Synthesis of self-healing polymers precursors from available bio-renewable raw materials.

D V Zakharova$^{1,2}$, A A Pavlov$^2$, A V Polezhaev$^{1,2}$

$^1$ Bauman Moscow State Technical University, 105005, Russia, Moscow, 2nd Baumanskaya str., 5/1
$^2$ A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), 119334, Russia, Moscow, Vavilova str., 28

E-mail: DZakharova@emtc.ru, avp@emtc.ru

Abstract. A series of a new diglycidyl derivatives of aromatic amines containing a furan fragment was obtained. The synthetic scheme consists of two stages: reductive amination and epoxidation. We used industrially produced inexpensive amines and furfural as starting material. Diepoxides obtained are key components for development of epoxy binders capable of intrinsic self-healing based on the reversible Diels-Alder reaction between furan and maleimide. To demonstrate the possibility of self-healing, the Diels-Alder reaction adduct of one of the products with N-phenyl maleimide was isolated and characterized by 2D NMR spectroscopy. The reversibility of the reaction was confirmed by DSC experiment.

1. Introduction

Epoxy binders are a crucial component of carbon and fiberglass composites that have a decisive influence on the performance of the composite. [1, 2] Polymer matrix bind fibers, protects them from environmental factors such as light, moisture, aggressive chemicals, e.t.c., and also contributes to the redistribution of mechanical stresses. [3, 4] The polymer matrix is always less durable than the reinforcing fiber. Defects in its structure, even microcracks, can significantly reduce the strength of a composite material. One of the problems of widespread use of a fiber-reinforced plastic is the complexity of prediction of defect formation and propagation in the epoxy binder layer.[4, 5] Development of self-healing materials is a possible solution to this problem. Two approaches, extrinsic and intrinsic self-healing were proposed. The first approach involves an introduction of microcapsules containing a healing agent and a catalyst into a polymer matrix. A healing agent releases from a microcapsule after cracking. [6] The main disadvantages of this approach are: the impossibility to predict the degree of cross-linking in the damaged area after the “healing” process, the limited amount of the “healing” agent and the irreversible nature of the epoxidation reaction. All the disadvantages mentioned above make the “healing” process possible only once. Moreover, to increase the self-healing ability, one should increase the number of microcapsules in the volume of the material, but at the same time, the mechanical properties might fall. [7-9] The “intrinsic” self-healing is based on the design of materials capable of independent internal self-healing that results from physical or chemical impacts, which provide the ability to rebound and repair damage due to the presence of specific functional groups in the material. [7] The reversible Diels-Alder reaction between furan and maleimide residues is a promising method...
for self-healing polymers design. [10]

Thus, we have proposed the synthesis of compounds via the Diels-Alder reaction between furan and maleimide residues. Such synthetic strategy leads to the formation of a highly cross-linked polymer structure and opens up new opportunities for its functionalization. Specific features of the polymer structure, the self-healing ability due to the sequential reverse and direct Diels-Alder reaction determines the improved mechanical properties of these compounds.

The creation of epoxy binders based on furan-containing compounds and maleimide cross-linking reagents was reported previously. Authors demonstrated self-healing properties of the compounds obtained as a result of the thermal cycling process. [7] We propose a synthetic strategy for getting new epoxy-containing monomers to create self-healing binders with improved thermomechanical properties. It is worth notice that one of the initial reagents of the synthetic scheme (Scheme 1) is furfural - a compound obtained from bio-renewable raw materials, in particular, from various agricultural wastes. [11-13] This reduces the cost of the target compound and makes the process of its production more environmentally friendly [14-16].

2. Results and discussion

Earlier, the Ming Qiu Zhang group demonstrated thermal remendability of the epoxy blend consist of N,N-diglycidylfurfurylamine, N,N’-(4,4-diphenylmethane)-bismaleimide and methyl hexahydrophthalic anhydride [1]. However, the described self-healing cycle was too long for practical application, and the mechanical characteristics were relatively poor. We suggest that these shortcomings can be corrected by introducing a hard aromatic scaffold into the structure of the epoxy component of the mixture and spacing the epoxy groups making their structure closer to well-known Bisphenol A and F - based epoxy resins.

