Degradable elastomer composites containing layered silicate.

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ABSTRACT

The aim of work was to obtain an elastomeric composites with both increased mechanical, thermal properties and a certain time of degradation. For this purpose the protein hydrolysates were used to prepare the rubber mixtures. The epoxidized natural rubber ENR was used as a polimeric matrix. The natural layered silicates as montmorillonites MMT were used as a filler. The application of hydrolysates resulted in increased susceptibility to degradation of ENR during the storage on land and composting. The hydrolysates improved the thermal resistance of vulcanizates, also they influenced on mechanical properties of a filled ENR rubber

Keywords: elastin, keratin, silk proteins, elastomeric composites, layered silicate

1 INTRODUCTION

There are several research activities focusing on obtaining environmental friendly polymer materials[1-3]. One of them refers to the polymers with an increased degree of degradability which can be obtained through the addition of natural biodegradable supplements to the synthetic polymers[4-6]. The aim of our study was to obtain an elastomeric composites with a good mechanical properties and determined time of degradability. There are some reports of the use of natural additives to improve the properties of rubber in the patent literature[7-9]. Herein as a fillers the modified and unmodified montmorllonites MMT have been applied to improve the mechanical properties of composites. It is known that layered silicates have several advantages when compared to traditionally used fillers i.e. they improve the mechanical strength of composites, increase barrier properties and reduce flammability[10]. Additionally the color of filler (white) allows to obtain low price, colorful materials. The most widely used layered silicate, montmorillonite has a complex three-layered structure (package) that contains two tetrahedral silicate layers and in between the octahedral layer. The thickness of the layer of montmorillonite is about 1 nm, the length range reaches about 100-150 nm. Number of packets per a unit cell varies from a few to several thousand.

Unfortunately preparation of a homogeneous mixture of rubber containing exfoliated layers of MMT is a difficult task because of incompatiblity of this filler with matrix caused by the chemical nature of its surface[10]. Usually montmorillonites are modified with organic compounds f.e. ammonium salts. to improve the compatibility with the polimeric matrix. In our work during preparation of rubber mixtures (based on epoxidized natural rubber) to improve the dispersion of MMT and the ratio of degradation and biodegradation of the final composites keratin, elastin, silk proteins derived from waste products were added.

2 OBJECT AND METHODS OF STUDIES

In the work the following layered fillers were used:
- unmodified montmorillonite K-10 (Sigma-Aldrich),
- Cloisite 15A – natural montmorillonite modified with a dimethyl, dihydrogenatedtallow, quaternary ammonium salt 2M2HT where HT is hydrogenated tallow (~65% C18, ~30% C16, ~5% C14) produced by Southern Clay Products

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.

An epoxidized natural rubber ENR with a degree of epoxidation equal to 50% mol. (Kumpulan Guthride Berhard, Malaysia) was used as a elastomer matrix.
Hydrolyzed proteins derived from elastin, keratin and hydrolyzed silk proteins (produced by Proteina, Lodz, Poland as a modifying and imrpoving the dispersion of MMT were used. Elastomer ENR was crosslinked with the addition of sulfur in a presence of accelerators (CBS). Mixing of the filler, hydrolizates and curing agents with the elastomer was done in an open two-roll mixing mill of laboratory size using selected processing parameters to increase the degree of exfoliation. Moulding was done at 15 MPa pressure in a laboratory-sized hydraulic press at 160°C temperature for the time necessary for a torque increase of moment of the rheometer by 90% ($\tau_{0.9}$). The stress-strain tests were done with a material testing machine Zwick 1435 according to ISO-37. The influence of the

natural components on the rheometric properties, curing kinetics, crosslink density and the network structure of vulcanizates was studied. The 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). Thermal ageing studies were carried out in a dryer with thermocirculation at 70°C in 7 days. .The aeging coefficient K was calculated according to equation:

