the Young's modulus and the glass transition temperature of ethylene-propylene copolymer [8]. Chen et al. [9] demonstrated that POSS molecules containing methyl groups aggregated and formed network structure in isotactic polypropylene (iPP) promoting the nucleation rate of iPP during crystallization. The functionalized POSS nano-structures has been widely studied in recent years as an active

filler accelerating the curing process and the properties of 3D-polymer network structure when incorporated into epoxy resin matrix [10]. It has been demonstrated that the glassy epoxy-POSS nanocomposites based on the DGEBA-3-3'-dimethyl-4,4'-diaminocyclohexylmethane epoxy matrix represent promising material which exhibited significantly improved properties including the electrical [11] and thermal [12] properties. The improvement of epoxy nanocomposites strength and toughness was observed after the incorporation of POSS-rubber core-shell nanoparticles [13]. The molecularly designed POSS-filler consisted of the rigid part (octameric polyhedral oligomeric silsesquioxanes, octa-POSS), the rubbery segments (n-butylacrylate) covalently bonded to inner POSS core and terminated with active amine functional groups thus it was able to bonding with epoxy matrix. The synthesis of novel POSS modified polyurethane elastomers was reported [14], for this purpose a partially opened POSS-diol cages were incorporated into the methylene di-isocyanate/poly(tetramethylene) glycol urethane network as a substitute chain extender, significant enhancements in physical structure, thermal stability and thermal degradation chemistry after the POSS modification were observed. In case of elastomeric materials POSS additives are widely used to improve the properties of polysiloxane rubber [15]. Usually various mixing conditions influence the morphology of octaisobutyl-POSS/polysiloxane elastomer composites as well as the POSS dispersion level. For the blends prepared at high mixing temperatures the highly crystalline octaisobutyl-POSS dissolved into silicone rubber and exhibited some physical interactions with silicone chains and thus during subsequent cooling fewer POSS crystals precipitated resulting in better properties of final material [15]. Meng et al. [16] prepared the octaisobutyl-POSS and allylisobutyl-POSS poly (methylvinyl-siloxane) composites by melt mixing, blends were chemically peroxide crosslinked. NMR analysis confirmed that allylisobutyl-POSS particles were grafted onto silicon rubber chains. Chemical bonds between allylisobutyl-POSS and matrix significantly improved the dispersion level and prevented the thermal degradation of composites comparing with octaisobutyl-POSS composites [16]. Liu et al. [17] demonstrated that the grafting of POSS molecules and their chemical incorporation into room temperature vulcanized (RTV) silicone rubber significantly enhanced thermal stability of RTV silicon rubber in both nitrogen and air atmosphere. Application of vinyl-POSS derivatives as multifunctional cross-linkers led to enhancement of mechanical properties and hardness of polydimethylsiloxane [18]. Effect was attributed to higher functionality of crosslinked network and uniform distribution of POSS cross-linker. The similar effect, the improvement of thermal and mechanical properties of vinyl terminated polydimethylsiloxane matrix after incorporation of vinyl-POSS derivatives was observed by Zhang et al. [19]. It was found that further significant enhancement in thermo-oxidative stability and mechanical properties of room vulcanized RTV silicone rubber occurred after the incorporation of hexal[(trimetoxysilyl)ethyl]-POSS domains together with the application of fumed silica as a filler, it was attributed to the synergistic effect between POSS and fumed silica [20]. The octamalemic acid-POSS (OM-POSS) additive can act as the adhesion enhancer on the properties of silicone rubber/silica nanocomposites. Sirin et al. [21] demonstrated that the utilization of OM-POSS in the silicon rubber influenced the peroxide curing characteristics, the crosslinking reactions started at lower temperatures as the POSS concentration increased. Additionally improved adhesion of POSS modified silicon composites to the rayon fiber was observed [21]. Compared to the POSS modified silicon rubber nanocomposites, relatively few researchers have studied the influence of POSS moieties on nitrile rubber. Glycidyl polyhedral oligomeric silsesquioxanes were applied as a cross-linking agent for carboxyl-terminated poly (acrylonitrile-co-butadiene) CTBN [22]. Synthetized polyhedral oligomeric silsesquioxanes (POSS) with hydroxyl groups were used as curing agent for fluorocarbon rubber (FKM) and carboxylated nitrile rubber (XNBR) [23]. The hydroxyl groups of POSS participated in rubber curing, the formation of crosslinks was confirmed by the increase in volume fraction of rubber in the swollen gel. Due to absence of carboxyl groups in nitrile rubber (NBR) the use of POSS as a NBR curing agent is restricted. Yang S.et al. [24] constructed novel network structure in $NBR/LiClO_4/POSS$ composites based on the coordination ability of electron-rich groups (-CN present in nitrile rubber, and -C-O-C- groups present in octa-(polyethylene glycol)-POSS) with metal cations $Li^+$. This novel type of crosslinks facilitated strong interface cohesion between POSS and elastomer matrix, increased the tensile strength. In our work two different octameric POSS with vinyl and methacrylate groups available for grafting and thus can act as multifunctional crosslinks for peroxide cured elastomers are proposed as a modifying agents for the silica and montmorillonite filled ethylene-propylene copolymer (EPM) and hydrogenated butadiene-acrylonitrile rubber (HNBR). Eight reactive groups give possibility of POSS incorporation into rubber network causing the enhancement of rubber crosslink density and the properties of cured material. The POSS participation in curing reactions is expected to influence the speed and time of curing. Recently fabrication of two or more elastomer blends is a very advantageous way of developing new materials combining properties of individual constituents. Blending of elastomers is carried out in order to improve chemical and ageing resistance, processing characteristics or mechanical properties. Components of rubber blends usually show thermodynamic incompatibility which results in poor interfacial adhesion and weak mechanical properties. Hybrid nanoparticles with different surface chemistries exhibit higher efficiency in compatibilizing immiscible polymer blends [25]. We propose the application of the nanometric silica and cationic layered double silicates acting as reinforcing fillers, together with octamethacrylate-POSS as an additive to ethylene-propylene copolymer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR and their EPM/HNBR blends. The rheometric curing characteristics of these materials, crosslink density and mechanical properties are analyzed. Additionally the UV-resistance of POSS modified hydrogenated nitrile rubber HNBR and its EPM/HNBR blends is investigated.

## II. Experimental

### A. Materials and Preparation

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 was obtained from Arlanxeo, ethylene-propylene copolymer EPM ( Dutral CO 054) containing 41 wt.% propylene was produced by Versalis Sp.A. Composites were crosslinked with 2.5 phr of (bis(1-methyl-1-phenyl-ethyl) peroxide) DCP (Sigma-Aldrich). Polyhedral oligomeric silsesquioxanes POSS were obtained from Hybrid Plastics. The 3 phr (parts per hundred of rubber ) of methacryl OM-POSS (MA0735) containing eight methacrylate groups and octavinyl OV-POSS (OL1170) containing eight vinyl groups were used for rubber composites formulations. As a reinforcing fillers were applied: 20 phr of fumed silica Aerosil 380 (Evonik) and 5 phr of montmorillonite Nanomer I.31PS, product of Nanomer Clay, contains according to product data sheet 0.5-5wt% (aminopropyl) triethoxysilane and 15-35 wt% octadecylamine. Rubber compounds, with the formulation given: EPM or HNBR (100 phr), $SiO_2$ (20 phr), OMt (5 phr), MA-POSS or OV-POSS (3 phr), DCP (2.5 phr) 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 about 40°C during 30 minutes.

