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Modifications of Epoxy Resins and their Influence on their Viscosity

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Modifications of Epoxy Resins and their Influence on their Viscosity

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Abstract. The material engineering of composites is currently one of the fastest growing fields of the technology. Research in this discipline currently focuses on two basic directions: a search for completely new materials and methods of modifying the properties of already known materials. Among the study belonging to the second group, research on the properties and modifications of polymers is a particularly dynamically developing field. Commonly, the most often used polymer types in construction engineering are: construction, coating, and adhesive polymers. The last group includes the so-called resins, e.g., epoxy, phenol, polyester, formaldehyde, and mixtures of these polymers. Their use is focused at combining construction materials, i.e. to strengthen structural elements. Their hardening process can be caused by two factors – the hardener (chemohardening polymers) or higher temperature (thermohardening polymers). These processes cause its cross-linking, i.e. the production of a crystallized resin structure to a permanent form. The conditions in which the resin was prepared have a big impact on its adhesion to the substrate during its application on the glued surfaces (early resin adhesion). This parameter largely depends on two important factors: the chemical composition of the resin and its viscosity. Changes of viscosity can have a measurable effect on the final effect of gluing. The following elaboration includes the results of modification tests of an epoxy resin with the addition of two inorganic fillers: microsilica (in the amount of 0.5% of resin weight) and carbon nanotubes (in the amount of 0.1% of resin mass). The epoxy resin commonly used in engineering for joining steel, concrete, carbon fiber, and glass elements was used. In addition, the ultrasound energy was used as a factor, which disintegrated the initial structure of the resin in liquid form and allowed the efficient mixingofthe resin with the filler. The influence of sonication and filler additives on the viscosity of the resin at temperature of 22 °C was determined. Based on the results obtained and observation of the ultrasound effect, the phenomena occurring at the interface of the liquid phase of the resin and the phase of individual fillers were explained. The increase of temperature of the resin under the influence of a dynamic action occurring during sonication was taken into account. The study conducted was the preliminary phase before investigating the influence of the modifications applied on the physical and mechanical parameters of the hardened resin.

1. Introduction

Polymers are a group of chemical substances, which consist of complex cyclic repeating chemical sequences (the monomers - "mers") which form a polymer chain [1]. Individual sequences are connected to each other by means of chemical bonds: ionic, coordinate, polarized, or hydrogen [2]. The type of bonds occurring between the individual mers determines the physico-mechanical, rheological, and operational properties of the polymer [1]. They are obtained by refining hydrocarbons directly contained in the crude oil or from other sources containing organic phases, e.g., phenolic, carboxylic, ester, hydrocarbon. The production of polymers is systematically growing, currently reaching the number of hundreds of millions of tons per year [3] and they are currently the most commonly produced materials widely used in many branches of the economy.

Among the very large group of polymers encountered in technology, e.g., in electronics, mechanics or bioengineering, the most commonly used in construction are [1]:

- fibre-forming, e.g., strengthening and reinforcing meshes,
- structural (resin concrete, support profiles, masking elements),
- coatings (hydrophobic coatings, varnishes, impregnates), insulating construction foils,
- adhesive (glues) – epoxy, polyester, phenol, formaldehyde, urea resins, and mixtures)
- special (e.g., with increased resistance to fire or UV radiation),

The main advantages of the construction polymers are [4]:

- very good strength parameters in relation to the element's mass, e.g., supporting beams,
- very good adhesion to wood, steel, concrete, and ceramics – in the case of adhesives,
- constantly decreasing costs of production and their price.

Gluing is the process of combining two or more elements made of the same or different materials using a suitable bonding material. The most commonly used adhesives in the construction industry include resins, such as [2]:

- epoxy,
- phenolic,
- formaldehyde,
- polyester,
- urea,
- combinations of the above types of resins.

