Temperature and chemical resistance of repair composite and microstructure monitoring depending on different type of binder and filler

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Abstract. Currently, we are carrying out several repairs to concrete structures that are permanently exposed to chemically aggressive environments and the effects of temperature and cyclic mechanical stress. It is therefore necessary to develop a highly resistant patching composite that would return the damaged objects to their original state or improve resistance to external attack. In this paper, results of the research, in which monitoring of the temperature was performed and chemical resistance of the polymer composites of repair, specifically with the epoxy matrix and a different type of filler, is presented. As a filler, we use secondary raw materials that are currently produced largely as a by-product of industrial production in the Czech Republic and abroad. It has been found that the type of filler used has not an impact on temperature resistance. but in chemical resistance plays a considerable role also used filler. The microstructure was also monitored before and after chemical stress.

1. Introduction

Newly developed mass is used for the rehabilitation of existing structures experiencing mechanical stress in chemically aggressive environments with higher temperatures. Epoxy resins (ER) are very useful in this environment because they are known to resist famously demanding conditions.

ERs fall into the category of polymers – thermosets that comprise molecules of two or more oxiranes. Their use is divided into several areas, notably electrical, fire retardant, paint (paints, varnishes, adhesives, etc.), and composite [1] ERs can be cured with various curing agents, especially those based on diols, diacids, anhydrides and diamines [1].

In the use of repair materials in demanding industrial and energy plants, chemical resistance is an important parameter. In this environment, aggressive liquids often appear, such as those with a strongly basic and strongly acidic character. The effect of various chemicals on the polymers may lead to a change in their physical properties. There may, for example, be swelling, colour change, chemical degradation of the polymer chains, bursting, crosslinking, or other possible disturbances. In a design environment, organic or inorganic acids are occurred, while organic acid (HCOOH, CH₃COOH, and CH₃CH₂COOH) are relatively weak acids and are therefore much less dissociated. Acting mainly as a solvent, and their effect leads to the formation of blisters on the surface and separation of the segments of the macromolecular chains [2]. Kalenda and Kalendová demonstrated that increased chemical resistance of polymer compositions can be achieved by introducing fillers that are capable of reacting with diffusing acid. Inert fillers or pigments (TiO₂, graphite, carbon black, chromium oxide), present
in the ER matrix, increase the diffusion of aggressive (corrosive) media because the penetration at the interface of the pigment/binder extends along the pigment particles [2].

For characterization of the polymer materials heat resistance, glass transition temperature \(T_g\). This temperature characterizes an upper temperature limit at which the polymer is still useful, was also showed to be very close to between the onset of the so-called diffusion control regime during the isothermal cure of thermostet and its glass transition, the influence of \(T_g\) on the chemorheology of a thermoset, and the correlation between internal stresses and \(T_g\). Many authors have dealt with these dependences, e.g. Hale et al. [3], who created a model equation expressing the relationship between \(T_g\) and other specific parameters. He found out that increase of \(T_g\) is caused by a decreasing in chain-end concentration, as well as formation of effective cross-links and further decrease in the configurational entropy.

2. Identification of materials
As a part of the research, we used two types of polymer resins. The developed patching composites labelled RC1 had a binder component epoxy comprising a resin, a filler such as a reference quartz sand Dorsilit (REF), waste packing transparent glass (WGT), and waste from the production of insulating mineral wool panels (WMTI). The development of repair composites began with a performance of 30%; the maximum tested performance was 85%, and after it exceeded 50%, the amount of filler was increased successively by 5%, because it is from this filling that the properties of the polymer mass are markedly changed. The amount of filler was expressed in weight percentage on the total weight of the fresh mixture.

Patching composites labelled RC2 as a binder component having a different type of epoxide, consisting of an ER (alkoxymethyl) oxirane (C12-C14 alkyl), solvent naphtha (petroleum), and light aromatic. Polyamine-based hardener contained benzyl alcohol, polymer with benzenamine, hydrogenated formaldehyde, 2,4,6-tris (dimethylaminomethyl) phenol, 4,4’-methylenebis (cyclohexylamine), followed by filler components that used quartz sand (Dorsilit), transparent waste glass (WGT), pulverised fly ash contaminated due to denitrification of the flue gas (PFA) and waste from mineral thermal insulation production without organic compound (WMTI). For composites of repair, RC2 was selected with an initial quantity of filler of 40%, making it suitable as a patching material with low viscosity in compositions such as RC1 with planned utilisation in the form of grout.

| Marking materials | Requirements for pre-treatment | Density [kg/m³] |
|-------------------|--------------------------------|-----------------|
| REF               | Need not be modified           | 2662            |
| WGT               | Grinding and sorting to fractions | 2534         |
| PFA               | Need not be modified           | 2390            |
| WMTI              | Need not be modified           | 2620            |