### B. Techniques

The size of the fillers (montmorillonite, silica) 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 (model of elastomer matrix) was determined. Before the measurements the dispersions were stabilized upon ultrasonic treatment (Bandelin Sonorex DT 255) during 15 minutes.

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 dibuthyl phthalate (DBP).

Room-temperature powder X-ray diffraction patterns were collected using a DRON 2EJ apparatus with (CuKα) radiation. Data were collected in the 2θ 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 (nλ=2dsinθ).

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.

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 and EPM/HNBR composites. The curing studies were done at 160°C according to ASTM D5289. The parameters: the optimum cure time ($\tau_{95}$), scorch time ($t_{\Delta2}$),

minimum elastic torque ($S'_L$), maximum elastic torque ($S'_H$) and delta torque ($\Delta S' = S'_H - S'_L$) 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 weighed. 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 weighed again. To determine the content of non-covalent crosslinks in the elastomer network, samples were swollen in toluene in a desiccator with saturated ammonia vapor (25% aqueous solution).

Stress-strain behavior was characterized using Zwick 1435 tensile machine. The moduli at 100, 200, 300% elongation ($SE_{100}$, $SE_{200}$, $SE_{300}$), 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. The loss on hysteresis after five cycles (300% extension) for rubber vulcanizates was measured using Zwick 1435 tensile machine for three testing type 1 dumb-bell specimens.

The glass transition temperatures $T_g$ were estimated on base on DSC measurements using a DSC1 equipment (Metler Toledo). The measurements were done using two steps method. In first step the temperature was decreased from 25°C to -100°C at a rate of 5°/min and then the second step heating to 100°C with the same heating rate. The $T_g$ temperatures were estimated from the second step.

Accelerated UV aging studies were carried out for rubber vulcanisates using UV2000 Atlas solar simulation chamber (Linsengericht, Germany) (UV-A, λ=342 nm). Sample aging lasted for 120 h during which alternating day (radiation intensity 0.7 W/m², temperature 60°C, duration 8 h) and night (without UV radiation, temperature 50°C, duration 4 h) segments were repeated. After aging stress-strain tests and crosslink density measurements were performed.

## III. Results and Discussion

### A. Characteristics of Applied Reinforcing Fillers

Particle size and the size of formed aggregates are very important parameters influencing the mechanical properties of filled elastomers. The distribution of the filler aggregates in the elastomer matrix can be the key factor to achieve the significant improvement of mechanical properties. An uneven dispersion and the occurrence of isolated large agglomerates acting as center initiating breaking during deformation lead to

deterioration of the rubber properties. From the other hand the presence of nanostructures with high surface area even at low concentration resulting in enhancement of the interphase contact between solid surface and elastomer and thus has strong impact on the reinforcing effect. Two commercially available for rubber industry fillers, nanometric silica and montmorillonite able to generate nanostructures after intercalation and exfoliation in elastomer, were applied as reinforcing fillers for modified with octavinyl-POSS and octamethacrylate-POSS ethylene-propylene EPM and hydrogenated butadiene-acrylonitrile HNBR rubbers. The nature of surrounding medium influences on the formation of more aggregated structures. Therefore, the aggregates sizes in water as well as in paraffin oil for both fillers were studied (Table I).

TABLE I. Size of filler aggregates measured in water and paraffin oil, the values of oil absorption parameters (OAP).

|  | silica | OMt |
|---|---|---|
| Agglomerate size, (water), [nm] | 126 – 1239 | 190 – 692 |
| The aggregate main fractions (water), [nm] | 186 | 286 |
| Number percentage <300 nm, (water), [%] | 74 | 51 |
| Agglomerate size (paraffin oil), [μm] | 0.3-3.2 | 0.3 – 5.5 |
| Number percentage >2μm, (paraffin oil), [%] | 88 | 76 |
| Oil absorption parameter OAP, [gDBP/100g] | 515.3 | 69.4 |

The sizes of the silica agglomerates, as measured in water, were within the range of 126 nm to more than 1.7 μm. OMt formed in water the aggregates within the smaller range than silica from 190 nm to less than 0.7 μm, although the number percentage of aggregates in size up to 300 nm was higher, more than 74%, for silica than for OMt – 51%. The size of montmorillonite agglomerates intensely increased in paraffin oil, and as measured, were within the range up to 5.5 μm indicating stronger tendency of this fillers to agglomerate in non-polar medium with higher viscosity. Silica in paraffin oil formed agglomerates within range up to 3.2 μm. Both fillers characterized high number percentage of fraction in size more than 2 μm. One of the filler characteristics contributed to reinforcing effect is the tendency to create "filler particles structure" as a result of particle/particle interactions. This tendency can be estimated on the basis of oil absorption parameters (OAP). The empty space (void volume) between aggregates and agglomerates linked together through physical interactions and creating network can be expressed as the volume of dibuthyl phthalate (DBP) absorbed by a given amount of filler (g DBP/100g filler). Ability of silica particles to create network structure in elastomer matrix is well known, the values of oil absorption parameter OAP for silica Aerosil 380 was 515.3 gDBP/100g filler (Table I). The octa-decylamine intercalated OMt montmorillonite used in our studies was additionally surface modified with (aminopropyl) triethoxysilane. The additional surface covering caused increase of oil absorption parameter, value of OAP 69.4 g DBP/100g filler, comparing with not modified montmorillonite Nanomer PGV, value of OAP 49.6 g DBP/100g filler, and montmorillonite modified only with

octadecylamine Nanomer I.30E, value of OAP 51.7 g DBP/100g filler. The SEM pictures, as shown at Fig. 1, indicated spherical nanometric (less than 100 nm) primary particles of Aerosil 380 silica forming more aggregated structures. The layered, plate-like particles of organic modified montmorillonite OMt Nanocore I.31 PS. (Fig. 2) formed grain structures with the diameters in micrometric scale.
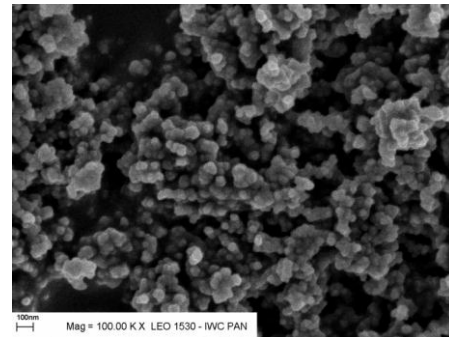

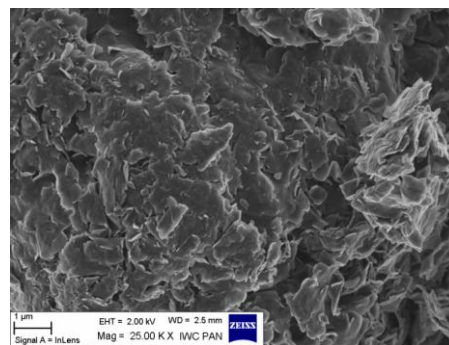Fig. 1. SEM image of silica Aerosil 380.


Fig. 2. SEM image of organic montmorillonite OMt Nanocore I.31 PS.