The resins differ primarily with the type of functional groups, on which the name of the resin depends, as well as the method of hardening. In this respect, they can be divided into the chemohardening resins (under the influence of a suitable catalyst – a hardener that initiates the process of crosslinking and hardening); and the thermohardening resins, in which the hardening process is initiated under the influence of a high temperature. The first group includes epoxy resins, i.e., the oligopolymers that are the reaction product of an epichlorohydrin and bis-phenol. Apart from the mentioned adhesive and strength properties, their additional features are chemical resistance, impermeability, and dielectricity. The main disadvantages include low resistance to high temperatures and UV radiation.

The last division of polymers concerns the method of obtaining a polymer chain by the reaction of: [1]:

- the poly-addition – in this reaction individual units are attached to the forming chain; this reaction is not accompanied by the secretion of by-products,
- the poly-condensation – the crosslinking reaction with the separation of by-products, most often H_2O.

In order to improve the resin parameters, appropriate additives, i.e., fillers, are used [5, 6]. Their quantity and type are selected for the type of the modification planned, the chemical composition of the polymer, the properties of the filler particles (shape, chemical composition, specific surface area), and the required end effect. An important aspect is also the issue of effective distribution of the filler in the resin's volume. For this purpose, the sonication (ultrasounds) is often used in the polymer technology [7, 8]. As a result of dynamic phenomena caused by the action of their energy (vibrations, change of temperature and pressure), filler's molecules can fill spaces between polymer chains or connect with them, most often by means of temporary atomic bonds. In the case of the ultrasound operation in adhesive resins, it is possible to choose their frequency and energy so that the viscosity and thus adhesion to the substrate during application of the adhesive layer before its curing can be appropriately changed. This has a very significant effect on the final adhesion at the interface with the substrate and the ultimate strength of this kind of joint. In addition, the ultrasounds can be used to detect damages and defects in plastic components.

The paper contains the results of research on the properties of the epoxy resins modified with the addition of fillers – microsilica and carbon nanotubes. The exact mixing of the fillers with the resin was obtained by the action of the ultrasound energy. The influence of the modifications applied on the viscosity of the resin before the addition of the hardener was investigated, and as a consequence, the early adhesion to the concrete substrate. In addition, due to the temperature rise of the adhesive due to vibrations, the temperature drop of the resin to the initial (usable) value was investigated. This study was the preliminary stage of the research aimed at determination of the impact of modifications on the physical and mechanical parameters of the hardened resins.

2. Materials, devices and methodology

The Epidian 52 resin was used, by means of which it is possible to glue concrete, ceramics, wood or metal elements. Its basic parameters are:

- shape/colour – thick, yellow-brown liquid with a characteristic smell,
- flash point – 64°C,
- gelation time (the Z-1 hardener) – 40min,
- epoxy number [mol/100g]: 0.51 – 0.55,
- density (in T = 22°C): 1.12 – 1.13g/cm^3,
- viscosity (T = 22°C): 400 – 800 mPas,
- solubility: insoluble in water, soluble in ketones, esters, alcohols, and aromatic hydrocarbons.

The catalyst used was the Z-1 hardener (triethylene-tetrachloro amine). The fillers used were microsilica and carbon nanotubes. The formulas of the composites tested are presented in Table 1.

Table 1. List of recipes of composites tested

Recipe designation	Type of resin	Type of addition/modification	The amount of filler [%]	The amount of hardener [%]
EP52	epoxy	----------------	----------------	7.6
EP52+UD	epoxy	sonication	----------------	7.6
EP52+Mk	epoxy	sonication and microsilica	0.5	10
EP52+NR	epoxy	sonication and carbon nanotubes	0.1	10

In the first phase of the research, the initial parameters (viscosity and density) of the unmodified resin at 22 °C were determined. Next, the resin was subjected to three types of modification (in accordance with Table 1). For each recipe, the same time of the ultrasound operation was taken, which was 3 minutes. After this time, the temperature of the resin and its viscosity were measured, which obtained a minimum value for each recipe. Then, the temperature drop and viscosity increase of the resin were investigated in intervals of 5 min until the resin reached the initial temperature. The amount of filler was related to the resin's mass.