3. Tests performed
3.1. Chemical resistance
Any changes to the properties were affected by the type and concentration of the chemicals, in addition to the time of exposure to the chemicals on the surface of the polymers. According to the formulas (25%RC1+75% REF, 25%RC1+75% WGT, 40%RC1+60% PFA, 30%RC2+70% REF, 30%RC2+70% WGT, 35%RC2+65% WMTI), set samples were prepared different polymer repair composite. Application was done through suitable means in a thick layer on the laboratory specimen slide, which had been cleaned and dried with acetone. Samples were allowed to polymerise for 7 days on a clean substrate at 20 ± 2 °C and then immersed in a sealable glass tube with the appropriate chemicals. Checking of the samples were carried out for 7 to 30 days after immersion in aggressive liquid solutions. The evaluation results were mainly visual, and the reaction mass according to
chemicals classified by the evaluation system are indicated in Tab.1. Second, some specimens were examined using the optical digital microscope VHX-950F Keyence.

**Table 2.** Evaluation system for accelerating chemical resistance tests designed with respect to the expected behaviours of the tested samples in the aggressive media.

| Rating | Description                                      |
|--------|--------------------------------------------------|
| *******| No changes                                       |
| *****  | Colour changes                                   |
| ****   | Swelling and colour changes                      |
| ****   | Peeling off from the glass                       |
| ***    | Peeling off from the glass and swelling included colour changes |
| **     | Peeling off from the glass and softening         |
| *      | Complete disruption                              |

Based on the expected use of the repair materials developed in industrial and energy plants, solutions were selected that are used in these plants to a great extent. Acetic acid (CH\(_3\)COOH), phosphoric acid (H\(_2\)SO\(_4\)), sodium hydroxide (NaOH), sodium chloride (NaCl), hydrogen peroxide (H\(_2\)O\(_2\)), and distilled water (H\(_2\)O), followed by petroleum products and gasoline were chosen.

3.2. **Temperature resistance**

Determination of heat resistance of polymers is usually carried out by setting the glass transition temperature (\(T_g\)) through differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). Samples for \(T_g\) were tested using DMA 2980 (TA Instruments). This is an analysis in which through periodic sinusoidal deformation of the sample clamped in the jaws of the system, the force required for this deformation is measured. Based on the course of the deformation and force (deformation subsequently converted to deformation stress) and their phase shift is determined by a dynamic modulus of elasticity and its components: elastic (Storage) and the Loss (loss) modulus. Measurements were performed in the temperature range of 40-130 °C at a heating rate of 5 °C / min, amplitude of 10 mm, and a frequency of 1 Hz. The dimensions of the samples were 35 (17.6 active) × 3.3 × 12.0 mm, and from each material, two samples were obtained.

3.3. **Coefficient of linear thermal expansion**

Coefficient of thermal expansion (\(\alpha\)) was determined for the chosen repair and grout materials. The samples’ dimensions were 20 × 20 × 100 mm, and measurement was carried out in the temperature range of 20-60 °C for approximately 18 hours. Coefficient of thermal expansion (\(\alpha\)) is an important parameter, particularly for polymers used in engineering applications. Low value of \(\alpha\) is often desirable for achieving dimensional stability.

4. **Results and discussion**

4.1. **Chemical resistance**

Evaluation of the chemical resistance of tested repair composites was conducted after 30 days of exposure to various corrosive media. It was found that the selected repair materials were resistant to strong inorganic acids and hydroxides (see Fig. 1 and Fig. 2). However, the materials were not resistant to acetic acid (CH\(_3\)COOH) at a concentration of 10%. After immersion in distilled water and saturated sodium chloride (NaCl), even after 30 days, there was no change. Gasoline, which is a primarily aliphatic hydrocarbon mixture obtained by fractional distillation of crude oil with added aromatic hydrocarbons and additives also had no effect on the degradation of the epoxy repair mass.
Table 3. Evaluation of chemical resistance of tested repair composites (RC1, RC2) after 30 days of immersion in different liquid aggressive solutions.

| Aggressive medium | Concentration | RC1 75% REF | RC1 75% WGT | RC1 60% PFA | RC2 70% REF | RC2 70% WGT | RC2 65% WMTI |
|-------------------|---------------|-------------|-------------|-------------|-------------|-------------|-------------|
| H$_2$SO$_4$       | 40%           | **********  | **********  | **********  | **********  | **********  | **********  |
| NaOH              | 40%           | **********  | **********  | **********  | **********  | **********  | **********  |
| CH$_3$COOH        | 10%           | *           | *           | *           | ***         | ***         | **          |
| Gasoline          | -             | **********  | **********  | **********  | **********  | **********  | **********  |
| NaCl              | 10%           | **********  | **********  | **********  | **********  | **********  | **********  |
| H$_2$O$_2$        | 30%           | *****       | *****       | **          | **********  | **********  | **********  |
| Distilled water   | -             | **********  | **********  | **********  | **********  | **********  | **********  |

Fig. 1. Samples RC1 75% WGT after 30 days immersion in aggressive liquid solutions.