XRD analysis of modified montmorillonite OMt structure (Fig. 3) revealed basal reflection corresponding to a Bragg diffraction peak at $2\theta = 4.10°$ and d-spacing of 2.16 nm.
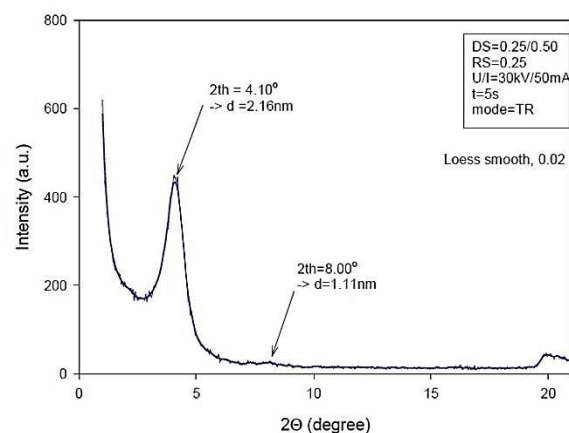

Fig. 3. X-ray diffraction pattern of organic modified montmorillonite OMt, Nanomer I.31PS.

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## B. Influence of POSS Modification on Curing of Filled Ethylene-Propylene Copolymer EPM and Hydrogenated Butadiene-Acrylonitrile Rubber HNBR

Crosslinking with peroxide is growing in popularity because of enhanced aging resistance of final cured rubber material. Organic peroxides, such as: dicumyl peroxide, are commercially used to vulcanize totally saturated elastomers. Upon heating the O-O bond in the peroxide breaks generating free radicals, which abstract an H-atom form elastomer backbone. The dicumyl peroxide at 2.5 wt % was added to each of the formulation. Apart from peroxide type used during crosslinking, the efficiency of this type of curing depends on used coagents. Usually as the components improving the efficiency of peroxide curing the chemical compounds containing methacrylate and acrylate groups are used [26]. POSS moieties with more than two functional groups available for the radical reactions could be good additives increasing the cure rate of saturated rubber. An Moving Die Rheometer was used to follow the reaction stages in vulcanization of ethylene-propylene copolymer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR.

The curing characteristics at 160 °C for rubber compositions are shown at Fig. 4-5, calculated rheometric parameters are compiled in Table II. The first step in the vulcanization is the induction or scorch period, it should be sufficiently long to allow the processing and shaping of the rubber compound. The peroxide curing rubbers generally characterize short induction and scorch times. The addition of octavinyl-POSS and octamethacrylate-POSS to silica and montmorillonite filled EPM and HNBR rubbers decreased the induction and scorch times comparing to unfilled rubber which may cause scorch problems in processing and molding at higher temperatures than 160°C. The induction period is followed by crosslinking reactions resulting in the increase of torque.

EPM (Figure 4) and HNBR rubber (Figure 5) after addition of 5 wt. % of organic modified montmorillonite OMt. The incorporation of both filler to ethylene-propylene rubber caused the decrease of torque increment ΔS comparing to unfilled EPM. This effect of fillers is believed to be related to acid-catalyzed decomposition of peroxide on the filler surface. It is known that many fillers including some clays can interfere with peroxides and lead to acidity-induced ionic peroxide decomposition. Effect strongly occurs for ethylene-propylene rubbers thus passivation of the clay is recommended [27]. In our studies the montmorillonite used was additionally surface modified with silane to reduce the acid catalyzed decomposition of peroxide.



Fig. 5. Normalized elastic component S' (dNm) of the torque as a function of time for hydrogenated butadiene-acrylonitrile rubber (HNBR).

TABLE II. Rheometric properties of EPM and HNBR rubber mixtures.

| | $S'_L$, dNm | $S'_H$, dNm | ΔS, dNm | $t_i$, s | $t_{A2}$, min | $\tau_{95}$, min | CRI, min$^{-1}$ |
|---|---|---|---|---|---|---|---|
| EPM | 0.71 | 8.58 | 7.87 | 32 | 2.8 | 17 | 7.0 |
| * SiO$_2$ | 2.69 | 8.39 | 5.70 | 20 | 1.4 | 12 | 9.4 |
| * SiO$_2$, OMt | 2.84 | 7.92 | 5.08 | 24 | 1.7 | 12 | 9.7 |
| * SiO$_2$ OMt OV-POSS | 3.02 | 19.8 | 16.8 | 19 | 0.6 | 8 | 13.5 |
| *SiO$_2$ OMt OM-POSS | 3.07 | 14.2 | 11.1 | 17 | 0.7 | 8 | 13.7 |
| HNBR | 0.94 | 10.1 | 9.12 | 24 | 1.9 | 18 | 6.2 |
| ** SiO$_2$ | 2.18 | 19.5 | 17.3 | 25 | 1.1 | 17 | 6.3 |
| ** SiO$_2$ OMt | 2.08 | 19.7 | 17.6 | 23 | 1.1 | 16 | 6.7 |
| ** SiO$_2$ OMt OV-POSS | 2.18 | 35.8 | 33.7 | 22 | 0.9 | 16 | 6.6 |
| ** SiO$_2$ OMt OM-POSS | 2.62 | 25.5 | 22.9 | 12 | 0.7 | 16 | 6.5 |
| EPM/HNBR | 0.81 | 8.75 | 7.94 | 26 | 2.4 | 19 | 6.0 |
| *** SiO$_2$ | 2.67 | 20.4 | 17.8 | 23 | 1.1 | 18 | 5.9 |
| *** SiO$_2$ OMt | 2.93 | 20.3 | 17.4 | 22 | 1.0 | 18 | 5.9 |
| *** SiO$_2$ OMt OV-POSS | 2.86 | 23.7 | 20.9 | 16 | 0.7 | 18 | 5.8 |

*-EPM, **-HNBR, ***-EPM/HNBR, $S'_L$ – minimum torque, $S'_H$ – maximum torque, $\Delta S = S'_H - S'_L$ – delta torque, $t_{A2}$ – scorch time, $\tau_{95}$ – the optimum cure time, CRI – cure rate index,
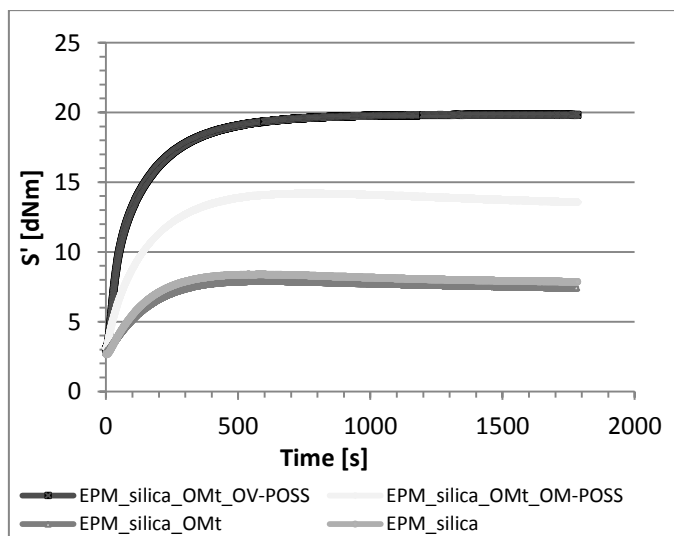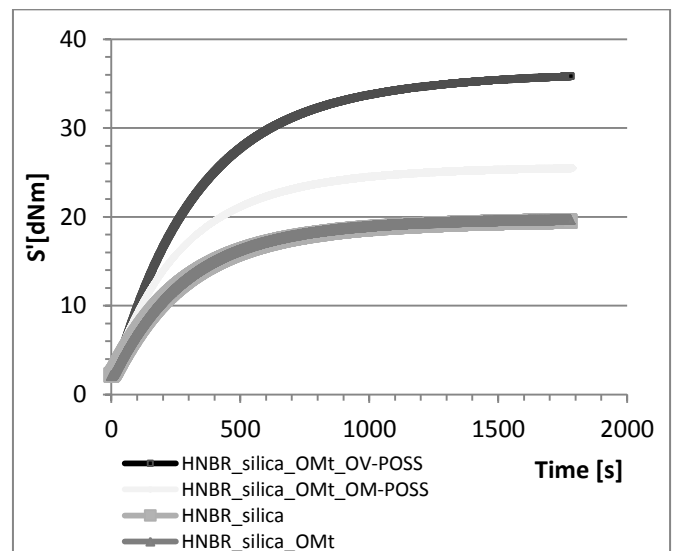


Fig. 4. Normalized elastic component S' (dNm) of the torque as a function of time for ethylene-propylene copolymer (EPM).

