The effect of triethylene glycol additive on the self-healing properties of epoxy binder

T V Petrova\textsuperscript{a}, V I Solodilov\textsuperscript{a}, V E Kabantseva\textsuperscript{a}, N V Karelina\textsuperscript{a}, A V Polezhaev\textsuperscript{a,b,}\textsuperscript{*}

\textsuperscript{a}Bauman Moscow State Technical University, 105005, Russia, Moscow, 2nd Baumanskaya str., 5/1
\textsuperscript{b}A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, 119334, Vavilova street 28

E-mail: avp@emtc.ru

Abstract. A triethylene glycol-modified epoxy composition based on diglycidylfurfurylamine (FuEp) and 1,1'- (methylene-di-4,1-phenylene)bismaleimide (BMI) was cured with methyl hexahydrophthalic anhydride (MHPPA). The components of the composition can reversely binds through Diels-Alder reaction between furan and maleimide moieties. We studied the effect of TEG additive on the rheological and thermophysical properties of the binder, as well as the ability through thermal treatment. All compounds were characterized with NMR and IR spectroscopy. It was shown that TEG significantly reduces the curing time and the glass transition temperature of the cured samples, which allows to speed up the process of self-healing.

1. Introduction

Self-healing materials belong to the class of "smart" materials that can partially or completely repair damage caused by external influence. [1-3]. Such materials should be able to self-heal cracks and other defects arising during the operation of the product. The development of various strategies and approaches to the creation of self-healing materials is one of the most important tasks in the creation of new composite materials. [4, 5].

There are two different approaches to the creation of such materials: intrinsic and extrinsic self-healing. In the case of extrinsic self-healing, the liquid reducing agent is placed in spherical capsules or hollow tubes. When a crack is formed, the liquid components spread out, filling the crack, and polymerize under the action of a hardener or catalyst that was previously inserted into the composite matrix. [6-11]. Thus, this type of self-healing only provides one-time recovery.

Intrinsic self-healing does not require the introduction of various healing agents. This method is based on the ability of materials to re-form covalent bonds between functional groups on the surface of a crack. To form these bonds, the monomeric components of the material must be fully or partially polymerized due to a reversible, under certain conditions, reaction. If damaged, this material may be subjected to depolymerization to release fragments that fill the crack, followed by reverse polymerization to the crosslinked state. [12-14].

Intrinsic self-healing is a more promising method for creating self-healing materials, as it allows self-healing to be controlled and repeated. Furan components of such polymers are usually synthesized from furfural - a product of processing plant raw materials, which is important from the point of view of...
"green" chemistry. [15, 16]. We present here a reversible self-healing approach based on reversible Diels-Alder reaction between furan and maleimide pair [17, 18, 19].

2. Experimental

2.1. Materials and methods
BMI (1,1’- (methylene-di-4,1-phenylene)bismaleimide, 95%, Sigma-Aldrich), MHHFA (hexahydro-4-methylphthalic anhydride, 98%, Acros Organics), triethylene glycol (TEG), furfurylamine (99 %, Acros Organics), epichlorohydrin (99%, Fluka), NaOH (Labtech), tetrabutylammonium hydrosulfate (98%, Acros Organics) were used without further purification. All solvents used: ethyl acetate, petroleum ether, hexane (all reagent grade) - were produced by the company "Component-Reactent".

IR-ATR spectra were obtained on a Thermo Nicolet iS10 spectrometer with a Fourier transducer using a germanium crystal in the range of 4000-650 cm-1. NMR spectra were recorded on a Bruker Avance 600 spectrometer 600 (600.1 MHz) in DMSO-d6. Calorimetric measurements were performed on DSC NETZH DSC 204 F1 Phoenix calorimeter in the temperature range from 20 to 200 °C with a heating / cooling rate of 10 K min-1 in argon atmosphere. Viscosity was determined on a rotational cone-plate viscometer Brookfield Cap 2000+ (rotation speed of 8 rpm, spindle No. 1).

