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COMPOSITES THEORY AND PRACTICE

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COMPOSITES BASED ON HIGH-MOLECULAR WEIGH EPOXY RESIN MODIFIED WITH POLYSULFIDE RUBBER

The desire to obtain unique properties of polymer materials and the ever growing competition in the plastics market have a direct impact on the intensification of research in materials science. This article regards innovative proposals to modify polymeric material (epoxy resin) to obtain new products (composites) with improved properties. The mechanical and chemical properties of composite materials based on epoxy resins modified with synthetic polysulfide rubber were determined. Moreover the effect of adding industrial waste (glass powder) on the structure and performance of the composites was estimated. The physical and mechanical properties of the composites as well as their chemical resistance to aggressive environments were determined. One of the applications for the innovative composite materials is to use them as a protective material, e.g. in construction for lightweight concrete.

Keywords: **composites, epoxy resin, polysulfide rubber**

MATERIAŁY KOMPOZYTOWE NA BAZIE WYSOKOCZĄSTECZKOWEJ ŻYWICY EPOKSYDOWEJ MODYFIKOWANEJ KAUCZUKIEM POLISIARCZKOWYM

Dążenie do otrzymania unikatowych właściwości materiałów polimerowych oraz stale rosnąca konkurencja na rynku tworzyw sztucznych mają bezpośredni wpływ na intensyfikację badań w zakresie inżynierii materiałowej. Niniejsza praca dotyczy innowacyjnej propozycji modyfikacji materiału polimerowego (żywicy epoksydowej) w celu otrzymania nowych produktów (kompozytów) o lepszych właściwościach. Określono właściwości chemiczne i mechaniczne materiałów kompozytowych na bazie żywic epoksydowych, zmodyfikowanych polisiarczkowym syntetycznym kauczukiem. Ponadto oszacowano wpływ dodatku recyklatu szklanego (w postaci proszku będącego odpadem przemysłowym) na strukturę oraz własności użytkowe kompozytu. Zdefiniowano fizyczne i mechaniczne właściwości kompozytów oraz ich odporność chemiczną w agresywnym środowisku. Jedną z propozycji aplikacyjnych nowatorskich materiałów kompozytowych jest zastosowanie ich jako materiału ochronnego m.in. w budownictwie na pokrycia lekkich betonów.

Słowa kluczowe: **kompozyty, żywica epoksydowa, kauczuk polisiarczkowy**

INTRODUCTION

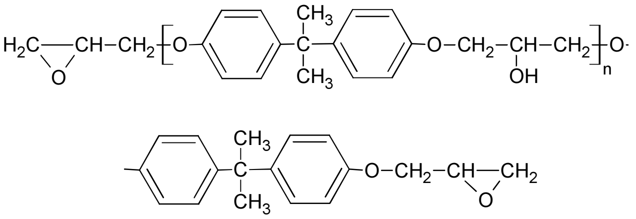
Epoxy resin due to its high specific strength and low density is very often used to create on its basis new composite materials that can be used in various spheres of human activity: industry, household goods, construction and others. Epoxy resin based composites have good mechanical and thermal properties, high chemical resistance and excellent adhesion to many materials [1]. In order to obtain new polymer materials with special properties, the epoxy resin is subjected to modification, stabilization or flexibilization. To obtain composite materials various kinds of fillers are used.

Recently, materials engineering activities have focused on the use of waste materials in order to recycle them. Due to its stable properties despite repeated processing, which is very beneficial from an economic and ecological point of view, glass is very readily used as a filler in composites. Many studies have been conducted on this subject [2, 3], for example, epoxy resin based composites or other polymers with added waste materials from industry, including glass. Based on analysis of the research in [4, 5], it can be concluded that producing composites based on an epoxy polymer with the addition of an inorganic filler material in a fine form, for example powder, appears to be the most promising at the present time. The introduction of such a resin filler has a beneficial effect on the properties of hardened plastics, contributes to lowering product costs, extends composite life, and reduces the exothermic effect of crosslinking.

