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A. Malicka-Soczka*, L. Domka**, A. Kozak***

KAOLIN MODIFIED WITH SILANE COMPOUNDS AS A FILLER USED IN RUBBER INDUSTRY

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Kaolin unmodified and modified with the following silanes: 3-aminopropyltriethoxysilane, N-2-aminoethyl-3-aminopropyltriethoxysilane and 3-metacryloxypropyltrimethoxysilane has been characterised as to its physico-chemical properties (DTA and SEM methods) and mechanical performance. The course of vulcanisation of rubber blends and physical properties of butadiene–styrene rubber (KER 1500) vulcanisates containing unmodified and modified kaolin have been determined. The vulcanisates filled with kaolin modified with silane compounds containing amine groups have been found to show better mechanical performance than those with kaolin modified with 3 metacryloxypropyltrimethoxysilane and unmodified kaolin.

key words: kaolin, surface chemical modification, rubber (KER 1500)

INTRODUCTION

One of the methods for obtaining polymer materials of improved physico-chemical properties, leading at the same time to reduction of the cost of their production is the introduction of mineral fillers into the polymer matrix. The most often used white fillers are kaolin and chalk (Alexandre, Dubois, 2000, Lebaron et al., 1999). The

* Department of Metalorganic Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

** Department of Macromolecular Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan

*** Department of Water Protection, Faculty of Biology, Adam Mickiewicz University, Umultowska 89, 61-614 Poznan, Poland

mechanism of polymer reinforcement by the fillers has been the subject of interest of many authors. It has been established that of the greatest importance is the activity of the fillers that depends on many parameters such as the surface area, degree of dispersion in the polymer system, polymer-filler and filler-filler interactions (Zaborski et al., 1993, Domka, 1990, 2008). The free hydroxyl groups on the surface of the filler molecules hinder a direct introduction of the filler into the hydrophobic polymer matrix, leading most often to the formation of agglomerations in the matrix. To minimise these tendencies the surface of the filler should be chemically modified with the use of the so-called promoters of adhesion and reinforcement (Domka, 2005, 2006). Such promoters are organic acids and their derivatives, surfactants, polyoxyethylene glycols, organic proadhesive compounds of zirconium and titanium and silane coupling agents, playing a particularly important role in the systems kaolin-polymers. Chemical modification of the fillers considerably changes the morphology of the filler molecule surface and affects the filler influence on the properties of the composite. Kaolin is used as a filler in numerous cheap blends that have to be resistant to wear, and used for shoe soles, shoes, floor covering, bicycle tyres and conveyer belts (Domka, 1983). The stiffening effect of kaolin in rubber blends is used in production of hoses, inner tubes, extruded cords and rings. As kaolin is neutral to human health, it is used for production of sanitary products, household appliances, toys and others. The kaolin resistance to acids permits its use in production of elasto- and plastomers (ebonite blends) used as anticorrosion covers and protective clothing.

EXPERIMENTAL

Kaolin KOG from the bed Surmin near Bolesławiec was studied. Modification of kaolin was performed with the following silane compounds : 3-aminopropyltriethoxysilane, N-2-aminoethyl-3-aminopropyltriethoxysilane and 3-metacryloxypropyltrimethoxysilane. The modification was made using 3 wt parts of the modifying agent per 100 wt parts of kaolin. To ensure homogeneous cover of kaolin surface, the modification was performed in a mixture of water and ethanol using different amounts of the solvent for different silane agents, see Table 1.

Table 1. Silane compounds used for kaolin surface modification and the composition of the solvent used

Silane agent	H_2O [cm^3]	EtOH [cm^3]
3-aminopropyltriethoxysilane	70	50
N-2-aminoethyl-3-aminopropyltriethoxysilane	80	50
3-metacryloxypropyltrimethoxysilane	50	50

Modification with the three silane agents was performed under the same conditions. Appropriate amounts of kaolin, modifying agent and solvent were placed in a glass vessel and stirred for 60 minutes by a homogenizer Universal Laboratory Aid type MPW-309. The modified kaolin was dried at room temperature, and filtered through the mesh size 75 μm.

The unmodified and modified kaolin samples were subjected to physico-chemical examination. Analysis of the morphology and microstructure of the samples studied were based on SEM images Fig.1. DTA measurements were performed in helium atmosphere; the results are presented in Fig. 2. Moreover, the rubber blends of the composition according to the Polish Norm PN-87/C-04258, containing unmodified and modified kaolin were studied (Table 2).

Table 2. Composition of the rubber blends studied

Components	Weight parts
Butadiene-styrene rubber (KER 1500)	100
Stearin	1
Titanium white	3
Kaolin unmodified	6.5
or modified with 3-aminopropyltriethoxysilane	6.5
or with N-2-aminoethyl-3-aminopropyltriethoxysilane	6.5
and with 3-metacryloxypropyltrimethoxysilane	6.5
Accelerator – Vulkacit	1
Sulphur	1.75

The course of vulcanisation of rubber blends was characterised by a vulcameter with oscillating rotor at 150 ºC according to PN-ISO 3417. The following physico-mechanical parameters of the vulcanisates were determined.

