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Synthesis of Furfurylideneacetones and Their Application as Active Diluents for Epoxy Resins Fabrication

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Abstract—A variety of furfural-acetone resins has been synthesized, and their ability to act as active diluent in the diglycidyl ether of Bisphenol A–tris(ethanolamino)titanate system has been estimated. The prepared resins decrease the compositions viscosity without deteriorating the polymers thermomechanical properties. The application of the developed systems open possibilities to prepare heat-resistant polymer composites based on the vegetable biorenewable source without pressure reactor molding.

Keywords: furfural-acetone resin, active diluent, bio-based chemicals, polymer composites

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Recently much attention has been paid to development of production of various chemical products from renewable raw materials. In this regard, furfural produced via acid-catalyzed dehydration of polysaccharide-containing agricultural wastes is a highly promising starting material [1, 2].

Furfural-based resins are fairly cheap fire-retarding and acid-resistant materials showing low viscosity and good set of physico-mechanical properties; hence, they are widely used as binders for production of polymer-concrete composites and antirust coatings [3, 4]. However, systematic studies of application of furfural-acetone resins and their mixtures with epoxy resins as binders for fiberglass and carbon-filled plastics have been scarce so far.

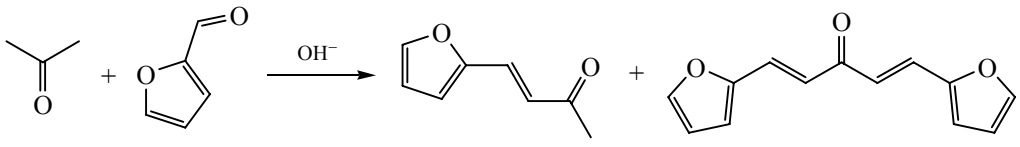
Modern technology of polymer composites preparation put strict limitations on rheological properties of the applied binders [5]. For example, efficient application of high-throughput methods like vacuum infusion and resin transfer molding (RTM) requires the viscosity of impregnating compositions to be below 300–400 mPa/s, whereas widely used epoxy derivatives of Bisphenol A show viscosity of above 3500 mPa/s. In order to reduce the composition viscosity, active diluents are applied, their nature and the applied ratio affect technological properties of the binder (viscosity and impregnation efficacy) as well as the final product properties (thermomechanical characteristics are often deteriorated).

This work aimed at preparation of furfural-acetone resin and its application as active diluent for the diglycidyl ether of Bisphenol A–tris(ethanolamino)titanate system. Furthermore, thermomechanical properties of the prepared polymer products were estimated (Scheme 1).

Furfural-acetone resin is a complex mixture of products formed in the course of base-catalyzed condensation of furfural and acetone. The major components are monofurfurylideneacetone MFA and difurfurylideneacetone DFA. Oligomers, isopropylideneacetone are among the minor components along with the starting furfural and acetone [6].

Furan ring and α,β-unsaturated carbonyl group of MFA and DFA can react with epoxy resins and their

Scheme 1.



Conditions of furfurolacetone resin preparation

Product	Acetone : furfurol	T, °C	Time, h	H_2O, eq.	NaOH, mol/L	DFA : MFA[a]
FA1	1 : 1	70–75	4	5	1.11	0.3 : 1
FA2	1 : 1	70–75	4	5	1.11	0.6 : 1
FA3	1 : 1	20–25	2	27	1.37	0.7 : 1
FA4	1 : 1	70–80	4	5	1.11	0.7 : 1
FA5	1 : 1.25	20–25	2	33	1.13	1 : 1
FA6	1 : 1.25	20–25	2	33	1.13	1.2 : 1
FA7	1 : 1.5	70–75	4	5	1.11	1.6 : 1
FA8	1 : 1.5	70–75	4	5	1.11	1.7 : 1
FA9	1 : 1.5	20–25	2	41	1.36	3.8 : 1

[a] MFA: monofurfurylideneacetone, DFA: difurfurylideneacetone.

hardeners, the furfural-acetone resin components being chemically incorporated into the formed polymer [7]. Individual MFA and DFA are solid low-melting compounds, but their mixtures are low-viscosity fluids at room temperature (≤100 mPa/s) [8]. It could be expected that the increase of DFA ratio in the mixture should result in the structures with higher crosslinking density (due to the higher content of reactive groups) that should enhance the thermomechanical properties of the final product [9]. In this work we varied conditions of furfural-acetone resin preparation [10, 11] in order to increase DFA yield; the preparation conditions are collected in the table. At NaOH concentration above 3 mol/L brittle powders (not applicable as active diluent) were produced instead of fluid resins.