The article presents a new proposal for the method of curing epoxy resin by using polysulfide rubber and the results of studies on the structure and properties of composites based on modified epoxy resin with the addition of glass powder.

MATERIALS AND METHODS

One of most of interesting construction materials is liquid epoxy resin with a molecular weight of 350÷450 [6]. The properties of the epoxy resin can be constituted by its modification, resulting in better stability or elasticity. The structure of the epoxy resin (DGEBA/propanol) is:



The microstructure of the epoxy resin is shown in Figure 1.

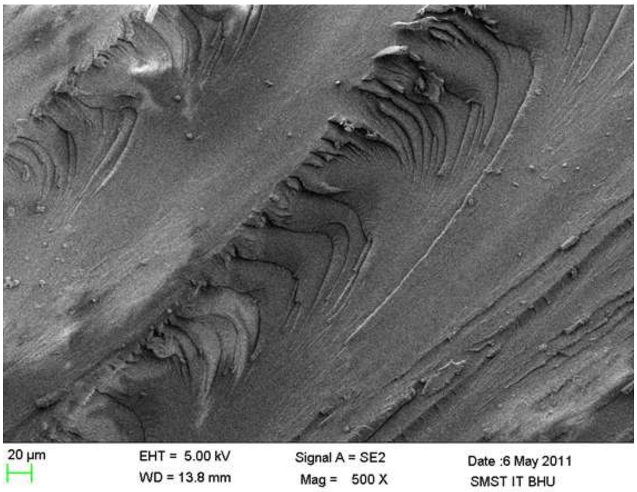
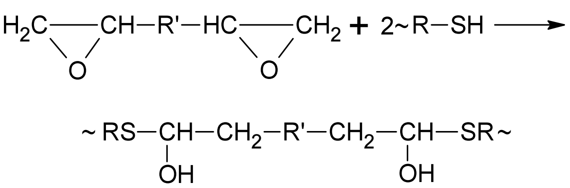


Fig. 1. Microstructure of epoxy resin, SEM micrograph [6]
Rys.1. Mikrostruktura żywicy epoksydowej, SEM

The structure of liquid polysulfide rubber (n = 6÷10) viscosity = 28 Pa · sec, HS- = 3.1% is:

$$HS\left(C_2H_4-O-CH_2-O-C_2H_4-S-S\right)_n C_2H_4-O-CH_3,$$

The process of reaction epoxy resin with luquide polysulsufe rubber is:



The optimal modification, maximizing the results is presented in Table 1.

TABLE 1. **Properties of modified liquid epoxy composite with polysulfide rubber [3]**
TABELA 1. **Właściwości żywicy epoksydowej modyfikowanej polisiarczkowym kauczukiem [3]**

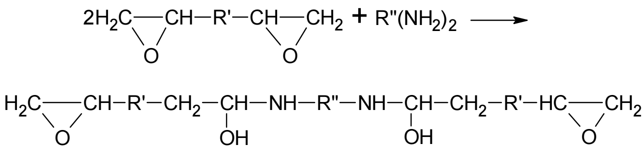
Molecular weight of epoxy resin	Concentration of polysulfide rubber per 100 molecular weight of resin	Tensile strength [MPa]	Shear strength [MPa]	Compression strength [MPa]	Operating temperature range [°C]
390*	20	45.7	12.1	114	–30… +150

* - hardener: polyethylene polyamine 100:5.

