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Viscosity and Free Surface Energy as Parameters Describing the Adhesion of the Epoxy Resin to the Substrate

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Abstract. The polymers engineering is a dynamically developing branch of technology. The main research directions are the search for new polymers and methods for modifying existing ones. Among the extensive group of polymers, construction, coating, and adhesive polymers are the most commonly used in the construction industry. The last family includes the epoxy resins that are used to combine two or more materials with different properties. Under the influence of the hardening agent (catalyst or temperature), the polymers are cross-linking to obtain a solid form. During the gluing process, the most important aspect is the resin preparation procedure and the state of the surface to which it will be applied. The adhesion of the resin to the substrate, the effectiveness and durability of the resulting mixture depend on three factors: resin's composition, viscosity, and adhesive parameters of hardened resin.

The paper contains the research results aimed at modification of the epoxy resin using inorganic fillers: microsilica and carbon nanotubes. An epoxy resin is commonly used for e.g., reinforcing structural elements. Ultrasounds were used as a disintegrating agent of the liquid resin structure, allowing mixing it with the filler. The effect of sonication and fillers on the viscosity of the resin at 22 °C was determined. Next, the free surface energy was evaluated, which is the factor determining the final adhesion. Based on the results obtained, the phenomena occurring at the interface between the liquid phase of the resin and the solid phase of the fillers were explained.

1. Introduction

Polymers are chemical substances composed of cyclic repeating chemical sequences (the so-called mers), which form a polymer chain [1]. The mers combine with each other using various types of chemical bonds: ionic, coordinating, polarized, or hydrogen [2]. The chemical composition of the polymer and the chemical bonds occurring between the sequences determine the intended use of a polymer. Viscosity and the final adhesion to the substrate (e.g., concrete, steel [3]) determine the suitability of a polymer. The viscosity affects the possibility of spreading the adhesive on the target surface, filling its irregular ities, and the resin adhesion after hardening. The cross-linking reactions occur at different times, from several hours to several days. The course of the reactions depends largely on the presence of specific polymer groups (phenolic, epoxide, and ester) and the type of factor initiating such a reaction. In the case of chemo-hardening polymers, the amine-based hardeners are most often used [1, 2]. Construction adhesives are hardened after just a few hours, and after a period of 2 days they usually get full adhesion to the substrate.

Among the very large group of polymers encountered in civil engineering the following ones are the most commonly used in construction [1]:
- fiber-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, UV radiation, low temperatures).

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

- very good strength parameters in relation to the weight of the element, e.g., beams,
- very good adhesion to wood, steel, concrete, and ceramics,
- constantly decreasing costs of obtaining polymers and their final price.

The epoxy resins are oligo-polymers that are the product of reaction of the epichlorohydrin and bis-phenol. In addition to the aforementioned properties, its additional features are chemical resistance, impermeability, and dielectricity. The main disadvantages include low resistance to high temperatures and UV radiation.

Fillers are additives, thanks to which it is possible to obtain specific properties and improve the parameters of resins [5, 6, 7]. Their quantity and type are selected due to the type of modification planned, the chemical composition of the polymer, the properties of the filler particles, and the required final effect. The amount of the filler is usually dependent on the resin's weight (volumetric dosing is less precise due to the sensitivity of the polymer to change in temperature and thus their density). It is also important to effectively distribute the filler in the volume of the resin. For this purpose, ultrasounds are often used in the polymer technology [8, 9, 10]. As a result of dynamic phenomena caused by the action of their energy (vibrations, change of temperature, pressure, cavitation), the filler molecules can fill spaces between polymer particles or connect with them, most often by means of temporary atomic bonds. Proper selection of the sonication energy and the amount of filler gives the possibility of appropriate change in the viscosity of the resin – the parameter that determines the initial, early adherence of the resin to the substrate. Then, the hardened polymer obtains proper adhesion to the substrate.

The paper contains the research results on the properties of epoxy resins modified with two fillers – microsilica and carbon nanotubes. The exact mixing of the fillers with the resin was obtained by the action of the sonication energy. The dependence of the early viscosity (at the time of the resin application to the target surface) on the final adhesion of the resin to the substrate was evaluated. For this purpose, the free surface energy was measured [8, 9, 11]. It is a parameter describing dependencies on the liquid-solid. The Owens-Wendt method was applied, which requires the use of two liquids with known dispersive and polar properties. The results obtained were the basis for determining the effectiveness of the modifications applied with regard to the possibilities of practical application, i.e., during strengthening and gluing of building elements. The research conducted was the first stage of research on the effectiveness of the modifications applied in the concrete reinforcing issues, i.e. strengthening by the FRP tape.