The MFA-to-DFA ratio in the prepared furfural-acetone resins was determined by ^{1}H NMR spectroscopy. The signal of methyl group at 2.3 ppm was assigned to MFA, whereas protons of ethylene and furfural fragments of both MFA and DFA resonated in weaker field. Hence, the required ratio of the components in the resin could be calculated as follows:

$$\text{DFA : MFA} = 0.3X - 0.5,$$

with X being a ratio of integral intensities of the signals at 7.7–6.2 ppm to that of the signal at 2.3 ppm.

Analysis of ^{1}H NMR spectra revealed that the resins with MFA to DFA ratio of 0.3 to 3.8 were produced (see table).

Viscosity of the prepared furfural-acetone resins was practically independent of the MFA/DFA ratio, being around 100 mPa/s. At the same time, the resin composition noticeably affected the viscosity of its mixtures with LE-828 epoxy resin (30 : 100); in particular, viscosity of such compositions grew with the increased DFA ratio in the system (Fig. 1). In order to roughly estimate the effect of furfural-acetone resin addition, viscosity of the LE-828 resin diluted with diglycidyl ether of polypropylene glycol (7 : 100 with diglycidyl ether of Bisphenol A) is given in the same plot. It is seen that the introduction of furfural-acetone resin noticeably reduced the composition viscosity as compared with the effect of conventional diluent.

Noteworthily, furfural-acetone resins with high DFA ratio (FA6–FA9) were unstable at storage and solidified within several days at room temperature. The resins could be liquefied by heating, but this was undesirable in view of the possible industrial application.

In order to select the most efficient active diluent of the stable resins FA1–FA5, the following should be considered. Firstly, decrease of DFA ratio in the mixture decreases viscosity of its composition with diglycidyl ether of Bisphenol A. Secondly, as was mentioned above, the increase of DFA content in the mixture enhances the final product properties due to the formation of the denser crosslink network.

Figure 1 demonstrates that the difference in viscosities of the compositions based on FA2 and FA5 was not extremely high, and the amount of the reactive

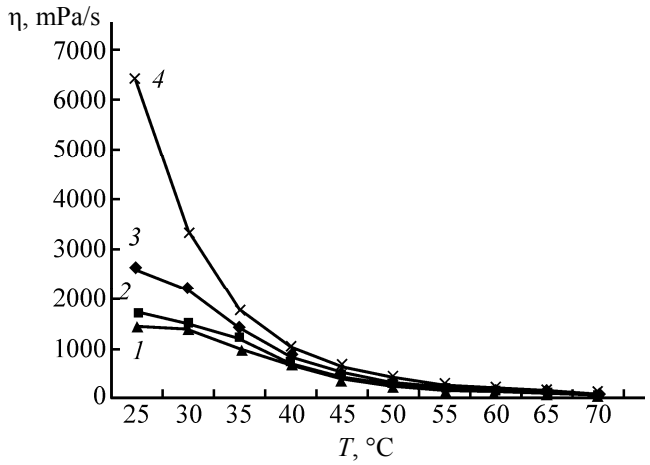


Fig. 1. Dynamic viscosity of mixtures of diglycidyl ether of Bisphenol A with (*1*) FA2 resin (100 : 30), (*2*) FA5 resin (100 : 30), (*3*) FA7 resin (100 : 30), and (*4*) diglycidyl ether of propylene glycol (100 : 7) as function of temperature.