No differences were observed in the normalized cure profiles (after incubation period), as measured for silica filled

As we expected the addition of both POSS moieties to rubber compositions resulted in changes of cure behavior.

Both POSS increased the torque increment ΔS during curing (table II). The effect was stronger for octavinyl-POSS than for octa-methacrylate-POSS suggesting that the octavinyl group present in OV-POSS were more accessible for radical grafting to elastomer chains during curing. The presence of POSS in both EPM and HNBR rubber compositions resulted in a substantial increase of maximum elastic torque $S'_H$ which is normally related to the increase of crosslink density. It is interesting to observe that for the silica and organic modified montmorillonite filled 50:50 wt. % EPM/HNBR blends the maximum elastic torque $S'_H$ values were almost similar to these observed for filled HNBR. The cure rate index was calculated according to equation:

$$CRI = \frac{100}{\tau_{95} - t_{\Delta 2}} \qquad (1)$$

where $\tau_{95}$ is the optimum cure time and $t_{\Delta 2}$ is the scorch time. The effect of POSS functionalization on the cure rate index is more pronounced for the ethylene-propylene EPM rubber. A strong increase of the cure rate index CRI and the reduction of optimum cure time $\tau_{95}$ is observed confirming the higher activity of POSS in the vulcanization process of ethylene-propylene rubber EPM than hydrogenated butadiene-acrylonitrile rubber HNBR. The incorporation of OM-POSS and OV-POSS did not show any significant effect on $\tau_{95}$ and CRI index of HNBR rubber and EPM/HNBR blends, although it influenced the formation and state of cured network increasing the maximum torque $S'_H$, and the increment of torque ΔS during curing.
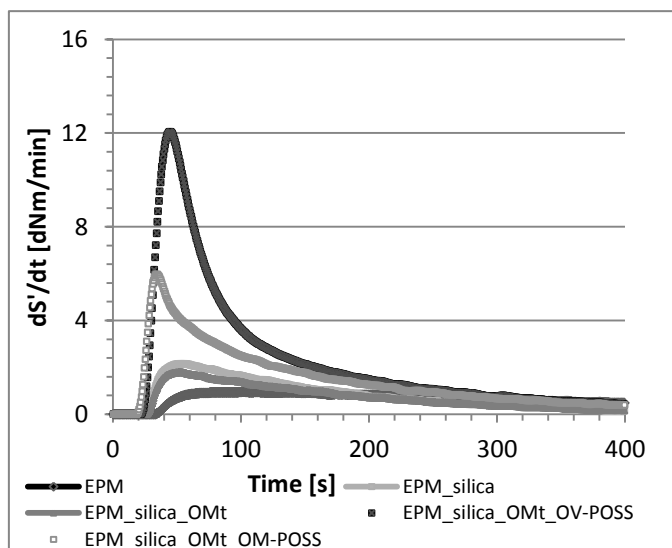


Fig. 6. The first derivative of the elastic component S' of torque versus reaction time (dS'/dt) for ethylene-propylene copolymer EPM.

The first derivative gives us information about how whether a function is increasing or decreasing and by how much it is increasing or decreasing. With respect to the reaction speed, which is given by the curves of the first derivative of elastic torque dS'/dt versus reaction time (Figures 6-8) higher influence of both POSS on the curing speed have been recorded for ethylene-propylene rubber than for hydrogenated butadiene-acrylonitrile rubber or blend of both

elastomers. The local maximum of the first derivative dS'/dt peak appeared at shorter time confirming that reaction speed was faster and the addition of POSS influenced the kinetic of reaction. The curing behavior of EPM/HNBR blends was similar to curing behavior of HNBR rubber, with much similar curves of the first derivative dS'/dt.
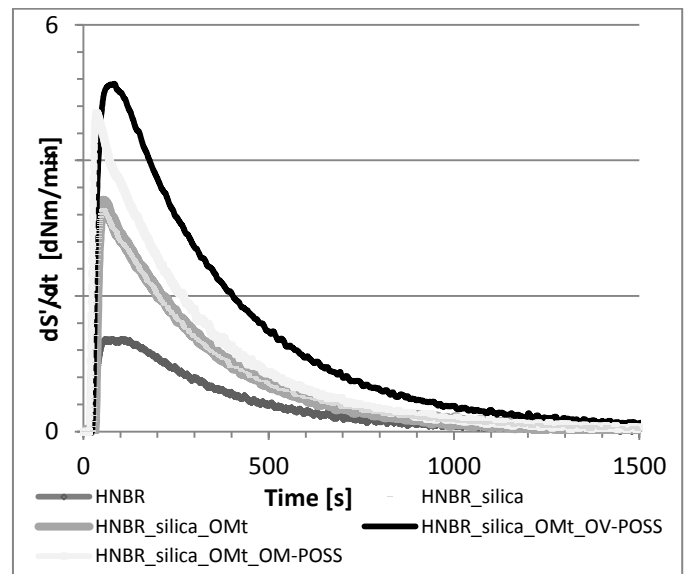


Fig. 7. The first derivative of the elastic component S' of torque versus reaction time (dS'/dt) for hydrogenated butadiene-acrylonitrile rubber HNBR.
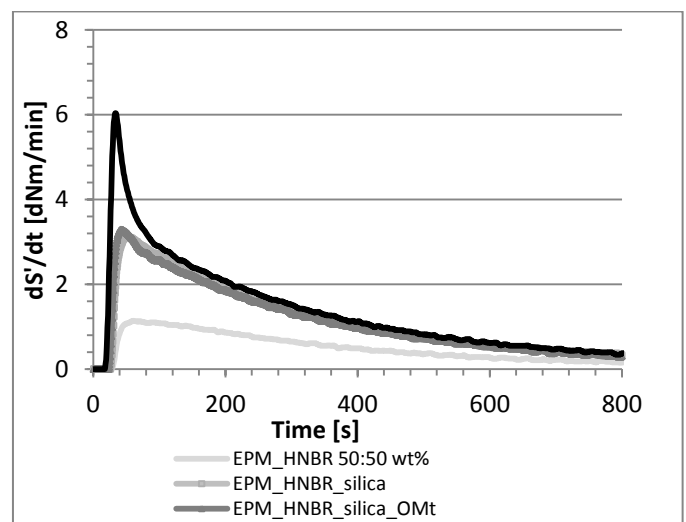


Fig. 8. The first derivative of the elastic component S' of torque versus reaction time (dS'/dt) for EPM/HNBR blends.

