Furfurylglycidyl ether: a new effective active diluent for epoxy resins from bio-renewable raw materials

T V Petrova¹, V I Solodilov¹, V E Kabantseva¹, N V Karelina¹, A V Polezhayev¹,²,*

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

E-mail: avp@emtc.ru

Abstract. New reactive diluents based on bio-renewable raw materials are widely explored as additives to traditional resins. We investigated the effect of furfurylglycidyl ether on the rheological and thermomechanical properties of a widely used epoxy binder with an anhydride hardener. It was shown that the addition of 5-15% active diluent significantly reduces the viscosity of the composition to the values optimal for RTM and vacuum infusion technologies for fiber-reinforced plastics and does not lead to a significant decrease in heat resistance and Young's modulus of the cured binder.

1. Introduction
Currently, epoxy resins are used as matrices for fiber-reinforced composites, surface coatings, adhesives, due to low cost, and specific properties such as heat and chemical resistance [1]. However, the high viscosity and poor processability of some commercial epoxy resins severely limit wide applications. An effective way to eliminate these disadvantages is the use of suitable reactive diluents so that there was no substantial loss of basic properties [2, 3]. Reactive diluents are usually low molecular weight compounds containing at least one reactive functional group. Such diluents reduce the viscosity of the resin, improve its workability, and react with monomers and oligomers to form homogeneous materials [4].

In the past decade, a lot of attention was paid to the development of substitutes for petroleum-based products due to their non-renewability. The move from petroleum-based monomers and building blocks to bio renewables involves the use of natural materials for the production of different materials. Furfural and other furan containing monomers are especially valuable because of production from a wasted source such as corn cobs, wood products or cereal byproducts such as the hulls of cottonseed, oats, and rice.[5-7]. Furan monomers can be obtained from hemicellulose as one of the main components of plant biomass contained in large quantities in agricultural waste. Furfural, as the most critical first-generation furan derivatives industrially produced up to 200 000 tons per year, both in wealth and in developing countries. More than 80% of furfural has usually converted to furfuryl alcohol (FA) through a simple reduction process [8].

In a recent publication [9], the authors suggested using furfurylmetacrylate obtained by acrylation of furfuryl alcohol as a replacement for styrene in a polyester resin. Furfurylglycidyl ether (FGE) is another...
FA derivative. FGE was explored as a monomer in the anionic polymerization with formation poly
(FGE) homo and deblock (with propylene oxide) copolymers [10, 11], for modifying natural polymers
such as chitosan [12], and for producing thermostable polymers by the Diels-Alder reaction [13, 14].
Furfurylglycidyl ether was recently reported as a very useful active diluent in epoxy compositions with
aliphatic amine hardener. It was shown that FGE effectively reduced the viscosity of the composition,
slightly decreases the glass transition temperature of the cured resin and does not lead to degradation of
mechanical properties [2]. However, there is no information on FGE use in exopy/anhydride binders.
Epoxy/anhydride resins are usually used for the production of high-performance composites with high
heat resistance and excellent mechanical properties.

We decided to investigate the potential of FGE as an active diluent in anhydride curing composition
and to investigate the rheological and thermomechanical properties of the composition before and after
curing.

2. Experimental

2.1. Materials and methods

The epoxy resin DER331 (epoxy value 23%, DOW Chemicals) was used without further purification,
furfurylglycidyl ether (FGE, epoxy value 27.92%, DOROS, Russia) was additionally distilled under
vacuum. Methylhexahydrophthalic anhydride (MHHPA, 98%, Acros Organics) and 2-methylimidazole
(2MI, Himex) were used as received.

The ATR-FTIR spectra were registered on a Thermo Nicolet iS10 spectrometer with a Fourier
transducer using a germanium crystal in the range of 4000-650 cm\(^{-1}\). The dynamic viscosity was
measured on a rotational cone-plate viscometer Brookfield Cap 2000\(^+\) (rotational speed of 10 rpm,
spindle No. 1). The study of the curing process of the samples was carried out by differential scanning
calorimetry (DSC) on NETZH DSC 204 F1 Phoenix calorimeter in the temperature range from 25 to
260 °C at the heating rate of 5 K/min\(^+\) under an argon atmosphere. Dynamic mechanical analysis
(DMA) of cured samples (20 mm x 6 mm x 2 mm, 3 samples for each composition) was carried out in
a three-point bending mode on a Netzsch DMA 242 E Artemis instrument within the temperature range
of 25-250 °C, with a heating rate of 2 K/min, at frequency of 1 Hz.

2.2. Resin formulation (DER331/FGE/MHHPA/2MI)

We prepared 7 combinations with different FGE content (FGE: 0, 5, 10, 15, 20, 25 и 30% with respect
to the DER331 resin) amount of hardener and catalyst was calculated with the following equation.

\[
m = X \cdot \frac{M_0}{M}
\]

\(M_0\) - hardener molecular mass (g/mol);
\(M\) - epoxy group molecular weight (43 g/mol);
\(X\) - amount of epoxy groups (g) per 100 g of resin (Russian standard 10587-84).