2.2. Synthesis of diglycidylfurfurylamine FuEp
The target substance was obtained by a modified literature method. [17]. Briefly, the synthesis was carried out in two stages. At the first stage, furfurylamine was slowly added to the epichlorohydrin, the product obtained, without isolation, was cyclized by the action of an alkali solution. Yield 33,9 g. 1H NMR (400 MHz, DMSO-d6, ppm): 3.1–2.4, 6.17–6.25 (=CH-CH= furan ring, 2H), 7.31 (-O-CH=C- furan ring, 1H), 3.7-4.07 (-NCH2, 2H). IR (ATR, cm-1): 3121, 3049, 2995, 2922, 2831, 1739, 1601, 1442, 1350, 1257, 1151, 1076, 1011, 917, 856, 830.

2.3. Synthesis of cross-linked polymer (FuEp/BMI/MGGFA/TEG)
BMI 0.451 g (1.3 mmol) was mixed with 0.526 g (2.5 mmol) of FuEp at 70 °C for 15 minutes. TEG was added to the mixture (1, 5 or 10% with respect to FuEp). The curing conditions were chosen in accordance with the optimum temperature for the formation of Diels-Alder bonds, so that most of the furan and maleimide groups reacted before the system was cured. Samples were cured with 0.680 g (4.0 mmol) of methyl hexahydrophthalic anhydride (MGGFA) at 70 °C for 24 h.

3. Results and discussion
Tian and coauthors showed [17] that a three-component binder consisting of FuEp, BMI and MHHFA can cure to form a cross-linked polymer that forms a double interpenetrating network: one part of the network was formed by a copolymerisation of epoxy and anhydride, and the second was formed through DA adducts between the maleimide BMI and the furan ring of FuE. Under heating to 120 °C in a cross-linked polymer, a retro-DA reaction occurred with the destruction of the bonds between furan and maleimide with the release of BMI, the subsequent prolonged curing at 60 °C leads to the reformation of the DA adducts, which resulted in the restoration of mechanical properties after damage (Scheme 1)
Scheme 1. Formation of a cross-linked polymer and reversible decomposition of DA adducts.

We repeated this work and noticed some shortcomings. For example, the restoration cycle proposed by the authors (20 minutes at 120 °C and 72 hours at 70 °C) is long and impractical for industrial use. Another significant drawback is the fragility of the resulting composition. It is known that one of the most commonly used technologies for manufacturing of fiber reinforced composite is vacuum infusion. This method requires the use of low viscosity binders to ensure good impregnation quality. We suggest that the addition of triethylene glycol could help to reduce all the above disadvantages. It is known that glycols act as a catalyst for an anhydride curable epoxy composition and also as a plasticizer. The addition of such a component can lead to a decrease in the curing time and a decrease in the glass transition temperature, and, consequently, to an acceleration of the self-healing process (Scheme 2).

Scheme 2. Formation of a cross-linked polymer in the presence of TEG and reversible destruction of DA adducts.
3.1. Synthesis and structure of the epoxy component of the binder (FuEp)

The epoxy component of the binder was obtained in two stages, at the first stage, furfurylamine was slowly added to epichlorohydrin, controlling the temperature, then the resulting mixture was treated with 40% NaOH solution, extracted and purified by silica gel flash chromatography (Scheme 3).

Scheme 3. Synthesis of an epoxy component.

The compound obtained was characterized with IR and NMR spectroscopies. Figure 1 shows the FTIR (ATR) spectrum of the FuEp. The bands at 3049 cm\(^{-1}\) (C–H of oxirane ring), 1257 and 857 cm\(^{-1}\) (C–O–C), and 918 cm\(^{-1}\) correspond to the oxirane cycle. Stretches of the furan ring in FuEp appeared as bands at 3122 cm\(^{-1}\) (C–H), 1508 cm\(^{-1}\) (C = C), 1351 cm\(^{-1}\) (C–N), 1152 cm\(^{-1}\) (C–O), and 1011 cm\(^{-1}\).

Fig. 1. FTIR spectrum of FuEp.

