Study of the curing process of epoxy-amine compositions by differential scanning calorimetry

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Abstract. The results of studying the process of curing epoxy resin ED-20 with various amine hardeners by differential scanning calorimetry are presented. The effectiveness of several tertiary amine curing accelerators has been evaluated. The completeness of curing of the epoxy resin and the stoichiometry of the compositions were evaluated by IR spectroscopy.

1 Introduction

Epoxy resins (ER) are highly reactive due to the presence of epoxy and hydroxyl groups in the oligomeric chains. The epoxy group is able to react with more than 50 functional groups of various chemical nature, as well as with substrates containing reactive groups on their surface, which leads to a high adhesive strength of ER after curing and the possibility of their use in the production of a large number of composite materials [1–4]. A large group of hardeners for ER are diamines and polyamines, which make it possible to obtain structural materials with high physical and mechanical properties and chemical resistance [5–8].

Primary aliphatic amines (ethylenediamine, hexamethylenediamine, polyethylenepolyamine) are low-viscosity liquids that are well compatible with ER and cure them at room temperature. However, the curing process with their participation is highly exothermic (the reaction of an amine with one equivalent of the epoxy group releases 103 kJ), as a result of which the curing system can heat up to 200-250°C, while thermo-oxidative processes begin to occur in the material with the formation of bubbles from gaseous decomposition products resins [9-11].

Alicyclic, arylaliphatic, heterocyclic di- and polyamines can be classified as structural and functional analogues of aliphatic polyamines. They have a similar structure, molecular weight, and functionality, effectively cure ER at room temperature, are toxic to about the same degree, but are less volatile than aliphatic polyamines and, in some cases, are more preferable as curing agents [12–14].

Aromatic di- and polyamines are less reactive than aliphatic ones due to the low mobility of the phenyl units. However, they are a good alternative to aliphatic amines. As a rule, these

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are solids, less often high-viscosity liquids, which solidify ER upon heating (usually in a stepwise mode).

To improve the complex of technological properties - to reduce viscosity, improve solubility in ER, increase the viability of compositions, ensure good wetting of reinforcing fillers and substrates, reduce the exothermic effect of the curing reaction - modified aromatic amine hardeners are used, which are eutectic mixtures of various amines, including aliphatic, ER curing agents, and other functional additives [15–19].

A separate group of ER curing agents are tertiary amines, which can serve as both hardeners and accelerators of the ER curing process. Tertiary amines are introduced in a nonstoichiometric amount with respect to the epoxy resin, which is selected experimentally [19]. Tertiary amines initiate the ionic polymerization of ER, which makes it possible to obtain acid and alkali resistant cured products with higher heat resistance than in the case of curing with amines. In addition, the use of catalysts makes it possible to lower the temperature, shorten the curing time, and eliminate the influence of undesirable side reactions [20, 21].

As mentioned above, ER curing is an exothermic process, which can be studied using the method of differential scanning calorimetry [22, 23], which was implemented in this work.

2 Experimental procedure

As the main component of the composition, we used the ED-20 epoxydian oligomer (GOST R 56211-2014), the properties of which are given in Table 1.

Table 1. Physical and chemical properties of ED-20 resin.

Property	Indicator
Appearance	Viscous transparent
Mass fraction of epoxy groups, %	20.0-22.5
Mass fraction of volatile substances, %, no more	0.8
Dynamic viscosity, Pa s, at 25°C	12-25
Gelatinization time, hour, not less	4.0

As a hardener, we used two different amine-type hardeners developed at the Scientific and Educational Center "Composites of Russia" of Bauman Moscow State Technical University - "Amikrost-1" and "Amikrost-2" different in composition, but with the same amino equivalent weight equal to 44.5.

Triethanolamine (TEA), 2,4,6-tri-N,N-dimethylaminomethylphenol (Agidol-53) and triethanolamine titanate (TEAT) were used as curing accelerators.

The curing process of the compositions was studied by measuring the thermal effect of the chemical reaction on a NETZH DSC 204 F1 Phoenix differential scanning calorimeter. The glass transition temperatures of the cured samples were determined by differential scanning calorimetry (DSC) on the same instrument. The measurements were carried out in the temperature range from 25 to 250°C at a heating rate of 10 K/min in argon (according to GOST R 57687-2017).