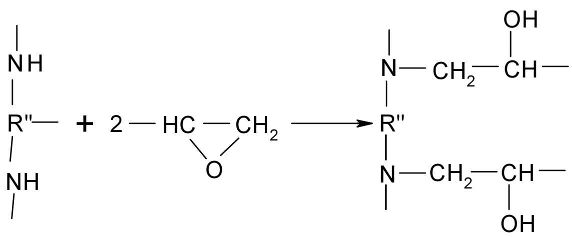
The structure of polyethylene polyamine is:

$$NH_2(CH_2CH_2NH)_nCH_2CH_2NH \qquad (n \geq 4)$$

If the composition is administered as activators of primary or secondary amines, the initially formed linear adducts:



Further secondary amines or adduct activators interact with the epoxy resin groups, which leads to the formation of cross-linked polymers:



In this study the epoxy resin was modified with a polysulfide rubber additive at a mass ratio of 100:20. The resin was melted and thoroughly homogenised for 30 minutes at 200°C. In the next step to obtain the composite materials, milled glass powder was added to the modified resin at mass ratios of 100:10; 100:20; 100:50; 100:100. The glass recyclate used was a material of a satisfactory quality and had a powder fraction consisting of fine glass grains of 0.45÷0.65 μm. This material, apart from grinding in a ball mill, was not subjected to any additional treatment. After mixing all the components, the composites were dried 2 hours in a dryer at 40°C to reduce internal stresses.

The obtained composites with different filler additives were subjected to structural analysis using an AFM microscope, chemical resistance W was determined by sample weight change after immersion in a chemical environment from 1 to 45 days, according to the formula:

$$W(t) = \frac{m(t) - m_0}{m_0} \cdot 100\%$$

where m_0 - the initial mass of the sample; $m(t)$ - mass after exposure to the aggressive environment for time t. The study was conducted in 20% aqueous solutions of sodium chloride, potassium hydroxide and hydrogen chloride.

Compressive strength was determined by the ISO 15109 procedure.

RESULTS AND DISCUSSION

The basic condition of the high strength of a composite material is the high quality of the connection between the components. The lack of a proper connection results in a decrease in the mechanical properties. The use of milled waste as a filler for the composites resulted in the fact that it is still difficult to achieve a good connection.

The microstructure of the composites (Fig. 2.a-c) can be divided into two phases: fractional inclusions of a crystalline structure and the polymer matrix. None of the composites revealed defects between the connections of the inorganic and organic components - the glass powder particles are have a smooth transition to the epoxy matrix. The inorganic component (glass recyclate) is unevenly distributed in the polymer matrix, indicating that a uniform composite structure is possible only by using special technical solutions or chemical surface active agents.

In Figure 3, the black circle indicates the wave-like modification of the epoxy resin structure. The white lines indicate an interesting phenomenon, namely glass powder grains are formed within the polymer molecules. This is possible due to the characteristic features of epoxy resin, namely the presence of long chains of cross-linked polymer. This result is very interesting in the context of the interfacial connections of the polymeric and inorganic materials.