![Figure 1. Comparison of two different approaches.](image)

Simple strategy for the synthesis of the epoxy resin type 3b was proposed. For the synthesis of the desired compounds commercially available, inexpensive, industrially produced diamines (1a – c) such as 1,4-phenylenediamine, 4,4'-diaminodiphenylmethane, 4,4'-sulfonyldianiline and (±)-epichlorohydrin were used as starting compounds (Scheme 1).

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At the first stage, the formation of secondary amino group can be carried out via standard reduction amination procedure using Na[BH(OAc)] as a reducing agent (Scheme 1, Method A, B). In order to increase the yield of the product 2b, an alternative two-step synthetic scheme was proposed (Scheme 1, Method B). Method B suggested isolation of the imine (2b') and its subsequent reduction with sodium
borohydride to amine (2b). Thus, it was possible to increase the yield of compound 2b from 14 to 40%.

Compounds (2a – 2c) were characterized by NMR (\(^1\)H, \(^{13}\)C) and IR spectroscopy.

A series of epoxidation reactions were carried out under various conditions targeting 3b (p. 1–5, Table 1). The reaction conditions consisted of (±)-epichlorohydrin as a reagent and solvent, silica gel as a catalyst and KOH in THF as a base resulted in the highest yield of the product (p. 4, Table 1). This reaction requires a long time due to low reactivity of aromatic diamines. The reaction progress was monitored by IR spectroscopy. We used the characteristic absorption band at 3410 cm\(^{-1}\) in the spectrum of the compound 2b corresponding to the secondary amino groups as references. The disappearance of the band mentioned above indicated completion of the reaction. The compound 3c cannot be obtained under the same conditions, which is probably due to a more electron-deficient character of the secondary amino groups of compound 2c compared to 2b.

Table 1. Variation of reaction conditions

| Substrate | Product | № | Conditions | % |
|-----------|---------|---|------------|---|
| ![Furan structure](image1) | ![Furan structure](image2) | 1. | NaOH, Na\(_2\)SO\(_4\), ZnCl\(_2\) | - |
| ![Furan structure](image3) | ![Furan structure](image4) | 2. | KOH, K\(_2\)CO\(_3\) | - |
| ![Furan structure](image5) | ![Furan structure](image6) | 3. | CH\(_3\)COOH | - |
| ![Furan structure](image7) | ![Furan structure](image8) | 4. | KOH, K\(_2\)CO\(_3\), EtN\(^+\)Cl\(^-\), MW irradiation | - |
| ![Furan structure](image9) | ![Furan structure](image10) | 5. | silica gel, 40°C, 24 h. | 48 |
| ![Furan structure](image11) | ![Furan structure](image12) | 2. | KOH, THF, 3 h., r.t. | - |

To demonstrate the ability of furan fragments to react reversibly with the maleimide derivatives via the Diels-Alder reaction we proposed the synthesis of a model compound — the product of the interaction of the difuran derivative 3b with N-phenylmaleimide (Scheme 2).
Adduct 3d was obtained from [4 + 2]-cycloaddition between compound 2b and N-phenylmaleimide after reflux for 24 h. Products of the Diels–Alder reaction are usually a mixture of diastereoisomers [1]: kinetic (endo) and thermodynamic (exo) reaction products. In the case of the compound 3d the formation of three isomers was possible (Figure 2): A (exo-exo), X (endo-endo) or Z (endo-exo). Only one set of signals was observed in the NMR spectra (\(^1H, ^{13}C\)) of the product 3d, corresponding to a symmetric product that is in agreement only with proposed structures A or X.

![Scheme 2. Synthesis of the target compound (3d) by Diels–Alder [4+2]-cycloaddition.](image)

**Figure 2.** Possible isomeric products (3d) in the Diels–Alder reaction.

An NMR study was carried out using the HMQC, HMBC, NOESY, COSY, NOE methods (the spectra are shown below) for the complete assignment of signals of the obtained compound (3d). Using the spectra of two-dimensional correlation (HMQC, HMBC), as well as the \(^{13}C\) DEPT spectrum, the assignment of \(^{13}C\) and \(^1H\) spectral signals is carried out unambiguously (Figure 3, 4).

