STUDY ON A THERMOPLASTIC ELASTOMER MATERIAL BASED ON WASTE POLYVINYLCHLORIDE REINFORCED BY PHOSPHOGYPSUM

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Abstract

The waste calcium sulfate (phosphogypsum) is a solid by-product generated from phosphoric acid production processes. The phosphogypsum (PG) represents a serious ecological problem that isn't solved globally. A potential possibility for its utilization is usage as mineral filler for polymer composite materials.

The aim of present work is development, properties study and formation process modeling of new polymer composite material based on waste Polyvinyl Chloride (PVC) reinforced by PG, modified by nitrile rubber. The main potential industry application of this material can be lining of flexible cables with low-grade thermal properties.

A new material for flexible cables coatings with tensile strength 10 MPa and elongation at break 500 % was developed using wastes from polymer industry. The main requirements for polymer composites used as electric insulation are a tensile strength not less than 10 MPa and elongation of not less than 300% and specific dielectric parameters. The new developed material provides fully match of these requirements.

Using statistical methods of experiment design the material forming process was studied. The numerical models for mechanical behavior of these materials were developed. These mathematical models allow to obtain exact receipt and for other compositions with early definite properties.

1 Introduction

In the present significant amounts of waste polymers were produced from the polymer technology. The biggest quantities are from rubber, polyolefin and polyvinyl chloride. The recycling of these wastes is very important from economical and environmental reasons. The effectiveness of the development of polymer products and technologies is mainly determined by the opportunities for waste reduction technology, as well as the development of significant high-level technologies for recycling industrial wastes and waste products. The literature describes various effective methods for recycling of plastic wastes [1-3]. Polyvinyl chloride is one of the most widely used polymers in the industry [1, 2]. In the polymer technology many recycling methods with varying degrees of effectiveness are proposed [2, 3].Generally, these wastes can be divided into two major groups - technological wastes that weren't subject to external conditions of aging and discarded products set out through a long period of UV radiation, oxidation, destruction and other weathering.

The thermoplastic elastomers are new classes of polymeric materials whose properties are similar to those of vulkanizates but unlike them are treated as ordinary thermoplastics [4]. Today when the use of wastes is very important the benefits of thermoplastic elastomers are clear and they show opportunity to create a non-waste technology [4].

In the shoes industry a significant amount of plasticized polyvinyl chloride in varying degrees was dropped and can be converted into different polymer compositions with new properties [5].

In plasticization process of polymers using high molecular weight polymeric plasticizers new compounds with properties of thermoplastic elastomers can be obtained [4]. At normal temperature they have such properties as rubber vulkanizates and at temperatures close to those of processing - such as thermoplastic materials. Such pair of polymers is a mixture of PVC and nitrile rubber and low molecular weight plasticizer in certain ratios.

A large scale study of processing of polyvinylchloride with nitrile rubbers was conducted [6-12].

The aim of present work is to study the possibility for converting technological waste from the footwear industry into a polymer blend with properties of thermoplastic elastomer and development of mathematical models for strain-strength and dielectric properties of the resulting compositions.

The availability of adequate mathematical models allows determining the receipt of compositions needed to practice characteristics.

2 Materials and testing methods

The characteristics of used materials are shown below:

1.Polyvinyl chloride, trade mark Develit S68

2.Acrylonitrile Butadiene Rubber (NBR), trade mark Europrene N 3945 ("Enichem Elastomerics" - Southampton, UK)

3.Phosphogypsum (waste $CaSO_4.2H_2O$)

4.Chalk ($CaCO_3$)

Receipts of developed compositions are shown in Table 1.

