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USE OF CLAY SORPTIVE MATERIALS IN THE SYNTHESIS OF POLYMER MATERIALS

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Abstract. The paper suggests the solution to the urgent problem of increasing the level of environmental safety of industrial wastewater treatment from heavy metal using natural and modified bentonite.The use of spent bentonite in the processes of filling polymers is investigated. The aim of the research was to study the influence of fillers on the crosslinking course and functional properties of vulcanized elastomeric mixtures. Test research compositions included chloroprene rubber and chlorosulfonated polyethylene. Nanofillers were used as a strengthening substance. Montmorillonite and spent montmorillonite saturated with copper ions were used as nanofiller.

Keywords: rubber, filling, montmorillonite, heavy metal ions.

1. Introduction

The combination of the elastomer with the crosslinking agent alone is often insufficient in terms of the functional properties of the final product, which is rubber material, so it is of high necessity to apply a suitable filler (active, semi-active, or passive) and many other additives. Only after crosslinking does the rubber mixture obtained in this way acquires the appropriate properties, largely adapted to the conditions in which the material will be used. The growth of market demands leads to the search for new substances with a strengthening effect. Therefore, in recent years, interest in nanofillers has significantly grown (Mokrousova at al., 2015).

An overview of recent research publications has shown that an important area of study today is to identify effective methods of regeneration and disposal of sorbents that have previously been used as sorbents in wastewater treatment and municipal wastewater. After all, the utilization of absorptive materials helps not only reduce the man-made load on the environment, but also to improve the technology of creating alternative materials due to the use of high-quality clay material (Malovanyy at al., 2020).

At present, used highly dispersed minerals are widely applied in many sectors of the economy, including the production of various consumer goods. However, the limited scientific research leads to a low level of application of used clay sorbents in polymer production processes. Their application is based on specific colloid-chemical properties, which are due to the crystal mineral structure. The most common types of minerals extracted in Ukraine are kaolin, montmorillonite, palygorskite, hydromica and a natural mixture of montmorillonite and palygorskite. The chemical composition and features of the crystal structure of highly dispersed minerals determine a complex of their sorption, exchange, coagulation properties and ability to disperse (Malovanyy at al., 2021). The relevance of this

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research for production is also due to the need to dispose of sorbents used for wastewater treatment, in particular for heavy metal ions treatment.

The influence of fillers – modified montmorillonite – on crosslinking and on functional properties of compositions containing styrene-butadiene rubber, chloroprene rubber or chlorosulfoned polyethylene was studied. Nanofillers were used as a reinforcing substance.

The purpose of the research paper was to study the use of montmorillonite and waste materials previously already used in water treatment technologies as an adsorbent. Such filled elastomeric compositions are expected to have satisfactory properties.

2. Research results

The influence of fillers that absorbed heavy metal ions (spent adsorption material) on crosslinking and properties of elastomeric mixtures was studied. A mixture of chloroprene rubber with styrene-butadiene (CR / SBR) was investigated (Malakhov, 2009). Copper (I) oxide (Cu_2O) was used as a vulcanizing agent for the tested mixtures of CSM / SBR and CR / SBR (Pagacz, Pielichowski, 2007).

The following materials of industrial production were used for the research:

1. Chloroprene rubber (CR) named Baypren 216, manufactured by Lanxess GmbH (combined chlorine content of about 40 %);

2. Chlorosulfonic polyethylene (CSM) under the trade name Hypalon 20, manufactured by DuPont (compatible chlorine content of about 29 %);

Nanobent ZR1 (montmorillonite modified with dimethylbenzyl-alkylammonium chloride);

Nanobent ZR2 (montmorillonite spent, waste water treatment technologies with a content of Cu^{+2} ions 3 %, modified with dimethylbenzyl-alkylammonium chloride)

Supplementary materials:

Vulcanizing group

• copper oxide (Cu_2O) from POCh S.A.