Shore hardness according to PN-80/C-04238

- Elasticity according to PN-88/C-04255
- Tearing strength - PN-ISO 34-1, method B, procedure (a)
- Tensile strength - PN-ISO 37, ore type 1
- Stress on elongation by 300 % and 500 %
- Grindability - PN-75/C-04235.
- Permanent deformation on compression at 30 Hz measured on Goodrich apparatus, according to PN-81/C-04292.

RESULTS AND DISCUSSION

Modification of the kaolin surface with the silanes used has insignificantly changed the agglomeration of particles; SEM photographs of the unmodified and modified kaolin samples show relatively large crystal structures. The most effective for disintegration of the agglomerations is the modification with 3-aminopropyltriethoxysilane, less effective is the modification with 3-metacryloxypropyltrimethoxysilane.

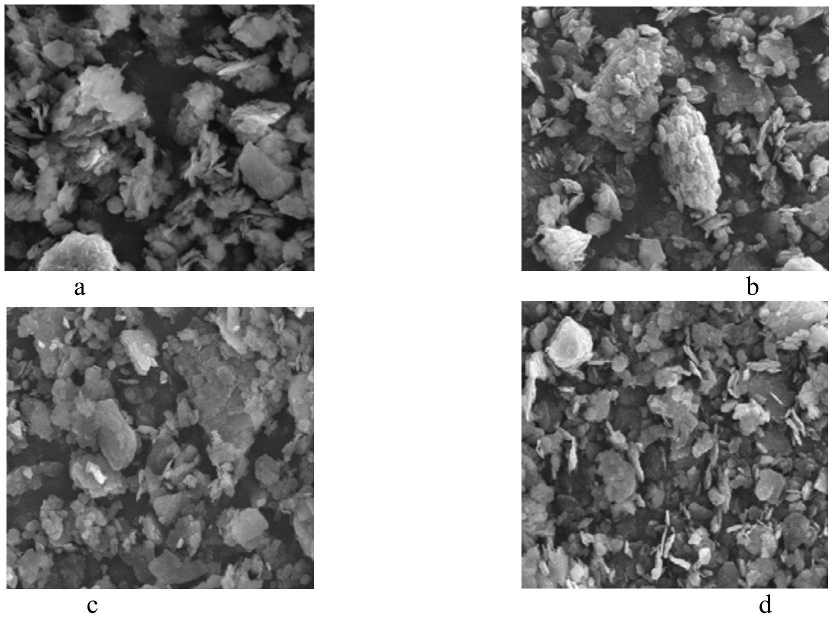


Fig. 1. SEM images of a) unmodified kaolin, b) kaolin modified with N-2-aminoethyl-3-aminopropyltriethoxysilane, c) kaolin modified with 3-metacryloxypropyltrimethoxysilane, d) kaolin modified with 3-aminopropyltriethoxysilane .

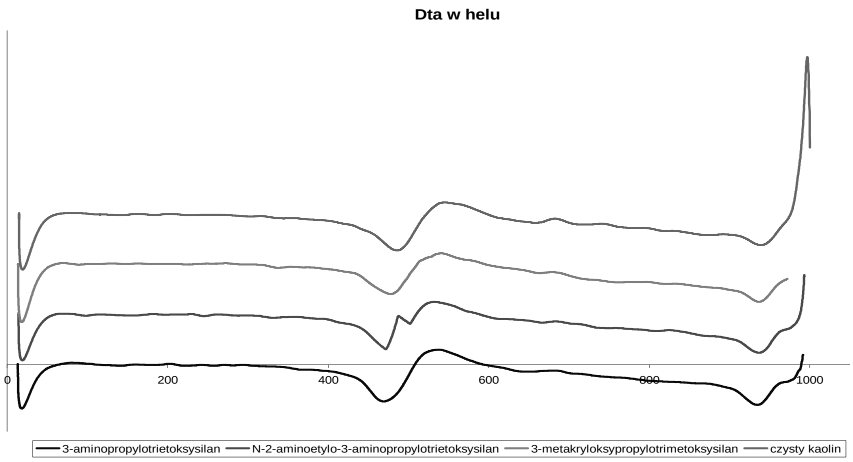


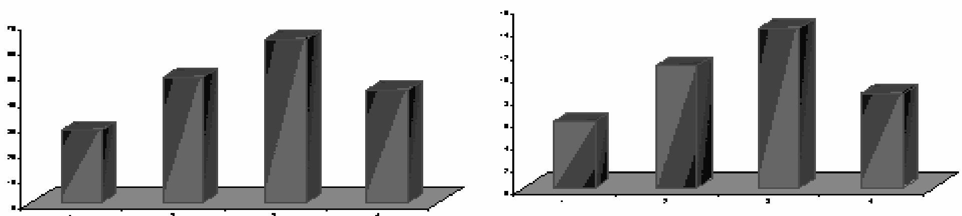
Fig. 2. DTA curves recorded for kaolin unmodified and modified with the silanes studied

