Elastomer composites containing layered fillers and hydroxyapatities

M. Lipińska*, M. Zaborski*, J. Pietrasik*, A.Masek *

*Technical University of Lodz, Institute of Polymer and Dye Technology, Stefanowskiego 12/16 Lodz 90-924, Poland, magdalena.lipinska@p.lodz.pl

ABSTRACT

Traditionally, as a filler of rubber carbon black is used. It is an active filler able to reinforce and improve the properties of finished rubber products. For ecological and economic reasons the research activity is focused on looking for new methods of surface modification of inactive fillers to enhance their strengthening performance in elastomers. In our work as a filler of elastomeric compounds a cation-exchangeable aluminosilicates-type montmorillonites with nanometric thickness of the tiles were used. This type of the filler can be used to obtain nanocomposites due to produce nanoscopic structures „in-situ" in polimer matrix by intercalation and exfoliation of single layers of filler [1].

Montmorillonites are incompatible with most polymers and therefore is necessary to modify them in order to increase layer-spacing and to facilitate the penetration of polymer chains [2]. The modification involves introducing various organic cations in place of sodium cation present between layers. Most commonly used for this purpose are ammonium or phosphonium salts. Modification increases the distance between the packages in the filler, and also due to adsorption of modifier on the surface increases the affinity to elastomeric matrix. In our work as a modyfing agent the ionic liquids were used. Surface properties of modified fillers, the zeta potential of suspended solids in the water, the oil absorption number, the impact of modifications on the tendency to agglomerate in the non-polar and polar medium were investigateded.

As a elastomer fillers also hydroxyapatites were used. There are legal requirements and environmental pressures to resolve the problem of the waste disposal by finding new applications for the products or byproducts obtained from waste streams. The meat industry makes a significant contribution to the volume of organic wastes produced per year. Identification of new applications for the components of these waste streams is an open issue of increasing importance. In our work the physicochemical properties of hydroxyapatite obtained from animal bones as well as the properties of the elastomer-hydroxyapatite composites were studied.

The modified fillers were used in two type of acrylonitrile-butadiene rubber, carboxylated XNBR and hydrogenated one HNBR. The effect of the application of fillers on the cross-linking density of the vulcanizates, rheometric and mechanical properties of filled systems was investigated. The ageing studies (thermal, atmospheric and under UV radiations) were conducted.

Keywords: layered silicates, intercalated composites, hydroxyapatities, elastomers,

1. Object and methods of studies.

In the work the commercially layered fillers as described below were used:

- unmodified montmorillonite **MMT**, Nanomer PGV (Nanoclay, USA) – hydrophilic bentonite nanoclay,

As the modyfing agents we used the ionic liquids as:

- didecyldimethyl ammonium saccharinate **SDDMA** (Industrial Chemistry Research Institute, Warsaw, Poland),
- didecyldimethyl ammonium acesulfamate **ADDMA** (Industrial Chemistry Research Institute, Warsaw, Poland).

Ionic liquids are currently defined as salts that are composed solely of cations and anions which melt below one hundred celsius degree. These salts have been studied for a variety of applications in electrochemistry, chemical synthesis and catalysis. In our work the selected described above ionic liquids were applied as modifying agents for surface modification of montmorillonites. This ionic liquids shows antimicrobial, antibacterial and antifungal activities.

The amount of ionic liquid added was 10 wt % / mass of the MMT filler. The modification was done from the filler aqueous dispersion by. the solvent evaporation. After the modification the filler was 48h dried in vacuum dryer at 80°C.