### C. Influence of POSS on Crosslink Density and Mechanical Properties of EPM and HNBR Rubber

The crosslink density of cured elastomer can be determined from swelling measurements. Crosslinked elastomers absorb solvent, swelling continues until the retractive forces in the extended molecular strands in the network balance the forces tending to swell the network. The Flory-Rehner's equation [28] (2) is widely used to determine the crosslinking density related to the amount of swelling in toluene according to equation:

$$\nu_T = -\frac{\ln(1-V_p) + V_p + \chi V_p^2}{V_S(V_p^{\frac{1}{3}} - \frac{V_p}{2})}$$ (2)

where $\nu_T$ is crosslink density, $V_p$ is the volume fraction of elastomer in the swollen gel and $V_s$ is the molar volume of solvent (mole/cm$^3$). The Huggins parameter ($\chi$) for elastomer–solvent interaction are given by the following equations [29, 30]:

$\chi = 0.501 + 0.273\ V_p$ (HNBR) (3)
$\chi = 0.425 + 0.34\ V_p$ (EPM) (4)
$\chi = 0.436 + 0.323\ V_p$ (EPM:HNBR 50:50 wt.%) (5)

The percentage of non-covalent crosslinks was determined by decomposition of present ionic crosslinks under the ammonia vapor treatment (*$\nu$) and was calculated according to the equation:

$$*\nu = \frac{\nu_T - \nu_A}{\nu_T} \cdot 100\%$$ (6)

where $\nu_A$ is the crosslink density determined for samples treated with ammonia, $\nu_T$ is the crosslink density determined for samples swollen in toluene. Mechanical properties of elastomer depend strongly on crosslink density. Both the level and the functionality of formed crosslinks are important. Octavinyl-POSS and octamethacrylate-POSS act as multifunctional crosslinks due to ability to incorporate into rubber network structure and creating more branched molecules. Peroxide curing, which takes place via a free radical mechanism, leads to carbon-carbon crosslinks, This way cured vulcanizates although characterize good ageing resilience have low mechanical strength properties. POSS molecules can be thought of as smallest possible particles of silica leading to a nano-reinforcement, when compounded with rubber. Additionally these nano-sized particles can participate via functional groups in curing reaction and cross-links formation simultaneously enhancing the crosslink density of vulcanizates.
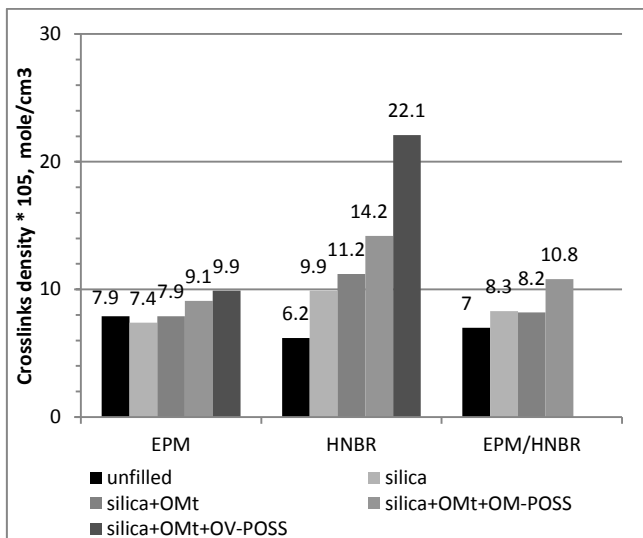


Fig. 9. Crosslink density $\nu_T$ of ethylene-propylene copolymer EPM, hydrogenated butadiene-acrylonitrile rubber HNBR and their EPM/HNBR blends calculated according to equation (2).

The values of calculated crosslink density and the percentage of non-covalent, ionic crosslinks destroyed by ammonia treatment are compiled at Figure 9 and Figure 10. All these results indicate strongly that octavinyl-POSS and octamethacrylate-POSS can participate in crosslinking reactions increasing the values of crosslink density for both rubber ethylene-propylene copolymer EPM and hydrogenated butadiene-acrylonitrile rubber HNBR. The more significant influence of POSS on the crosslink density was observed for hydrogenated butadiene-acrylonitrile rubber HNBR and its blend EPM/HNBR. The increase of rubbers crosslink density was stronger after addition of octavinyl POSS than octamethacrylate POSS suggesting that vinyl groups were more active during curing and formed 3D-network with higher functionality.
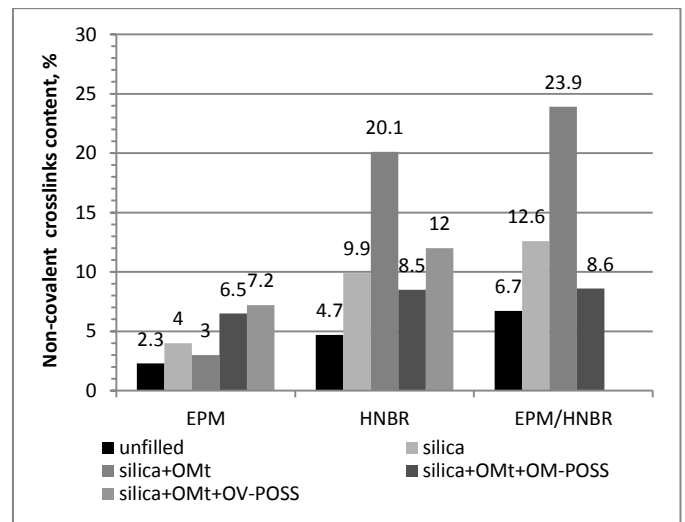


Fig. 10. The percentage of non-covalent crosslinks *$\nu$ for ethylene-propylene copolymer EPM, hydrogenated butadiene-acrylonitrile rubber HNBR and their EPM/HNBR blends calculated according to equation (6).

The increase of crosslink density was also observed for the vulcanizates of hydrogenated butadiene-acrylonitrile rubber HNBR containing silica and montmorillonite. The mixing and dispersing of silica is easier in more polar HNBR rubber than in EPM rubber because of its surface energy characteristic. The facilitated dispersion caused the higher filler/polymer contact and filler/polymer interphase interactions resulting in the higher amount of bounded and occluded rubber on filler surface. This bounded and occluded rubber prevented swelling increasing the values of crosslink density of HNBR rubber. The montmorillonite particles used in our studies were surrounded by the silane modifier containing amine groups, which made them more compatible with the HNBR polymer matrix improving their dispersion and as it took place for the silica filled HNBR rubber the amount of bounded and occluded rubber on filler surface was higher. For this way modified montmorillonite the formed HNBR network structure consisted of covalent crosslinks as well as of extra-network non-covalent crosslinks probably formed as a result of some physical interactions with the nitrile groups present in elastomer chains, as is shown in Figure 10. The addition of the POSS moieties, very active in the curing reaction, led to

formation of more rigid three-dimensional network, with higher functionality covalent crosslinks effecting and restricting the possibility of creation of labile, non-covalent crosslinks. Therefore, a combination of silica, OMt and POSS resulted in decrease of the percentage of non-covalent crosslinks in formed network, although the total crosslink density of HNBR vulcanizates and its EPM/HNBR blend was higher.