It was previously shown [17], that the difference in chemical shifts and multiplicities of proton signals (H13 and H14, Figure 3) of the endo- and exo-isomers make it possible to determine the structure of the Diels–Alder reaction product unambiguously. Authors compared the vicinal constants of the spin-spin interaction \(3J_{HH}\), to determine the isomer. Constants \(3J_{HH}\) are dependent on several structural parameters, but most importantly on the H – C – C – H dihedral angle in the molecule. For protons 13 and 14 the constant should be approximately equal to 5.8 Hz in the case of the endo-isomer and close to zero for the exo one. According to the COZY spectrum, the vicinal constant of spin-spin interaction for H11 - H13 is zero, and the constant \(3J_{H12,H14}\) is less than 1 Hz. The combination of these factors leads to
the fact that the signal at 5.23 ppm, corresponding to the bridge proton H14, degenerates into a singlet. Thus, the above facts and literature information [17-19] confirm our assumption about the preparation of the (exo-exo)-isomer.

Figure 3. $^1$H-NMR spectrum of compound 3d.
Reversibility of the Diels-Alder process was shown using DSC (Figure 5). It was shown that the Diels-Alder reverse reaction occurs at an unusually high temperature (173°C). This temperature was found to be significantly higher than values found in the literature for the furan-maleimide adduct (usually 110-130 °C). [20-22] We have suggested that such a high temperature of the reverse Diels-Alder reaction was achieved due to the formation of intramolecular hydrogen bonds between the protons of the NH groups and the oxygen atoms of the maleimide fragments. However, this phenomenon requires further studying.

Figure 5. DSC curve of compound (3d). Heating from 0 to 210°C / 5K/min. T (rDA) = 173.20°C.
3. Experimental

Furfural (99.5%) was purchased from “Komponent-reaktiv” and purified by vacuum distillation. Sodium borohydride ((98%, Acros Organics), 1,4-phenylenediamine (98%, Sigma), 4,4'-diaminodiphenylmethane (97%, Aldrich), 4,4'-sulfonyldianiline (97%, Acros Organics), (±)-epichlorohydrin (99%, Fluka), aniline (99.8%, Acros Organics), maleic anhydride (99%, Aldrich) were purchased from Aldrich and used as received.

NMR spectra were recorded by a Bruker Avance 600 NMR Spectrometer (600.1 MHz), using residual proton signal of deuterated solvent as reference, chemical shifts were reported as parts per million downfield from tetramethylsilane (TMS). ATR-FTIR was performed on Nicolet iS10 spectrometer in the range of 4000 to 650 cm$^{-1}$ on a germanium crystal. The thermal behavior was examined by DSC, with a NETZH DSC 204 F1 Phoenix calorimeter within a temperature range of 0 to 210 °C at heating/cooling rates of 5K min$^{-1}$ in an argon atmosphere.

3.1. N,N'-difurfuryldiamines synthesis (2a-c)

3.1.1. N,N'-difurfuryl-p-phenylenediamine (2a).

To obtain sodium triacetoxyborohydride acetic acid (4.470 ml) was added dropwise to the solution of sodium borohydride (0.980 g, 25.79 mmol) in 1,2-dichloroethane (50 ml) maintaining the temperature between 0 and 5°C. Then the reaction mixture was stirred at room temperature for 3 h. Afterwards, 1,4-phenylenediamine (0.975 g, 9.03 mmol) (1a), furfural (1.490 ml, 18.05 mmol) and molecular sieves (4 Å) was added. The mixture was stirred at room temperature for 24 h. After the reaction completed (TLC monitoring), 50 ml of 0.1 N aq NaOH was added. The product was extracted with EtOAc (15 ml × 3), and the organic layer was dried (Na$_2$SO$_4$) and concentrated under reduced pressure. The product was purified by flash chromatography on silica gel eluting with Petroleum ether/EtOAc (1:1) to give an orange powder (0.998 g, 41 %). mp 74°C. 