As an ultrasound source, the UP 400S stationary sonicator was used, which emits the24kHz frequency waves and has a power range regulation from 0 to 400W. The viscosity measurement was performed using the Fungilab rotational viscometer – H type, using the R2 spindle with a measurement accuracy of 0.1 mPas. The temperature of the resins was measured using a laboratory thermometer with an accuracy of 0.1 °C and a range of measured temperatures from 25 °C to 150 °C. The view of the test bench is shown in Figure 1.

Figure 1. The test stand – the sonicator and rotational viscometer.

The amount of filler and the optimal sonicator operation time was determined experimentally after a series of tests including the selection of the appropriate ultrasonic energy (400 W was assumed for the test). The optimum filler quantity was determined due to the possibility of its effective and regular distribution in the resin's volume. It should also be noted that for accurate measurements of rheological properties (viscosity) it was important to maintain a constant initial temperature (22 °C).

3. Results and discussions

Figure 2 shows the course of the viscosity variations depending on time for recipes with modifications applied. Figures 3 and 4 show the values of temperature and viscosity for particular recipes at the time of switching off the sonicator, while Figure 5 shows the viscosity values when the resin reached the initial temperature of 22 °C.

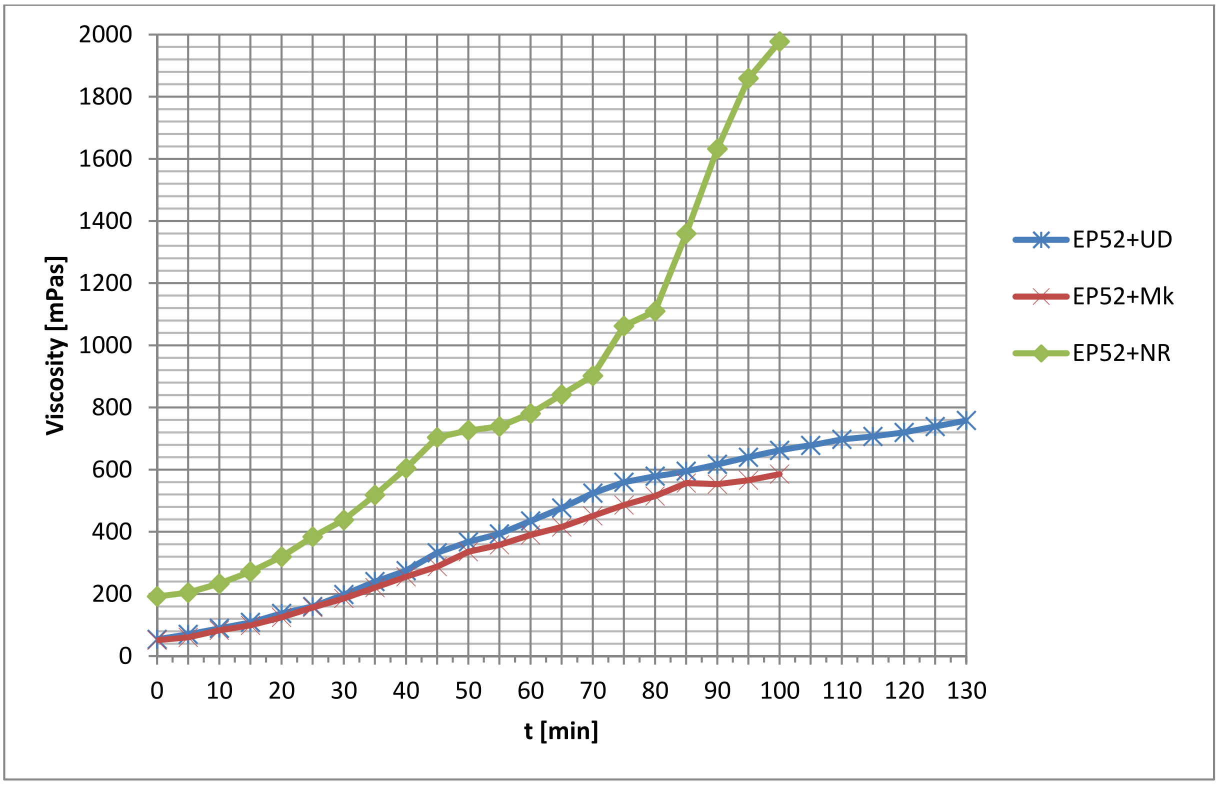

Figure 2. The course of viscosity changes depending on time.

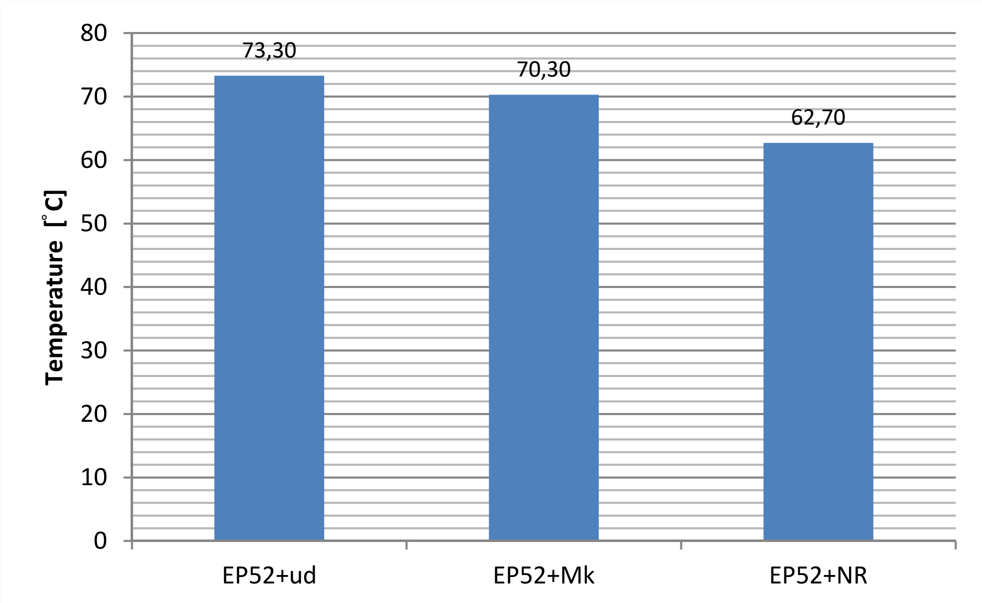

Figure 3. Temperatures of individual composites at the moment of switching off the sonicator.

