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The Mechanical Properties Improvement of Polyurethane Rubbers by Using Titanium Oxide and Calcium Carbonate Modifiers (Additives)

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Abstract: *The structure of polyurethane and the physico-chemical properties of its components are considered. The most promising modifiers have been selected:* TiO_2*,* $CaCO_3$*. The features of the preparation of the studied polyurethane mixture, its composition, manufacturing technology and equipment are described in detail. The geometric properties, manufacturing processes and testing methods of samples are presented. The graphical dependencies of the influence of the parameters of sample preparation on their mechanical properties such as hardness, tensile stress at break, Jung's modulus are given. The rational parameters of the technology for the production of samples modified with fillers to give them stable mechanical properties have been set. The maximum proportions of these fillers in polyurethane rubber are limited to 30-35%. It is proved that the addition of* TiO_2 *and* $CaCO_3$ *to the composition of polyurethane rubbers gives them special properties that allow them to expand the range of their industrial usage.*

Keywords*: titanium oxide, calcium carbonate, polyurethane rubber*

1. Introduction

One of the polymer compounds advantages is that the use of modifiers can significantly improve their mechanical properties. The new polymer compounds not only with improved mechanical properties, but also with increased corrosion resistance and lower cost compared to analogues can be obtained by including polymers in compounds such as aluminum oxides (Al_2O_3), glass fiber and carbon components [1].

The polymer compounds are more actively used in additive technologies than other materials due to the simplicity of preparation, economy and specific physicochemical properties. However, the polymer original materials have very low wear resistance and hardness. The mechanical properties investigation of polymer composites based on low density polyethylene (LDPE) with modifiers TiO_2, AL_2O_3, $CaCO_3$ as reinforcing materials has shown that the tensile and flexural strength grow up with an increase in the amount of aluminum and calcium carbonate, and an increase in the plasticity of the samples leads to a decrease in their impact toughness [2].

The issue investigation of improving mechanical properties by modifying the epoxy matrix with small particles of Al_2O_3, SiO_2 и TiO_2 has shown that the flexural strength is higher for the epoxy resin variant modified by SiO_2, and hardness and impact toughness increase when the epoxy compound is modified by aluminum oxide [3].

There are known studies on the use of SiO_2 as a cheap filler for polyurethane (PU), which was obtained by the reaction of polyol with isocyanate at room temperature, followed by the addition of SiO_2 in different proportions and pouring it into a mold to get samples. The results have shown that the use of silicon dioxide in polyurethane improves the mechanical properties such as hardness and Jung`s modulus, but as the proportion of silicon dioxide increases, the same properties begin to worsen [4].

In another study the material was produced by adding rice husk to polyurethane (RH) and the inclusion of the resulting composition as a filler to polyethylene glycol (polyol). The impact strength

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and tensile and flexural strength of the material produced in this way grow up with an increase in the amount of RH and reducing the particle size of rice husk. This is due to the large reaction area between OH and NCO. It was found that when the resulting material was added to dimethylformamide (DMF) and the amount of increased RH, the swelling volume was less. If the resulting material is added to water, the volume of swelling is greater due to the water absorption of the group OH RH [5].

The researchers [6] succeeded in obtaining polyurethane material from rape and sunflower oils with (4,4 methylen-bis-(phenylisocyanate(MDI)) and investigating the influence of titanium dioxide on its properties. The samples were prepared by mixing polyol with different proportions of MDI. It has been found that the mechanical properties of this improve by adding TiO_2.

The use of calcium carbonate as a modifier in thermoplastics leads to an improvement in Jung`s modulus, but reduces the impact strength, impact toughness and elongation at break [7]. When studying the influence of calcium carbonate on the mechanical properties of thermoplastic polyurethane based on recycled poly(ε-caprolactone), taking into account their water solubility, it was found that calcium carbonate $CaCO_3$ does not affect Jung`s modulus in the temperature range from 20°C to 50°C, improves mechanical properties at temperatures up to 65°C and increases the melt fluidity of thermoplastics [8].

The study [9] showed that the addition of both nano-fillers improved the mechanical properties of the composite, including an increase in tensile strength, flexural strength, and impact strength. The best mechanical properties were observed for the composite with a combination of Al_2O_3 and SiC nano-fillers. The improvement in mechanical properties was attributed to the enhanced interfacial bonding between the matrix and the fibers, as well as the reinforcement effect of the nano-fillers.

The study [10] resulted in showing that the addition of Precipitated Calcium Carbonate (PCC) increased the hardness and tensile strength of the composites. However, the elongation at break decreased with increasing PCC content. The thermal stability of the composites was improved by the addition of PCC. The results suggest that PU/PCC composites have potential applications in industries such as automotive, construction, and packaging.