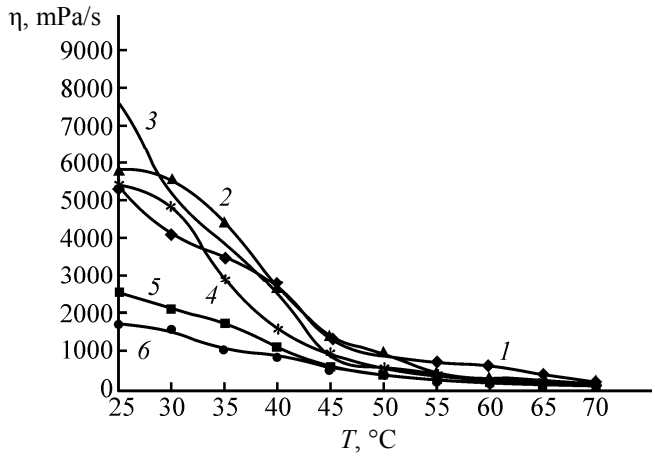


Fig. 2. Dynamic viscosity (*1*) of epoxy resin LE-828 and of mixtures of diglycidyl ether of Bisphenol A with FA5 resin: (*2*) 100 : 5, (*3*) 100 : 10, (*4*) 100 : 15, (*5*) 100 : 20, and (*6*) 100 : 25 as function of temperature.

groups should be critical for the final choice. Therefore, FA5 resin was selected for further detailed studies.

Figure 2 displays temperature dependences of viscosity of the LE-828:FA5 mixtures with varied components ratio. For the sake of comparison, the same figure shows a similar plot for the pure LE-828 resin. It is seen that the introduction of FA5 resin to diglycidyl ether of Bisphenol A up to the ratio of 100 : 15 did not result in significant viscosity decrease, whereas starting from the ratio of 100 : 20 the furfural-acetone resin was efficient in reducing the mixture viscosity.

Indeed, the viscosity of a composition should not exceed 300–400 mPa/s in order to be molded via the RTM method; furthermore, in view of the energy costs such viscosity should be attained at the lowest possible temperature. As seen from data in Fig. 2, the LE-828 resin was sufficiently fluid at above 65°C. Introduction of 20 parts of FA5 resin per 100 parts of the epoxy resin decreased the lowest temperature to reach acceptable viscosity down to 45°C.

Let us consider the effect of FA5 diluent on thermomechanical properties of the hardened resin.

Figures 3 and 4 show temperature dependences of elasticity modulus E' and the loss factor tan δ of the cured binder prepared at varied content of the FA5 resin.

Noteworthily, the shape of the shown temperature dependences was not affected by the amount of the active diluent. With the increased FA5 content, the glass transition temperature of the samples was lowered as documented by the shift of the inflection at the E' curves and of the maximum at the tan δ curves. The presence of a single peak at the tan δ curves pointed at the homogeneity of the prepared compositions, i.e. the absence of any phase separation in the course of curing of the epoxy-furan compositions.

DSC curves of the compositions recorded during the first heating cycle revealed the exothermic peak of curing of the epoxy-furan binding with tris-(ethanolamine)titanate at 95 to 180°C (with maximum at 140–160°C). The exothermal effects during the subsequent heating cycles confirmed the complete curing during the first heating. Furthermore, the DSC traces recorded during the second and the third heating cycles clearly revealed the glass transition process of the crosslinked sample. The single glass transition observed in the curves further confirmed the curing samples homogeneity.

Importantly, the FA5 resin content did not influence the position and thermal effect of the composition curing; hence, the furfural-acetone resin did not affect the catalytic curing reaction of the epoxy component.

At the same time, the increase in the FA5 resin content in the composition decreased the glass transition temperature of the final product. Independently of the technique (DSC or DMA), the observed difference between the glass transition points was