Figure 2 presents the DTA curves for the kaolin samples studied. The endothermic peaks at 470 ºC and 500 ºC are much sharper for the kaolin sample modified with N-2-aminoethyl-3-aminopropyltriethoxysilane than for unmodified kaolin. For the unmodified kaolin the endothermic peak occurs at 490 ºC, whereas for the samples of modified kaolin this peak is shifted to lower temperatures by 10 or 20 ºC. For kaolin modified with 3-metacryloxypropyltrimethoxysilane it is shifted by 10 ºC, while for kaolin modified with silane containing amine groups by 20ºC (Lebaron P.C., 1999)

Table 3. Physico-mechanical characterisation of vulcanizates filled with kaolin unmodified or modified with the silanes studied

Parameter	unit	Sample number			
		1	2	3	4
Conditions of vulcanisation	min	50	20	15	50
Shore hardness	ShA	54	58	60	56
Elasticity	%	44	50	50	46
Tearing strength	kN/m	28.3	49.0	63.6	43.9
Tensile strength	MPa	5.9	10.9	14.2	8.4
Stress on elongation by 300% 500%	 MPa MPa	 2.1 2.7	 8.3 10.6	 8.2 12.3	 4.6 5.8
Grindability	cm^3	0.169	0.199	0.097	0.131
Permanent deformation	%	13.0	1.63	1.86	2.70

Table 3 presents results of the physico-mechanical tests of vulcanisates filled with modified and unmodified kaolin. According to the results of these tests, samples studied can be divided into 2 groups. Grup 1 includes tests involving blends and vulcanisates containing unmodified kaolin (Alexandre, Dubois 2000) and kaolin modified with 3-metacryloxypropyltrimethoxysilane (Domka, 1990), while grup 2 includes tests involving blends and vulcanisates containing kaolin modified with 3-aminopropyltriethoxysilane (Lebaron, 1999) and N-2-aminoethyl-3-aminopropyltriethoxysilane (Zaborski et al., 1993). The most important mechanical parameters are shown in Fig. 3.



a b

Fig. 3. Diagrams illustrating the tearing strength (a) and tensile strength (b) of the vulcanizates obtained

The blends filled with kaolin modified with silanes containing amine groups (Lebaron et al., 1999, Zaborski et al., 1993) are characterised by higher elasticity, hardness and stress on elongation by 300 % and 500 %, greater grindability and tensile strength than those with kaolin unmodified or modified with 3-metacryloxypropyltrimethoxysilane silane. High tensile strength was obtained for the rubber filled with kaolin modified with silanes containing amine groups (Lebaron et al., 1999, Zaborski et al., 1993). The results have shown that the use of kaolin modified with silanes with amine groups as filler improves the tensile strength and grindability of the material filled. The parameters characterising vulcanizate 1 were much poorer then those obtained for the other samples (Zaborski et al., 1993).

CONCLUSIONS

The modification of kaolin with silane agents was found to reduce the agglomeration of particles and change the positions of the peaks on the DTA curves towards lower temperature. The use of kaolin modified with silane agents containing amine groups as filler of rubber blends has permitted a considerable shortening of the time of vulcanisation and has improved the tensile strength and tearing strength of the vulcanisates. Particularly beneficial was the influence of 3-aminopropyltriethoxysilane and N-2-aminoethyl-3-aminopropyltriethoxysilane on the grindability of the vulcanisates

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Próby kaolinu niemodyfikowanego jak również kaolinu modyfikowanego za pomocą następujących silanów: 3-aminopropylotrioksysilan, N-2-aminoetylo-3-aminopropylotrioksysilan i 3 metakrylooksypropylotrioksysilan, zostały scharakteryzowane pod katem właściwości fizykochemicznych (analiza DTA i SEM) oraz właściwości mechanicznych. Przeprowadzono procesy wulkanizacji mieszanek gumowych oraz określono fizykochemiczne właściwości wulkanizatów z gumy butadienowo-styrenowej, które zawierały modyfikowany lub niemodyfikowany kaolin. Wulaknizaty z wypełnieniem kaolinowym, który to kaolin był modyfikowany związkami zawierającymi grupy aminowe wykazywały lepsze właściwości mechaniczne niż wulkanizaty zawierające kaolin niemodyfikowany lub kaolin modyfikowany 3-metakryloksypropylotrioksysilanem.

słowa kluczowe: kaolin, powierzchniowa modyfikacja, guma KER 1500