The study [11] found that the composites with microfillers showed increased tensile strength, flexural strength, and impact strength compared to the control sample without microfillers. Moreover, the addition of microfillers also improved the thermal stability and reduced water absorption of the composites. The study suggests that the incorporation of microfillers can enhance the performance of natural fiber-reinforced polyester composites and make them suitable for various applications in the automotive, construction, and packaging industries.

Filler-containing polymer compounds are in great demand due to their low cost and wide range of applications. Due to their use, it is possible to adapt a wide range of polymeric materials to work in a particular working environment and without loss of quality and increase in cost. It should be noted that polyurethanes are an important class of polymers produced on an industrial scale by reacting polyol with diisocyanate using additional catalysts [12,13].

The aim of the study is to search for optimal ratios of the components that make up the polyurethane rubber in order to obtain rational properties. For this, it is necessary to study the effect of fillers such as titanium dioxide TiO_2 and calcium carbonate $CaCO_3$ on the mechanical properties of polyurethane elastomer.

2. Methods and materials

2.1. Test materials

- Rubber polyurethane

Polyurethane belongs to thermoplastic or thermosetting elastomers. Thermoplastic polyurethane consists of linear segmented block copolymers, and copolymers consist alternately of hard (HS) and soft (SS) segments.

The solid segment consists of diisocyanates and short-chain extensions, such as diamines, diols, which are rigid and highly polar, while soft parts formed from long linear chains of a dipole or polyol are flexible and weakly polar.

Thermosetting polyurethane is formed using one or a combination of the following factors:

- the use of polyol with more than two functional groups;
- replacement of natural glycol with a trifunctional hydroxyl compound;
- using an NCO/OH ratio greater than 1;
- insertion of segments (SS, HS, CE);
- use of isocyanates with more than two functional groups.

Figure 1 shows the structure of a polyurethane elastomer and Figure 2 shows a soft segment, a hard segment and a crosslinking agent in a polyurethane rubber structure.

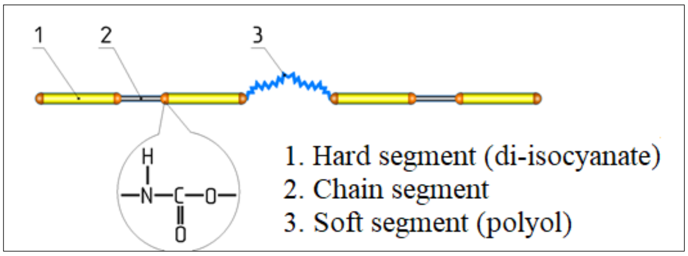

Figure 1. Polyurethane structure

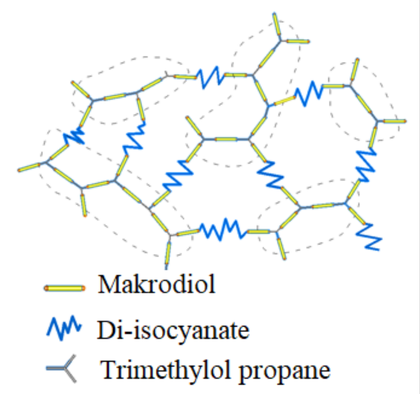

Figure 2. Soft segments, hard segments and a crosslinking agent in a polyurethane rubber structure in the structure of polyurethane rubber

Polyurethane rubber (Polyurethane Elastomer) was used in the study, which is a thermosetting polymer obtained by the reaction of polyols and diisocyanates produced by Sigma-Aldrich.

The equation below shows the reaction of isocyanate (isocyanate, R-NCO) with polyol (polyol, R'-OH), which occurs with the formation of polyurethane (polyurethane, R-NH-COOR'):

$$R\text{-}NCO + R'\text{-}OH = R\text{-}NH\text{-}COOR'$$

The polymerization reaction and the final properties of polyurethane are influenced by the physical properties, chemical composition and size of the component molecules.

Table 1 shows the properties of polypropylene glycol and diisocyanate

Table 1. Physical and thermal properties of polypropylene glycol and diisocyanate

Name	Polypropylene Glycols	Toluene diisocyanate
Physical state	Liquid	Liquid
Chemical formula	$C_3H_8O_2$	$C_9H_6N_2O_2$
Molecular weight, g/mol	1500-2000	174.16
Thermal conductivity, W/m.K	0.34	-
Density, g/cm^3	1.036	1.214

2.2. Cross-linker

In the production of polyurethane rubber castor oil (castor oil, chemical formula $C_{57}H_{104}O_9$, density 0.961 g/cm^3) was used as an additional material for polymer chains and it ensured their strength.

