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Article

Benzoxazine Copolymers with Mono- and Difunctional Epoxy Active Diluents with Enhanced Tackiness and Reduced Viscosity

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Abstract: The influence of epoxy active diluents, 1,4-butanediol diglycidyl ether (BD) and furfuryl glycidyl ether (FUR), in the mixtures with benzoxazine monomer based on bisphenol A, formaldehyde and m-toluidine (BA-mt), on the properties of a matrix was disclosed in this work. Resins were modified to achieve good tackiness at room temperature and reduced viscosity. The influence of mono- and difunctional modifiers on the process of curing was studied by way of differential scanning calorimetry and oscillatory rheology. The addition of BD and FUR shifted the curing peak to higher temperatures and significantly reduced viscosity. Preferable tackiness at ambient temperature was achieved with 10 phr of epoxy components in mixtures. However, cured blends with difunctional epoxy BD had an advantage over monofunctional FUR in enhanced tensile strength with remaining glass transition temperature at the level of neat benzoxazine (217 °C).

Keywords: benzoxazine; epoxy active diluents; benzoxazine curing; oscillatory rheology; furfuryl glycidyl ether

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1. Introduction

Polymer composite materials (PCM) are one of the most popular and rapidly developing types of materials today. Carbon fiber is used as a reinforcing fiber in the production of structural elements. The widespread use of PCM is growing every day in both strategic and civil industries. Polymer composites are used in the aerospace and nuclear industries, in the automotive industry, power engineering, construction, shipbuilding, bridge building, pipeline transport, and consumer goods. The level of technologies for serial production of carbon composite materials and the degree of their application in industry determines the scientific and technical potential of any country.

One of the main disadvantages of PCM is their high flammability due to the organic nature of the matrix [1–3]. This reason limits the wider application of PMC in the transport interior industry. Thus, the search for new benzoxazine resin mixtures with improved properties is an urgent task.

Benzoxazines have been developed as a new class of resins for PCM that appeared on the market at the beginning of the 21st century [4]. This is an addition-type phenol-formaldehyde resin rather than a condensation type. Benzoxazines are beneficial compared to the latter as they do not release volatiles during curing and have the following advantages: self-curing at elevated temperatures, high modulus, surpassing most of the known types of resins, near zero shrinkage during curing, low water absorption, excellent dielectric properties, flexibility of molecular design, enhanced flame resistance [5,6]. So, most polybenzoxazines fit V-1 category according to the UL-94 standard, but some of them relate to the highest V-0 flammability category [1,7].

Nowadays, benzoxazine monomers are a promising basis for creating resins that fit the requirements of different PCM technologies such as prepreg, RTM (Resin Transfer Molding), autoclave and so forth. This makes it possible to replace traditional phenol-formaldehyde and epoxy resin [8]. For example, many corporations have branded benzoxazine resins and prepregs. Flexible molecular design allows researchers to create benzoxazines with a wide variety of properties. For example, phenolphthalein benzoxazine resin has a glass transition temperature of 195–200 °C and belongs to the V-0 non-combustible category, while the bisphenol A based benzoxazine has a glass transition temperature of 173 °C and belongs to the category V-2.

One of the technological disadvantages of neat benzoxazine monomers is the glassy state of resin at room temperature and a narrow processing window. The lack of tack and drape at room temperature makes them difficult to use as a resin for prepreg technology. The viscosity at a processing temperature (80–130 °C) above 1 Pa·s limits their application, for example, in vacuum infusion technology, where the necessary condition for impregnation is a viscosity of the resin that is less than 0.5 Pa·s.

Thus, along with developing modifiers that improve mechanical, thermal and flame retardant properties, it is of great importance to search for viscosity regulator components that allow us to control the technological properties of benzoxazine resins without deteriorating the performance characteristics of polymer [9–11].

Such components can be active diluents in the form of monobenzoxazines or low-viscosity di- and monofunctional epoxy resins. Good compatibility of benzoxazine with epoxy resins and the ability to copolymerize with them due to hydroxyl groups formation during the self-cure process allows us to obtain a dense polymer network. Thanks to such favorable aspects, blends of benzoxazines and epoxy or novolac resins are widely reported in the literature [12–15].

A higher crosslinking density of benzoxazines and epoxy copolymerrization leads to a great change in the mechanical properties of the cured composition. Thus, in [11], with an addition of epoxy resin of 30 wt%, the glass transition temperature, flexural strength and deformation increased significantly in comparison with benzoxazine polymers. By varying the ratio of copolymers, this type of resin could be applied to specific performance requirements.

Another important advantage of composites based on a benzoxazine/epoxy mixture is the decrease of processing temperature at which an appropriate viscosity is reached. The high processing temperature could yield preliminary curing. So, mixtures with a concentration of cycloaliphatic epoxy resin of more than 25 wt% provided a proper viscosity for infusion processing [15].

The knowledge of the rheological properties of curing is important from the point of view of prepreg, infusion, RTM and other technologies for producing composite materials. Rheological parameters directly depend on the extent of the chemical reaction, if chemical processes with an increase in molecular weight occur, in particular leading to the formation of a three-dimensional network. Viscosity values could be determined by imposing constant (rotational) or periodic (oscillatory) shear strains on the material. Oscillatory mode is applied when a wide range of curing processes, including gelation and vitrification, are to be studied. In this case, small-amplitude oscillations are necessary conditions for measurement to proceed in a linear viscoelasticity region [16].

Some works combine different monitoring methods to conduct a comprehensive review of the process of curing. For example, in the study [17], the authors investigated the kinetics of curing with the two methods being compared: rheology and traditional differential scanning calorimetry. Various aspects of the rheology of curing processes including T–T–T diagrams (time–temperature–transformation) [18,19], homogeneous and heterogeneous curing, and the possibility of relaxation transitions in curing were studied in the works of Malkin A. and Kulichikhin S. [20,21].