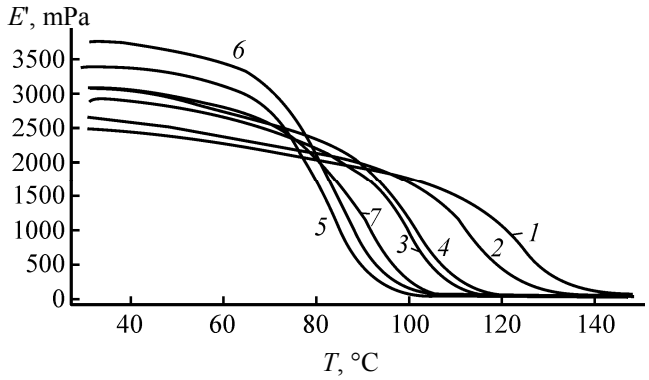


Fig. 3. Elasticity modulus of epoxyfurane compositions prepared from various mixtures of diglycidyl ether of Bisphenol A with FA5 resin, wt %: (*1*) 100 : 0, (*2*) 100 : 5, (*3*) 100 : 10, (*4*) 100 : 15, (*5*) 100 : 20, (*6*) 100 : 25, and (*7*) 100 : 30.

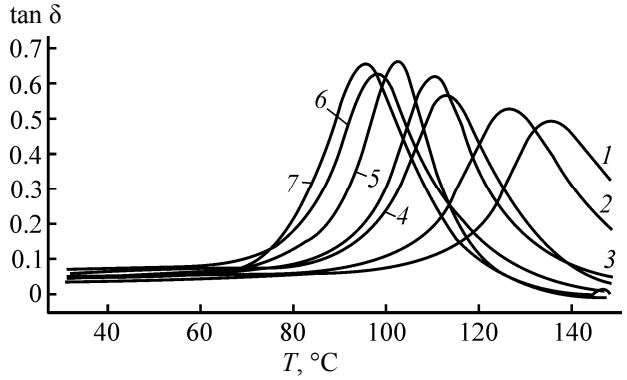


Fig. 4. Loss factor of epoxyfurane compositions prepared from various mixtures of diglycidyl ether of Bisphenol A with FA5 resin, wt %: (*1*) 100 : 0, (*2*) 100 : 5, (*3*) 100 : 10, (*4*) 100 : 15, (*5*) 100 : 20, (*6*) 100 : 25, and (*7*) 100 : 30.

about 20°C at the FA5 resin content of 10 : 100 and about 30°C at 30 : 100 of FA5 resin.

Let us now consider the mechanical properties of the cured polymers. Tensile strength of the examined matrices σ, their initial elasticity modulus *E*, and the elongation at break ε are collected in Figs. 5 and 6.

As seen from the presented data, the elasticity modulus of the material was practically independent of the FA5 resin content. The scattering of the data was likely due to the insufficient quality of the prepared specimens. Note that the constant elasticity modulus at varied concentration of the diluent was not always observed in previous studies. For example, the introduction of rubber into the epoxy resin resulted in monotonous decrease in the product elasticity with the content of the modifier [11, 12]. In the case of modification of epoxy resin with DEG-1, the measured elasticity modulus was independent of the diluent concentration [13], similarly to the case of the FA5 resin discussed here.

The tensile strength σ of the studied samples followed a curve with a maximum at 25 wt % of the FA5 resin, the composition strength being 45% higher than that of the non-modified reference composition. The tensile strength enhancement was observed in the case of the DEG-1 active diluent [14], but the observed effect was on the order of magnitude of the data scatter in the latter case.

Elongation at break of the studied samples followed the curve with a maximum as well; the highest elongation was attained at 20 wt % of the FA5 resin, being 40% higher than that of the reference sample. Similar effect was earlier observed at the modification of epoxy resins with rubbers and DEG-1 [14], being likely due to plasticization of the matrix (that was indirectly confirmed by the decreased glass transition temperature).

To conclude, we prepared a series of furfural-acetone resins differing in the components ratio and studied their effect on industrial and utilitarian properties of the resulting epoxy binder. The optimal set of properties was observed in the case of the resin with equal amounts of MFA and DFA. The furfural-acetone resin was shown to significantly reduce the viscosity of the system but only slightly decrease the glass transition temperature of the final polymer. Application of the developed systems opens possibility to use the resins produced from the renewable sources to prepare low-viscous binders and further processing of the heat-resistant materials avoiding pressure reactor procedures.