Iron acetylacetonate Fe(AA)$_3$ powder containing 12% iron was used as an accelerator for the reaction of polyol and isocyanate, which has the following characteristics: melting point 180°C; density 1.348 g/cm^3.

2.3. Fillers used

- Titanium dioxide TiO_2 produced by the company BASF Aktiengsellschaft is a white powder that does not dissolve in water. The grain size is 5 µm.
- Calcium carbonate $CaCO_3$. Odorless and tasteless powder that does not dissolve in water. The grain size is 15 µm. Table 4 shows some of its properties. Figure 6 shows the structure of this substance. Table 2 shows some of its properties

Table 2. Properties of titanium dioxide and calcium carbonate

Name	Titanium dioxide	Calcium carbonate
Physical state	Powder	Powder
Chemical formula	TiO_2	$CaCO_3$
Molecular weight, g/mol	79.87	100.0869
Boiling point, °C	2972	decomposes
Melting point, °C	1870	1339
Density, g/cm^3	3.9	2.7

2.4. Sample preparation method

The samples were prepared by mixing an accelerator (0.25%) with polyol (77.75%) and a crosslinking agent (11%). The composition was simultaneously heated to 65°C. and stirred with a magnetic stirrer until complete homogeneity. The furnace is connected to a vacuum pump to pump evaporating moisture out of the heating zone. The heating was carried out for 24 h at a constant temperature of 65°C Figure 3, after which titanium oxide and calcium carbonate were added to the mixture in portions as a filler in a percentage of 0 to 35% with continuous heating at 65°C and mechanical stirring until complete homogeneity. The mixture was then cooled to the following temperatures: the titanium oxide-containing mixture was cooled to 30°C; the calcium carbonate-containing mixture was cooled to 20°C. Isocyanate (11%) was added to the cooled mixtures with stirring for 30 min. Glass molds were made to create the billets. The glass mold consists of: a base with the size 30 cm by 30 cm; walls, width from 1 cm to 2 cm in the amount of 4 pieces. The thickness of the base is not regulated, the thickness of the walls was 3 mm. This made it possible to create a thickness of the poured mixture of 3 mm. The mixture was poured into the assembled mold, gently and slowly stirred and levelled along the walls of the mold with a spatula. To solidify the mixture, the molds with the samples were placed in a drying oven to keep it at 65°±1°C for the required time Figure 4 .

Figure 3. Drying furnace

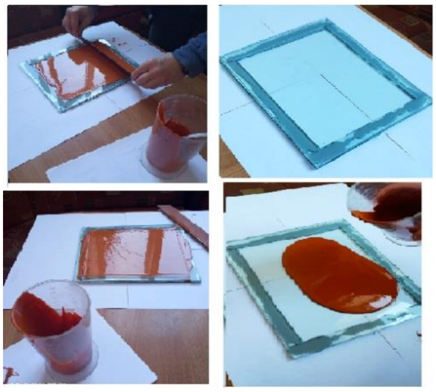

Figure 4. Blank creation process

2.5. Sample testing methods

For the production of test samples, a heater with a mechanized magnetic stirrer is used equipped with special blades that ensure a good mixing process.

Before testing, the samples were cut out of the plates according to the ASTM D882 standard in size, as shown in Figure 5. The samples obtained for testing are shown in Figures 6, 7.

The samples were tested on a universal testing machine CY 6040 Figure 8 equipped with a 1000 N strain gauge at a tensile rate (100 mm/min). The permissible relative error of load measurement comprised ±1%. Hardness was measured on the Shore-A scale Figure 9.

A micrometer for soft materials was used for measurements with an accuracy of 0,01mm Figure 10.

An electric furnace was used for the process of hardening the sample by heat treatment Figure 11.

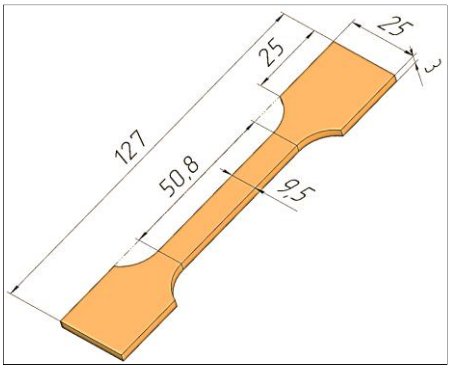

Figure 5. Geometric parameters of the test sample

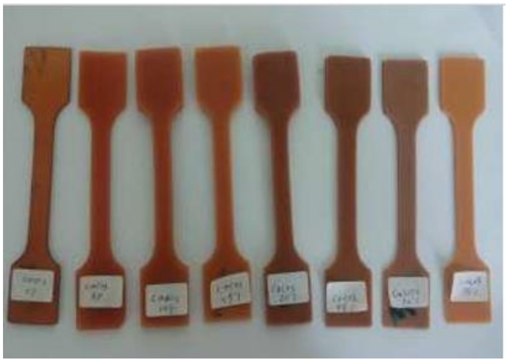

Figure 6. Tensile test samples (PU+(0-35% $CaCo_3$)