3 Results and discussion

The work studied the curing processes of various epoxy-amine compositions, the composition is given in table 2.

Table 2. Composition of epoxy-amine compositions.

Code	The content of the component, weight part (wt.p.)					
	ED-20	**Amikrost-1**	**Amikrost-2**	**Agidol-53**	**TEA**	**TEAT**
ESA-3	100.0	22.0	-	-	2.0	-
ESA-10	100.0	22.0	-	2.0	-	-
PAB-1	100.0	11.0	11.0	2.0	-	-
PAB-5	100.0	-	22.0	2.0	-	-
PAB-6	100.0	5.5	16.5	2.0	-	-
PAB-7	100.0	-	22.0	3.0	-	-
PAB-8	100.0	-	22.0	-	2.0	-
PAB-9	100.0	-	22.0	-	-	2.0
PAB-10	100.0	-	22.0	5.0	-	-
PAB-11	100.0	-	22.0	1.5	1.5	-
PAB-13	100.0	-	22.0	1.0	-	-

Table 3 shows the curing temperature parameters of the investigated compositions and the glass transition temperatures of the cured compositions, determined by DSC. From the data obtained, it can be seen that when using the Agidol-53 accelerator, a separate stage of curing is observed with a maximum at a temperature of 110-115°C. This phenomenon deserves separate consideration.

Table 3. Temperatures of maximum thermal effects during ER curing and glass transition temperatures of cured epoxy-amine compositions.

Code	Curing peak at temperature, °C	$T_{gl.tr.}$, °C
ESA-3	190.1	115.5
ESA-10	112.6 and 199.2	121.4
PAB-1	110.5 and 179.3	129.5
PAB-5	110.5 and 166.4	146.0
PAB-6	111.1 and 172.0	139.6
PAB-7	109.0 and 164.3	137.6
PAB-8	159.7	126.4
PAB-9	165.9	125.0
PAB-10	112.6 and 154.7	115.0
PAB-11	161.9	145.1
PAB-13	165.5	170.2

Figure 1 shows the curing curves of ESA-3 and ESA-10 compositions. The ratio of ED-20: hardener "Amikrost-1" is the same in them, but ESA-10 contains 2.0 wt.p. Agidol-53, and in the composition of ESA-3 - 2.0 wt.p. TEA. On the curing curve of the ESA-10 composition, the presence of Agidol-53 is manifested by the appearance of a low-temperature curing peak with a maximum at 112.6°C. From the comparison of high-temperature curing peaks, it can be seen that for this system "ED-20:Amikrost-1" the TEA accelerator is more efficient than the Agidol-53 accelerator. In particular, the peak cure temperature for ESA-3 is almost 10°C lower than for ESA-10. However, the glass transition temperature of both cured compositions is low and is 115.5°C for ESA-3 and 121.4°C for ESA-10.

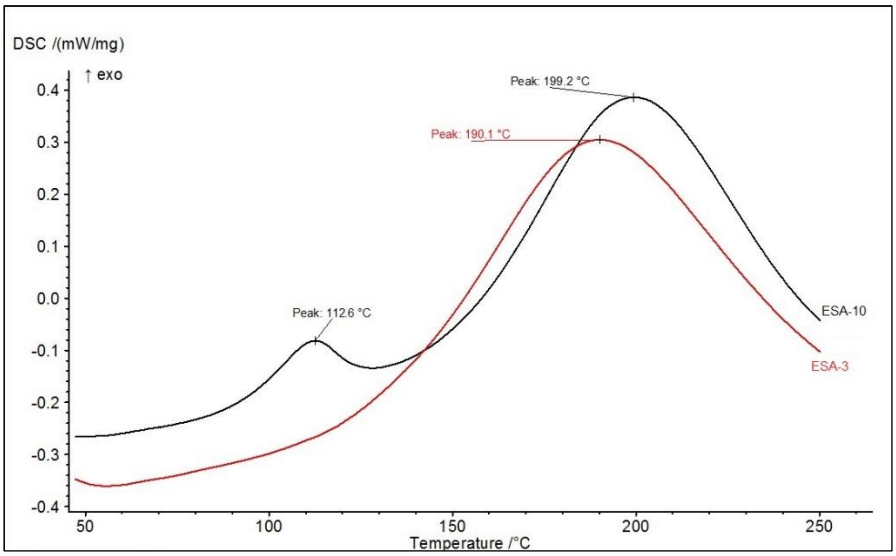

Fig. 1. DSC curing curves of ESA-3 and ESA-10 compositions.