All samples were cured for 3 h at 100°C, 6 h at 140°C.

3. Results and discussion

The low processability of highly viscous binders limits their widespread use, and therefore active
diluents are widely used. Unlike solvents, active diluents cure with epoxy resin and do not require
subsequent removal. We investigated the viscosity of the binder with the content of FGE from 5 to 30%
with an interval of 5%. Temperature dependence was shown for each composition (Table 1, Figure 1).
As expected, the viscosity significantly decreases with increasing amount of active diluent, and with
increasing temperature. The data show that FGE effectively reduces the viscosity of the Bisphenol A-
based epoxy resin, which is consistent with previously obtained data [2, 3].

Table 1. The dependence of viscosity on temperature and FGE content.
To study the effect of the active diluent content on the heat and the curing temperature of the binder, the DSC method was applied with the following mode: isotherm 10 min, 25 °C; heating, from 25-260 °C, 5 K/min; cooling to 25 °C, 20 K/min; isotherm 5 min. As can be seen from the results in Table 2, the FGE additive has almost no effect on the position of the maximum of the curing exotherm, which is in the around 160 °C. The enthalpy of curing process is significantly reduced, but it is unlikely that this is due to a real decrease in the amount of heat released. The measurement was carried out in open crucibles and a sufficiently rapid heating leads to the partial evaporation of volatile active diluent from a crucible, which leads to underestimated values of enthalpy. However, the remaining parameters, such as T_{onset} and T_{max}, which are crucial to the speed of curing, remain unchanged. Thus, we can conclude that the use of an active diluent does not require changes in the standard temperature curing regimes.

Table 2. DSC measurement results for formulations with different FGE content.

| FGE content/% | T_{onset}, °C | T_{max}, °C | ΔH, J/g |
|--------------|--------------|-------------|---------|
| 0%           | 125,1        | 164,0       | 356,0   |
| 10%          | 128,4        | 158,5       | 340,9   |
| 20%          | 132,7        | 160,5       | 201,0   |
| 30%          | 142,5        | 159,6       | 170,3   |

To study the effect of the active diluent on the mechanical properties of the cured composition, we measured the cured samples of the binder using the three-point bending method on a DMA instrument.

![Fig. 1. The dependence of viscosity on temperature and FGE content.](image-url)
The binder was cast into silicone molds in the form of bars (80 x 10 x 12 mm - length, width, thickness), cured in the following mode: 3 hours at 100 °C and 6 hours at 140 °C. From one bar received 3 small samples for DMA size 20x6x2mm were cut. The measurements were carried out at a heating rate of 2 K/min in the range of 25–250 °C at a frequency of 1 Hz with a proportionality coefficient of 1.1 and an absolute amplitude of 60 μm and a maximum dynamic force of 10 N. The measurement results are shown in Table 3 and Figure 2. The glass transition temperature Tg of the studied samples decreases linearly with an increase in the amount of active diluent: for pure resin, the value is 156 °C was obtained, and for the composition with 30% FGE - 117 °C. This disadvantage is characteristic of any active diluents [2, 3]. It should be noted that the glass transition temperature does not drop as much as in the case of active diluents based on aliphatic alcohols or glycols. The reduction in viscosity required for such technological processes as vacuum infusion is achieved already at 5–10% of FGE. At these concentrations a decrease in heat resistance of 10–15 °C can be considered insignificant.

### Table 3. DMA results

| Content  | E1' (MPa) at 45°C | E2' (MPa) at 45°C | E3' (MPa) at 45°C | Sample 1, Tg, °C | Sample 2, Tg, °C | Sample 3, Tg, °C | Average Tg, °C | Average E', MPa |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|---------------|
| DER331   | 3898            | 3830            | 3936            | 156,4           | 156,6           | 155,4           | 3888           | 156,1         |
| 5%FGE    | 3377            | 3342            | 3747            | 149,7           | 149,5           | 147,1           | 3489           | 148,8         |
| 10%FGE   | 4175            | 3337            | 3120            | 142,9           | 143,2           | 142,2           | 3544           | 142,8         |
| 15%FGE   | 3885            | 3113            | 3499            | 136,9           | 135,5           | 134,0           | 3499           | 135,5         |
| 20%FGE   | 4695            | 4236            | 3678            | 130,2           | 129,6           | 129,7           | 4203           | 129,8         |
| 25%FGE   | 4478            | 4847            | 4072            | 124,0           | 121,1           | 124,9           | 4466           | 123,3         |
| 30%FGE   | 4405            | 4231            | 4308            | 117,6           | 116,5           | 117,7           | 4315           | 117,3         |

The effect of the amount of FGE on the Young's modulus is non-linear: the addition of 5-15% FGE to the epoxy-diane resin leads to a slight decrease in the modulus from 4 to 3.5 GPa, a further increase in concentration leads to an increase in the modulus to 4.5 GPa. However, it should be noted that such quantities of diluent are deliberately non-technical, so the use of this effect is not practical in real systems.