Figure 7. Tensile test samples (PU+(0-35% TiO_2))

Figure 8. The tensile testing device

Figure 9. The hardness tester

Figure 10. Micrometer

Figure 11. Thermo-furnace

3. Results and discussions

To select the rational ratio of the components of the polyurethane rubber mixture the results of studies in the sources were analyzed [14-16]. In the preparation of polyurethane rubber mixtures, a mixture having a polyol-to-isocyanate ratio (5/1) and a diol-to-triol ratio (5.3/1.1) is of interest. A number of experiments were conducted to select the basic ratio for further research.

The table of preliminary experiment 3 shows the mixtures with a percentage indication of their composition and presents the following designations characterizing the reaction.

The results of preliminary tests regarding the selection of the optimal ratio of the components of the polyurethane rubber mixture have shown that a structure with a homogeneous surface without bubbles was obtained in the PU12 sample, and therefore this ratio of the components was taken as the basis for samples preparation and their further study.

During the experiment it was found that the process of reacting the components of the PU12 mixture into a polymer fabric at room temperature of 29°C takes a long time, about 48 h, but the samples obtained have good elastic properties. As a result of chemical interactions between the mixture components there is a slight increase in temperature, and, therefore, reactions of materials used in studies with polyurethane rubber can be described as heat-distributing agents. Figure 6 shows the graphical dependence of the mixture temperature on time and indicates the maximum extreme temperature of the "maturity" of the mixture, the value of which is T = 42°C. This temperature transition usually indicates the end of chemical reactions between the components of the mixture. The decrease in the temperature of the mixture is due to heat loss because of heat exchange with the external environment. This is due to the fact that the experiment shown in Figure 12 was not carried out with a heat-insulated environment.

Table 3. Data from the initial experiment

Sample	Accelerator, %	Polyol, %	Crosslinking agent, %	Isoc-yanates, %	Results
PU1	0	71.05	14.75	14.20	there was no reaction;
PU2	1	70.05	14.75	14.20	very fast reaction, inhomogeneous structure of the mixture is filled with bubbles of different sizes (difference in solidification time + loose areas)
PU3	0.5	70.55	14.75	14.20	very fast reaction, inhomogeneous structure of the mixture with large volume bubbles (difference in solidification time + loose areas)
PU4	0.25	70.08	14.75	14.20	relatively fast reaction, inhomogeneous saturation of the mixture structure with bubbles and inhomogeneous hardness
PU5	0.25	71.75	15	13	relatively fast reaction, inhomogeneous hardness, a small number of bubbles of different sizes
PU6	0.25	73.75	15	11	the average reaction rate, the structure of the mixture contains small diameter bubbles
PU7	0.25	74.75	15	10	slow reaction, bubble inclusions in the structure of the mixture
PU8	0.25	75.75	15	9	slow reaction, large surface bubbles are present on the surface of the mixture, sticky surface, the sample is characterized by low tensile strength and low elongation
PU9	0.25	74.75	14	11	average reaction rate, numerous small bubbles in the structure of the mixture
PU10	0.25	75.75	13	11	the structure of the mixture contains several large bubbles
PU11	0.25	76.75	12	11	homogeneous structure of the mixture without bubbles, high tensile strength at break, good elongation
PU12	0.25	77.75	11	11	homogeneous structure of the mixture without bubbles, high tensile strength at break, high elongation
PU13	0.25	78.75	10	11	inhomogeneous structure of the mixture, unstable solidification time