Figure 2 shows DSC curing curves for ESA-10, PAB-1, PAB-5 and PAB-6 compositions, in which Amikrost-1 (ESA-10), Amikrost-2 (PAB-5) was used as a hardener and their mixture 1:1 (PAB-1) and 1:3 (PAB-6). The content of the accelerator Agidol-53 in all these compositions was 2.0 wt.p. The resulting curing curves have pronounced inflections with maxima at 110-112°C, related to the curing of ED-20 accelerator Agidol-53. The temperature maximum of the second peak of curing shifts from 199.2°C for the ESA-10 composition with the Amikrost-1 hardener to 166.4°C for the PAB-5 composition with the Amikrost-2 hardener through intermediate 179.3°C (PAB-1) and 172.0°C (PAB-6) with a mixture of two hardeners (Table 2). This is evidence that the Amikrost-1 hardener reacts with ED-20 resin at a higher temperature than the Amikrost-2 hardener. It should be noted that the glass transition temperature of the cured compositions, on the contrary, decreases from 146.0°C for PAB-5 to 121.4°C for the ESA-10 composition (Fig. 3).

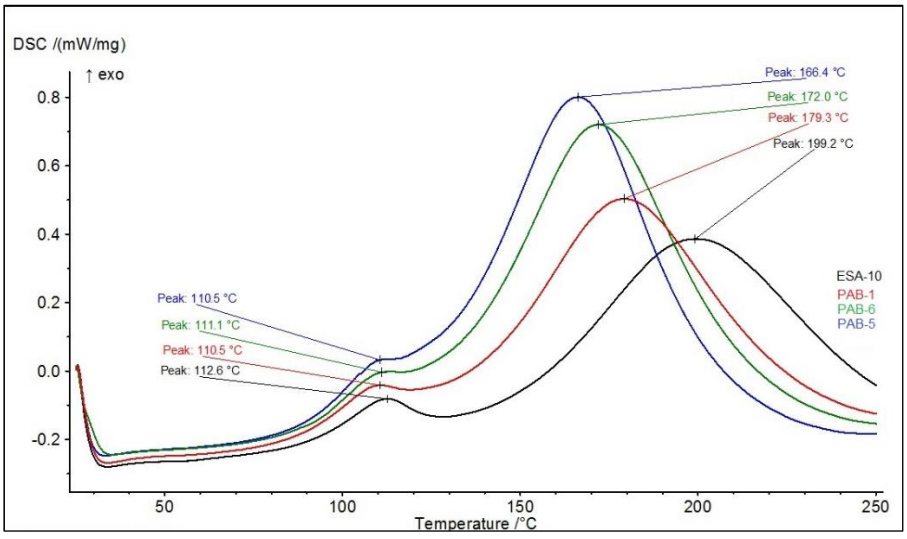

Fig. 2. DSC curing curves for ESA-10, PAB-1, PAB-5 and PAB-6 compositions.