$$K = (TS*EB)_{aged} / (TS*EB)_{unaged}$$

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

3 RESULTS AND DISCUSSION

The particle size of the used fillers in the aqueous medium was examined. Before making the measurements the aqueous dispersions were subjected to ultrasonic waves to improve their stability. The particle size of montmorillonite K-10 was 104 nm at 55.18% by number
Cloisite 15A characterized strong agglomeration and as a result created the agglomerates larger than 2μm (fig 1-2).
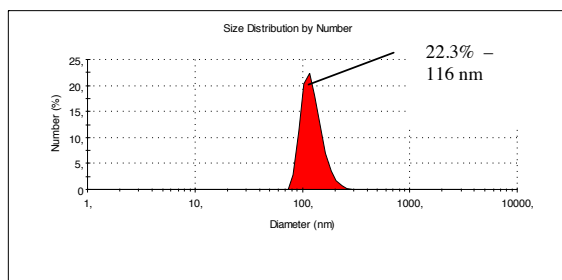

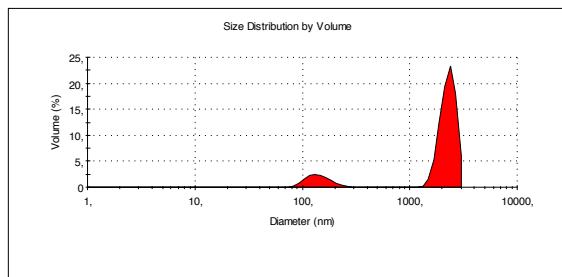Fig. 1. Size distribution by number for the Cloisite 15A

Fig. 2. Size distribution by volume for the Cloisite 15A

The oil absorption parameter was calculated on the basis of the amount of dibutyl phthalate oil absorbed by the filler particles, this parameter can characterize the tendency of the filler to create „own structure" in elastomer matrix. The value of this parameter was, respectively: Cloisite 15A - 54.4 [ml/100g], montmorillonite K-10 93.4 [ml/100g]. Higher trend in the absorption of dibutyl phthalate and the

smallest particle size characterized the unmodified filler montmorillonite K-10.
The influence of the hydrolysates application on the curing time of ENR mixtures was studied (fig 3.). Hydrolysates decreased the curing time of ENR mixtures. This effect was also observed for the filled rubber mixtures containing K-10 or Cloisite 15A (table 1, 2)
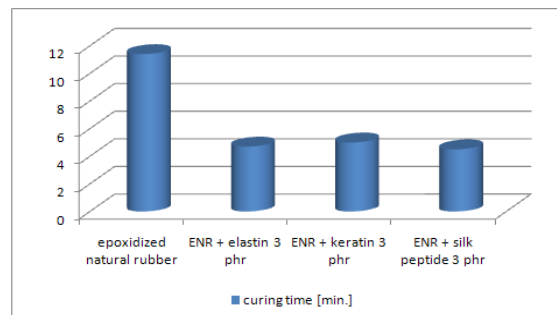

Fig. 3. Influence of the applied hydrolysates on the curing time of ENR mixtures.

	M_{min}, dNm	ΔM	$\tau_{0.9}$, min
Unfilled ENR	1.7	9.4	11.4
K-10, 5 phr	3.0	36.3	5.3
K-10, elastin, 3 phr	2.2	10.1	4.3
K-10, keratin, 3 phr	1.7	16.4	3.8
K-10, silk proteins, 3 phr	3.0	39.8	4.6

Table 1: Curing time $\tau_{0.9}$, minimum torque moment of blends M_{min}, increase of torque moment during curing ΔM for EPR mixtures.

	M_{min}, dNm	ΔM	$\tau_{0.9}$, min
unfilled ENR	1.7	9.4	11.4
Cloisite 15A, 5 phr	3.0	36.3	5.3
Cloisite 15A, 5 phr elastin, 3 phr	2.2	10.1	4.3
Cloisite 15A, 5 phr keratin, 3 phr	1.7	16.4	3.8
Cloisite 15A, 5 phr silk proteins, 3 phr	3.0	39.8	4.6

Table 2: Curing time $\tau_{0.9}$, minimum torque moment of blends M_{min}, increase of torque moment during curing ΔM for EPR mixtures.