In the case of prepreg materials, tack is one of the major properties that governs the ability of prepreg to be laid up. However, there is no standard method for measuring the tackiness of material. The tack of a material can be estimated by the sensation one experiences when removing one's finger from any sticky material (finger test) but it is only a qualitative assessment [22]. One of the quantitative tack measurements is the probe tack test [23,24]. It consists of a probe that comes into contact with the material to characterize it, then the probe is removed and the force and/or energy of separation is measured. In this case, contact formation and separation phases are clearly dissociated, so the contact parameters are easy to control, and each step of debonding could be clearly observed.

This work was devoted to the study of the dilution effect of 1,4-butanediol diglycidyl ether (BD) and furfuryl glycidyl ether (FUR) in blends with benzoxazine monomer (BA-mt) based on bisphenol A and m-toluidine. The practical purpose was to reach a favorable tack, expand the processing window and enhance or maintain some thermal and mechanical properties. The fundamental issue was to compare the effect of mono- and difunctional epoxy resins on the properties of mixtures with benzoxazine.

2. Materials and Methods

2.1. Starting Materials

Bisphenol A (4,4′-(Propane-2,2-diyl)diphenol) was supplied by Kazanorgsintez PJSC, Kazan, Russia and was used without further purification. M-toluidine (Acros Organics, Geel, Belgium) was distilled twice under vacuum before use. Paraformaldehyde (Acros Organics, Geel, Belgium) was used without further purification. Excipients were used without preliminary purification. Solvents were purified according to known methods, and their physical characteristics corresponded to literature data [25].

1,4-Butanediol diglycidyl ether (BD) (Macromer, Vladimir, Russia) and furfuryl glycidyl ether (FUR) (DOROS, Yaroslavl, Russia) were used as epoxy diluents without preliminary purification. The viscosity of BD at 25 °C was 30 mPa·s and the FUR viscosity was 6 mPa·s. The chemical formulas of the used epoxy compounds are presented in Figure 1.

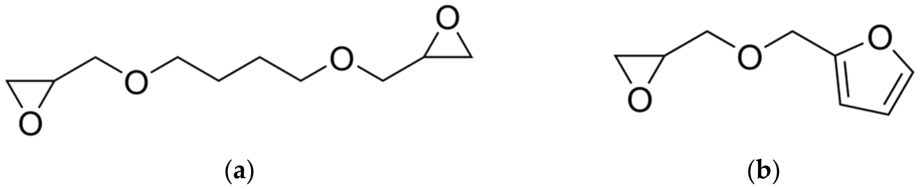


Figure 1. Chemical structures of epoxy diluents BD (**a**) and FUR (**b**).

2.2. Synthesis of Benzoxazine Monomer Based on Bisphenol A, M-Toluidine and Paraphormaldehyde (BA-mt)

Benzoxazine BA-mt (bis(3-(m-tolyl)-3,4-dihydro-2H-1,3-benzoxazine) is a well-known monomer. It was synthesized using the method reported in the literature [26]. The product yield was 95%. Completely cured BA-mt has a glass transition temperature of 217 °C for samples cured under the following conditions: 2 h 180 °C, 4 h 200 °C, 1 h 210 °C.

2.3. Composition Preparation

In order to determine the effect of epoxy compounds on the properties of benzoxazine monomer BA-mt, the following formulations, presented in Table 1, were prepared.

Table 1. Formulations of blends in parts per hundred resin BA-mt (phr).

Formulation	BD [2], phr	FUR [3], phr
BA-mt [1]	0	0
BB-5	5	0
BB-10	10	0
BB-15	15	0
BF-5	0	5
BF-10	0	10
BF-15	0	15

[1] BA-mt—bis(3-(m-tolyl)-3,4-dihydro-2H-1,3-benzoxazine, [2] BD—1,4-butanediol diglycidyl ether, [3] FUR—furfuryl glycidyl ether.

The mixtures of BA-mt and epoxy resin were obtained by stirring components at 110 °C for 10 min to achieve a homogeneous transparent solution. Subsequent degassing of the systems was performed at 110 °C for 15 min at a residual pressure of 1.0 kPa. The obtained compositions were either used as received for curing study or were cured at 180 °C–2 h + 200 °C–4 h + 210 °C–1 h for further thermal analysis and tensile tests.

2.4. Measurements

The ^1H and ^{13}C NMR spectra were obtained in DMSO-d_6 solutions with a Bruker AV-400 spectrometer (Bruker Corporation, Bremen, Germany) operating at 400 and 100 MHz, respectively. The signals, due to the deuterated solvents, were used as internal references. The chemical shifts of the signals were calculated relative to the signals of tetramethylsilane, which were used as references. The spectra were processed with the help of the MestReNova Lab software package (version 12.0.4, MESTRELAB RESEARCH, S.L, Santiago de Compostela, Spain).

A differential scanning calorimeter DSC 204 F1 Phoenix (Netzsch, Selb, Germany) was used for monitoring thermal effects [27]. The temperature characteristics of the curing and glass transition temperatures of cured specimens were determined according to ISO 11357-5:1999 [28] and ISO 11357-2:1999 [29], respectively. The heating rate for all measurements was 10 °C/min. All tests were performed in the temperature range from minus 50 °C to 300 °C in a nitrogen atmosphere at a rate of flow of 40 mL/min. The weight of the samples ranged from 5 to 10 mg. For data processing, Proteus Thermal Analysis version 8.0.2 software (Netzsch, Selb, Germany) was used.