Fig. 2. Samples RC1 60% PFA after 30 days immersion in aggressive liquid solutions.

For the selected composite (RC1 65% OIDM) showed, indicating somewhat lower chemical resistance than for other formulations (see Fig. 3 and Tab. 3). This difference may be due to a different filler – particularly the particle size and shape and its chemical composition.

Fig. 3. Samples RC2 65% WMTI after 30 days immersion in aggressive liquid solutions.

The surface of some samples was further investigated by optical microscopy after chemical stress to observe the influence of aggressive media on infringement material. Based on the images from the optical microscope, the action of the sulfuric acid did not disturb the surface (Fig. 4, Fig. 5). On the samples that were exposed to acetic acid, considerable deterioration of the surface and cracking were found (Fig. 6).
4.2. Temperature resistance
Examination of the heat resistance by repair composites was conducted by determining glass transition temperature ($T_g$). $T_g$ is a very important parameter for epoxy thermosets and epoxy matrix composites because it determines the conditions for the use of these types of materials. In most applications, epoxy resins are used at a temperature below $T_g$ (the glassy state). Different $T_g$ values can be justified through different ways of preparing materials [4]. Results of the determination of $T_g$ of DMA are shown in Fig. 7 and Fig. 8; the abscissa indicates temperature in [$^\circ$C], and the y-axis shows the values the of elastic modulus (left) and loss modulus (right). The highest $T_g$ was calculated from the value of the dissipation factor (tan $\delta$), which, upon reaching the $T_g$, was at maximum. Graphical comparison set $T_g$ can be observed in Fig. 9. Based on the results, it is evident that $T_g$ does not significantly affect the filler used, but rather the binder type (ER) and the principle of its curing. All test materials were a $T_g$ higher than 70 $^\circ$C, ensuring safe use even at higher temperatures in severe environments.
4.3. Coefficient of linear thermal expansion

The dilatometric curve of the selected repair composite RC1, which is primarily intended for use in the remediation of thermally and chemically stressed structures, is shown in Fig. 10. The results of the coefficient of thermal expansion (α) are given in Tab. 4.
Table 4. Values of the coefficient of linear thermal expansion (α) of different polymer repair composites.

| Formulation         | ΔT [K] | L₀ [mm] | α [K⁻¹] |
|---------------------|--------|---------|---------|
| RC1-75% REF         | 30     | 99.1965 | 40.1·10⁻⁶ |
| RC1-75% WGT         | 29     | 99.0962 | 55.3·10⁻⁶ |
| RC1-60% PFA         | 24     | 99.2088 | 52.8·10⁻⁶ |
| RC2-70% REF         | 27     | 99.1794 | 55.5·10⁻⁶ |
| RC2-70% WGT         | 26     | 99.1856 | 55.3·10⁻⁶ |
| RC2-65% WMTI        | 33     | 99.1565 | 40.9·10⁻⁶ |

The determined values of the coefficient of thermal expansion (α) confirmed the generally known evidence that polymer-based materials exhibit higher values of α compared with silicate materials. In the case of repair materials for the repair of concrete structures, the same or similar coefficients of thermal expansion (α) that show a concrete bed are required [5]. For conventional concrete, α = 14·10⁻⁶ K⁻¹ [6]. The developed materials did not fulfil this requirement completely because of the achieved values of α between 40·10⁻⁶-55·10⁻⁶ K⁻¹ (Tab. 4). In case of the rehabilitated part of the structure loading by cyclic temperature variation, small cracks could occur in the tested repair materials due to the higher stress at the connection point of the remediation material to the substrate. However, because of the high cohesion of repair materials to the substrate and a lower modulus of elasticity, repair composites can be developed that are capable of effectively resisting even alternating temperature changes. This assumption still needs to be verified in practice.

5. Conclusion
Based on the determined values of thermal resistance by means of DMA analysis, and the results of the Tₕ, it can be concluded that the type of filler used has no effect on the temperature resistance of repair composites developed using epoxy resin (ER), which is planned mostly used for the repair of concrete structures. Heat resistance is mainly affected by the type of binder used. The results showed that even the coefficient of thermal expansion is influenced primarily by the type of binder used, in this case the epoxy resin, and not by the type and amount of filler.

Regarding the chemical resistance, the worst degradation of the test fuel was caused by acetic acid (10% CH₃COOH). Therefore, repair composites should not be used in environments where an
aggressive medium is present. It was also found that these composites are resistant to strong solutions of inorganic acids and alkalis.

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