Development of branched aromatic maleimides as components of self-healing binders for polymer composites

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Abstract. Various modifications of epoxy resins with maleimides and polyimide fragments result in the formation of heat-resistant materials with excellent mechanical and electrical properties together with high chemical, corrosion, and radiation resistance. Such materials can be used in the aerospace industry, electronics, instrument making, and other industries. The ability of some epoxy-maleimide resins to react with furanic groups through thermo-reversible Diels-Alder reaction open a new area in composite material science - self-healing binders. Self-healing materials can restore their structure and mechanical properties after a damage that results in an increase of the service life several times and, therefore, reduce their cost. In this paper, maleimides were modified by diglycidyl ethers to obtain not previously described polyethers, capable of self-healing of mechanical properties after damage. All compounds were characterized by ¹H NMR.

1. Introduction
Thermosetting resins are widely used in industries, for example, as adhesives or binders for fiber-reinforced composite materials for the aerospace industry [1]. The most widely used of thermosets are epoxy resins and polyimides. Epoxy resins are known as materials with high tensile strength, modulus of elasticity, excellent adhesive properties, low shrinkage during curing, high chemical and corrosion resistance. The simplicity of chemical modification and processing also increase the utility of epoxy resins. However, applications of epoxy resins in aerospace and some other areas are limited with their insufficient thermal stability and sometimes poor mechanics [2]. Polyimides showed a unique combination of extremely high thermal and heat resistance, excellent mechanical and electrical characteristics in together with high chemical and radiation resistance, which leads to their widespread use in the aerospace industry, electronics, electrical engineering, instrument engineering and others [3]. However, polyimides have some disadvantages, such as poor processability, fragility, and high cost. Therefore, the development of various modifications of epoxy resins with polyimides in order to obtain materials with suitable properties and an acceptable cost has attracted the attention of scientists for a long time [4-14].

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Also, epoxy resins modified with maleimide fragments, are of particular interest to developers of self-healing binders based on thermo-reversible Diels-Alder reaction between furan and maleimide as a diene and dienophile, self-healing process could occur within the 100-150°C range. [15-20]. We demonstrate here a modification of maleimides with diglycidyl ethers to obtain polyethers not previously described, potentially capable of self-healing of mechanical properties after damage.

2. Experimental

2.1. Materials and methods
Maleic anhydride (p.a., Khimreaktiv, Russia), 4-aminophenol (97%, Acros Organics, Italy), 3,5-diaminobenzoic acid (98%, Acros Organics, United Kingdom), 5-aminoisophthalic acid (94 %, Aldrich Chemistry, India), sodium acetate anhydrous (99%, Acros Organics, Spain), acetic anhydride (tech., Ya.M. Sverdlov factory, Russia), acetonitrile (99%, Component-Reactiv, Russia), para-toluenesulfonic acid monohydrate (98%, Sigma-Aldrich, USA), 1,4-butanediol diglycidyl ether (Khimekslimited, Russia), diglycidyl ether of diethylene glycol DEG-1 (NIIKHIMPOLIMER, Russia), 4-dimethylaminopyridine DMAP (99%, Acros Organics, USA), tetrabutylammonium hydroxide sulfate (98%, Acros Organics, India), triphenylphosphine, TTP (99%, Acros Organics, China), hexamethyl triethylammonium bromide, CTAB 97%, Acros Organics, USA), epichlorohydrin (≥ 99%, Fluka Analytical, Germany), sodium hydroxide (p.a., Labtech, Russia), anhydrous sodium sulfate (p.a., Labtech, Russia), phosphorus oxide (V) (p.a., Component- Reagent, Russia), acetic acid (p.a., OOO Baum-Lux , Russia), acetone (p.a., Component- Reagent, Russia), chloroform (r.g., Component-Reagent, Russia), toluene (p.a., Component- Reagent, Russia), ethyl alcohol (medical antiseptic solution, 95%, Ferein, Russia), 4-dimethylformamide DMF (99%, Acros Organics, USA). DEG-1 was purified by vacuum distillation; the remaining reagents were used without further purification. ATR FTIR spectra were recorded on a Thermo Fisher Scientific Nicolet iS10 (USA) spectrometer. All 1H-NMR spectra were recorded on a Bruker Avance 600 spectrometer (600.15 MHz). The values of chemical shifts (δ, ppm) in the spectra were determined relative to the residual signal of the solvent.