Rheological measurements were carried out on a modular rheometer Anton Paar MCR302 in oscillation mode at a frequency of 1 Hz, a shear strain of 1% and a gap of 0.5 mm using plate–plate geometry, 25 mm in diameter. We conducted experiments at 180 °C. Rotational measurements were carried out at 120 °C for 2 h at a rotational speed of 200 rpm using the same geometry and gap. Tack properties were evaluated by the probe tack test, conducted on plate–plate geometry of 5 mm in diameter with the following two intervals: Driving to the measuring gap of d = 0.5 mm with a set force of 1 N; Moving up the measuring plate with a constant removal speed of v = 10 mm/s.

Tensile tests of cured resin specimens were carried out for five specimens of each composition with a crosshead speed of 1 mm/min using the universal testing machine 50ST (Tinius Olsen, Great Britain), according to ISO 527-2:2012.

3. Results and Discussion

3.1. Synthesis and Characteristics of BA-mt

The synthesis of benzoxazine monomer BA-mt was performed by way of the scheme in Figure 2. Synthesis was carried out in toluene solution with 10% paraformaldehyde excess at 85 °C.

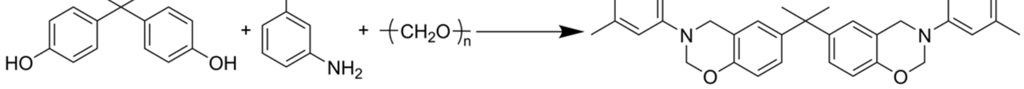
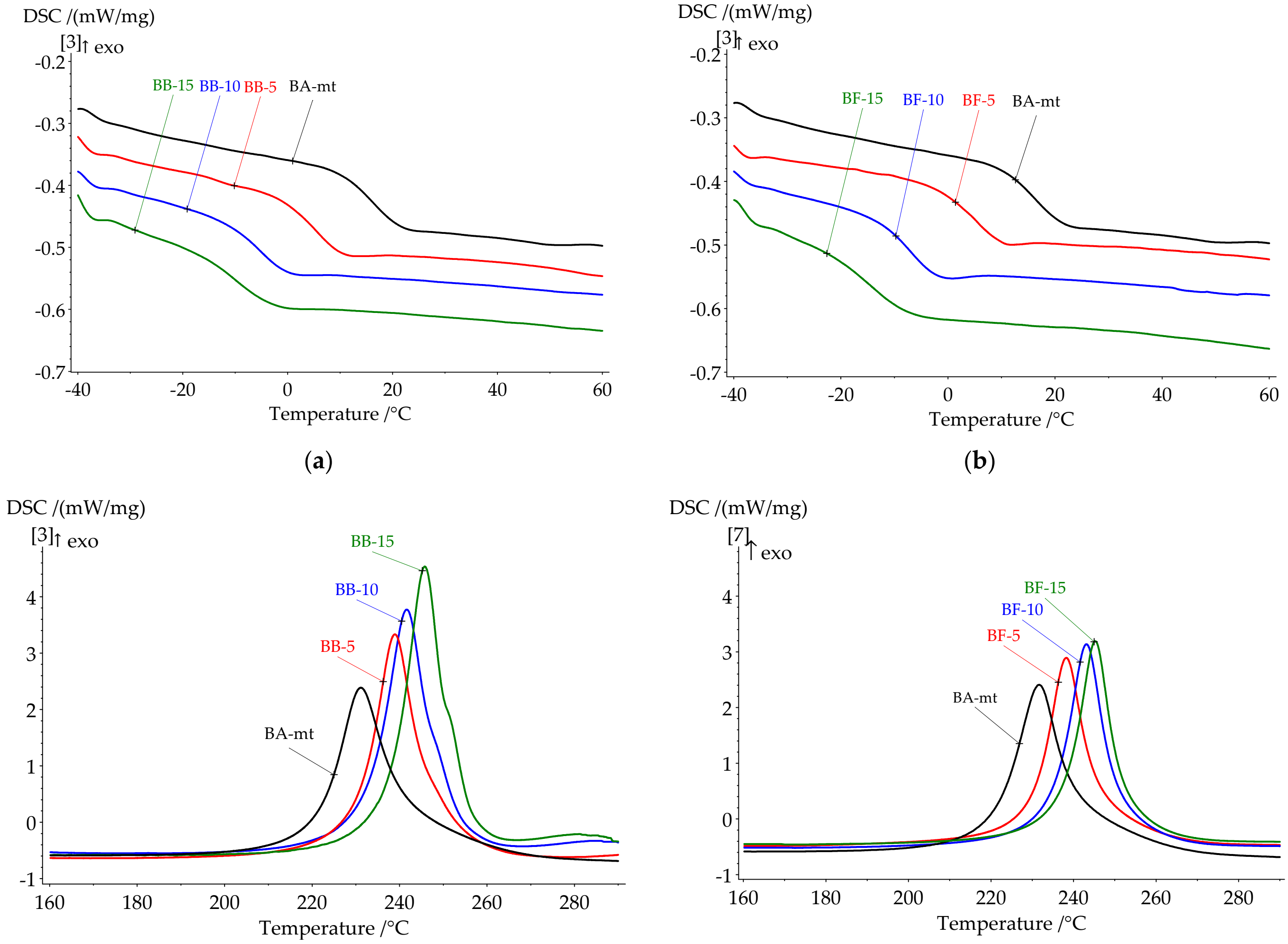


Figure 2. Synthetic scheme of benzoxazine monomer BA-mt.