![Figure 2. The dependence of the elastic modulus on the FGE content.](image)}

To confirm the completeness of the reaction, the binder was characterized by ATR-FTIR spectroscopy. As can be seen from the spectra in Figure 3, the bands of the carbonyl group of the
anhydride hardener at 1785 and 1861 cm\(^{-1}\) completely disappear, as does the strip of the epoxy group at 889 cm\(^{-1}\), which confirms the complete course of curing.

**Figure 3.** IR-ATR spectra of uncured (top) and cured (bottom) compositions with 20% of FGE4.

4. Conclusions
New active diluent - furfurylglycidyl ether was investigated in composition with Bisphenol A-based epoxy resin and anhydrite hardener. Rheological studies demonstrated high efficiency in reducing viscosity, a DSC study showed that the FGE additive does not affect the nature of the curing reaction, and testing of samples with the DMA method revealed a slight drop in heat resistance and the Young’s modulus after addition of 10-15% FGE to the commercial epoxy.

Acknowledgments
This work was supported by Russian Foundation of Basic Research (RFBR) grants 18-29-18036 and 18-29-18037. NMR experiments were performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

References
[1] Ellis B and ebrary Inc. 1993 *Chemistry and technology of epoxy resins* (London ; New York: Blackie Academic & Professional)
[2] Karami Z, Nademi F, Zohuriaan-Mehr M J and Rostami A 2017 An efficient fully bio-based reactive diluent for epoxy thermosets: 2-[(Oxiran-2-y1m ethoxy) methyl] furan versus a petroleum-based counterpart *J. Appl. Polym. Sci.* 134 44957
[3] Sinha A, Islam Khan N, Das S, Zhang J and Halder S 2018 Effect of reactive and non-reactive diluents on thermal and mechanical properties of epoxy resin *High Perform. Polym.* 30 1159-68
[4] Johansson K and Johansson M 2006 A model study on fatty acid methyl esters as reactive diluents in thermally cured coil coating systems *Prog. Org. Coat.* 55 382-7
[5] Bessonov I V, Kopitsyna M N, Polezhaev A V and Nelyub V A 2016 A mechanistic study of the reaction between furfural-acetone resins and polyamines *Pol. Sci. Ser. D* 9 17-21
[6] Bessonov I V, Polezhaev A V, Kuznetsova M N, Nelub V A, Buyanov I A, Chudnov I V and Borodulin A S 2013 Rheological and thermal analysis of low-viscosity epoxy-furan
composites Pol. Sci. Ser. D 6 308-11
[7] Gandini A, Lacerda T M, Carvalho A J F and Trovatti E 2016 Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides Chem. Rev. 116 1637-69
[8] Suib S L 2013 New and future developments in catalysis catalysis by nanoparticles. (Amsterdam; Waltham, MA: Elsevier) p 1
[9] Zhang Y, Li Y, Thakur V K, Wang L, Gu J, Gao Z, Fan B, Wu Q and Kessler M R 2018 Bio-based reactive diluents as sustainable replacements for styrene in MAE OS resin RSC Advances 8 13780-8
[10] Barthel M J, Rudolph T, Crotty S, Schacher F H and Schubert U S 2012 Homo- and diblock copolymers of poly(furfuryl glycidyl ether) by living anionic polymerization: Toward reversibly core-crosslinked micelles J. Pol. Sci Pol. Chem. 50 4958-65
[11] Wagner M, Barthel M J, Freund R R A, Hoeppener S, Traeger A, Schacher F H and Schubert U S 2014 Solution self-assembly of poly(ethylene oxide)-block-poly(furfuryl glycidyl ether)-block-poly(allyl glycidyl ether) based triblock terpolymers: a field-flow fractionation study Pol. Chem. 5 6943-56
[12] Na H-N, Park S-H, Kim K-I, Kim M K and Son T-I 2012 Photocurable O-carboxymethyl chitosan derivatives for biomedical applications: Synthesis, in vitro biocompatibility, and their wound healing effects Macromol. Res. 20 1144-9
[13] Tian Q, Rong M Z, Zhang M Q and Yuan Y C 2010 Synthesis and characterization of epoxy with improved thermal remendability based on Diels-Alder reaction Polym. Int. 59 1339-45
[14] Platonova E O, Vlasov E, Pavlov A A, Kireynov A, Nelyub V A and Polezhaev A V 2019 Self-healing polyurethane based on a difuranc monomer from biorenewable source 136 47869