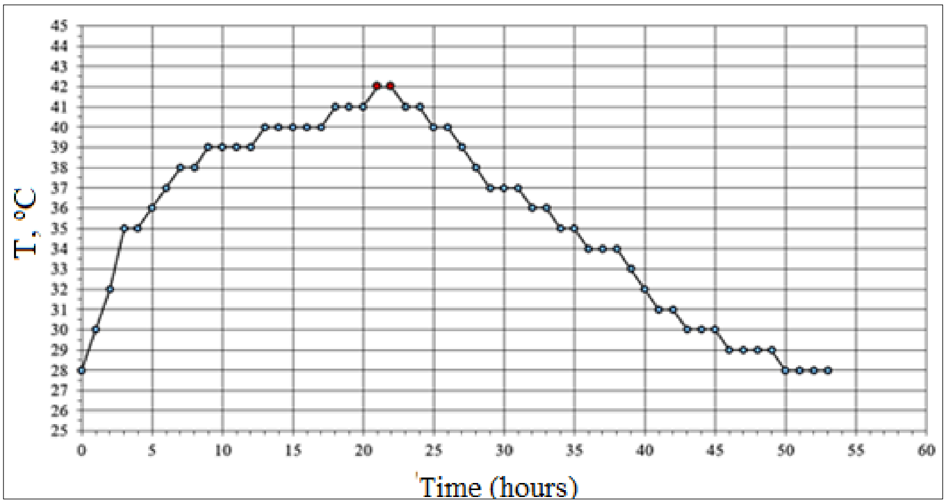

Figure 12. Cold curing curve for polyurethane at a test temperature

of 29°C and a relative humidity of 35%

When studying the "maturity" of the cooled mixture, it is found out that the test sample has a high viscosity and stickiness, which indicates the incompleteness of the chemical reactions necessary to achieve the required structure. Proceeding from this and in order to reduce the time of "maturation" of the mixture, degassing of samples by lowering the atmospheric pressure in a thermal furnace was applied to accelerate the maturation process and avoid the formation of air bubbles in the mixture.

The test studies have been carried out to find the stability of some mechanical properties (surface hardness and tensile stress).

The changes due to Shore A surface hardness were studied depending on temperature and heating time for samples of pure polyurethane foam (without filler). From Figure 13 it is concluded that there is congruence of hardness values at temperatures of 65°C, 75°C and 85°C after 6 h, while the mixture should be created at 50°C for 9 h.

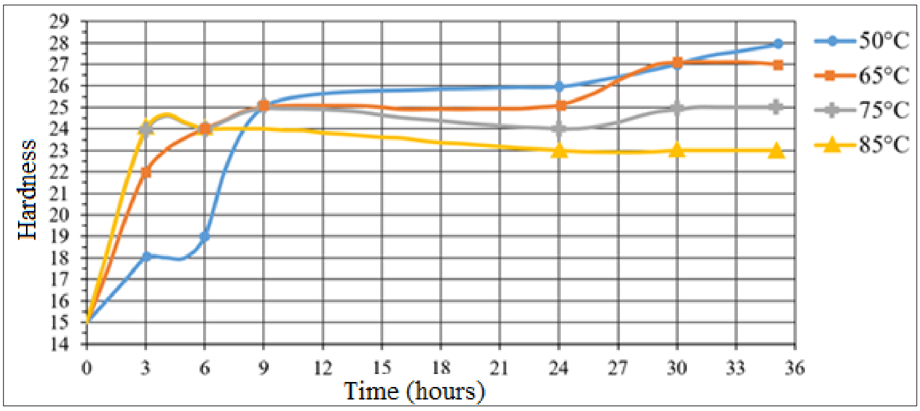

Figure 13. Curves of changes due to Shore A hardness values of pure polyurethane foam samples depending on the heating temperature and time

The stability of the hardness values is observed after the mixture has exceeded the "ripening temperature", with the exception of the test at 85°C, at which the hardness decreases slightly. The reason for this may be the beginning of thermal decomposition in polyurethane after the completion of the "maturation process" of the mixture. This is an important result from a practical point of view, which indicates that:

- the heating temperature of the mixture affects the "maturation" of the mixture, the elasticity and structural integrity of the samples and the stickiness of their surface. It should be noted that the production time of samples by cold curing requires several days;
- to obtain the required characteristics, constant hardness and achieve the "maturity" of the mixture, it is necessary to heat the samples to the temperature values indicated in Figure 13.

To determine the rational values of the heating temperature, the experiment was conducted to study the ultimate tensile strength of standard samples.

Figure 14 shows graphical dependences of tensile stresses at break depending on the time and temperature of manufacturing of a pure polyurethane rubber sample.

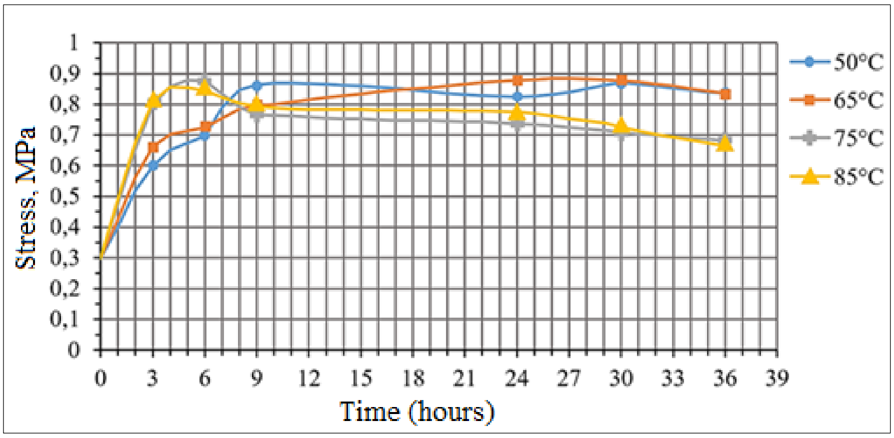

Figure 14. Graphical dependences of tensile stresses on the time and temperature of producing a pure polyurethane rubber sample