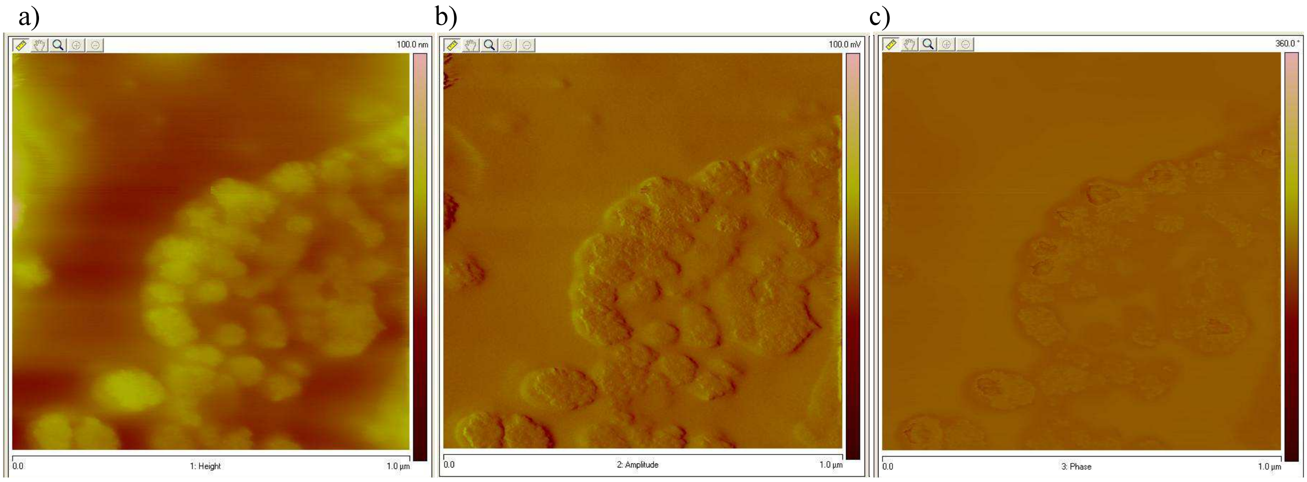


Fig. 2. The structure (AFM) of composite materials based on epoxy polymers modified with synthetic polysulfide rubber with glass powder filler

Rys. 2. Struktura (AFM) kompozytu na bazie zmodyfikowanej żywicy epoksydowej z dodatkiem proszku szklanego

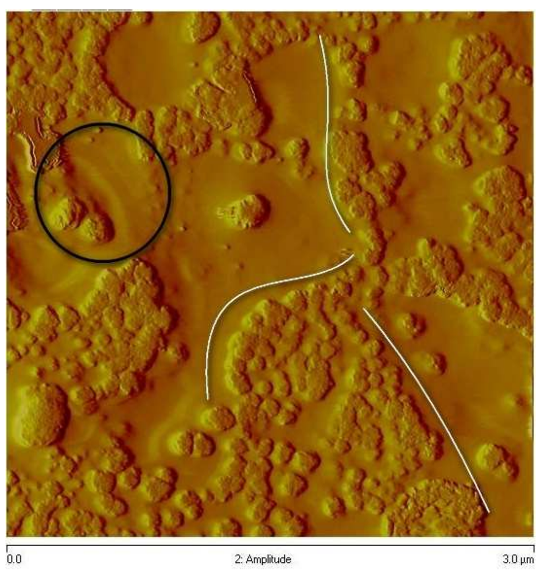


Fig. 3. The structure (AFM) of composite materials based on epoxy polymers modified with synthetic polysulfide rubber with glass powder filler

Rys. 3. Struktura (AFM) kompozytu na bazie zmodyfikowanej żywicy epoksydowej z dodatkiem proszku szklanego

The composite studies have also shown that the use of glass powder filler affects the overall performance of the composite. The chemical resistance of the composites in the acidic HCl environment decreases with the addition of powdered glass (Figs. 4 and 5), whereas it increases by the action of NaCl alkali salts and in the alkaline environment of KOH (Figs. 4 and 6).

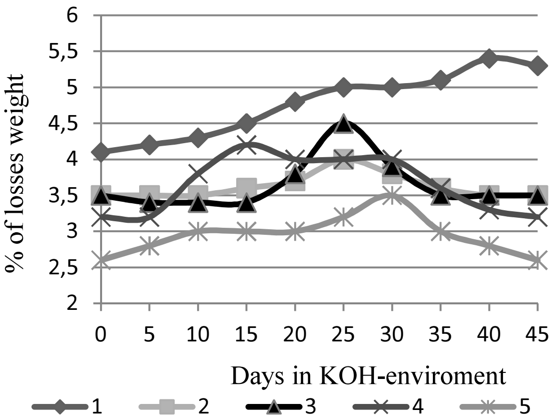


Fig. 4. Chemical resistance to KOH. Mass proportion epoxy/polysulfide rubber to powdered glass: 1 - 100:0; 2 - 100:10; 3 - 100:20; 4 - 100:50; 5 - 100:100

Rys. 4. Odporność chemiczna w KOH. Udział masowy żywica/kauczuk do proszku szklanego: 1 - 100:0; 2 - 100:10; 3 - 100:20; 4 - 100:50; 5 - 100:100

Figures 4-6 illustrate that the chemical resistance of materials filled with a modifier in the form of glass is higher than that of epoxy resin alone. When immersed in an aggressive environment, the composite samples underwent a loss in weight only within a certain time range, after which a drop was not recorded. This can be attributed to the fact that the first glass particles were washed away and then the resulting spaces were filled with particles of the aggressive chemical environment (potassium and oxygen).