• stearic acid (stearin) from Chemical Worldwide Business S.A company.

The mixtures were prepared on laboratory rollers with the following cylinder dimensions: the diameter – 200 mm, the length – 450 mm, the temperature – 433 K. The total preparation time of each mixture did not exceed 10 minutes. The mixtures were settled for about 24 hours before vulcanization (Michalska, 2016).

The composition of the elastomeric mixtures is presented in Table 1.

The fillers were added to the polymer hot solution at the beginning of mixing. After cooling and settling, the components of the vulcanizing group were added. Vulcanization was carried out on an electric press. Crosslinking of elastomeric mixtures was carried out by placing in steel moulds between the plates of the hydraulic press, heated electrically, at a temperature of 433K. Crosslinking took place during the time determined by the kinetics of vulcanization (30 min), under the pressure of 300 bars. The obtained moulds were conditioned for 24 hours. Appropriate samples were then cut from the vulcanizate to test the research specimens.

Table 1

The composition of the elastomeric mixtures Butadiene Styrene Rubber (SBR)/Chloroprene Rubber (CR)

Test samples	1 (control sample)	2	3	4
CR	80	80	80	80
SBR	20	20	20	20
Cu_2O	4	2	4	4
Stearyna	1	1	1	1
ZR1	–	–	5	–
ZR2	–	7	–	5

The results of determining the kinetics of vulcanization of the test samples are presented in Table 2. It is determined that the presence of fillers affects the crosslinking of mixtures of CSM / SBR with copper (I) oxide. The formation time (t02) for the unfilled mixture was 1.06 minutes. Among the mixtures containing montmorillonite, the shortest firing time (t02 = 1.02 min.) is achieved when the consumption of filler from used montmorillonite is 5m.h., and this figure is 0.5 min. lower than for the worst option 2. That is, the time of structure formation depends both on the filler content and the expense of copper oxide (I).

The minimum swirling moment for mixtures containing fillers reaches higher values compared to the control sample. This means that the fillers affect the viscosity of the mixture, significantly increasing it. The highest value of the minimum torque is observed for sample 2, which indicates that the fillers' density and viscosity affect the value of M_{min} in the first place.

The largest values of the increase in torque after a given heating time (ΔM30, ΔM40, dNm) were observed in mixture 2 containing the maximum of montmorillonite at the same total consumption of Cu_2O, with the values of all samples higher than the control sample without filling. This may be evidence that the degree of crosslinking is affected by both the cost of the filler and

the vulcanizer. Analysis of the values of Table 2 allowed establishing the minimum vulcanization time of the samples – 30 minutes.

Table 2

Characteristics of the filler ability to structure formation

Sample	1	2	3	4
t_{02} [min]	1.06	1.07	1.04	1.02
M_{min} [dNm]	0.51	1.04	0.70	0.62
ΔM_{30} [dNm]	3.18	5.43	4.67	4.75
ΔM_{40} [dNm]	3.99	6.58	4.86	5.30
ΔM_{60} [dNm]	1.06	1.07	1.04	1.02

The obtained values of bulk equilibrium swelling (Fig. 1) confirm the conclusions made on the basis of kinetic analysis of CR / SBR / Cu_2O mixtures. Vulcanizates containing supplementary copper ions in the filler were more crosslinked and less swollen in toluene and heptane.

In general, vulcanizates swell better in toluene than in heptane. This is due to the greater thermodynamic similarity of toluene with the investigated rubber mixture.

The results of studies of the physico-mechanical properties of CR / SBR vulcanizates are presented in Table 3. The research results reveal that the lowest tensile strength has sample 2, but after aging the material its properties are the best. Also, sample 2 is characterized by high elongation of native samples and samples after thermal oxidation. However, summarizing the indicators of stress – elongation, it should be noted that sample 4 is closer in value to both the control sample and sample 3.