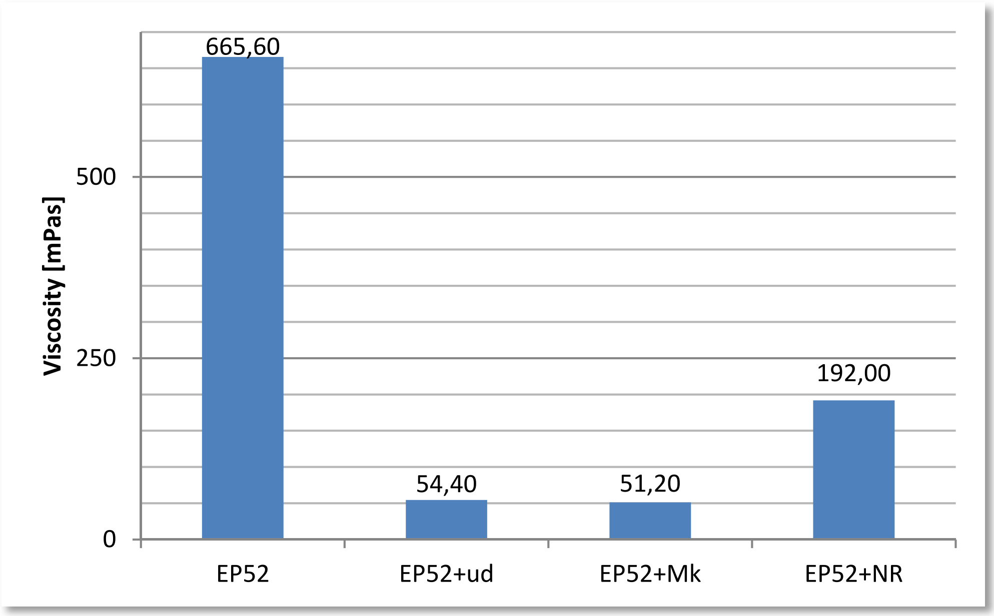

Figure 4. Viscosity values of composites at the time of switching off the sonicator compared to the viscosity of the unmodified resin.

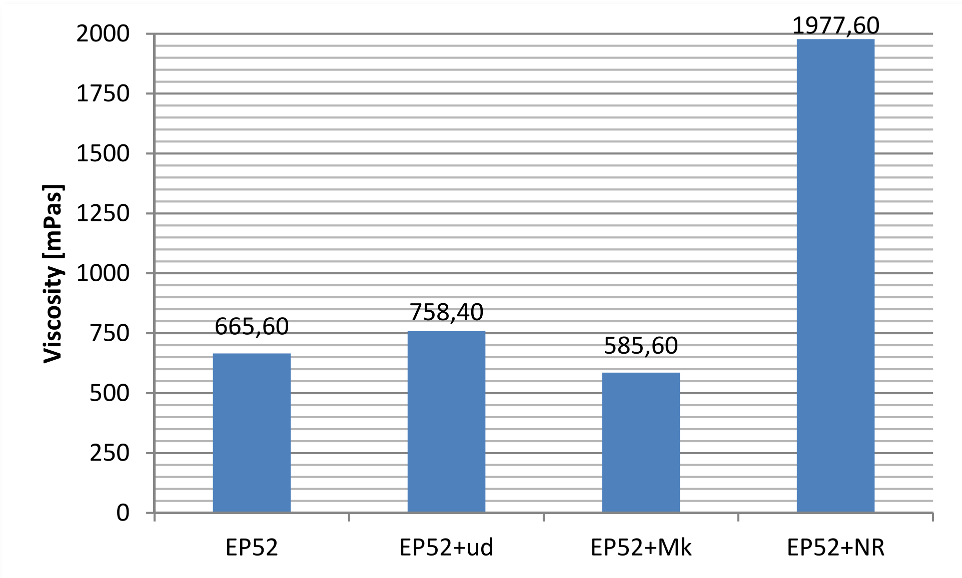

Figure 5. The final viscosity value for the resins tested.

Based on the results obtained, it should be stated that the value of the final viscosity (before adding the hardener) is significantly influenced by the type of the modification used. Each of the ways of preparing the resin causes a different character of changes taking place in its structure.

In the case of modification with the action of the ultrasound energy, the following phenomena were observed.

At the power level applied and a constant frequency of 24 kHz, significant changes occur in the resin's volume. The main reason for this is the occurrence of cavitation and temperature changes, and thus the density of the medium – vibrations caused by the sonication cause low dynamic movements of the system, which at the time become more dynamic. There is a partial disintegration of the polymer chains, some of them are relocated, ruptured, and tidied up. At the same time, due to the temperature increase in the medium, its viscosity decreases which leads to continuous movement and mixing of the masses located at the sonicator head with masses located near the walls of the vessel. What is interesting is that the temperature value obtained at the moment of switching off the sonicator is even higher than the flash point of the resin, while the viscosity value is only 8% of the initial viscosity. As a result of cooling, the viscosity of the resin increases again, which is related to the reassembly of the polymer chains. Its final value is, however, 14% higher than in the case of the unmodified resin. This effect is caused by the ordering of the resin's structure, which was disintegrated during the operation of the ultrasound energy. This translates into an increased early adhesion of the resin to the concrete substrate at the time of application (gluing) and dispensing of the hardener.