Benzoxazine monomer BA-mt, chosen for our study, was obtained according to the method described in [30]. The monomer was characterized by ^1H and ^{13}C (Figures S1 and S2 in Supplementary Materials) and DSC (Figure S3 in Supplementary Materials). The ^1H NMR spectrum corresponded to the structure of synthetized BA-mt. Signals at the area δ_H = 4.67 ppm (Ar–CH$_2$–N) and δ_H = 5.42 ppm (O–CH$_2$–N) corresponded to methylene groups in the oxazine ring. The broadened signal at 4.25–4.5 ppm corresponded to the methylene protons of oligomeric compounds. The presence of oligomerized monomer in the product was either confirmed by a slight broadening of the DSC peak corresponding to the benzoxazine curing. Other thermal characteristics are T_{peak} = 233.3 °C and ΔH = 320.1 J/g.

3.2. DSC Measurements of the Curing Process and Polymers

For monitoring the process of curing and detecting the glass transition temperature of the uncured and cured blends under study, DSC scans were proceeded in a range from −50 to 300 °C (Figure 3). That allowed us to correlate tack with the physical process of vitrification. The parameters of curing and glass temperatures are listed in Table 2.



(**a**) (**b**)

(**c**) (**d**)

Figure 3. DSC curves of glass transitions of uncured blends with BD (**a**) and with FUR (**b**) and exothermic peaks of curing for blends with BD (**c**) and FUR (**d**).

Table 2. Characteristic temperatures and enthalpy values for the curing process and glass temperatures for uncured and cured specimens.

Formulation Index	Resin					Polymer
	T_g, °C	T_{onset}, °C	T_{peak}, °C	T_{end}, °C	ΔH, J/g	T_g, °C
BA-mt	16	225	233	242	346.1	217
BB-5	5	230	239	248	352.6	214
BB-10	−5	232	242	250	355.2	217
BB-15	−8	237	246	253	359.2	216
BF-5	3	300	240	246	325.2	208
BF-10	−8	235	242	251	315.5	205
BF-15	−13	237	245	252	306.9	204

Both BD and FUR contributed to the shift of the exothermic reaction's peak to the higher temperature region. This change could be explained by the dilution effect caused by epoxy resins, which resulted in the slower ring opening polymerization (ROP) of benzoxazine. In addition, epoxy may influence the distribution of the hydrogen bonds, which are responsible for both the reactivity and stability of the resins. Moreover, the reaction between the phenolic-OH groups of benzoxazine, generated via ROP, with the epoxy groups yields oligomers of high molecular weights, which may sterically hinder the benzoxazine curing [31]. The presented curves of curing had only one peak, whereas in many works two peaks were explicitly observed during curing [32]. This fact could be explained by the small amount of epoxy in blends and by the relatively high heating rate of 10 °C/min resulting in peaks overlapping. The fact that there were actually two peaks could be demonstrated on the system BB-15 in Figure 4, where when using the Peak Separation function in Proteus, two peaks were indicated. We propose that the second peak was invisible in blends with FUR as the monofunctional epoxy FUR in fact had an epoxy equivalent of 154, while for the difunctional epoxy BD it was 101, therefore in the same amount of modifier there were more epoxide groups in BD than there were in FUR.

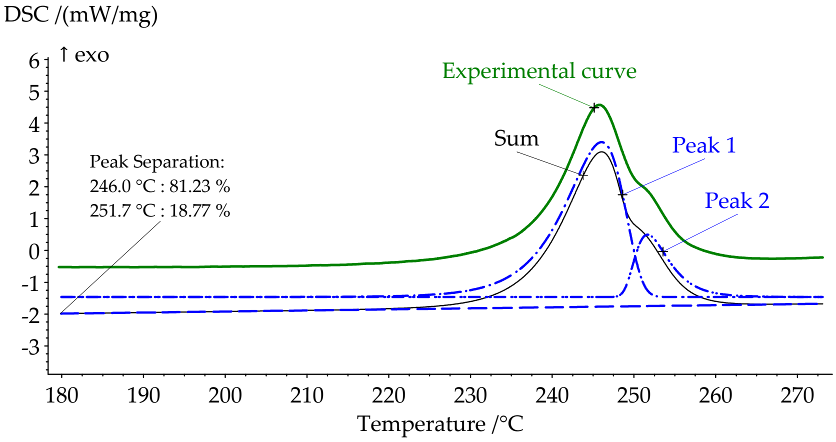


Figure 4. Peak separation for system BB-15.

There was almost no difference between characteristic temperatures of curing for blends with BD and with FUR. The addition of 5 phr of diluents increased the peak temperature from 233 °C to 238 °C, while the addition of 15 phr shifted the peak to 245 °C. The values for the overall heat of the polymerization of blends with BD increased with the increasing BD concentration. Whereas for blends with FUR, the values of heat released decreased until 306 J/g. According to Ishida and Rodriguez [33], the average of the total heat of polymerization for benzoxazine from DSC experiments was 316 J/g. The obtained results of enthalpy (346.1 J/g) and glass transition temperature (217.4 °C) for the synthesized BA-mt appeared to be in a good agreement with the literature data [26], where the enthalpy of polymerization BA-mt was 325 J/g and the glass temperature was 209 °C.

Glass transition temperatures (Tg) of uncured blends are listed in Table 2. It was demonstrated that the addition of FUR decreased the glass temperature more than BD, thus T_g for BB-10 and BF-10 were −4.8 °C and −8.1 °C respectively, that is, 20 °C lower than for neat BA-mt (15.6 °C). In general, the addition of diluents changed the state of the resin at room temperature (RT) from glassy to viscous.