Our investigation showed that application of hydrolysates increase the tensile strength of ENR vulcanisates (table 3-4, fig. 4). We observed that the strengthening effect of filler significantly enhanced in a presence of hydrolyzed keratin proteins and silk proteins. Probably these hydrolysates allowed to obtain better dispersion of the filler in rubber

matrix. The addition of hydrolysates did not affect the elongation at break.

	SE$_{100}$, MPa	TS, MPa	Eb, %
---	0.68	10.70	777
elastin	0.67	12.77	772
keratin	0.80	18.54	787
silk proteins	0.71	13.59	774

Table 3: Mechanical properties of ENR vulcanisates containing 3 phr of hydrolysates. SE$_{100}$ – 100% modulus, TS – tensile strength, Eb – elongation at break.

	SE$_{100}$, MPa	TS, MPa	Eb, %
unfilled ENR	0.68	10.70	777
K-10, 5 phr	0.73	15.11	801
K-10, elastin, 3 phr	0.78	12.50	761
K-10, keratin, 3 phr	0.95	18.54	704
K-10, silk proteins, 3 phr	0.77	17.68	794

Table 4: Mechanical properties of ENR vulcanisates containing K-10 (5 phr) and hydrolysates (3 phr). SE$_{100}$ - 100% modulus, TS-tensile strength, Eb-elongation at break.
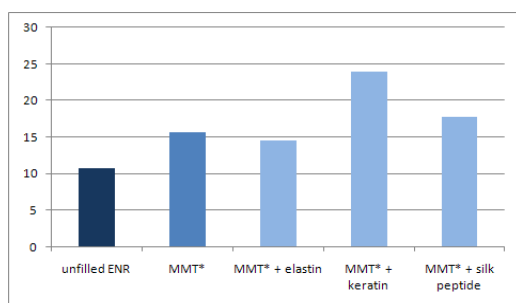

Fig. 4: Tensile strength [MPa] of ENR vulcanisates containing 5 phr of Cloisite 15A.

	W$_1$	W$_1$- W$_5$
---	3.04	1.23
elastin	2.66	1.44
keratin	1.79	1.05
silk proteins	2.35	1.22
K-10	3.41	1.84
K-10, elastin	2.92	1.65
K-10 keratin	2.09	1.18
K-10 silk proteins	2.54	1.25
Cloisite 15A	2.35	1.06
Cloisite 15A, elastin	3.64	2.29
Cloisite 15A, keratin	3.66	2.45
Cloisite 15A, silk proteins	4.44	2.68

Table 5: Hysteresis of ENR. W$_1$ – hysteresis during 1st strain, W$_5$ – hysteresis during 5th strain.

In tables 5 are presented the results of hysteresis measurements. The application of hydrolysates did not influence on the hysteresis of ENR vulcanisates.

From fig. 5 it follows that crosslink density of ENR vulcanisates increased considerably when hydrolysates are added to rubber mixture. Moreover this effect is also observed for the vulcanisates containing Cloisite 15A (table 6) . Keratin increased the content of ionic crosslinks in the elastomer network Δν.
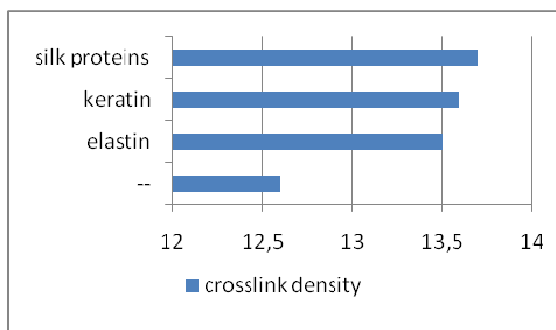

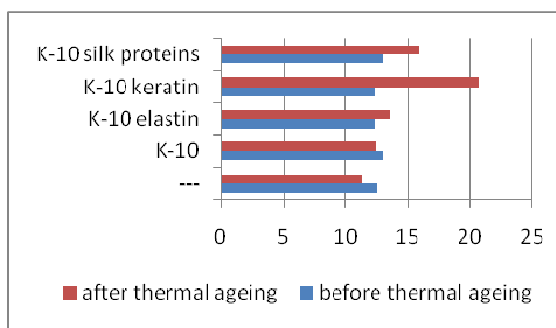Fig. 5: Crosslink density $\nu*10^5$ (mole/cm^3) of ENR vulcanisates containing different hydrolysates.