The graphical dependences of Figure 13 and Figure 14 resemble, which shows a relatively similar effect of temperature on the characteristics of the mixture. The measurements were carried out with the samples that had reached the state of "maturity". It has been established that the samples made at 50°C and 65°C have the relatively stable tensile stress values, at the same time there is a decrease in the tensile stress values of samples made at 75°C, 85°C. This effect is due to the thermal destruction of samples when heated to temperatures of 75°C and 85°C.

The analysis of the study results has shown that the samples made at 65°C can be considered promising, this is a conditionally averaged temperature between 50°C and 75°C.

The practical experiments with fillers have shown a decrease in the time to reach the state of "maturity" of the mixture. Thus, to achieve the "maturity" of pure polyurethane rubber at a temperature of 65°C it takes 9 h, and it takes up to 3 h for polyurethane rubber with a content of 30% titanium dioxide filler.

Figure 15 shows the graphical hardness dependences of rubber polyurethane samples with a content of 30% titanium dioxide filler for different heating times and temperatures.

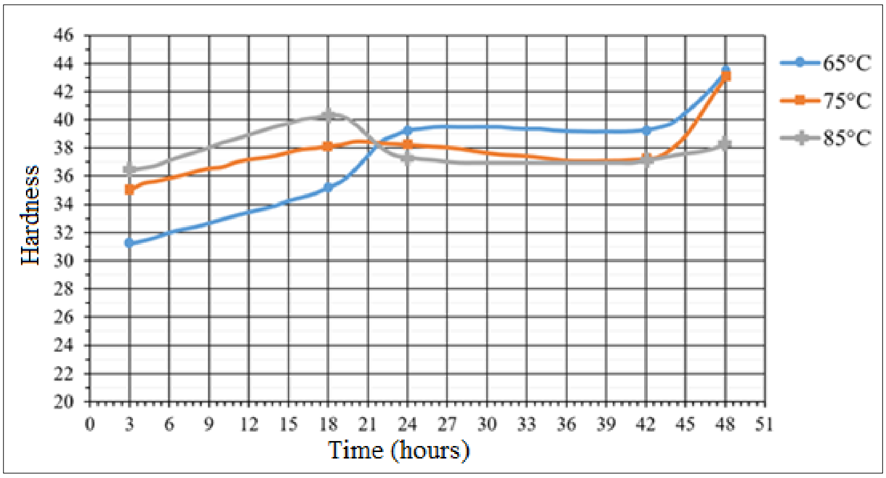

Figure 15. The surface hardness dependence of polyurethane rubber containing 30 % TiO_2 on the temperature and heating time

As can be seen from Figure 15, after 3 h the "maturation" of the mixture still continues, that is, despite the achievement of the required consistency and texture by the samples, the "maturation" process was not completed, so the heating was continued. The final achievement of surface hardness occurs for 24 h and for heating at temperatures of 65°C, 75°C, 85°C. This is the minimum required keeping time to achieve complete "maturation" of the sample, after that, with continued heating, the stability of the surface hardness indicators is noted. The result obtained is important, as it shows the need to heat the sample to achieve the "maturity" of the mixture.

A similar study was conducted for the polyurethane rubber samples containing 30% $CaCO_3$ Figure 16.

It can be seen from Figure 16 that in order to achieve the stable hardness heating is required for at least 18 h at these temperatures.

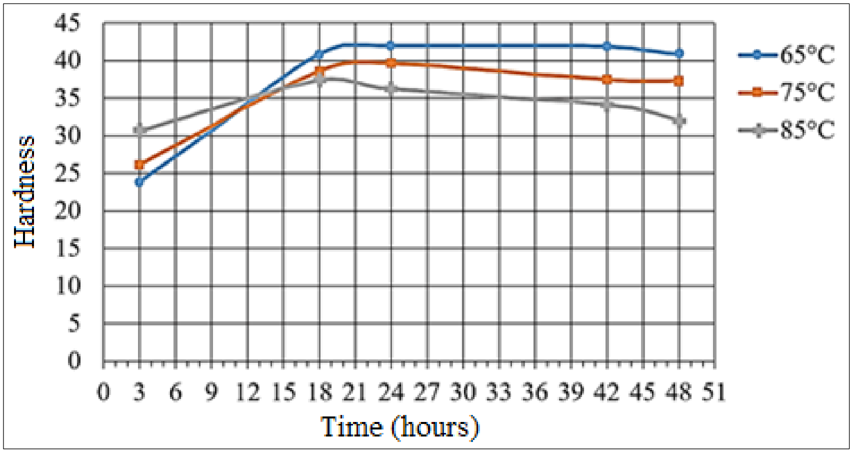

Figure 16. The values dependence of the surface hardness of polyurethane rubber containing 30% $CaCO_3$ on the temperature and heating time