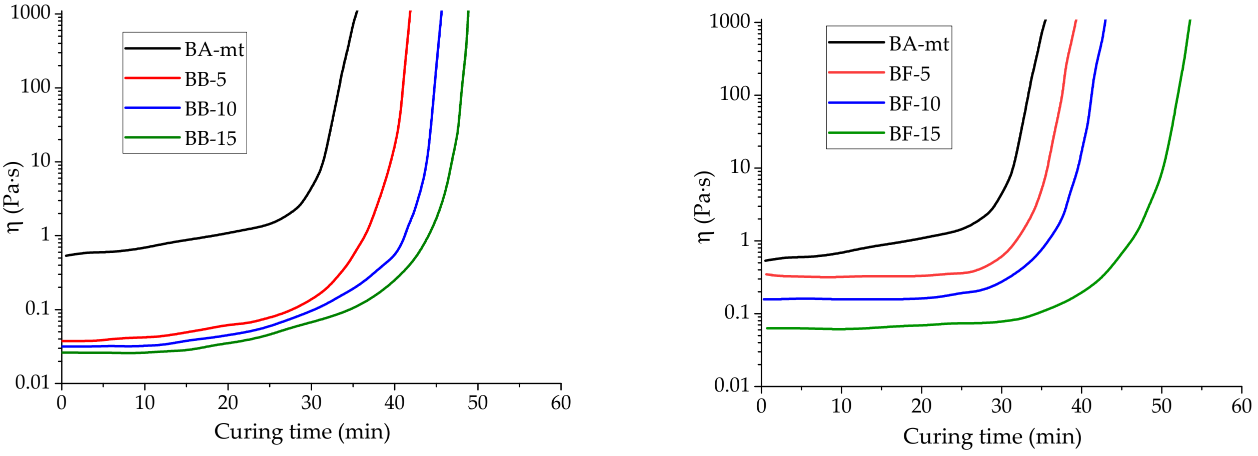
Polymerized compositions were characterized by measuring glass transition temperature (Table 2) and tensile strength (discussed in Section 3.4). The addition of 5 phr BD to BA-mt led to a lower T_g = 214.2 °C compared to neat BA-mt (217.4 °C). This could be explained by a change in the spatial regularity of the formed polybenzoxazines network and a decrease in the number of hydrogen bonds between hydrogen atoms in phenolic groups and nitrogen in polymerized benzoxazines. However, a further increase of BD concentration led to an increase of glass temperature to the level of 217 °C. We propose that this happened due to the copolymerization of benzoxazine and difunctional epoxy resulting in a rigid polymer network. On the other hand, the addition of the FUR modifier could not increase the density of the network as there was only one epoxide group in its structure. Thus, the larger the amount of FUR in the blend, the lower the glass transition temperature observed. The values of T_g for BF-5, BF-10, BF-15 were 207.7 °C, 205.3 °C and 203.8 °C, respectively.

3.3. Rheological Study

3.3.1. The Influence of Epoxy Diluents on the Processing Characteristics of the Resins

To estimate how diluents effect some processing parameters, we defined gelation time at a curing temperature, measured the change in viscosity at an approximate processing temperature during 2 h and presented the viscosity of blends at 40 °C. Then, the process of curing was considered from the point of view of structure formation.

The viscosity dependence on time at an isotherm of 180 °C for the compositions under study are presented in Figure 5. The obtained viscosity curves were characterized bya sharp viscosity increase starting at 1 Pa·s for neat BA-mt. The epoxy diluents did not alter the general character of the viscosity curves. However, the addition of modifiers reduced the initial values of viscosity and increased the lifetime of the resin compositions.



(**a**) (**b**)

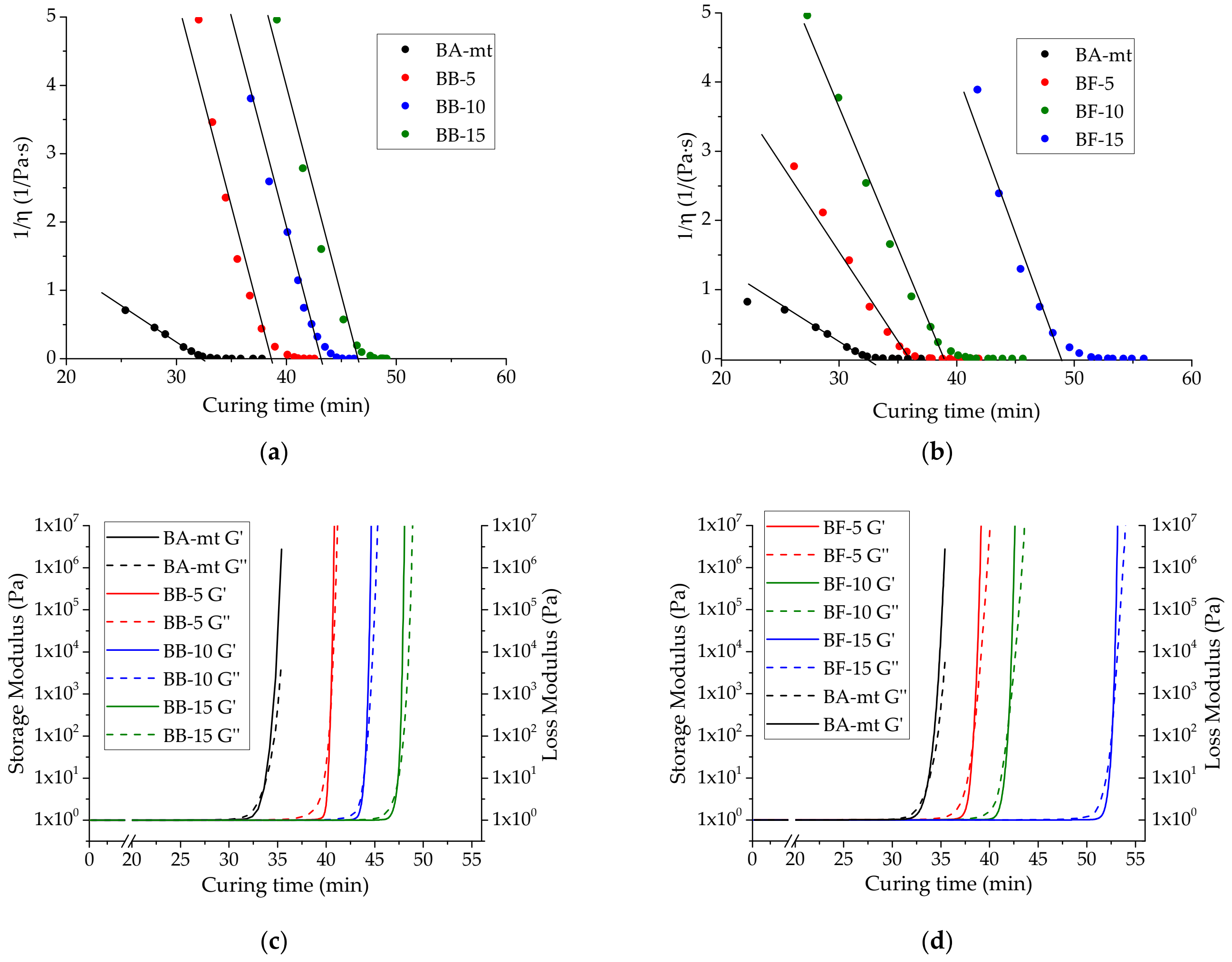
Figure 5. Dependencies of viscosity on curing time at 180 °C for compositions with BD (**a**) and FUR (**b**).