2.2. Synthesis of N-(4-hydroxyphenyl)maleamic acid 1
In a three-neck flask with reflux, 64.8 g (0.66 mol) of maleic anhydride were dissolved in acetone (525 ml) at the room temperature. Then 65.4 g (0.60 mol) of p-aminophenol was added to the solution in portions over 30 minutes and stirred for 1.5 hours. The precipitate was filtered, washed with acetone and dried in vacuum over P2O5. 115.8 g (yield 93%) of the target substance was collected as lemon-yellow crystalline precipitate.

Spectrum 1H-NMR (DMSO-d6): 13.19 (s, 1H, -COOH), 10.50 (s, 1H, –NH), 7.42 (d, 2H, J = 8.9, Ar), 6.74 (d, 2H, J = 8.9, Ar), 6.48 (d, 2H, J = 12.4, =CH-C(O)-NH), 6.29 (d, 2H, J = 12.4, =CH-COOH).

2.3. Synthesis of N-(4-hydroxyphenyl)maleimide 2
70.40 g of acid 1 and 5.12 g of p-toluenesulfonic acid were boiled in a mixture of DMF (36 ml) and toluene (400 ml) at 110 °C with a Dean-Stark nozzle for 5 hours until the precipitate dissolved completely and the stoichiometric amount of water was collected. After evaporation of toluene, the thick solution was poured with water, the precipitate was filtered, washed with 5% NaHSO4 solution and water, dried in vacuum over P2O5. 50.40 g (yield 78%) of the target substance was received as bright yellow crystalline precipitate. 1H-NMR (DMSO-d6): 7.34 (d, 2H, J = 8.8, Ar), 7.17 (d, 2H, J = 8.8, Ar), 6.84 (s, 2H, -CH = CH-maleimide ring).

2.4. Synthesis of 3,5-bis[((2Z)-3-carboxyprop-2-enoyl)amino]benzoic acid 3
9.70 g (0.1 mol) of maleic anhydride and 5.02 g (0.033 mol) of 3,5-diaminobenzoic acid were boiled in chloroform (300 ml) for 20 hours. The precipitate was filtered, washed with chloroform and dried in vacuum over KOH. 11.31 g (98.0% yield) of the desired substance was obtained as light green crystalline
precipitate. $^1$H-NMR (DMSO-d6): 11.05 (s, 3H, -OH), 10.62 (s, 2H, -NH), 8.38 (s, 1H, Ar), 8.02 (s, 2H, Ar), 6.52–6.24 (m, 4H, - (O) C-CH = CH-C (O) -).

2.5. Synthesis of 3,5-bis(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzoic acid 4

5.45 g (0.016 mol) of acid was stirred with 0.4 eq. (0, 51 g, 0.0063 mol) of sodium acetate in acetic anhydride (120 ml) at 90-100°C for 1.5 hours. Then the solution was poured onto ice, 750 ml of cold water was added, left for 10 minutes, then vigorously stirred for 1 hour. The precipitate was filtered, washed with ~ 300 ml of cold water and dried in vacuum over KOH. 2.41 g (yield 49.2%) of the target substance was received in the form of beige crystalline precipitate. $^1$H-NMR (DMSO-d6): 12.96 (s, 1H, -OH), 8.07-7.96 (m, 2H, Ar), 7.69 (s, 1H, Ar), 7.26 (s, 4H, -CH = CH- maleimide ring).