2. Materials, Devices and Methodology

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

- state/color – thick, yellow-brown liquid with a characteristic smell,
- ignition temperature – 64 °C,
- gelation time (the Z-1 hardener) – 40 min,
- epoxide number [mol/100g]: 0.51 – 0.55,
- density (at T = 22 °C): 1.12 – 1.13 g/cm^3,
- viscosity (at T = 22 °C): 400 – 800 m·Pa·s, (1m·Pa·s = 10^{-3} Pa·s) ,
- solubility: insoluble in water, soluble in ketones, esters, alcohols, aromatic hydrocarbons,
- hardener: the Z-1 (triethylene-tetrachloro amine).

The fillers used are microsilica and carbon nanotubes. The amount of filler was related to the weight of the resin and it was determined experimentally. The recipes of the composites evaluated are shown 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 stage of the research, the initial parameters (viscosity and density) of the unmodified resin at 22 °C were determined. Next, the polymer was subjected to the three types of modifications shown in Table 1. For each recipe, the same time of sonication (3 minutes) was assumed (time and power of sonication was determined experimentally). After this time, the initial viscosity of the resin and its temperature was measured. Then the temperature drop and the viscosity increase was measured at intervals of 5 min until the resin reached the initial temperature. The ultrasounds source was the UP 400S stationary sonicator, which emits 24kHz waves and have a power range regulation from 0 to 400 W (Figure 1). The viscosity measurement was made using the Fungilab type H rotational viscometer with the use of the R2 spindle (measurement accuracy up to 0.1 m·Pa·s). The temperature of the resin was measured with a laboratory thermometer with an accuracy of 0.1 °C and with a range of measured temperatures from -25 to 150 °C.

a)   b)   c)
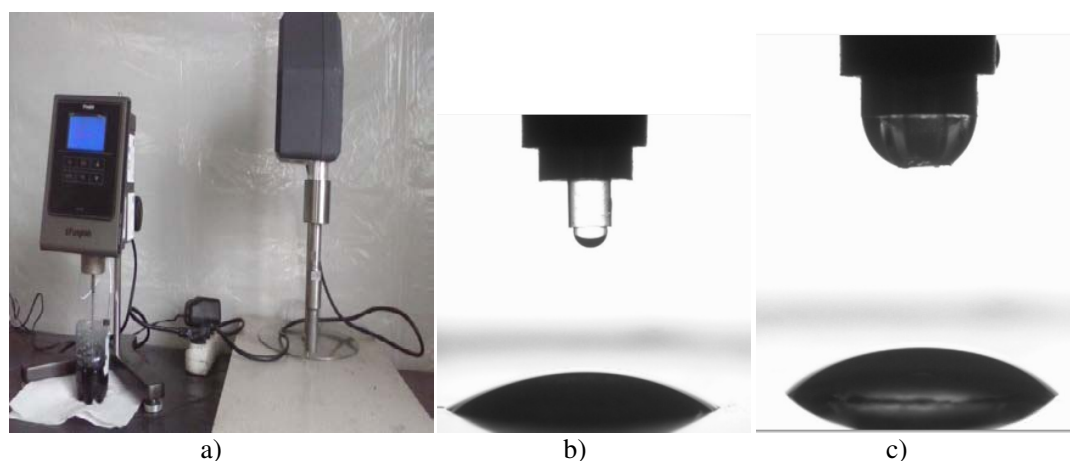
Figure 1. The test stand: a) the sonicator and the rotational viscometer, b) the drop of distilled water, c) the drop of diiodomethane

The surface free energy (SFE) was determined according to the Owens-Wendt method, which consists in measuring the wetting angle of the hardened resin surface. This angle is measured between the horizontal straight line and the tangent to the drop in two variants (for two different liquids Figures 1b and 1c). These liquids were diiodomethane, which had a dispersive component value of 50.8 mJ/m^2 and zero polar component (highly dispersive), and distilled water (highly polar liquid) with a dispersive component value of 51 mJ/m^2 and polar 21.8 mJ/m^2. The SFE is determined as the sum of the dispersive and polar component for each sample. For each series, 30 SFE measurements were made. In order to perform the accurate measurements of rheological properties (viscosity and SFE), it was important to maintain a constant final temperature (22°C); The use of this temperature was necessary to be able to compare the parameters measured, and it was set according to the guidelines and recommendations for this type of research.

3. Results and Discussions

Table 2 shows the results obtained: the initial viscosity μ_0 (at the time of switching off the sonicator), the final μ (after the resin reached 22ºC), and the dispersive components γ_d, polar γ_p, and the total value γ_0 of the SFE. The results obtained were compared with the results for the unmodified resin.