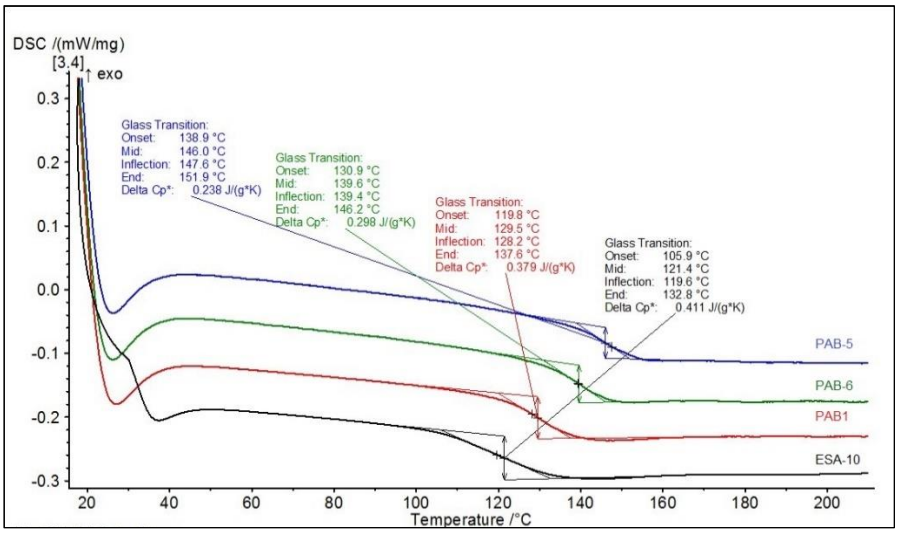

Fig. 3. Determination of the glass transition temperatures of cured PAB-5, PAB-6, PAB-1 and ESA-10 (the curves are located as the content of "Amikrost-2" increases, Table 2).

In Table 3 consists of the curing parameters of the compositions PAB-5, PAB-8 and PAB-9, in which AG-53, TEA and TEAT were used as accelerators in an amount of 2.0 wt.p. respectively. The ratio of "ED-20: hardener "Amikrost-2" = 100.0 wt.p.: 22.0 wt.p. in all the described compositions. On the PAB-5 curing curve, there is a separate characteristic peak of ED-20 curing with the Agidol-53 accelerator at 110.5°C. The curing peak maxima from the interaction of ED-20 with the Amikrost-2 hardener are observed at approximately the same temperatures in the case of Agidol-53 and TEAT (166.4°C and 165.9°C), and in the case of TEA, the temperature maximum of the curing peak is slightly lower - at 159.7°C. It should be noted that with the Agidol-53 accelerator, the glass transition temperatures of the cured compositions are significantly higher than with the TEA and TEAT accelerators.

On Figure 4 shows the DSC curing curves of the ED-20 compositions with the Amikrost-2 hardener, taken in the ratio of wt. p. = 100:22, but containing different amounts of the accelerator Agidol-53 (from 1.0 to 5.0 wt. p.) - compositions PAB-13, PAB-5, PAB-7 and PAB-10. The nature of the depicted curves shows that the Agidol-53 accelerator reacts with ED-20 faster than the Amikrost-2 hardener, the peak of the thermal effect of the reaction is observed at 110-112°C. However, the heat released as a result of this stage of curing when the content of the accelerator 1÷3 wt. p. (PAB-13, PAB-5, PAB-7), practically does not affect the course of the curing process of ED-20 with the Amikrost-2 hardener (the curing peak is at temperatures of 164-166°C) and only when the content of the accelerator is 5 wt. p. there is a noticeable decrease in the maximum reaction temperature of the main curing to 154.7°C (PAB-10). At the same time, the negative effect of increasing the amount of the Agidol-53 accelerator on the heat resistance of the cured compositions can be seen (Fig. 5): the glass transition temperature decreases from 170.2°C (PAB-13) to 115.0°C (PAB-10).