2.6. Synthesis of 5-[(2Z)-3-carboxyprop-2-enoyl]amino]benzene-1,3-dicarboxylic acid 5

To the solution of 2.89 g (0.0295 mol) of maleic anhydride in glacial acetic acid (55 ml), 5.16 g (0.0285 mol) of 5-aminoisophthalic acid were added with vigorous stirring. In 5 hours, the precipitate was filtered, washed with water and dried in vacuum over KOH. 2.42 g (yield 30.4%) of the target substance was received in the form of light beige crystalline precipitate. $^1$H-NMR (DMSO-d6): 12.89 (s, 3H, -OH), 10.72 (s, 1H, -NH), 8.50 (s, 2H, Ar), 8.23 (s, 1H, Ar), 6.55–6.36 (m, 2H, - (O) C-CH = CH-C (O) -).

2.7. Synthesis of 5-[(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzene-1,3-dicarboxylic acid 6

1.46 g (0.0052 mol) of acid was mixed with 0.25 g (0.003 mol) of sodium acetate in acetic anhydride (25 ml) at 90°C for 17 hours. Then the solution was poured into ice water, extracted with diethyl ether, the organic layer was dried over sodium sulfate, filtered, evaporated, and the residue was recrystallized from ethyl alcohol. Received 0.97 g (yield 71.5%) of the target substance in the form of beige crystalline precipitate. $^1$H-NMR (DMSO-d6): 12.92 (s, 1H, -OH), 7.98 (s, 2H, Ar), 7.65 (s, 1H, Ar), 7.23 (s, 2H, -CH = CH-maleimide ring).

3. Results and discussion

Self-healing polymers based on the Diels-Alder thermo-reversible reaction are very promising due to their ability to restore the structure and mechanical properties repeatedly. A modification of the epoxy binder with furan fragments is most often used for the introduction of diene groups, and bismaleimide or other dimaleimides are added to the binder as a dienophile [1, 21-23]. The price of dimaleimides is quite high and it greatly increases the final cost of the developed materials.

Most of the work on self-healing polymers is devoted to the synthesis of furan components, and a single diphenylmethane (bismaleimide) has been often used as the dienophile. We consider that the use of new maleimides based on inexpensive aromatic amines will significantly expand the possibilities of creating new self-healing polymers. In this regard, we developed a series of various branched aromatic maleimides. It is also should be noted that in this paper mainly simple methods of synthesis allowing to obtain high-purity compounds without additional purification were used.

The proposed synthetic scheme begins with the synthesis of simple aromatic maleimides from commercially available p-aminophenol, 3,5-diaminobenzoic acid and 5-aminoisophthalic acid. The reaction was carried out in two stages with the preparation of maleamic acid and subsequent cyclization by acetic anhydride or p-toluensulfonic acid. Maleimides 2, 4, 6 of high purity were obtained during the work. The most likely reason of small yields in the preparation of compounds 2, 4 and 5 is their partial solubility in water (Scheme 1).
On the next stage maleimide containing precursors bearing active functional groups were reacted with inexpensive and commercially available epoxydes such as epichlorohydrine and diglycydyl ethers of aliphatic diols. First we used literature procedure [24] for the synthesis of compound 7, however, could not obtained the product due to the probable ring opening of the maleimide ring under basic conditions. The courses of reactions targeted compounds 8 and 9 were monitored by disappearance in IR spectra of an epoxy groups bands at 837, 912, 1275 and 1519 cm\(^{-1}\) for compound 8 and 855, 910, 1336 and 1479 cm\(^{-1}\) for compound 9, respectively. However, NMR analysis showed the presence of a mixture of reaction products. Thus, it was decided to abandon attempts to obtain esters of N-(4-hydroxy phenyl)maleimide. We are working now on the synthesis of compounds 10 and 11, since known methods for similar compounds described in the literature [25] require optimization. At the next stage, we are planning to synthesize Diels-Alder adducts from these compounds, to study the process of curing the obtained materials with various amines and to determine the ability of these binders to self-healing after mechanical damage.

**Figure 1. Synthesis of maleimides**
Figure 2. Schemes for producing ester precursors of resins

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