In order to compare with those ionic liquid- modified fillers commercially available modified by octadecylamine montmorillonite was also examined:

- **I.30 E** – clay surface modified with 25-30 wt% octadecylamine (Nanoclay, USA),

The size of montmorillonites aggregates was determined using a Zetasizer NanoS90 apparatus (Malvern). The size of particles in water dispersions ($0.2g/dm^3$) was measured based on the dynamic light scattering DLS method. The oil absorption parameter was measured using Oil Absorption Brabender equipment. The elastomers used in this work were:

- hydrogenated butadiene-acrylonitrile rubber HNBR, containing 34% of acrylonitrile mers (Therban A 3407, Bayer), The composition of the prepared rubber mixes in this case was as follows: HNBR 100 phr, filler 5 or 10 phr, crosslinking agent DCP (dicumyl peroxide, Sigma Aldrich) 2 phr.
- carboxylated butadiene-acrylonitrile rubber XNBR (Krynac X7.50) containing 27 wt% acrylonitrile and 6.7 wt% carboxylic groups produced by Bayer AG was used. Nonstoichiometric hydroxyapatities extracted from the cortical part of the long pig bones were used as a filler to obtain XNBR elastomer composites

The rubber mixes were made by a laboratory two-roll mill at a temperature of approximately 35°C. Mixing of the filler and curing agents with the elastomer was done using selected processing parameters to increase the degree of exfoliation. The condition of vulcanization were determined by oscillating disc rheometer WG-2. The samples were vulcanized at 160°C for the time necessary for a torque increase of rheometric moment by 90% ($\tau_{0.9}$). Crosslink density of the vulcanisates was calculated from equilibrum swelling in toluene. In order to determine the content of ionic crosslinks in the elastomer network samples were swollen in toluene in a dessicator with saturated ammonia vapour (25% aqueous solution). The mechanical properties of the vulcanisates were determined according to ISO-37 using a ZWICK 1435 universal machine. Thermal ageing studies were carried out in a dryer with thermo circulation at 70°C in 7 days. Atmospheric ageing studies were carried out using Atlas Weather Ometer Ci 4000 equipment, in 100 h using selected day and night panels with parameters as: day panel – time 240 minutes, energy of radiation 0,7 W/m^2, humidity 60%, night panel – time 120 min., humidity 50%. The UV ageing studies were carried out using Atlas UV 2000 equipment. The parameters of the process were: time 100 h, day panel – 320 min., energy of radiation 0,7 W/m^2, temperature 60°C, night panel – 160 min., temoerature 50°C.

For every type of ageing studies the ageing coefficient K (1) was calculated according to equation:

$$K = (TS*EB)_{aged} / (TS*EB)_{before\ aging} \quad (1)$$

where TS – tensile strength, EB – elongation at break.

Results and discussion

One of the key factors to achieve the significant improvement of mechanical properties of the polymer composite is attributed to the filler particle size as well as its disspersion/distribution in the matrix. The reduction in aggregates size formed by the primary particles results in an better contact between the filler and elastomer chains. Moreover it determines the size of the interphase between the surface and an elastomeric matrix what strongly influences on the mechanical properties. The aggregates can be the "weak centre" in which breaking of the material ocurrs. The particle sizes of used montmorillonites were investigated (fig 1). Before making the measurements the aqueous dispersions were subjected to ultrasonic waves to improve their stability.

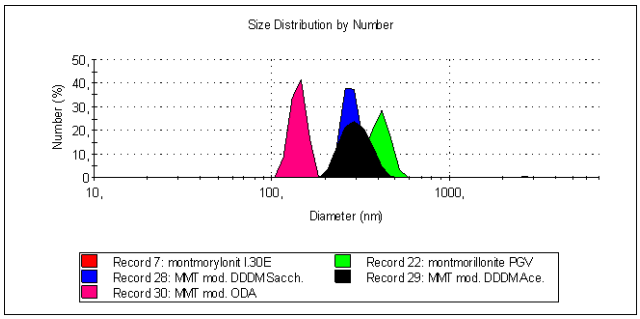

Fig. 1. Size distribution by number for the water dispersion of studied montmorillonites (green – unmodified PGV, blue – MMT modified with didecyldimethyl ammonium saccharinate, black – MMT modified with didecyldimethyl ammonium acesulfamate, pink – MMT modified with octadecylamine)

Both modified with ionic liquids layered silicates showed higher tendency to agglomerate and as a result formed aggregates with higher size than it was in case of octadecylamine modified montmorillonite.