Fig 6: Crosslink density $\nu*10^5$ (mole/cm^3) and crosslink density after thermal ageing ν_T*10^5 (mole/cm^3) of ENR vulcanisates containing different hydrolysates and K-10 monmorillonite.

The influence of thermal ageing of the crosslink density and mechanical properties of vulcanisates was studied (fig 6, table 6). We observed an increase of crosslink density after thermal ageing in elastomeric composites containing used hydrolysates. This effect was not observed in case of unfilled or filled only with montmorillonites vulcanisates. The crosslink density for these vulcanisates decreased after thermal ageing.

	ν, mole/cm^3	$\Delta\nu$, %	ν_T mole/cm^3
Cloisite 15A	12.7	0.6	12.6
Cloisite 15A, elastin	13.4	0.6	13.8
Cloisite 15A, keratin	18.6	0.8	18.8
Cloisite 15A, silk proteins	13.2	0.6	14.6

Table. 6: Crosslink density $\nu*10^5$ (mole/cm^3) , the content of ionic crosslinks in the elastomer network $\Delta\nu$ and crosslink density after thermal ageing ν_T*10^5 (mole/cm^3) of ENR vulcanisates containing different hydrolysates and Cloisite 15A.

As is shown in tables 7 – 9 the application of hydrolysates influenced on the aeging coefficient K. Hydrolysates improved thermal resistance of unfilled vulcanisates, vulcanisates characterized higher values of the aeging coefficient K . Addition of modified montmorillonite Cloisite 15A to ENR led to decrease value of the aeging coefficient K. Probably lower thermal resistance is caused by the presence of aquaternary ammonium salt used to modification of montmorillonite. In case of vulcanisate containing unmodified montmorillonite K-10 this effect did not occurred, the aeging coefficient K was higher in comparision to unfilled vulcanisate.

	TS, MPa	Eb, %	K
---	7.80	669	0.62
elastin	10.59	682	0.73
keratin	16.42	607	0.68
silk proteins	15.87	756	1.14

Table 7: Mechanical properties after thermal ageing of ENR vulcanisates containing 3 phr of hydrolysates. TS – tensile strength, K - the aeging coefficient

	TS, MPa	Eb, %	K
Cloisite 15A	15.98	762	0.56
Cloisite 15A, elastin	16.89	703	1.08
Cloisite 15A, keratin	25.04	636	0.92
Cloisite 15A, silk proteins	14.20	644	0.65

Table 8: Mechanical properties after thermal ageing of ENR vulcanisates containing Cloisite 15A (5 phr) and 3 phr of hydrolysates. TS – tensile strength, K - the aeging coefficient.

	TS, MPa	Eb, %	K
K-10	14.36	759	0.90
K-10, elastin	9.92	663	0.69
K-10, keratin	14.66	578	0.65
K-10, silk proteins	14.70	694	0.73

Table 9: Mechanical properties after thermal ageing of ENR vulcanisates containing K-10 montmorillonite (5 phr) and 3 phr of hydrolysates. TS – tensile strength, K - the aeging coefficient

4 CONCLUSIONS

The addition of hydrolizates decreased curing time of ENR rubber crosslinked by sulphur curing system. It was found that the mechanical propereties of filled ENR vulcanizates were better in composites containing keratin and silk proteins. The hydrolysates improved the thermal resistance of vulcanizates, also they influenced crosslink density of a filled ENR rubber. The SEM studies showed that the application of hydrolyzed proteins derived from elastin, keratin and silk as a modifying substance improved the dispersion of the MMT in the ENR matrix. The application of hydrolysates resulted in an increased susceptibility for degradation of ENR during the storage on land and composting.

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