The resins used in technology meet a variety of requirements. One of the most important parameters of any resin is the gelation time at a certain temperature (or at a certain curing mode). The gelation time is expressed by the time interval from the beginning of the measurement to the moment of loss of fluidity, that is, to the moment of the beginning of the formation of a three-dimensional structure. Gelation time could be determined by extrapolating the time dependence of the shear viscosity η or the complex shear viscosity η^* on the time axis in the section where $\eta \to \infty$ or $\eta^* \to \infty$. This could be realized due to the Cox–Merz rule that states that η is the same function of γ as η^* is of ω [34]. To determine the gel point is to measure the maximum possible viscosity of the system and to plot the dependence of the reciprocal viscosity $1/\eta$ on time at the final stages of curing [35]. This dependence at the final stage of the experiment is usually well approximated by a straight line, the intersection of which with the *x*-axis determines the time at which the system reaches an infinite viscosity, that is, a gel point τ_{gel}. Another determination of gelation time is the crossover point—the point at which the storage shear modulus (G') is equal to the loss shear modulus (G'')—associated with the transformation of viscous liquid into a solid. The gelation times and crossover points of the obtained compositions are presented in Table 3 and Figure 6.

Table 3. Gelation and crossover points at 180 °C, viscosity at 40 °C and tackiness at 25 °C for compositions under study.

Formulation Index	**Gelation at 180 °C**		**η at 40 °C, Pa·s**	**Tack at 25 °C**		
	τ_{gel}, min	**$\tau_{(G' = G'')}$, min**		**Thumb Test**	**σ_{max}, mN/mm^2**	**W_{adh}, μJ/mm^2**
BA-mt	32	34	59,000	no	376 *	345 *
BB-5	38	38	7900	low	-	-
BB-10	43	42	850	medium	615	514
BB-15	46	53	210	medium	-	-
BF-5	36	41	5340	low	-	-
BF-10	40	45	503	medium	499	2630
BF-15	49	47	100	medium	-	-

* measured at 40 °C.



(**a**) (**b**)

(**c**) (**d**)

Figure 6. Dependencies of reciprocal viscosity 1/η on curing time at 180 °C for compositions with BD (**a**) and FUR (**b**) and dependencies of Storage Moduli and Loss Moduli for compositions with BD (**c**) and FUR (**d**).

The use of epoxy diluents as a modifier for BA-mt benzoxazine resin provided the increase in gelation time and crossover time. The mono-functional additive FUR monotonously changed the gelation time of the composition through different amounts of additive. The di-functional epoxy BD significantly increased the gel time and crossover time of the composition when 15 phr was added.

To estimate the influence of epoxies on the approximate processing window, isotherms at 120 °C were carried out over 2 h (Figure 7). The change of viscosity at elevated temperatures for different blends was from 0.30 to 0.45 Pa·s for neat BA-mt, from 0.12 to 0.16

for composition with 10 phr BD and from 0.08 to 0.17 for composition with 10 phr FUR. Blends with difunctional epoxy BD provided a higher viscosity increase rate than the monofunctional one. However, both additives significantly reduced the viscosity at 120 °C and the viscosity increase rate in comparison with the neat benzoxazine.

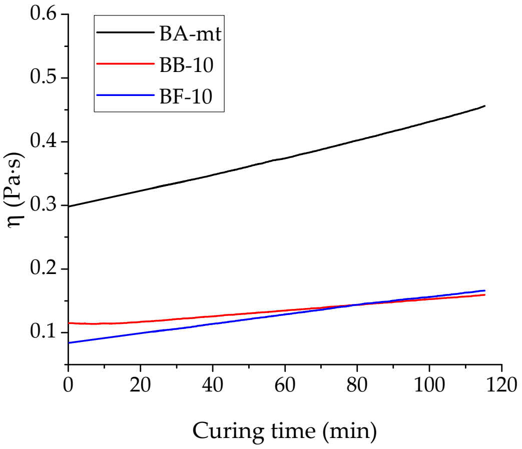


Figure 7. Dependencies of shear viscosity on the time at 120 °C for neat BA-mt, BB-10 and BF-10.