Ingredients	**mass %**	**Ingredients**	**mass %**	**Ingredients**	**mass %**
Waste PVC	100	Waste PVC	100	Waste PVC	100
Europrene N 3945	0-230	Europrene N 3945	25	Europrene N 3945	0-230
		Fresh PVC	0-30	Fresh PVC	25
Phosphogypsum	60	Phosphogypsum	60	Chalk	0-80

Table 1. Recipes of the developed compositions

The compositions were prepared on mixing rolls at 160 °C at mixing time of 5 min. Before blending Europrene N 3945 was plasticized on cold rolling mixer for about 10 min. Components are introduced in the following order: technological waste of PVC, fresh Europrene N 3945 and chalk. Compositions of the resulting samples were prepared in the following regime: temperature 160 °C, time of pre-pressing 3 min; pressure of 30 MPa, pressing 5 min; cooling rate 50 °C/min. The strain-strength characteristics were determined on a tensile testing machine "INSTRON", model 4203 according to ASTM D638 [13]. Dielectric properties were obtained according to ASTM D876 [14] on apparatus "SCHERING BRIDGE" Company "CEAST" at 50 Hz and the specimen thickness of 1 mm.

3 Results and discussion

Preliminary studies of the relationship between waste content and nitrile rubber (Europrene N 3945) demonstrate that the ratios of technological waste and nitrile rubber in compositions as 80:20 can be used for obtaining of material with properties of thermoplastic elastomer. The carried out experiments showed that mechanical properties such tensile strength, Young modulus and elongation at break change are in the interval, respectively: 7.48-11.22 MPa, 3.52-9.05 MPa и 411-580 %. These characteristics satisfy the requirements of these polymer mixtures with properties of thermoplastic elastomers subjected to static loads.

These thermoplastic elastomers may have potential application for covering of the flexible electric cables, which would significantly increase productivity due to failure of the process of rubber vulcanization. There are requirements for materials for flexible cables coating and they must have a tensile strength not less than 10 MPa and an elongation at break not less than 500 %. The mechanical properties of the developed compositions as function of the ratios of waste PVC and the amount of Europrene N 3945 were studied. The results from tensile tests are shown in fig. 1-4.

The studies reveal that the used technological waste of PVC is high-plasticized material and strain-strength characteristics of the resulting mixtures with properties of thermoplastic elastomer are lower than the requirements for coating cables. This requires the incorporation of additional amounts of fresh PVC in 2-30 mass %.

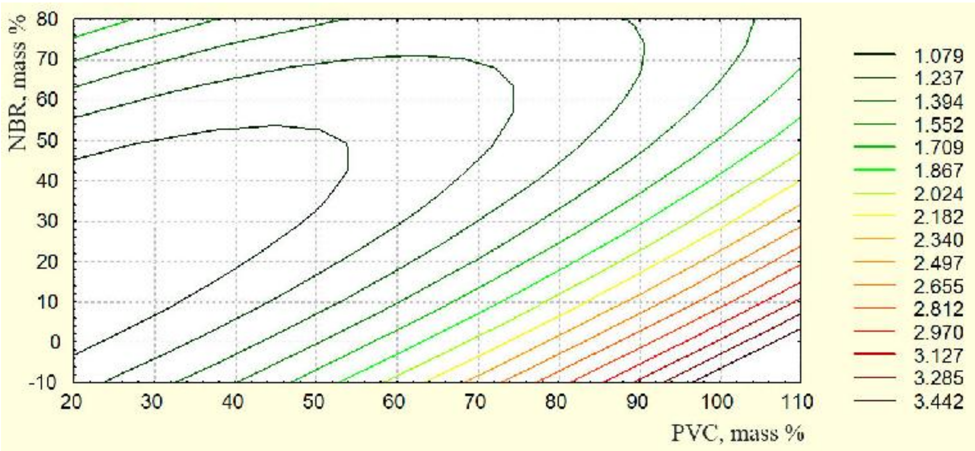


Figure 1. Results for tensile strength as function of the ratio between technological PVC waste and Europrene N 3945 on developed PVC compositions.