Having established the influence of POSS on the vulcanization process and crosslink density of cured rubbers, we then examined their mechanical properties, the results are given in Table IV. For the filled rubber as a parameter estimating the reinforcing effect of various fillers and their mixtures can be used the reinforcing index RI proposed by Kohija and Ikeda [31]. Reinforcing index for vulcanizates was calculated according to equation:

$$RI = \frac{N}{N_0} * \frac{m_F}{100} \qquad (7)$$

where N, $N_0$ are values of selected mechanical parameters for vulcanizates filled and without fillers adequately, $m_F$ is mass of fillers 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, particle size, activity of surface) as well as the nature of surrounded matrix thus the reinforcing index RI allows to determine and compare the reinforcing effect of various fillers in selected elastomer [32]. From the values presented in Table III, it can be clearly observed that the applied fillers, nanometric silica and organic modified montmorillonite had a strong impact on the mechanical properties of ethylene-propylene copolymer EPM, hydrogenated butadiene-acrylonitrile rubber HNBR and their blends EPM/HNBR, the higher values of modulus at 100% of elongation $SE_{100}$ and tensile strength TS were reported. The reinforcing effect of fillers and POSS was observed. However the greater changes in the values of RI indexes were noted for ethylene-propylene rubber EPM indicating stronger reinforcing effect of fillers in this elastomer than in hydrogenated butadiene-acrylonitrile rubber HNBR. As we expected the modification of vulcanizates by the addition of POSS moieties caused strong increase of modulus at 100% of elongation and decrease in elongation at break $E_B$ resulting from the increase of crosslink density. Furthermore, it was found that the addition of small quantities (3phr) of octametacrylate POSS into ethylene-propylene rubber EPM and its blend EPM/HNBR resulted in a remarkable increase in tensile strength TS and reinforcing index $RI_{TS}$ comparing to reinforcing effect caused by silica and montmorillonite. The observed improvements, the higher values of tensile strength are possibly due to the better dispersion of POSS nanoparticles which was caused by the grafting and incorporation of POSS particles into cured rubber structure. Stress-strain curves under tension and subsequent retraction create a hysteresis loop. Hysteresis loss is the ratio of the rate dependence for two components (viscous and elastic component) of deformation energy. During deformation of rubber some irreversible processes occur, and a part of mechanical energy is converted

into heat and other form of energy. The loss of mechanical energy measured as the hysteresis loss is a parameter which plays an important role in applications where cured rubber is subjected to repeated deformation. The hysteresis loss at first deformation $W_1$ and the difference between energy loss at first and fifth cycle of deformation $\Delta W = W_1 - W_5$ were determined (Table III). The filler-filler network formed by reinforcing fillers breaks down during the deformation of samples. Hysteresis loss increases with an increase of breakdown of this network. Both POSS strongly influenced the hysteresis loss at first cycle $W_1$ for filled samples, the loss of deformation energy after five cycles of deformation for this way modified silica and montmorillonite filled EPM, HNBR vulcanizates and their blends increased.

TABLE III. Mechanical properties of ethylene-propylene EPM, hydrogenated butadiene-acrylonitrile HNBR vulcanizates and their 50:50 wt% EPM/HNBR blends.

| | $SE_{100}$, MPa | $RI_{SE}$ | TS, MPa | $RI_{TS}$ | $E_B$, % | $W_1$ J | $\Delta W$ J |
|---|---|---|---|---|---|---|---|
| EPM | 0.73 | - | 1.69 | - | 1222 | 0.05 | 0.03 |
| * SiO₂ | 0.92 | 0.25 | 4.14 | 0.49 | 1409 | 0.11 | 0.10 |
| * SiO₂, OMt | 1.15 | 0.39 | 5.41 | 0.80 | 1368 | 0.14 | 0.13 |
| * SiO₂ OMt OV-POSS | 1.76 | 0.68 | 7.00 | 1.16 | 601 | 0.21 | 0.18 |
| *SiO₂ OMt OM-POSS | 1.41 | 0.54 | 9.40 | 1.56 | 637 | 0.20 | 0.18 |
| HNBR | 0.90 | - | 9.67 | - | 757 | 0.05 | 0.03 |
| ** SiO₂ | 1.75 | 0.39 | 18.49 | 0.38 | 668 | 0.12 | 0.10 |
| ** SiO₂ OMt | 1.67 | 0.46 | 22.01 | 0.57 | 728 | 0.15 | 0.12 |
| ** SiO₂ OMt OV-POSS | 3.19 | 0.99 | 25.10 | 0.73 | 397 | 0.35 | 0.31 |
| ** SiO₂ OMt OM-POSS | 1.73 | 0.54 | 24.00 | 0.69 | 626 | 0,25 | 0.21 |
| EPM/HNBR | 0.74 | - | 5.60 | - | 713 | 0.05 | 0.04 |
| *** SiO₂ | 1.45 | 0.39 | 9.80 | 0.35 | 645 | 0.16 | 0.13 |
| *** SiO₂ OMt | 1.45 | 0.49 | 10.4 | 0.46 | 690 | 0.19 | 0.16 |
| *** SiO₂ OMt OV-POSS | 2.01 | 0.76 | 16.4 | 0.82 | 554 | 0.25 | 0.21 |

*-EPM, **-HNBR, ***-EPM/HNBR, $SE_{100}$ –modulus at 100% elongation, TS – tensile strength, RI – reinforcing index , $RI_{TS} = (TS_F/TS_0)*m_{allfillers}/100$, $RI_{SE} = (SE_F/SE_0)*m_{allfillers}/100$, $E_B$ – elongation at break, $W_1$ – the energy loss during the first cycle of deformation, $\Delta W = W_1 - W_5$ – the difference between energy loss at first and fifth cycle of deformation

TABLE IV. Glass transition $T_g$ temperatures of silica and montmorillonite filled ethylene-propylene EPM, hydrogenated butadiene-acrylonitrile HNBR vulcanizates and their 50:50 wt% EPM/HNBR blends.

| | $T_g$, °C | $T_g$, °C |
|---|---|---|
| EPM_silica_OMt | -55.6 | - |
| EPM_silica_OMt_OV-POSS | -54.4 | - |
| EPM_silica_OMt_OM-POSS | -54.6 | - |
| HNBR_silica_OMt | - | -24.7 |
| HNBR_silica_OMt_OV-POSS | - | -23.6 |
| HNBR_silica_OMt_OM-POSS | - | -23.7 |
| EPM_HNBR_silica_OMt | -55.3 | -22.8 |
| EPM_HNBR_silica_OMt_OM-POSS | -53.7 | -22.6 |

Table IV shows the variation in glass transition temperatures $T_g$ indicated by DSC measurements for the filled cured rubbers. The incorporation of POSS particles to rubber slightly increased glass transition temperature of filled vulcanizates as could be expected analyzing the data of crosslink density. The participation of both POSS in curing

reactions and formation of the more crosslinked, with higher functionality, rubber 3D-network shifted the glass transition temperature of the HNBR and EPM vulcanizates towards higher values due to restricted chains mobility and higher immobilized elastomer phase on the POSS particles surface. For the EPM/HNBR blends the existence of two transitions was observed indicating that elastomers were immiscible and two phases existed. The incorporation of octamethacrylate POSS had no impact on the glass transition temperature of HNBR phase, the glass transition temperature referring to EPM phase was shifted to higher values of temperature indicating that octamethacrylate POSS was preferentially located and grafted to EPM phase.