Table 2. Results of research

Series	EP52	EP52+UD	EP52+Mk	EP52+NR
Viscosityμ_0 [mPas]	665.6	54.4	51.2	192
Viscosityμ [mPas]	--------	758.4	585.6	1977.6
Dispersive component [mJ/m^2]	42.7	40.1	42.03	40.87
Polar componentSFE [mJ/m^2]	22.67	32.33	30.6	23.57
TotalSFE [mJ/m^2]	65.43	72.43	72.6	64.43

The results indicated that the final viscosity as well as the individual components of the SFE strictly depends on the type of modification applied. Sonication leads to the dynamic changes in the volume of the resin. An important result of this change is the rise of temperature and pressure drop of the polymer and a violation of its original structure. This changes the structure of the composite and allow the resin to connect with the filler particles and the hardener, mainly in course of the crosslinking reaction. These changes affect the way the filler molecules are arranged, which enter the polymer chain. Sonication cause temporary breaking of the polymer chains, which makes it possible to reorganize them and attach filler molecules. However, the type of such a connection closely depends on the shape of the filler molecules. The sonication energy causes the destruction of long polymer chains and the increase in the viscosity due to the presence of free ends of the individual mers; this affects the parameters of the hardened resin, i.e., a higher SFE value (due to the presence of the free chain ends, while the internal structure is ordered, especially the polar component, directly related to the presence of the free chemical bonds at the ends of polymer chains(Figure 2).The presence of microsilica changes this process; due to intermolecular interactions, microsilica entered into the polymer chains and binds to free polymer endings. This reduces the viscosity and SFE, however, it is not decreased compared to the SFE of the resin modified only by sonication. On the surface of the resin, a thin layer composed of microsilica particles and components of the polymer chain is present (Figure 2), which increases the final adhesion, e.g., to the concrete substrate. Carbon nanotubes, due to the action of ultrasounds, break down and combine with the polymer chains because they are chemically compatible with the main element that forms a polymer – carbon; this causes the initial increase in the initial viscosity. As a result of further interactions, the free polymeric ends are connected to each other by means of nanotubes. The lack of free ends of the polymer chains was noticed based on the results of the SFE value.

The method of "entering" the filler particles into the polymer chains affected the final viscosity. The microsilica is not directly connected to the resin molecules, but only enters into the open spaces between the polymer chains, which reduces the viscosity of the resin. Carbon nanotubes densify the polymer network, consequently increasing the viscosity of the adhesive.

a)   b)

c)   d)
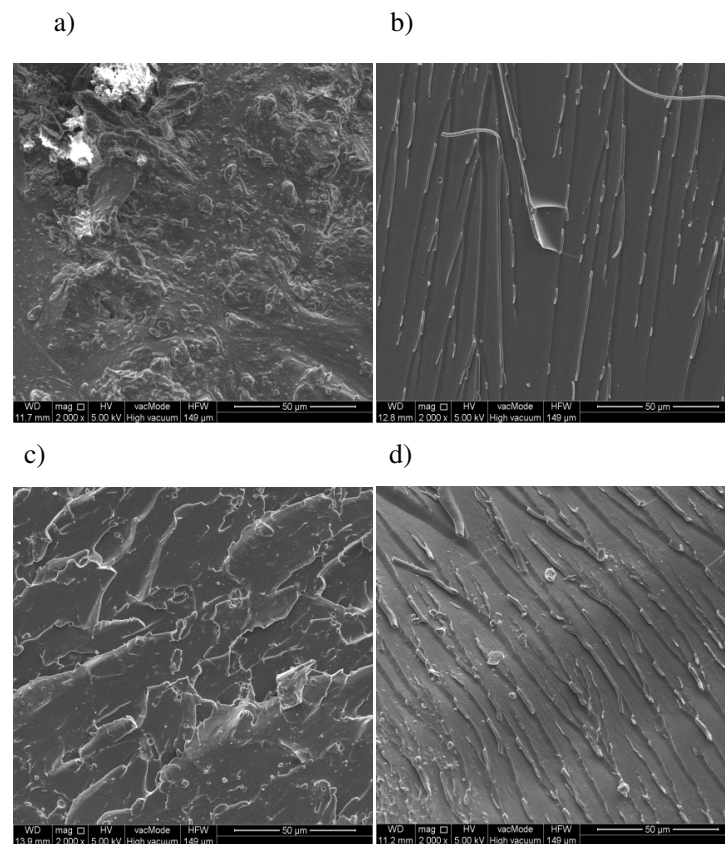
Figure 2. SEM Picture of the samples a) EP52, b) EP52+UD, c) EP52+Mk, d) EP52+NR

4. Conclusions

The results obtained gave a clear picture of how the resin subjected to the modifications behave on the target surface. The type of modification and filler used may depend on the target conditions under which the particular polymer composite will be operated.

The conclusions obtained are very important from a practical point of view. Modifications applied in the case of the EP52+UD and EP52+NR, due to the marked increase in the final viscosity, may be useful in the case of bonding materials at elevated temperatures, or in case when the surface of the substrate is smooth and even, less rough, and less adhesive. The use of the microsilica, on the other hand, may be useful in the case of bonding at lower temperatures or when the application surface is uneven and porous.

The results will be used during the next tests regarding the effectiveness of the modifications during the process of gluing the FRP tapes and reinforcing the concrete elements.

5. Acknowledgments

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