3.1.2. 4,4'-methanediylbis[N-(furan-2-ylmethyl) aniline] (2b)

Method A

To obtain sodium triacetoxyborohydride acetic acid (2.550 ml) was added dropwise to the solution of sodium borohydride (0.537 g, 14.13 mmol) in 1,2-dichloroethane (30 ml) maintaining the temperature between 0 and 5°C. Then the reaction mixture was stirred at room temperature for 3 h. Afterwards, 4,4'-diaminodiphenylmethane (0.979 g, 4.95 mmol) (1b), furfural (0.820 ml, 9.89 mmol) and molecular sieves (4 Å) was added. The mixture was stirred at room temperature for 24 h. After the reaction completed (TLC monitoring), 30 ml of 0.1 N aq NaOH was added. The product was extracted with EtOAc (= 15 mL × 3), and the organic layer was dried (Na$_2$SO$_4$) and concentrated under reduced pressure. The product was purified by flash chromatography on silica gel eluting with Petroleum ether/EtOAc (5:2) to give light yellow powder (0.205 g, 14 %), mp 52.4°C. 1H-NMR (DMSO-d$_6$, δ, ppm., J, Hz): 4.11 (s., 4H), 5.24 (s., 2H), 6.24 (d., J = 3.1, 2H), 6.36 (dd., J1 = 1.8, J2 = 3.2, 2H), 6.48 (s., 4H), 7.54 (m., 2H). 13C-NMR (DMSO-d$_6$, δ, ppm.): 41.11, 106.62 110.33, 113.90, 139.99, 141.69, 154.06.

Method B

Furfural (0.170 ml, 2.02 mmol) was added to the solution of 4,4'-diaminodiphenylmethane (0.200 g, 1.01 mmol) in MeOH (5 ml). The reaction was carried out with vigorous stirring at room temperature for 3 h. The obtained precipitate was collected by filtration, washed with MeOH and dried on air, giving a brown product (2b') with yield 58% (0.207 g).
Reduced pressure. Product 0.000

Organic layer was dried (Na$_2$SO$_4$) and concentrated under reduced pressure. Seum ether/EtOAc

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NMR (CDCl$_3$, δ, ppm., J, Hz): 3.96 (s., 2H), 6.69-6.71 (m., 2H), 7.12 (d., J = 2.7, 2H), 7.20 (d., J = 8.1, 4H), 7.27 (d., J = 8.2, 4H), 7.93 (s., 2H), 8.42 (s., 2H). $^{13}$C-NMR (CDCl$_3$, δ, ppm): 112.54, 116.79, 121.16, 129.54, 134.90, 139.38, 146.35, 147.83, 149.06, 152.02.
The product (2b') (1.000 g, 2.94 mmol) was dissolved in MeOH (50 ml). NaBH$_4$ (0.503 g, 13.24 mmol) was added at 0°C. The reaction mixture was stirred at room temperature for 48 h. After the reaction completed (TLC monitoring), 30 ml of 0.1 N aq NaOH was added. The product was extracted with EtOAc (15 mL x 3), and the organic layer was dried (Na$_2$SO$_4$) and concentrated under reduced pressure.
The product was purified by flash chromatography on silica gel eluting with Petroleum ether/EtOAc (5:2) to give light yellow powder (0.693 g, 69%).

3.1.3. 4'-sulfonylbis[N-(furan-2-ylmethyl)aniline] (2c)
To obtain sodium triacetoxyborohydride acetic acid (4.470 ml) was added dropwise to the solution of sodium borohydride (0.98 g, 25.79 mmol) in 1,2-dichloroethane (50 ml) maintaining the temperature between 0 and 5 °C. Then the reaction mixture was stirred at room temperature for 3 h. Afterwards, 4,4'-sulfonyldianiline (2.239 g, 9.03 mmol) (1c), furfural (1.49 ml, 18.05 mmol) and molecular sieves (4 Å) was added. The mixture was stirred at room temperature for 72 h. After the reaction completed (TLC monitoring), 50 ml of 0.1 N aq NaOH was added. The product was extracted with EtOAc (15 mL x 3), and the organic layer was dried (Na$_2$SO$_4$) and concentrated under reduced pressure. Product was obtained as light orange powder (2.847 g, 78%). $^{1}$H-NMR (DMSO-d$_6$, δ, ppm., J, Hz): 4.28 (d., J = 5.8, 4H), 6.30 (d., J = 3.2, 2H), 6.37 (t., J = 3.0, 2H), 6.69 (d., J = 8.8, 4H), 7.06 (t., J = 5.9, 2H), 7.51 (d., J = 8.8, 4H), 7.56 (d., J = 1.1, 2H). $^{13}$C-NMR (DMSO-d$_6$, δ, ppm): 39.11, 107.34, 110.44, 111.56, 128.42, 128.58, 142.30, 151.65, 152.22.