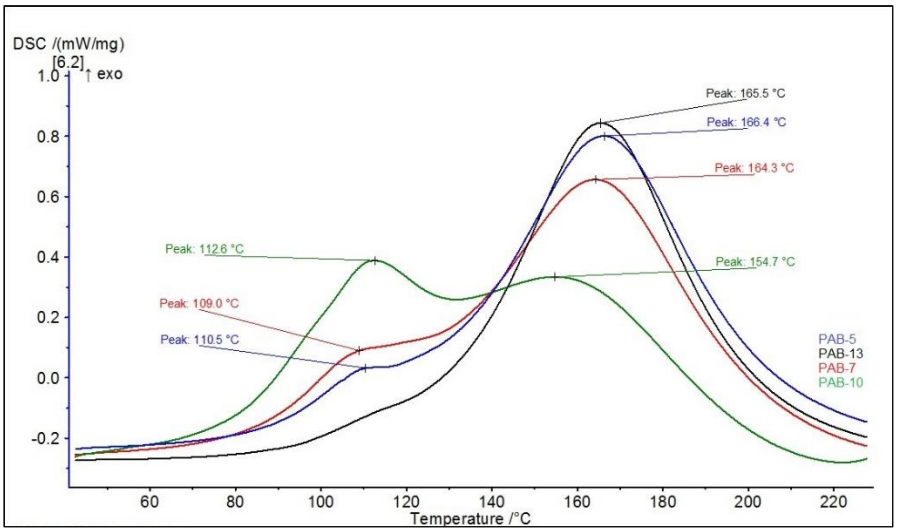

Fig. 4. DSC-curves of curing ED-20 with hardener "Amikrost-2", taken in the ratio of wt.p. = 100:22. The content of the accelerator AG-53: PAB-13 (1 wt.h.), PAB-5 (2 wt.p.), PAB-7 (3 wt.p) and PAB-10 (5 wt.p.).

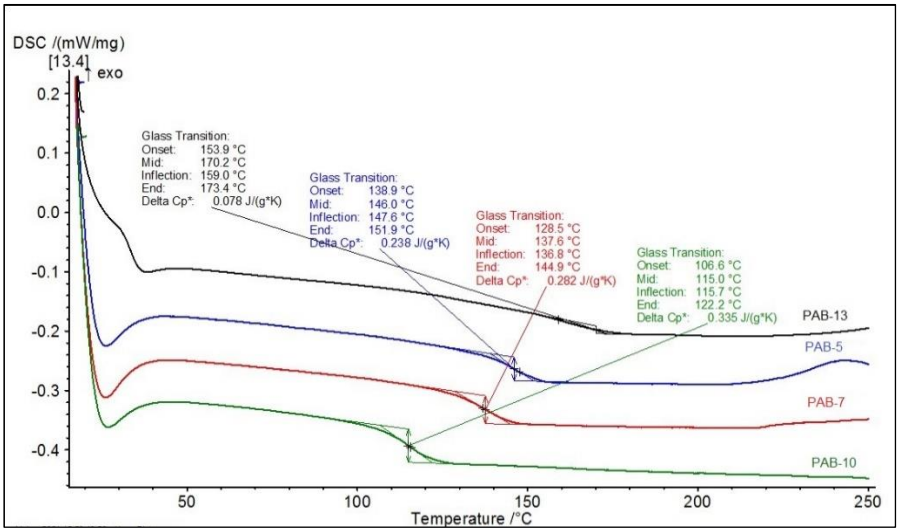

Fig. 5. Determination of the glass transition temperatures of PAB-13, PAB-5, PAB-7 and PAB-10 compositions. The content of the accelerator AG-53: PAB-13 (1 wt.p.), PAB-5 (2 wt.p.), PAB-7 (3 wt.p.) and PAB-10 (5 wt.p.).

The joint use of the Agidol-53 and TEA boosters seems to be very interesting. For example, the studied composition of PAB-11 based on ED-20 and the hardener "Amicrost-2" in the ratio = 100.0 wt.p.: 22.0 wt.p. contains equal amounts of both accelerators (1.5 wt.p.). The composition cures surprisingly with a single temperature peak at 161.9° C. and after curing has a very high heat resistance. The glass transition temperature of cured PAB-11 is 145.1°C.

4 Conclusions

1. In the Scientific and Educational Center "Composites of Russia" BMSTU has developed advanced liquid mixed amine hardeners "Amikrost-1" and "Amikrost-2". Their effectiveness in curing epoxy resin ED-20 has been proven.
2. It has been established by DSC that the hardener "Amikrost-1" cures ED-20 at a higher temperature than "Amikrost-2".
3. The influence of the content of the accelerator Agidol-53 in the composition on the process of curing the epoxy oligomer ED-20 with the hardener "Amikrost-2" was studied.
4. It has been established that when using the Agidol-53 accelerator, it is necessary to select the optimal conditions for the stepwise curing of the epoxy oligomer.
5. The prospects for the simultaneous introduction of a mixture of two accelerators Agidol-53 and Triethanolamine into the cured system are shown.
6. It was found that the use of the hardener "Amikrost-2" leads to the production of heat-resistant cured epoxy compositions with a glass transition temperature of about 170°C.

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