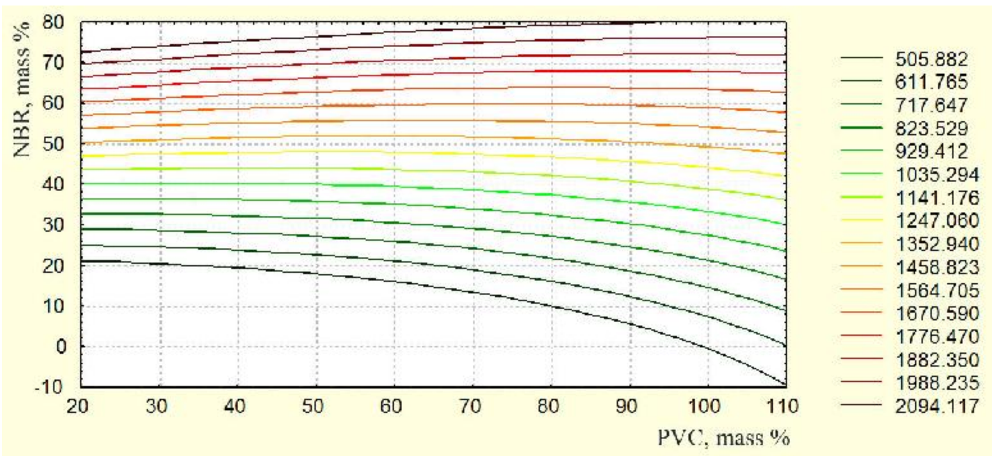


Figure 2. Results for Young modulus as function of the ratio between technological PVC waste and Europrene N 3945 on developed PVC compositions.

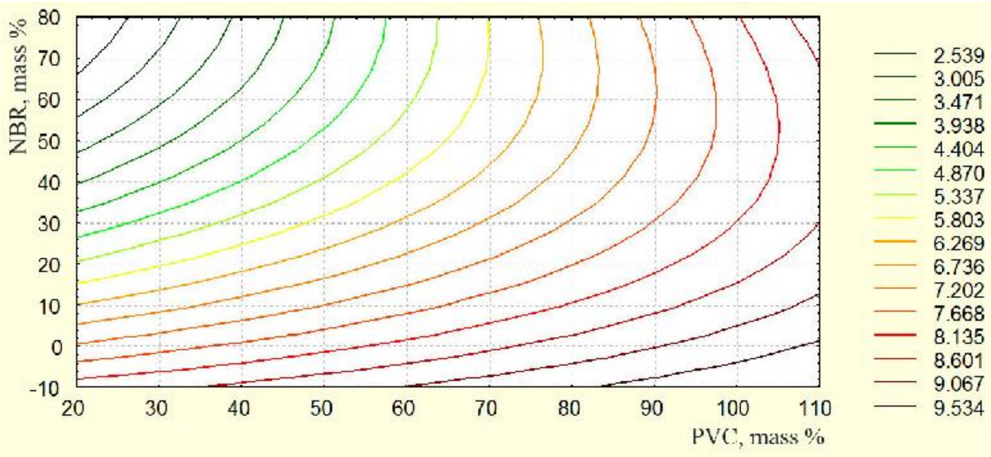


Figure 3. Results for elongation at break as function of the ratio between technological PVC waste and Europrene N 3945 on developed PVC compositions.

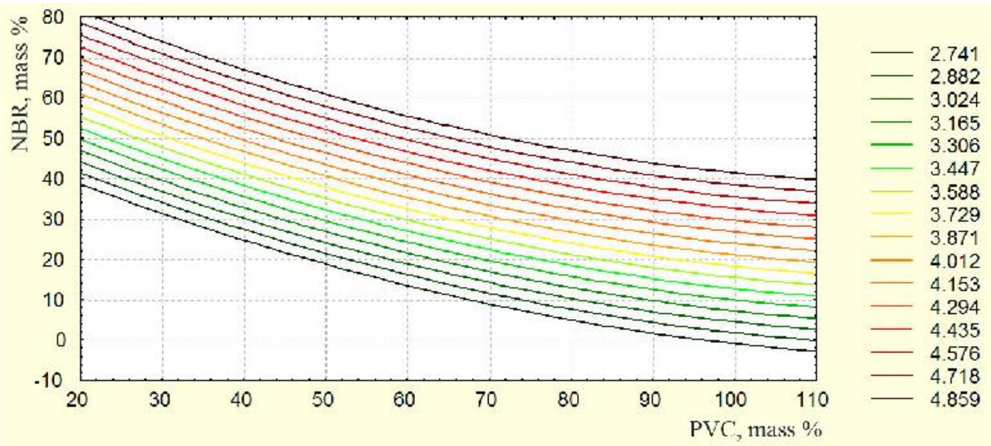


Figure 4. Results for energy at break as function of the ratio between technological PVC waste and Europrene N 3945 on developed PVC compositions.