As mentioned in Section 3.2, blends with epoxies were not in a glassy state at 25 °C instead of neat BA-mt. Values of viscosity measured at 40 °C are listed in Table 3. FUR turned out to be 30%–40% more efficient in the reduction of viscosity compared to BD. Thus, values of viscosity for compositions with 10 phr of BD and FUR were 850 Pa·s and 503 Pa·s respectively and the viscosity of neat BA-mt was 59,000 Pa·s.

Actually, benzoxazines have unfavorable tackiness, thus the incorporation of epoxy is to contribute not only to reduced viscosity, but also to enhanced tack properties, which is important, for instance, for prepreg technology [36,37]. Thermoset tack is a measure of mechanical resistance that needs to be overcome in order to separate the resin and the substrate. Tack is governed by a complex interaction of adhesive and cohesive phenomena that are influenced by environmental parameters as well as by intrinsic properties of the material itself. Probe tack testing is the mechanical simulation of the subjective thumb tack test [38]. In our work, tack properties were preliminarily evaluated by the thumb tack test to choose the representative formulations for further study. RT blends with 10 phr of modifier turned out to have the most appropriate tack properties, while neat benzoxazine was almost in a glassy state at RT without demonstrating any tack. That is why to compare the tack of compositions with neat resin, the probe tack test was conducted at 45 °C for BA-mt and at 25 °C for BB-10 and BF-10. The further increase of epoxy concentration in compositions led to lower viscosity and cohesive character of separation. Results of the probe test are presented in Table 3 and Figure 8.

As expected, the addition of epoxy diluents increased the maximum tack stress of benzoxazine resin. However. the addition of 10 phr BD resulted in the same character of stress-displacement curve as neat benzoxazine. However, the addition of 10 phr FUR significantly affected the work of adhesion values. Some assumptions should be made about the effect of the diluents on tackiness. Neat benzoxazine resin at the chosen experimental temperature is near the relaxation transition (glass transition). However, due to the increased fluidity of the modified systems (reduced relaxation time) associated with the introduction of active diluents, the stickiness properties are more pronounced compared to unmodified benzoxazine. The resulting effect allows for a shorter period of time to interact between the environment and the surface of the measuring geometry.

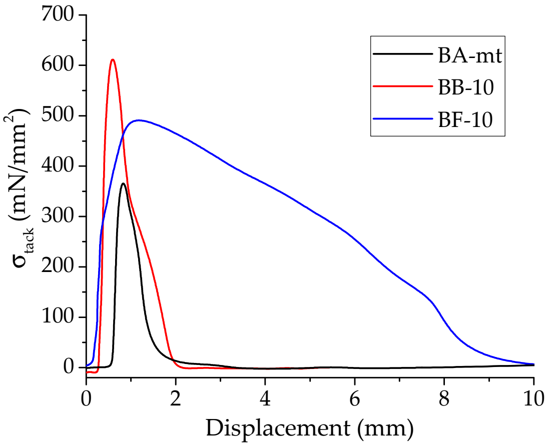


Figure 8. Stress-displacement curves for probe tack test separation for neat BA-mt at 45 °C, BB-10 and BF-10 at 25 °C.

3.3.2. Structure Formation during Curing of Modified Compositions

The rheological study of the curing process requires the determination of viscosity dependence on time. Since the change in viscosity during curing is the result of a combination of physical and chemical processes, the viscosity function could be represented as follows:

$$\eta(t,T,\alpha) = \eta(T)\eta(t,\alpha), \quad (1)$$

where $\eta(T)$—the temperature dependence of viscosity; $\eta(t, \alpha)$—the dependence of viscosity on time and degree of conversion. At a constant temperature $\eta(T)$ takes on a constant value of η_0.

It was found that, for all compositions under study, the change of viscosity η with the curing time could be satisfactorily described by the exponential equation:

$$\eta = \eta_0 \exp(k_\eta\ t), \quad (2)$$

where k_η—viscosity increase rate constant and η_0—initial viscosity.

The obtained equation is valid only for the initial stages of curing until the gelation point. This expression is also valid for the dependence of the complex viscosity on time, since the nature of the change in both functions is identical.

The viscosity increase rate constants were calculated (Table 4) using the initial area of the obtained curves. Epoxy diluents decreased the viscosity increase rate constants of the compositions. The addition of mono-functional FUR epoxy diluent led to a more than five times decrease in the rate constant. The effect of BD addition to the benzoxazine resin was not so significant, but the decrease of the rate constant was uniform for every added amount of epoxy additive.

Table 4. The viscosity increase rate constants of compositions under study.

Formulation	**BA-mt**	**BB-5**	**BB-10**	**BB-15**	**BF-5**	**BF-10**	**BF-15**
k_η, min^{-1}	0.039	0.032	0.028	0.020	0.009	0.007	0.006