3.2. N,N'-difurfurildiepoxydiamines synthesis (3a-c)

3.2.1. The product of the epoxidation of compound 2b (3b)
1.112 g (3.11 mmol) of 4,4'-methanediyldibis[N-(furan-2-ylmethyl)aniline] (2b) was dissolved in (-)-epichlorohydrin (4 ml), silica gel and molecular sieves (4 Å) was added. After reaction mixture was stirred at 80°C for 10 h silica gel and molecular sieves was filtered and the excess of (-)-epichlorohydrin was removed under reduced pressure. To solution of obtained oil in THF (3 ml) was added 1N aq KOH (9.30 ml, 9.32 mmol) and tetramethylammonium chloride (0.010 g, 0.09 mmol), and then mixture was stirred at 50 °C for 5 h.

3.3. Diels–Alder reaction

3.3.1. N-phenylmaleimide synthesis
A mixture of aniline (29.362 mL, 0.323 mol), maleic anhydride (32.855 g, 34.0 mmol) in dry acetone (200 ml) was stirred at room temperature for 1 h. The precipitated was filtered and washed with dry acetone (15 mL x 3), then dried in a desiccator overnight to give 3-phenylcarbamoyl-acrylic acid as pale yellow powder. 57.417 g, 93% yield. A mixture of 3-phenylcarbamoyl-acrylic acid (10.000 g, 52.36 mmol), acetic anhydride (25.700 mL, 272.62 mmol), sodium acetate (2.147 g, 26.18 mmol) was stirred at 50°C for 2 h, then the solution was diluted with H$_2$O (30 mL) and stirred at 70°C for 2 h. The precipitated was filtered, dried overnight in a desiccator to give 7.165 mg (80%) of final product. $^{1}$H-NMR (CDCl$_3$, δ, ppm., J, Hz): 7.18 (s., 2H), 7.33-7.35 (m., 2H), 7.40-7.41 (m., 1H), 7.47-7.51 (m., 2H).

$^{13}$C-NMR (CDCl$_3$, δ, ppm): 126.81, 127.74, 128.88, 131.57, 134.66, 169.94 (C=O).
3.3.2. *Product of Diels-Alder reaction (3d)*

N-phenylmaleimide (0.193 g, 1.12 ммоль) was added to the solution of 4,4’-methanediylbis[N-(furan-2-ylmethyl) aniline] (2b) (0.200 г, 0.56 ммоль) in THF (5 ml). The reaction mixture was stirred at room temperature for 24 h, and then poured into ice. The reaction mixture was left for 30 minutes in an ice bath. The product was obtained by filtration, washed with THF and dried on air. Product of Diels-Alder reaction (3d) was obtained as white powder with yield 44% (0.172 g). 1H-NMR (DMSO-d6, δ, ppm., 600 MHz) δH(ppm): 3.18 (d., J = 6.5, 2H), 3.26 (d., J = 6.6, 2H), 3.46-3.49 (dd., J1=5.5, J2=14.0, 2H), 3.62 (s., 2H), 3.83-3.86 (dd., J1=6.8, J2=14.1, 2H), 5.23 (s., 2H), 5.36 (t., J=6.1, 2H, NH), 6.53 (d., J=5.5, 2H), 6.60 (m., 6H), 6.90 (d., J = 8.3, 4H), 7.24 (d., J = 7.7, 4H), 7.42 – 7.45 (t., J = 7.3, 2H), 7.49 – 7.52 (t., J = 7.7, 4H) 13C-NMR (DMSO-d6, δ, ppm): 39.42 (C27). In 13C-NMR spectrum peak of C27 hidden behind the solvent peak (DMSO-d6). 2D HMQC experiment was conducted to determine the signal of C27, 42.77, 48.64, 50.51, 80.72, 91.41, 112.50, 126.92, 128.50, 128.97, 129.04, 129.88, 132.13, 137.10, 138.38, 146.77, 174.39, 175.63. Found (C_{43}H_{36}N_{4}O_{6}): C, 73.21, H 5.17, N 8.02; Calculated: C 73.28, H 5.15, N 7.95%.

3.3.3. *DSC-experiment.*

For the experiment 12.8 mg of the compound 3d was used. Experimental conditions: heating from 0 to 210 °C / 5K/min. T (rDA) = 173.20°C.

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