Additional quantities of incorporated fresh PVC show that the mechanical characteristics of the compositions change significantly (fig. 5), i.e. using certain amounts of fresh PVC can improve the mechanical characteristics and obtain compositions satisfying the requirements for covering of flexible cables and many other products.

To reduce internal stresses in the compositions and to improve manufacturability for processing by extrusion and reduce the cost of products we have explored the possibility of filling of the thermoplastic elastomer by one of the most widely used mineral fillers for PVC and rubbers - chalk.

The values shown in fig. 6 illustrate the changes in strain-strength characteristics of thermoplastic elastomer depending on the degree of filling by chalk.

With increasing degree of filling strain-strength characteristics are amended in relatively low, except for the Young modulus. The studies show that when filling of thermoplastic elastomer with chalk is in the range 10-80 mass% resulting compositions have good processing and changes in their characteristics is within limits.

The used content of phosphogypsum (waste $CaSO_4.2H_2O$) up to 100 mass % increases the oxygen index of the composition by 4 units and improves the flame retardant properties of the material. This effect is commensurate with those of the widely used $Al(OH)_3$.

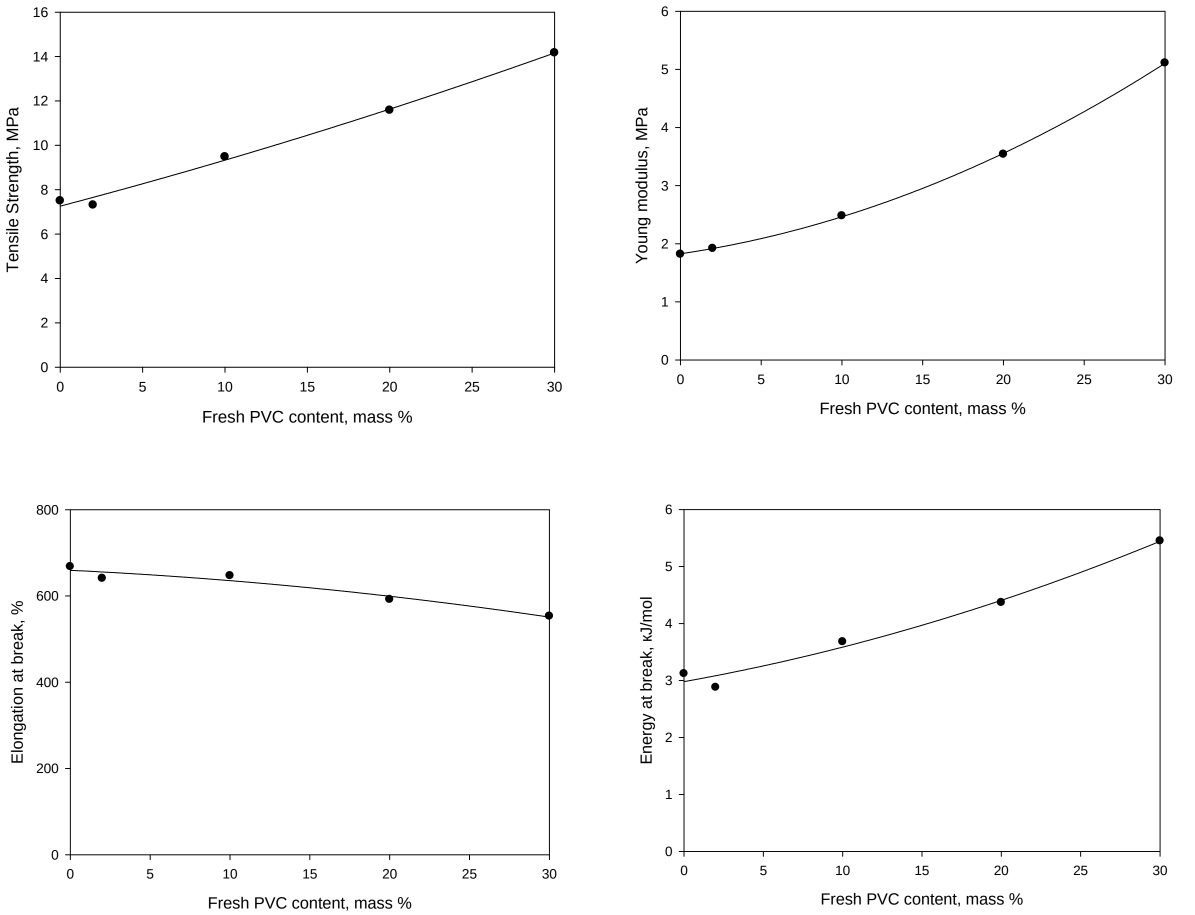
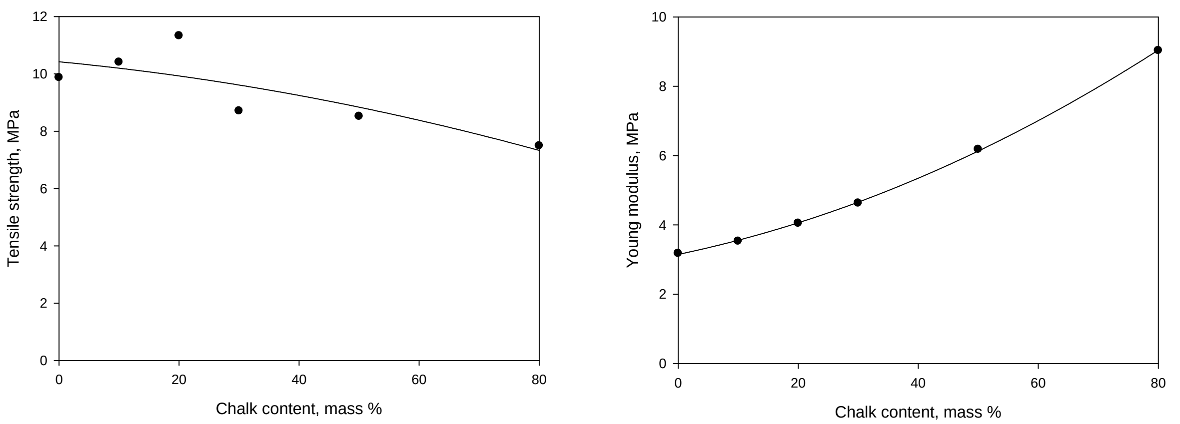
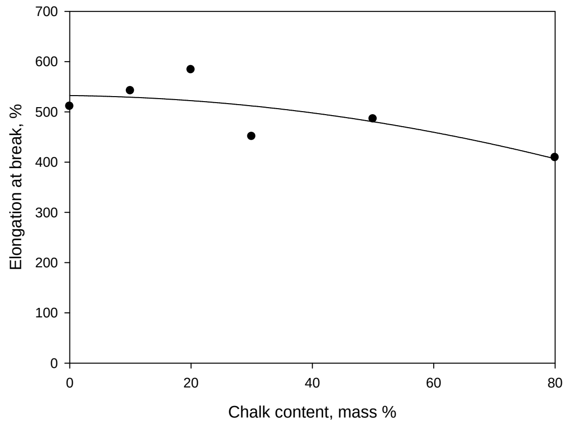


Figure 5. Results of tensile tests on developed PVC compositions depending on fresh PVC content.

Previous developed tests and recipe composition have shown that technological wastes from PVC shoes industry in certain ratios with other components (NBR, chalk) and various degree of filling can become thermoplastic elastomer material which satisfy the requirements for lining of cables.