. Table 1: D-spacing within the clay galleries measured by X-ray diffraction

filler	d-spacing, nm
unmodified montmorillonite	1,30
octadecylamine	2,16
didecyldimethyl ammonium saccharinate	1,40
Didecyldimethyl ammonium acesulfamate	1,36

By X-ray diffraction the d-spacing within the clay galleries was measured. Modification with saccharinate and acesulfamate only slightly increased the distance between the packages in the filler (table 1). Probably the modification occurred mainly on the particle surface.

We examined the morphology and particle shape of the fillers used by SEM microscopy [3]. Unmodified montmorillonite strongly agglomerated, the particle surface is characterized by undulating structure. Application of ionic liquids to modify montmorillonite effected on the morphology of the agglomerates surface. Both didecyldimethyl ammonium saccharinate and didecyldimethylammonium acesulfamatereduced the size of agglomerates formed. The surface of modified particles is more developed and undulated with many petals, layers and wrinkle structure.

Table 2: The curing time τ_{90} **(min)** and crosslink density ν***10-**^{5} **(mole/cm**^{3}**) ,** 100% modulus SE_{100} **(MPa),** tensile strength **TS (MPa),** elongation at break E_b **(%)** of HNBR vulcanizates.

filler	τ_{90}	ν*10-^{5}	SE_{100}	TS	E_B
unmodified MMT	21	6,7	0,9	5,8	792
octadecylamine	18	8,7	1,1	12,1	742
DDDMA saccharinate	20	7,8	0,9	11,1	713
DDDMA acesulfamate	18	8,5	1,0	11,6	732

The mechanical properties of the vulcanisates were determined using a Zwick universal machine. In the table 2 the properties of HNBR vulcanisates containing 10 phr of the fillers are collected. We observed the influence of the type of montmorillonite used on the curing time. Depending of the modifing agents the curing time decreased. The modification influenced also on the crossling density of the vulcanisates. Montmorilonites are incompatible with polymers and the modification with various organic cations containing long hydrocarbons chains allows to improve the comptibility between filler and matrix what influences on mechanical properties and falicitate the dispersion of the filler in polymer. The HNBR vulcanisates filled with modified with ionic liquids MMT characterized higher tensile strenght and 100% modulus. The effect was similar to this achived in case of commercially products modified with ammonium salts. The effect was connected with the improvement of dispersion. Our studies showed (fig. 2) that the modification of MMT had negative effect on the ageing of HNBR vulcanisates. The presence of ammonium salts caused the changed in values of ageing coefficients. The vulcanisates containing modified montmorillonite were less resistant against UV radiation and weathering ageing in comparision to vulcanisate filled with unmodified MMT.

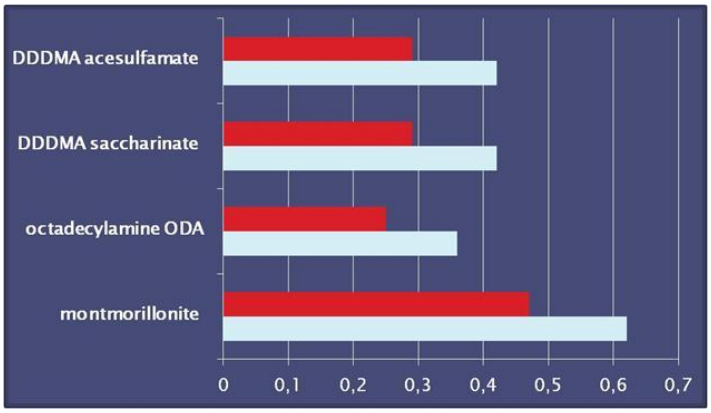

Fig 2.: The value of the ageing coefficient K calculated for HNBR vulcanizates containig modified MMT. Ageing coefficient K for HNBR vulcanizates (red – UV ageing, Light blue – wheathering ageing)