Figure 17 shows the graphs of changes in the hardness of polyurethane rubber depending on the percentage of filler for a heating temperature of 65°C. It has been noticed that the added fillers cause a clear improvement in the condition of the surface and increase the hardness values of polyurethane rubber. Moreover, the sample hardness increased with an increase in the proportion of each of the fillers. The maximum percentages of these fillers in the mixture reached (30-35%), higher percentages are difficult to create due to the practical difficulties in mixing and obtaining a homogeneous mixture.

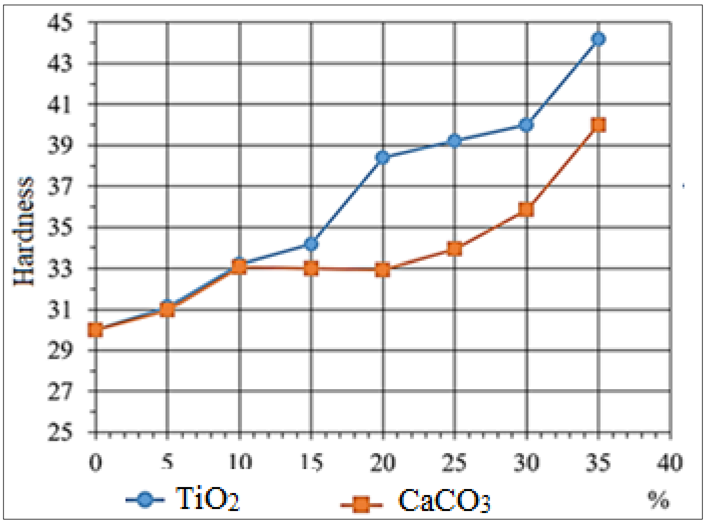

Figure 17. The dependence of hardness on the percentage of filler in polyurethane rubber: a) TiO_2; b) $CaCO_3$

The additional experimental studies were conducted to clarify the effect of $CaCO_3$ and TiO_2 on other mechanical properties. Figure 18 shows the graphical dependence of Jung's modulus from the proportion of TiO_2 in polyurethane rubber. The analysis of the graphical dependence shows an increase in the hardness of the produced samples with an increase in the percentage of titanium dioxide in the mixture: with a ratio of TiO_2 in the mixture - 0%, the Jung's modulus is 0.41 MPa; with a ratio of TiO_2 in the mixture - 35%, the Jung's modulus is 0.74 MPa. This result shows that the hardness of polyurethane rubber can be influenced by the addition of TiO_2, which expands the prospects for its use in industry.

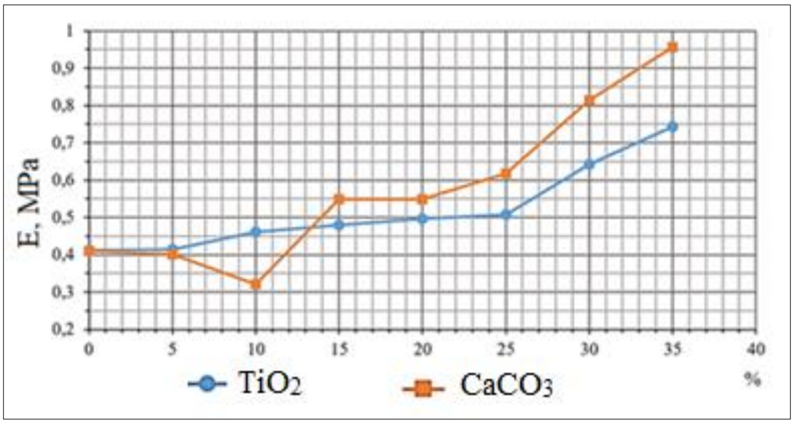

Figure 18. The Jung's modulus dependence on the percentage of filler in polyurethane rubber: a) TiO_2; b) $CaCO_3$

The effect of $CaCO_3$ on the Jung's modulus of polyurethane rubber was studied similarly, and, as shown in Figure 18, the Jung's modulus grows up with an increase in the proportion of calcium carbonate in the mixture. The analysis shows that the addition of calcium carbonate in proportions above 30% provides a higher Jung's modulus than for the same proportions of titanium oxide. The noticeable effect of calcium carbonate on the surface hardness and Jung's modulus of polyurethane rubber samples shows the prospects of its application in industry.