In the \(^1\)H NMR spectrum (Figure 2), the FuEp peaks at 3.1–2.4 ppm appeared from protons of oxirane rings (“5”). The furan cycle was showed by peaks at 6.17–6.25 ppm (= CH – CH =, 2H) and 7.31 ppm (= O – CH = C–, 1H), which corresponds to protons, denoted as 2, 3, and 1, respectively. The characteristic peak at 3.7-4.07 ppm (-NCH2-furan ring, 2H) corresponds to the methylene group in position "4". The data obtained unequivocally confirm the structure of the synthesized epoxy component.
3.2. Obtaining a binder (FuE / BMI / MHHFA / TEG) and the study of its properties

A binder was obtained by mixing of the components in a solution of dichloromethane, followed by removal of the solvent in high vacuum. The resulting viscous solution was kept at 80 °C for 10 minutes to ensure the formation of DA adducts between the furan and maleimide components. We studied the dependence of the viscosity of the composition FuEp / BMI / MHHFA from the amount of added triethylene glycol. Viscosity measurement showed a significant dependence of the dynamic viscosity on the TEG content, as well as on temperature. Thus, the introduction of 1% TEG into the binder resulted in a decrease in viscosity from 3.21 to 0.75 Pa * s. Adding more TEG does not linearly decrease viscosity, but has only a minor effect.

The DSC method was used to determine the maximum curing exotherm temperature for the binder, as well as the glass transition temperature of the cured material. The results of thermal analysis are presented in Table 1. At the first heating of the composition, an exothermic peak appears on the DSC curve, corresponding to the reaction of copolymerization of epoxide and anhydride hardener and TEG.
The decrease in the maximum of the exotherm when adding TEG shows that TEG acts as an accelerator in the curing process.

The addition of 1% of TEG lead to a drop of the maximum of the exotherm by 45 °C, but at the same time reduced the glass transition temperature, and hence the upper limit of the heat resistance of the polymer, by 30 °C. The increase in the concentration of triethylene glycol in this composition, in our opinion, is inexpedient, so further changes in the characteristics were insignificant. Also, DSC analysis allowed to indirectly assess the degree of self-healing. Samples of a composition with 1% TEG were subjected to thermal cycling according to the following program: 120 °C for 20 minutes to completely destroy DA adducts between furan and maleimide, and then kept at 60 ° C for various periods of time. After that, the samples were measured by the DSC method. To assess the degree of reduction of the DA adducts, the area of the endothermic peak of the Diels – Alder back reaction was used, which is proportional to the number of bonds formed, which in turn indicates the completeness of the reduction (Figure 4).

![Figure 4](image-url)

**Figure. 4.** DSC thermograms of samples containing 1% of TEG treated for 60 °C for 16, 32,48, 64, and 80 h.

The peak areas of the Diels-Alder reverse reaction for samples with different TEG contents are shown on Tab. 2. As can be seen, for samples with the content of 1% TEG, after 32 h, almost complete restoration of bonds is observed. An increase in the holding time does not contribute to a significant increase in the peak area and varies within 5%. For samples with higher TEG content, the glass transition temperature decreased and the glass transition curve overlaps with the signal corresponding to the Diels-Alder reverse reaction; therefore, it was not possible to separate these peaks and correctly analyze their areas.
Table 2. The results of measurements of the peak area of the Diels-Alder back reaction depending on the time of keeping the samples in the furnace and the TEG content

| Time, h | 16   | 32   | 48   | 64   | 80   |
|--------|------|------|------|------|------|
| TEG content, % | Square of the peak, J/g | Square of the peak, J/g |
| 0      | -9,69 | -10,06 | -11,79 | -13,39 | -12,36 |
| 1      | -18,76 | -19,63 | -20,82 | -21,02 | -22,15 |
| 5      | -13,69 | -38,60 | -18,29 | -20,22 | -40,71 |
| 10     | -27,86 | -12,98 | -27,70 | -28,34 | -13,05 |

We also carried out an optimization of the composition of the binder in order to determine the optimal TEG content, providing a reduction in viscosity for values acceptable for vacuum infusion and at the same time minimal loss of heat resistance (Fig.5). It was shown that an increase in the TEG content above 1% is unnecessary.

4. Conclusions
It was found that the optimal content of triethylene glycol in the composition with FuEp/BMI/MHHFA T about 1%. The addition of TEG makes possible to achieve a reduction of the temperature of the reaction of the epoxy ring opening from 148 °C to 107 °C, as well as to reduce the viscosity by 76%.

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