The nature of the increase in viscosity in the process of curing is complex. The increase in viscosity is determined by the change in molecular weight and the structure of molecules. It is assumed that, when building the dependence of viscosity on time in logarithmic coordinates, the obtained curves could be separated into two or three linear sections. Each area obeys a power law according to the Malkin–Kulichikhin equation [39]:

$$\eta = (f \cdot k \cdot \tau)^{n,} \quad (3)$$

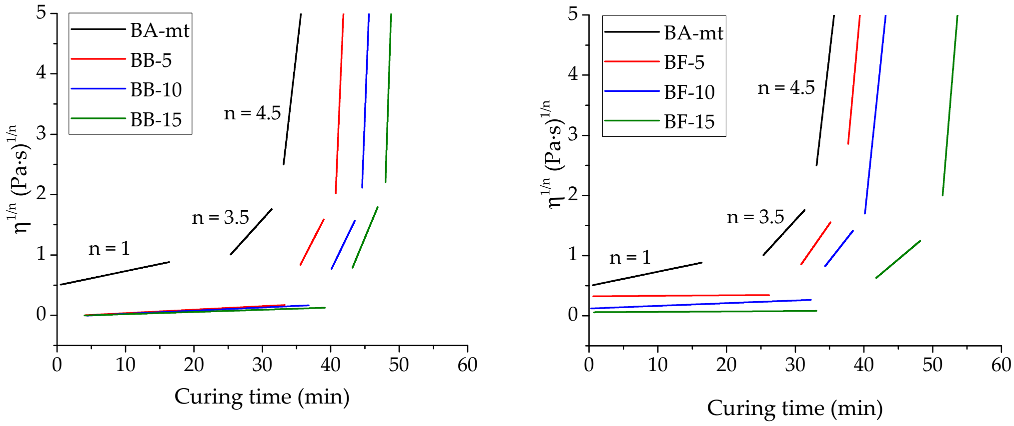
where f is the functionality of the oligomer; k is the viscosity increase rate constant (min^{-1}); τ is the time (min); n is a constant.

Certain structural transformations occur in each area: when n = 1, the molecular weight of the linear chains of the oligomer increases; when 1 < n < 3.5, a fluctuation network of entanglements of macromolecules arises; at 3.5 < n < 4.5, the three-dimensional cross-linking process begins to predominate until the system loses its fluidity, that is, until gel point.

We used the modified form of Equation (3) [40] to determine these characteristic areas in the compositions under study:

$$[\eta(\tau)]1/n = f \cdot k \cdot \tau. \quad (4)$$

The results of approximation are presented in Figure 9 and Table 5. All compositions were characterized by a long period of linear molecule growth and a very short time of fluctuation network formation; the second stage rapidly turned to the third one of a three-dimensional cross-linking process. Thus, the modifiers mostly altered the first stage due to the dilution effect.



(**a**) (**b**)

Figure 9. Dependencies of viscosity on curing time in the coordinates of the modified Malkin–Kulichikhin equation at 180 °C for compositions with BD (**a**) and with FUR (**b**).

Table 5. The characteristic times of the process of structuring for compositions under study.

Formulation Index	**Time, min**		
	$\tau_{n=3.5}$	$\tau_{n=4.5}$	τ_{gel}
BA-mt	20	33	32
BB-5	34	40	38
BB-10	38	44	43
BB-15	41	47	46
BF-5	28	36	36
BF-10	33	39	40
BF-15	40	50	49

The obtained values of the characteristic times were compared with the gel formation times, obtained by the classical approach. It turned out that characteristic time corresponding to the beginning of the three-dimensional cross-linking process was in good agreement with the gelation time. This fact proved the relevance of applying the Malkin–Kulichikhin equation to the benzoxazine curing process.

3.4. Tensile Properties of Cured Compositions

Tensile tests were carried out to estimate the mechanical properties of cured compositions. The mean strength values are presented in Table 6. Tensile properties were obtained only for BA-mt and BB-10 and BF-10 compositions due to their superior rheological and thermal performance.

Table 6. Tensile strength of cured BA-mt, BB-10 and BF-10.

Formulation Index	σ, MPa
BA-mt	47
BB-10	55
BF-10	45

A slight increase in tensile strength in the BB-10 composition indicated that the modifier was embedded in the three-dimensional network and its elasticity increased due to flexible ether groups. However, monoglycidyl ether led to the formation of a less rigid network, which was reflected in a slight decrease in tensile strength.

4. Conclusions

This work disclosed that 1,4-butanediol diglycidyl ether (BD) and furfuryl glycidyl ether (FUR) in compositions with benzoxazine monomer BA-mt yielded improved tackiness of blends, reduced viscosity and higher temperature of curing. Some of the compositions demonstrated enhanced thermal and mechanical properties.

The benzoxazine/epoxy blends possess good tack at RT compared to neat benzoxazine, which is nearly in a glassy state at RT. Epoxy diluents efficiently decreased the glass transition point of uncured resin: a decrease in T_g was more than 20 °C for compositions with 10 phr of BD or FUR. However, epoxy additives affected the polymerization process. The peak polymerization temperature shifted to a high temperature region in the case of both BD and FUR addition.

The use of epoxy compounds in an amount of 10 phr provided a significant decrease in viscosity. The favorable tackiness was achieved with 10 phr of epoxy components in mixtures. The shift of the DSC polymerization peak resulted in an increased gel time and lifetime of the compositions. The viscosity increase rate constants of BB-10 and BF-10 were 5.5 and 1.5 times less than for neat BA-mt. Structure formation was characterized by the Malkin–Kulichikhin equation, which appeared to be applicable to the benzoxazine curing process. The characteristic time corresponding with the beginning of the three-dimensional cross-linking process was in a good agreement with the gelation time.

Moreover, the addition of 10 phr FUR decreased T_g at 13 °C and tensile strength at 4%. On the other hand, the addition of 10 phr BD decreased T_g only at 1 °C and led to an increase in tensile strength at 17%. The difference in the properties of the resulting polymers was associated with the difference in the functionality of the used epoxy resins BD and FUR.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/jcs5090250/s1, Figure S1: ^{1}H NMR spectrum of benzoxazine BA-mt. Figure S2: ^{13}C NMR spectrum of benzoxazine BA-mt. Figure S3. DSC curve of BA-mt.

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