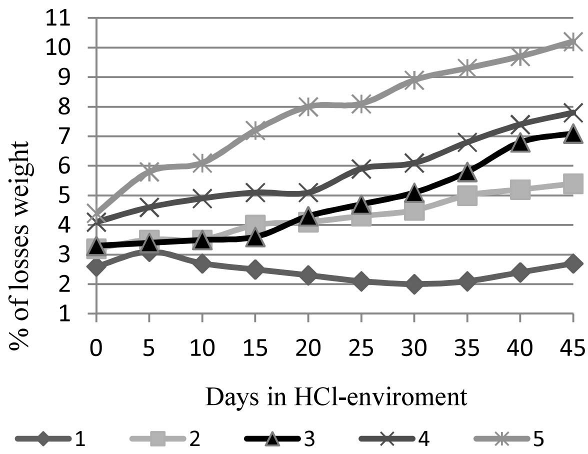


Fig. 5. Chemical resistance to HCl. Mass proportion epoxy/polysulfide rubber to glass powder: 1 - 100:0; 2 - 100:10; 3 - 100:20; 4 - 100:50; 5 - 100:100

Rys. 5. Odporność chemiczna w KCl. Udział masowy żywica/kauczuk do proszku szklanego: 1 - 100:0; 2 - 100:10; 3 - 100:20; 4 - 100:50; 5 - 100:100

The chemical resistance of epoxy resin based composites in the HCl acid environment (Fig. 5) after the addition of glass filler decreases and it is proportional to the amount of glass powder added.

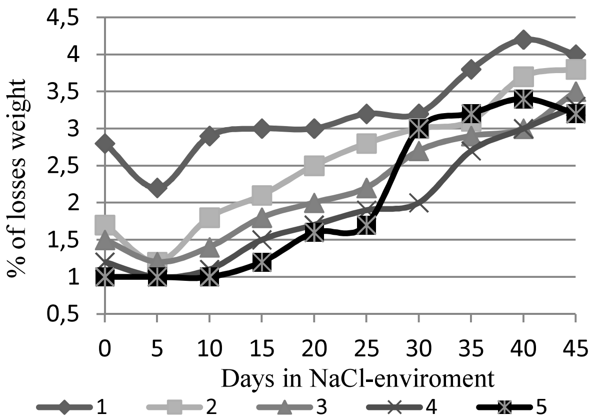


Fig. 6. Chemical resistance to NaCl. Mass proportion epoxy/polysulfide rubber to glass powder: 1 - 100:0; 2 - 100:10; 3 - 100:20; 4 - 100:50; 5 - 100:100

Rys. 6. Odporność chemiczna w NaCl. Udział masowy żywica/kauczuk do proszku szkalnego: 1 - 100:0; 2 - 100:10; 3 - 100:20; 4 - 100:50; 5 - 100:100

The results of chemical resistance in the NaCl environment (Fig. 6) indicate that the addition of glass recyclate to the modified resin results in a significant increase in chemical resistance up to 30 days. After 30 days in the reactive environment the chemical resistance is reduced due to activation of the leaching of components in the glass composites.

CONCLUSIONS

Within the study composites based on modified epoxy resin containing glass, as a new material proposal, were produced. The obtained results allow the authors to conclude that the content of glass recyclate has a significant effect on the properties of the composites.

The addition of glass raw material as post-production waste is economically justified and additionally increases the chemical resistance to alkalis and salts. The chemical resistance of the composites to the acidic HCl environment corresponds to the low chemical resistance of the glass itself.

One of the applications for the innovative composite materials is to use them as a protective material, e.g. in construction for lightweight concrete.

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