### D. Resistance to UV Radiation of POSS Modified HNBR and EPM/HNBR 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 copolymer EPM and hydrogenated butadiene-acrylonitrile rubber have more enhanced ageing stability than unsaturated as for example natural rubber. The exposure to UV irradiation can initiate photo-oxidation which leads to deterioration of mechanical properties and therefore the life-time of the product is limited in outdoor application. The proposed by us the hydrogenated butadiene-acrylonitrile HNBR vulcanizates containing silica and organic modified montmorillonite characterized the crosslinked network structure in which besides the covalent bonds also the high amount of non-covalent crosslinks was present. It was interesting to study if the exposure to UV irradiation can lead to crosslink destruction and deterioration of mechanical properties. To estimate the effect of UV ageing on mechanical properties the UV aging coefficients ($K_{UV}$) were calculated according to the equation:

$$K_{UV} = \frac{(TS \cdot E_B)_{after\ aging}}{(TS \cdot E_B)_{before\ aging}} \tag{8}$$

where TS is tensile strength, $E_B$ is elongation at break measured for the vulcanizates before and after UV ageing. The percentage of decrease or increase for the nominal parameters $\Delta N_{UV}$ after UV ageing were calculated following to the equation:

$$\Delta N_{UV} = \left( \frac{N_{after\ ageing} - N_{before\ ageing}}{N_{before\ ageing}} \right) * 100\% \tag{9}$$

where N are the nominal values of parameter such as: TS – tensile strength, $E_B$ – elongation at break, $\nu_T$ – crosslink density calculated from the equilibrium swelling in toluene, $\nu_A$ – crosslink density calculated from the equilibrium swelling in toluene under the ammonia vapor treatment adequately before and after UV-ageing. The percentage of non-covalent crosslinks for the vulcanizates after UV ageing was determined by decomposition of present ionic crosslinks under the ammonia vapor treatment ($*\nu_{ageing}$) and was calculated according to the equation:

$$* \nu_{ageing} = \frac{\nu_{TUV} - \nu_{AUV}}{\nu_{TUV}} \cdot 100\% \tag{10}$$

where $\nu_{AUV}$ is the crosslink density determined for UV-aged samples treated with ammonia, $\nu_{TUV}$ is the crosslink density

determined for UV-aged samples swollen in toluene. Table 6 summarizes the changes in mechanical properties and crosslink density of hydrogenated butadiene-acrylonitrile HNBR vulcanizates and their EPM/HNBR blends after the samples were exposed to UV radiation. The exposure of silica and montmorillonite OMt filled HNBR vulcanizates and its blend EPM/HNBR to sunlight resulted in higher stiffness and a loss of elasticity which is reflected by the significantly reduced elongation at break $E_B$ as well as the higher values of modulus at 100% elongation. The UV radiation caused increase of crosslink density $\nu_T$ calculated from the equilibrium swelling in toluene. The increase of crosslink density $\nu_A$, the parameter calculated for samples treated with ammonia vapor confirms that crosslink destruction occurred and previously formed crosslinks decomposed after UV ageing and rearranged into other types of crosslinks including carbon-carbon crosslinks and non-covalent crosslinks. The percentage of non-covalent crosslinks $*\nu_{ageing}$ for the silica and montmorillonite filled vulcanizates was more than doubled after ageing. Based on the obtained $I_{UV}$ values, which correspond to the UV-stability, the highest UV protection was provided by octamethacrylate-POSS ($K_{UV} = 0.61$) than octavinyl-POSS ($K_{UV} = 0.45$). Despite reduced tensile strength, the HNBR vulcanizates modified by the addition of octamethacrylate POSS showed after UV-ageing lower deterioration in elongation of break $E_B$ and higher percentage of non-covalent crosslinks $*\nu_{ageing}$. The higher UV-stability observed for the octamethacrylate-POSS modified HNBR rubber comparing to HNBR vulcanizates containing octavinyl-POSS can be explained by the higher tendency to form non-covalent crosslinks under elevated temperature condition during ageing what it is confirmed by higher values of $*\nu_{ageing}$ after UV-exposure. This behavior balanced the deleterious effect of UV radiation on breaking of the polymer chains.

### IV. CONCLUSIONS

Both fillers, silica and montmorillonite characterized strong tendency to formation of more aggregated structures as indicated by SEM studies and DLS measurements for the filler dispersions in paraffin oil, higher viscosity model of non-polar elastomer. The surface covering of octadecylamine intercalated montmorillonite with aminopropylo-triethoxysilane led to increased values of oil absorption parameter OAP estimating higher tendency to creation of filler network. The presence of aminopropylotriethoxysilane caused stronger physical interactions between filler particles comparing to unmodified montmorillonite PGV and intercalated only by octadecylamine. Fumed silica Aerosil 380 and aminopropyltriethoxysilane/octadecylamine modified montmorillonite OMt were applied, together with polyhedral oligometric silsesquioxanes POSS, as reinforcing fillers in ethylene-propylene EPM, hydrogenated butadiene-acrylonitrile rubber HNBR and their 50:50 wt.% EPM/HNBR blends. Octavinyl-POSS and octamethacrylate-POSS improved the efficiency of peroxide curing, significantly increasing the values of maximum elastic torque $S'_H$ and the values of torque increment during curing $\Delta S$, both parameters

are related to the increase of crosslink density what was confirmed by swelling studies. The curing reaction started after shorter induction time indicating changes in cure behavior. A higher enhancement of the cure rate index CRI and the reduction of vulcanization time was observed in case of the POSS modified ethylene-propylene copolymer EPM confirming the stronger influence of POSS addition on curing behavior of EPM than on HNBR. The changes in first derivative dS'/dt curves recorded for POSS modified rubbers confirmed that the curing reactions occurred with higher speed and efficiency. As we supposed the octamethacrylate-POSS and octavinyl-POSS participated in crosslinking reactions changing the structure of formed cured rubber network. Remarkable enhancement of modulus at 100% elongation and tensile strength for octavinyl-POSS and octamethacrylate-POSS modified EPM copolymer and its blend EPM/HNBR was noted. The presence of two different immiscible phases was reported by appearance of two glass temperatures related to EPM and HNBR phases. The octamethacrylate-POSS provided higher UV-aging stability and lower deterioration in elongation at break $E_B$. Under UV-treatment the rearrangement of previously formed crosslinks occurred resulting in higher amount of non-covalent crosslinks after ageing.

## REFERENCES

[1] W. Zhang, G. Camino, R. Yang," Polymer/polyhedral oligomeric silsesquioxane (POSS) nanocomposites: An overview of fire retardance", *Progress in Polymer Science*, vol. 67, pp. 77-125, 2017.

[2] K. N. Raftopoulos, K. Pielichowski, "Segmental dynamics in hybrid polymer/POSS nanomaterials", *Progress in Polymer Science*, vol. 52, pp. 136-187, 2016.

[3] A. Ullah, J. Alongi, S. Russo, "Recent findings in (Ti) POSS-based polymer systems", *Polymer Bulletin*, vol. 67, pp.1169-1183, 2011.

[4] J-C. Huang, C-B. He, Y. Xiao, K.Y. Mya, J. Dai, Y.P. Siow, "Polyimide/POSS nanocomposites: Interfacial interaction, thermal properties and mechanical properties", *Polymer*, vol. 44, pp. 4491-4499, 2003.

[5] Y. L. Liu, H-C. Lee, "Preparation and properties of polyhedral oligosilsequioxane tethered aromatic polyamide nanocomposites through Michael addition between maleimide-containing polyamides and an amino-functionalized polyhedral oligosilsequioxane", *Journal of Polymer Science: Part A: Polymer Chemistry*, vol. 44, pp. 4632-4643, 2006.

[6] N. Tz. Dintcheva, E. Morici, R. Arrigo, F. P. La Mantia, V. Malatesta, J.J. Schwab, "Structure-properties relationships of polyhedraloligometric silsesquioxane (POSS) filled PS nanocomposites", *eXPRESS Polymer Letter*, vol. 6(7), pp. 561-571, 2012.