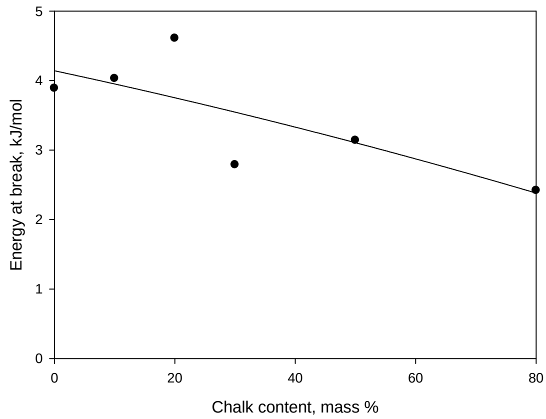


Figure 6. Results of tensile tests on developed PVC compositions depending on chalk content.

To study the mutual influence of components, the presence of synergism and many other effects has been conducted full factorial design experiment of type 2^n (where n is the number of studied factors). Preliminary studies allow selecting the narrowest range of variation of input factors. The selected input factors are:
x_1 is content of nitrile rubber Europrene N 3945;
x_2 is content of fresh Develit PVC S-68;
x_3 is content of chalk.
For these output parameters are derived mathematical models of the type:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 + b_{123} x_1 x_2 x_3 \quad (1)$$

Assessment of the absolute values of the coefficients deduced in mathematical models show that on the strain-strength performance of the resulting thermoplastic elastomer significantly influenced by the amount of waste PVC and fresh PVC, the ratio between polyvinyl chloride waste and Europrene N 3945 80:20 respectively. For the tensile strength values of the coefficients b_1 and b_3 are respectively 1.64 and 0.2 (2). The extent of interaction of these two factors b13 shows that imported fresh PVC reduces the negative impact of imported filler on the strength. After checking for significance by the criterion of Fisher equation for tensile strength has form (2) shown below:

$$y = 10.05 + 1.64 x_1 - 1.27 x_2 - 0.2 x_3 + 0.39 x_1 x_3 \quad (2)$$

The Young modulus strongly influenced by fresh imported PVC, rubber content and quantity of chalk. A minus sign before the coefficient x2 shows that the amount of Europrene N 3945 reduces the cost of module composition which is consistent with the theory of plastification of polymers, an additional amount of filler and PVC have a positive influence. Equation has form (3):

$$y = 3.74 + 0.91 x_1 - x_2 + 0.14 x_3 + 0.34 x_1 x_2 + 0.12 x_1 x_3 \quad (3)$$

The elongation at break of the compositions generally increases with introduction of a plasticizer and lowers the value of adding fresh PVC and mineral filler. The strongest influence is for fresh PVC (b_1 = - 27.05). The same order is the impact and the amount of chalk (b_3 = -21.9). For elongation at break are particularly relevant double interactions. This shows the importance of all factors in the equation (4) except b123 and it assumes the shape (4):

$$y = 555 - 27x_1 + 62x_2 - 21.9x_3 + 20.7x_1x_2 + 13.5x_1x_3 + 7.3x_2x_3 \quad (4)$$

The equation for the energy at break has the form (5):

$$y = 4.1 + 0.54x_1 - 0.17x_3 + 0.22x_1x_2 + 0.24x_1x_3 \quad (5)$$

The studies have shown that the mathematical models for the dielectric parameters are on the borderline of adequacy. Nevertheless, they provide sufficient information about the impact of input parameters, their interaction and the trend in changes in dielectric parameters.

4 Conclusions

A new material based on technological waste of PVC from shoes industry was developed. This composition is reinforced by phosphogypsum and contents also nitrile rubber and chalk. The potential use of this thermoplastic elastomer is for flexible cables coatings with tensile strength 10 MPa and elongation at break 500 %. Performing factorial design experiment mathematical models for mechanical properties were obtained. These equations are adequate and can perform calculations for obtaining of new recipes of materials with required properties.

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