Figure 19 also shows the graphical dependence of tensile stresses during the tensile test for polyurethane rubber depending on the proportion of TiO_2 filler in the mixture. The figure shows a clear increase in voltage values with an increase in the proportion of titanium oxide - from 0.660 MPa at 10% to 1.9365 MPa at 35%. That is, the values of the strength of the samples during tensile tests increases approximately three times.

TiO_2 and $CaCO_3$ fillers have high adhesion with rubberized polyurethane and they limit the development of damage within its structure. Due to the high adhesive properties of polyurethane and as a result of a good and homogeneous distribution of filler particles inside the base material, a highly cohesive structure is formed between the components of the mixture.

Figure 19 shows the graphical dependence of the tensile stress during tensile tests on the percentage of titanium oxide and calcium carbonate in the polyurethane rubber mixture.

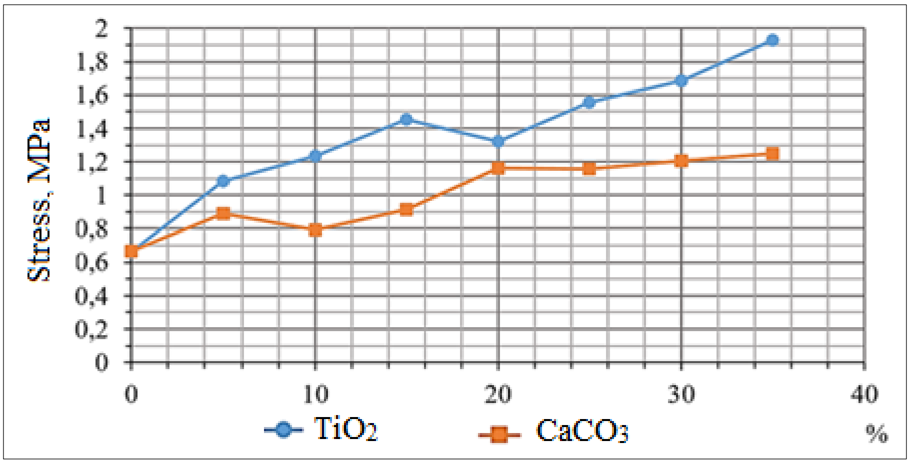

Figure 19. The graphical dependence of tensile stresses at break on the percentage of filler in polyurethane rubber: a) TiO_2; b) $CaCO_3$

The analysis of the obtained dependences shows that with an increase in the proportion of titanium oxide, there is an improvement in the tensile stress at break by three times: with a value of 0% titanium oxide the voltage is 0.660 MPa; with a value of 35% titanium oxide the voltage is 1.937MPa.

TiO_2 and $CaCO_3$ molecules are stress concentrators inside the polyurethane rubber, which has high adhesion to the filler particles. Due to the high adhesive property of polyurethane and as a result of a good and homogeneous distribution of filler particles inside the base material, a highly cohesive structure is formed between the components of the mixture.

The results presented in Figures 18, 19 show that the addition of TiO_2 and $CaCO_3$ to the composition of polyurethane rubber allows to expand the range of their application by giving special properties to polyurethane rubber products. The study of the percentage effect of additives on the properties of polyurethane rubber makes it possible to obtain a product with properties that distinguish it from other compounds.

4. Conclusions

The production of a material with high mechanical properties from polyurethane foam with the addition of TiO_2 and $CaCO_3$ requires a 24 h exposure at a temperature of 65°C.

Fillers TiO_2 and $CaCO_3$ significantly improve the surface condition and increase the hardness values of polyurethane rubber. The hardness of the material increases with the increasing proportion of each filler. The effect of increasing hardness when using TiO_2 filler is higher than when using $CaCO_3$. The maximum proportions of these fillers in polyurethane rubber are limited to 30-35%.

The analysis of the proportion influence of TiO_2 filler in polyurethane rubber on the tensile strength has shown that the strength grows up with the increasing filler content.

The study shows that the use of TiO_2 and $CaCO_3$ as modifiers is an effective way to improve the mechanical properties of polyurethane rubbers. TiO_2 can be used to increase their strength and stiffness, and can also increase their UV resistance, which expands its use for products that will be displayed outdoors. $CaCO_3$ can also be used to increase the stiffness and strength of polyurethane rubbers, but is cheaper than TiO_2.

It is proved that the addition of TiO_2 and $CaCO_3$ to the composition of polyurethane rubbers gives them the special properties that allow them to expand the range of their industrial usage in the creation of molds for casting standard and architectural and artistic products made of concrete and gypsum.

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