[7] R. Misra, B. X. Fu, S. E. Morgan, "Surface energetics, dispersion, and nanotribomechanical behavior of POSS/PPhybrid nanocomposites", *Journal of Polymer Science Part B: Polymer Physics*, vol. 45, pp. 2441-2455, 2007.

[8] B. X. Fu, M. Y. Gelfer, B. S. Hsiao, S. Phillips, B. Viers, R. Blanski, P. Ruth, "Physical gelation in ethylene-propylene copolymer melts induced by polyhedral oligomeric silsesquioxane (POSS) molecules", *Polymer*, vol. 44, pp. 1499-1506, 2003.

[9] J. H. Chen, Y-D. Chiou, "Crystallization behavior and morphological development of isotactic polypropylene blended with nanostructured polyhedral oligomeric silsquioxane molecules", *Journal of Polymer Science Part B: Polymer Physics*, vol. 44, pp. 2122-2134, 2006.

[10] W. Hao, J. Hu, L. Chen, J. Zang, L. Xing, W.Yang, "Isoconversional analysis of non-isothermal curing process of epoxy resin/epoxide polyhedral oligomeric silsesquioxane composites", *Polymer Testing*, vol. 30, pp. 349-355, 2011.

[11] J. Boček, L. Matějka, V. Mentlík, P. Trinka, M. Šlouf, "Electrical and thermomechanical properties of epoxy-POSS nanocomposites", *European. Polymer Journal*, vol. 47, pp. 861-872, 2011.

[12] Y. Ni, S. Zheng, K. Nie, "Morphology and thermal properties of inorganic-organic hybrids involving epoxy resin and polyhedral oligomeric silsesquioxanes", *Polymer*, vol. 45, pp. 5557-5568, 2004.

[13] W. Thitsartarn, X. Fan, Y. Sun, J. Chee, Ch. Yeo, D. Yuan, Ch. He, "Simultaneous enhancement of strength and toughness of epoxy using POSS-Rubber core-shell nanoparticles", *Composites Science Technology*, vol. 118, pp. 63-71, 2015.

[14] J.P. Lewicki, K. Pielichowski, M. Jancia, E. Hebda, R. L. F. Albo, R. S. Maxwell, "Degradative and morphological characterization of POSS modified nanohybrid polyurethane elastomers", *Polymer Degradation Stability*, vol. 104, pp. 50-56, 2014.

[15] L. Liu, M. Tian, W. Zhang, L. Zhang, J. E. Mark, "Crystallization and morphology study of polyhedral oligomeric silsesquioxanes (POSS)/polysiloxane elastomer composites prepared by melt blending", *Polymer*, vol. 48, pp. 3201-3212, 2007.

[16] Y. Meng, Z. Wei, L. Liu, L. Liu, L. Zhang, T. Nishi, K. Ito, "Significantly improving the thermal stability and dispersion morphology of polyhedral oligomeric silsesquioxane/polysiloxane composites by in-situ grafting reaction", *Polymer*, vol. 54, pp. 3055-3064, 2013.

[17] Y. Liu, Y. Shi, D. Zhang, J. Li, G. Huang, "Preparation and thermal degradation behavior of room temperature vulcanized silicone rubber-g-polyhedral oligomeric silsesquioxanes", *Polymer*, vol. 54, pp. 6140-6149, 2013.

[18] D. Chen, S. Yi, W. Wu, Y. Zhong, J. Liao, Ch. Huang, "Synthesis and characterization of novel room temperature vulcanized (RTV) silicone rubber using vinyl-POSS derivatives as crosslinking agents", *Polymer*, vol. 51, pp. 3867-3878, 2010.

[19] Y. Zhang, Y. Mao, D. Chen, W. Wu, S. Yi, S. Mo, Ch. Huang, "Synthesis and characterization of addition-type silicone rubbers (ASR) using novel cross linking agent PH prepared by vinyl-POSS and PMHS", *Polymer Degradation and Stability*, vol. 98, pp. 916-925, 2013.

[20] D. Chen, Y. Liu, Ch. Huang, "Synergistic effect between POSS and fumed silica on thermal stabilities and mechanical properties of room temperature vulcanized (RTV) silicone rubbers", *Polymer Degradation and Stability*, vol. 97, pp. 308-315, 2012.

[21] H. Sirin, M. Kodal, B. Karaagac, G. Ozkoc," Effects of octamaleamic acid-POSS used as the adhesion enhancer on the properties of silicone rubber/silica nanocomposites", *Composites Part B*, vol. 98, pp. 370-381, 2016.

[22] R. Konnola, C. P. R. Nair, K. Joseph, "Cross-linking of carboxyl-terminated nitrile rubber with polyhedral oligomeric silsesquioxane, cure kinetics", *Journal of Thermal Analysis and Calorimetry*, vol. 123, pp. 1479-1489, 2016.

[23] S. Sahoo, A.K. Bhowmick, "Polyhedral oligomeric silsesquioxane (POSS) nanoparticles as new crosslinking agent for functionalized rubber", *Rubber Chemistry and Technology*, vol. 80(5), pp. 826-837, 2007.

[24] S. Yang, H. Fan, Y. Jiao , Z. Cai, P. Zhang, Y. Li, "Improvement in mechanical properties of NBR/LiClO₄/POSS nanocomposites by constructing a novel network structure", *Composites Science and Technology*, vol. 138, pp. 161-168, 2017.

[25] G. Chen, P. Li, Y. Huang, M. Kong, Y. Lv, Q. Yang, G. Li, "Hybrid nanoparticles with different surface chemistries show higher efficiency in compatibilizing immiscible polymer blends", *Composites Science and Technology*, vol. 105, pp. 37-43, 2014.

[26] R. N. Datta, "Rubber-Curing Systems" in: A. K. Bhowmick (Ed.)," Current topics in elastomer research", CRC Press Taylor and Francis Group, New York, pp 415-460, 2008.

[27] S. Sengupta, M. Esseghir, J. M. Cogen, "Effect of formulation variables on cure kinetics, mechanical, and electrical properties of filled peroxide cured,ethylene-propylene-diene monomer compounds", *Journal of Applied Science*, vol. 120, pp. 2191-2200, 2011.

[28] P. J. Flory, J. Rehner, "Statistical mechanics of cross-linked polymer networks. II. Swelling", *Journal of Chemical Physics*, vol. 11, pp. 521-526, 1943.

[29] M. Maciejewska, M. Zaborski, A. Krzywania-Kaliszewska, "Mineral oxides and layered minerals in combination with itaconic acid as coagents for peroxide crosslinking of hydrogenated acrylonitrile-

butadiene elastomer", *Comptes Rendus Chemie*, vol. 15, pp. 414- 423, 2012.

[30] M. Lipińska, M. Zaborski, C. Dębek, "Układy elastomerowe modyfikowane pochodną oksazoliny, Elastomer vulcanizates modified with oxazoline derivative", *Przemysł Chemiczny*, vol. 89(4), pp. 462-467, 2010.

[31] S. Kohjiya, Y. Ikeda, "Reinforcement of general purpose grade rubbers by silica generated in situ", *Rubber Chemistry and Technology*, vol. 73(3), pp. 534-550, 2000.

[32] F. M. Helaly, S. H. El-Sabbagh, "Bone-meal waste and $Ca(HPO_4)_2$ as reinforcing filler for NR and CR and their blends compared with conventional white filler", *Journal of Elastomer and Plastics*, vol. 34(4), pp. 335-348, 2002.