As a filler for carboxylated butadiene-acrylonitrille rubber hydroxyapatites was also used. The properties of pig bone HAP were determined by light diffraction (Malvern Zetasizer NanoS90), nitrogen adsorption (Sorty 1750, Carlo Erba), thermogravimethry (Setaram Setsys TG-DTA 16/18), and energy dispersive X-ray spectroscopy (Siemens D500). HNBR. The properties of the filler are collected in table 3. HAP used in present studies contained a fraction of water (4,8%) and carbonate groups (3,5%) incorporated into structure.

Table 3: Physicochemical properties of hydroxyapatite extracted from the cortical part of the long pig bones.

Agglomerates size	2600, nm
Surface area	71, m^2/g
Thermal stability	-4,8% 200°C - 3,5% 800°C
Crystalinity	72%
Crystal size	353A

Caroboxylated acrylonitrile-butadiene rubber and zinc oxide (100 nm, BET 42,5 m^2/g) were used to preapare rubber mixtures. The composites contained different amount of HAP (10, 20, 40 phr).

The reinforcing activity of fillers is associated with the strength properties of vulcanizates. It apears that HAP can be an active filler for XNBR. The stiffness of the XNBR vulcanizates containing HAP increased with the amount of the filler added to the composite. The tensile strength of the system filled with the 40 phr of HAP was significantly higher than the value for the unfilled one (table 4).

Table 4: Mechanical properties of XNBR composites containing HAP. 100% modulus **SE_{100} (MPa),** tensile strength **TS (MPa),** elongation at break **E_b (%)**

	SE_{100}	TS	E_b
XNBR, ZnO	1,6	15,9	659
XNBR, ZnO, 10 HAP	1,9	15,4	624
XNBR, ZnO, 20 HAP	2,7	21,2	598
XNBR, ZnO, 40 HAP	6,0	28,0	495

It appeared that hydroxyapatite increased the cross-linking density of the vulcanizates, as calculated from the swelling in toluene. The number of ionic crosslinking points $\Delta\nu/\nu$ (T), whose formation could take place with the participation of Ca^{2+} was particularly high when the 40 phr of HAP was added to the composite (table 5).

Table 5: Crosslink density of XNBR composites.

	$\nu*10^{-5}$ (T)	$\nu*10^{-5}$ (A)	$\Delta\nu/\nu$, %
XNBR, ZnO	2,5	2,8	15
XNBR, ZnO, 10 HAP	4,5	2,9	35
XNBR, ZnO, 20 HAP	4,8	4,2	12
XNBR, ZnO, 40 HAP	8,2	3,2	60

$\nu*10^{-5}$, mole/dm^3 – crosslinking density calculated from the equilibrium swelling in (T) toluene or (A) toluene under the ammonia atmosphere, $\Delta\nu$ – concentration of ionic cross-links ($\Delta\nu = \nu$ (T) – ν (A) – the relative changes of cross-links under the ammonia treatement)

CONCLUSIONS

The application of ionic liquid influenced on the cross-linking density of the vulcanizates, rheometric and mechanical properties of HNBR.
The application of montmorillonites as well as hydroxyapatites led to a significant improvement in mechanical properties of rubber.
Tthe ageing studies (thermal, atmospheric and under uv radiations) showed that the modification of montmorilonite with ammonium salts had strong effect on ageing properties of vulcanisates.

REFERENCES

[1] P. Pages, T. Lacorte, M. Lipinska, F. Carrasco, J. Appl. Pol. Sci., vol. 108, 2107, 2008

[2] S. Sinha Ray, M. Okamoto, Prog. Polym. Sci., Vol 28, 1539, 2003

[3] M. Lipinska, A.Laskowska, M. Zaborski, *Materials Sci. Forum*, vol. 714, 73, 2012

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