Addition of microsilica changes the composite's parameters. The ultrasound energy, in addition to the mentioned phenomena, also causes the dispersion of the filler particles in the resin's volume. On the basis of the observations, it was found that microsilica is evenly distributed in the resin at the time of preparation, however the final temperature is lower than in the case of the recipe for the previous modification – this is related to the absorption of a part of a thermal energy by microsilica particles. However, the reduction of the final viscosity value to 88% of the original value is important. This effect results from the spherical structure of the microsilica particles which, during cooling, enter between the voids between the polymer chains, simultaneously reducing the degree of compaction of the resin's structure. This causes a reduction in the viscosity, and thus also the early adhesion to the substrate, but at the same time it allows for more precise penetration of the resin in the unevenness of its surface.

In the case of modifications with the addition of the carbon nanotubes, other dependencies were observed. The ultrasound energy causes the disruption of not only the polymer chains, but also the carbon nanotubes, which is also related to their specific structure, the effect is a significant increase in their specific surface area. Their single, free bonds may be partially bound to free bonds coming from the chains, whereby the resin structure becomes more dense and sticky – the initial viscosity after the sonication process reaches 29% of the initial value, which is also related to the medium temperature increase, however clearly lower than in the case of the two previous recipes. However, it is worth paying attention to the value of the final viscosity, which is almost 3 times higher than the comparison value – in this case the type of filler used clearly increases the adhesion of the glue to the substrate.

The test results obtained are very important from a practical point of view. Modifications applied in the case of EP52+UD and EP52+NR may be useful in the case of gluing materials at elevated temperatures, or in the case when the surface of the substrate is smooth and even, not rough and not very adhesive. The use of microsilica additive may be useful in the case of bonding at lower temperatures or uneven and porous surfaces.

4. Conclusions

The performed tests constitute a preliminary stage of the analysis defining the influence of applied epoxy resin modifications on the physico-mechanical properties of the hardened resins. They are important because only learning about the entire mechanism of disintegration and changes in rheological parameters of liquid resins enables effective explanation of phenomena occurring during the hardening process. The method of modification and the type of filler used have a significant impact on the viscosity of the resin. The use of the ultrasounds allows disintegration of the internal structure of the resin, the distribution of the filler, and significantly affects the initial adhesion of the glue to the substrate.

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References

[1] J. F. Rabek, “Modern knowledge about polymers”, Wyd. Naukowe PWN, vol 1, pp.3 – 20, 2013
[2] Z. Florjańczyk, S. Penczek, „Chemistry of the polymers”, Oficyna Wydawnicza Politechniki Warszawskiej, t. 2, pp.10 – 55, 2002.
[3] Z. Floriańczyk, M. Dębowski, E. Chwojnowska, K. Łokaj, J. Ostrowska, „Synthetic and natural polymers in modern polymeric materials”, *Polimery,* vol. 54, pp. 609-694, 2009
[4] W. Szlezyngier, Z. K. Brzozowski, „Plastics: chemistry, manufacturing technology, properties, processing, application”, FOSZE, t. 2, 2012.
[5] A. Gnatowski, “Influence of the type of filler on the properties of selected polymer mixtures”, *Composites,* vol. 5/2, 2005
[6] B. Ellis, „Chemistry and technology of epoxy resins”, Springer, 1993
[7] S. Fic, A. Szewczak, D. Barnat – Hunek, G. Łagód, “Processes of fatigue destruction in nanopolymer-hydrophobised ceramic bricks”, *MATERIALS*, nr 1, vol. 10, 2017
[8] S. Fic, A. Szewczak, M. Kłonica, „Adhesive properties of a low molecular weight polymer modified with nanosilica and disintegrated with ultrasounds for hydrophobization of building ceramics”, *Polimery,* vol. 11-12, pp. 730-734, 2015.