Based on the research results of elastomers elastic-deformation properties (Fig. 2), we conclude that the lower the value of the modulus of elasticity ΔG' is, the less extensive the structure of the filler the vulcanizate has. The tests reveal that sample 4, containing used bentonite in the amount of 5 ppm, received the highest value of the elasticity modulus ΔG'= 1.971 MPa, i.e., it has the most branched structure of the filler. Of all the filled vulcanizates, control sample 1 was characterized by the lowest value of ΔG '= 1.536 MPa. Thus, the elasticity modulus can be an indirect indicator that characterizes the filling efficiency of the polymer (Pagacz, Pielichowski, 2007).

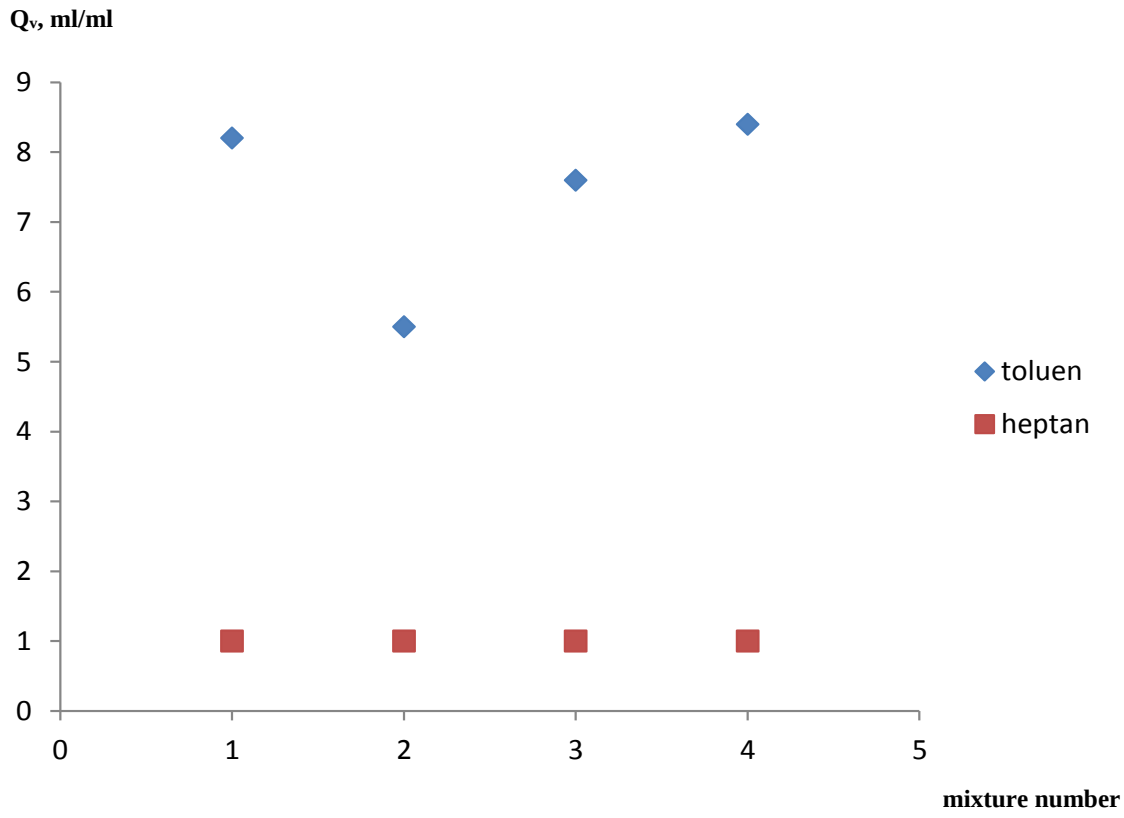

Fig. 1. Equilibrium bulk swelling of test samples in inorganic solvents

Table 3

Characteristics of the deformation of vulcanized elastomers

Samples	1		2	3	4
	Mechanical properties of samples				
S_{e100}[MPa]	1.14±0.04		2.23±0.01	1.01±0.02	1.14±0.03
S_{e200}[MPa]	1.52±0.07		2.53±0.02	1.36±0.06	1.56±0.03
S_{e300}[MPa]	1.89±0.10		2.77±0.04	1.76±0.08	1.99±0.05
TS_b[MPa]	9.93±0.30		4.62±0.04	9.99±0.28	7.74±0.14
	Mechanical properties of samples after thermal oxidative aging				
S'_{e100}[MPa]	0.49±0.02		0.62±0.05	0.66±0.03	0.71±0.02
S'_{e200}[MPa]	0.88±0.07		1.09±0.06	1.15±0.06	0.04±0.06
S'_{e300}[MPa]	-		1.64±0.06	-	-
TS'_b[MPa]	1.31±0.03		1.78±0.03	1.56±0.10	1.52±0.05

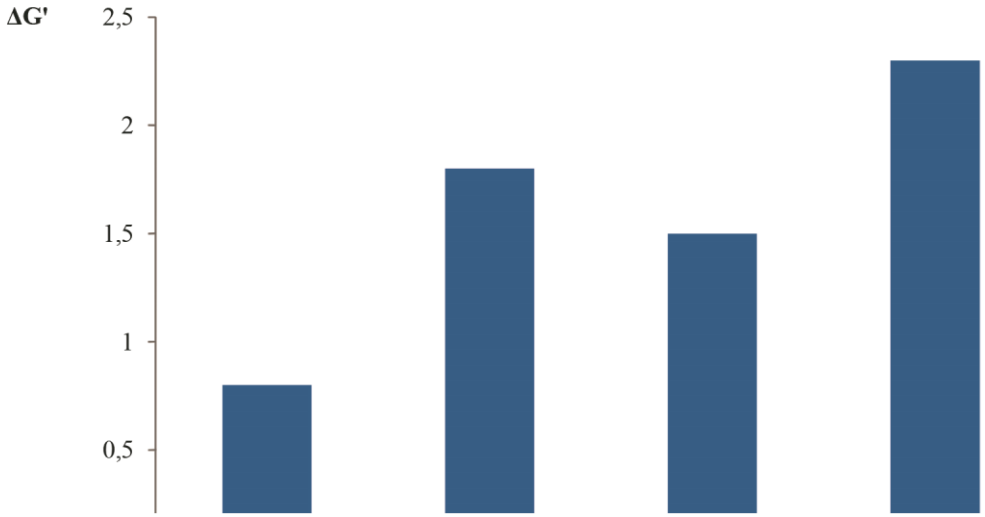

Fig. 2. Dependence of the difference of the elasticity modulus on the type of filler CR / SBR samples

The burning time in the air and the oxygen index of the tested vulcanized elastomers were determined. The results are presented in Table 4.

Table 4

Burning time in air and oxygen index of vulcanizates CR / SBR / Cu_2O

Samples of elastomer mixtures				
Parameter, unit of measurement	1	2	3	4
Average burning time in the air				
t_s [s]				
	< 5	< 5	< 5	< 5
Oxygen Index				
OI [%]	33	31	35	36

Analyzing the aforementioned research results, we can conclude that the tested vulcanized elastomers are non-combustible due to the classification of the determined oxygen index. The OI value of all vulcanizates exceeded 28 %. The highest value of the oxygen index is sample 4 (OI = 37 %).

3. Conclusions

The use of bentonite in the production of polymers provides the high-quality formation of the polymer structure due to specific colloidal and chemical properties of the main mineral of bentonite clays – montmorillonite. The application of bentonite, previously used in water treatment technologies, further solves the problem of efficient utilization of used adsorption materials.

The degree of elastomer crosslinking is affected by both the expense of the filler and vulcanizer. The montmorillonite origin has little effect on the processes of structure formation of CSM / SBR mixtures.

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