EXPERIMENTAL

The LE-828 epoxy resin was used as a model object. The active diluent (furfural-acetone resin) was prepared following the procedure adopted from [10, 11]. The diluent content in the epoxy resin was varied between 0 : 100 and 30 : 100 (w/w). The studied mixtures were prepared at 50°C under continuous stirring during 6 h, followed by degasation. As a result, the modifier was fully mixed with the epoxy resin. Tris(ethanolamino)titanate was used as a curing agent (14 wt %).

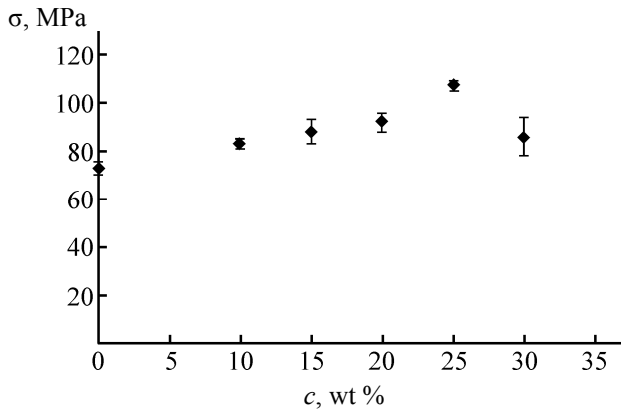


Fig. 5. Strength of epoxy matrices modified with FA5 resin as function of the content of the latter.

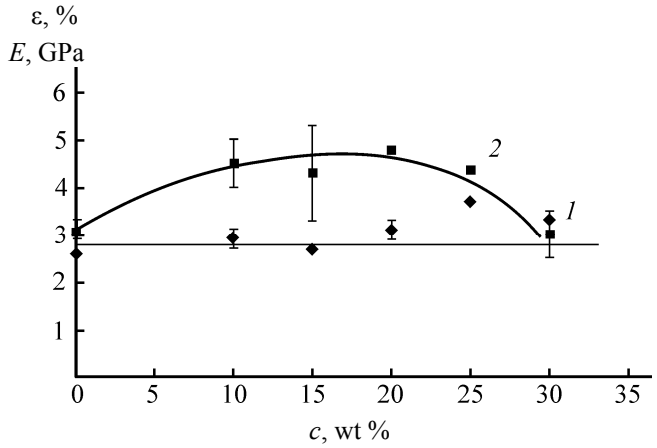


Fig. 6. (*1*) Elasticity modulus *E*' and (*2*) elongation at break ε of epoxy matrices modified with FA5 resin as function of the content of the latter.

Viscosity of the samples was measured with a Brookfield-LV viscometer (cone-plate, 30–900 s^{-1} at constant temperature). A LOIPLT 200 thermostat was used in experiments at elevated temperature (up to 70°C). The measurements were repeated in triplicate, and the results were averaged.

Three types of specimens were prepared for physico-mechanical testing. To do so, the resin was poured into the silicon forms and evacuated several times at 70°C during 1 h. The compositions were then cured during 2 h at 100°C, 2 h at 140°C, and 2 h at 160°C; the cured samples were shaped with a milling machine to get the 56 × 10 × 4.5 mm specimens for DMA testing and shoulder-blade specimens (2 mm cross-section and 35 mm length) for elongation testing.

Thermomechanical tests were performed using a Netzsch DMA 242 E Artemis analyzer (three-point loading, the measurement base of 50 mm; heating rate of 2 K/min at 25–300°C; the oscillation frequency of 1 Hz). Each composition was tested at least in triplicate.

The elongation tests were performed using a Zwik Z-100 machine at constant temperature of 25°C and the elongation rate of 1 mm/min. Deformation was monitored with a makroXtens extensometer. 6 Specimens were tested for each composition.

Thermophysical tests were performed using a Netzsch DSC 204 F1Phoenix differential scanning calorimeter. Each specimen was sequentially tested three times at 20–200°C under argon, the heating rate 10 K/min. The non-cured samples were so tested. The glass transition temperature of the sample cured in the calorimeter was determined by averaging the inflection points at the second and the first heating cycles; each composition was independently tested in duplicate.

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