

Rheological research of the curing processes of the epoxy-amine compositions based on ED-20 resin

N. Pavlukovich^{1,2*}, A. Leshtaev¹, V. Buryakov¹, I. Polikarpova¹, M. Orlov¹, I. Storozhuk^{1,2}, V. Nelyub¹, and A. Borodulin¹

¹Bauman Moscow Technical University, 2-ya Baumanskaya ul., 5, build. 1, 105005 Moscow, Russia

²A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova str., 28, 119991 Moscow, Russia

Abstract. In this paper the rheological properties of various epoxy-amine compositions based on the ED-20 epoxy resin were studied. The effectiveness of curing accelerators from among tertiary and quaternary amines has been evaluated. The rheokinetics of the curing processes were studied by the method of rotational viscometry. The times to reach the gel point of the studied systems are determined.

1 Introduction

At present, polymer composite materials play an important role in the creation of modern types of aviation and space technology. Among them, the most popular and commercially developed are composites based on carbon fabrics and epoxy resins of various chemical structures and compositions [1–9]. To develop the technology for obtaining the considered composite materials based on new modified binders, it is necessary to study the curing process of epoxy compositions [10–12].

The first stage of the curing process of an epoxy binder is gelation, and this process can be studied using the viscometry method [10]. Information about the rheological characteristics of the material is important for assessing the dependence of its fluidity on the composition of the curable composition, determining the optimal temperature for the process, and, based on this, predicting the behavior of the thermoplastic during impregnation, thin-layer application, dipping or pouring into molds.

For many systems, the change in viscosity (η) versus time (t) during curing is quite satisfactorily described by the exponential dependence equation [13]:

$$\eta = \eta_o \cdot \exp(k_\eta \cdot t) \quad (1)$$

where η_o – the initial viscosity, k_η – the viscosity increases constantly.

However, the application of this formula does not allow one to determine the true gelation time at which $\eta \rightarrow \infty$.

* Corresponding author: pavlukovich@yandex.ru

Various methods for determining the gel point are known from the literature [14–17]. What they have in common is fixing the point in time when the curing system loses its ability to flow. The most reasonable way to determine the gel point is the method of determining the maximum achievable value of the viscosity of the system under study and plotting the dependence of the inverse viscosity $1/\eta$ on time in the final stages of curing. Extrapolation of the value $1/\eta$ to the zero value makes it possible to determine the gel point with an error not exceeding 5% [18].

In this paper, the study of the reokinetics of structuring various epoxy-amine compositions based on the epoxy oligomer ED-20 and the mixed liquid amine hardener “Amicrost-1” with an amine equivalent weight of 44.5 developed at the Scientific and Educational Center “Composites of Russia” of Bauman Moscow State Technical University was carried out. The effect of various accelerators from among tertiary and quaternary amines on the curing process has been studied. The time to reach the gel point of the system was determined by extrapolating the dependence $1/\eta=f(t)$ to zero.

2 Experimental part

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

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

The developed mixed hardener “Amikrost-1” is a “hot” curing hardener, so the study of rheokinetics was carried out at elevated temperatures.

Triethanolamine (TEA), 2,4,6-tri-*N,N*-dimethylaminomethylphenol (Agidol-53), triethanolamine titanate (TEAT), and alkyldimethylbenzyl ammonium chloride (KatAB) have been studied as curing accelerators.

Rheological studies of the compositions were performed by rotational viscometry on a Brookfield LVDV-E viscometer. Dependences of viscosity (η) on time (t) were obtained at temperatures of 100 and 150 °C.

3 Results

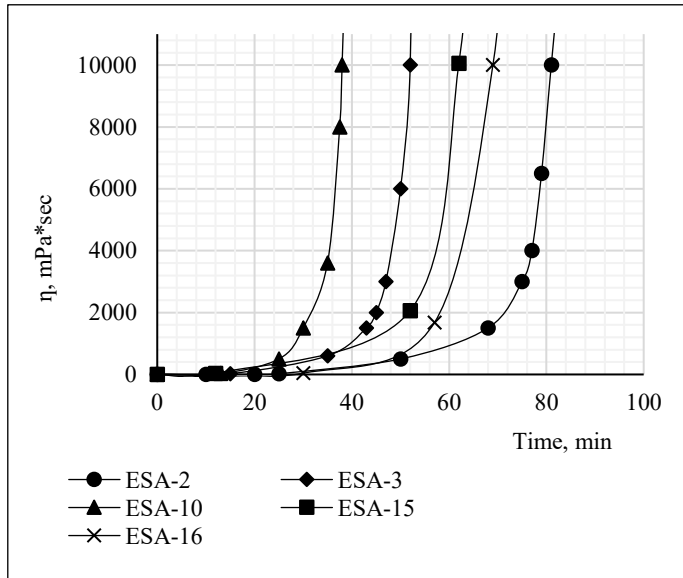
The paper studied the curing kinetics of various epoxy-amine compositions, the proportion of which is given in Table 2.

Table 2. The proportion of epoxy-amine compositions.

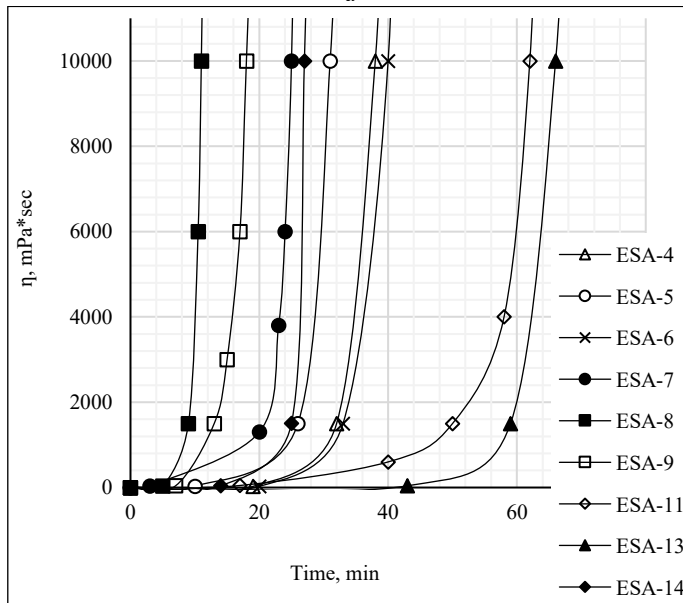
Code	Component's content, weight part (wt.p.)					
	ED-20	Aminokrost-1	Agidol-53	TEA	TEAT	KatAB
ESA-2	100.0	21.0	-	-	-	-
ESA-3	100.0	21.0	-	2.0	-	-
ESA-4	100.0	30.0	-	2.0	-	-
ESA-5	100.0	30.0	2.0	-	-	-
ESA-6	100.0	30.0	1.0	-	-	-
ESA-7	100.0	30.0	3.0	-	-	-
ESA-8	100.0	30.0	5.0	-	-	-
ESA-9	100.0	30.0	1.5	1.5	-	-
ESA-10	100.0	21.0	2.0	-	-	-

ESA-11	100.0	30.0	-	0.6	-	-
ESA-13	100.0	30.0	-	-	-	-
ESA-14	100.0	30.0	-	3.0	-	-
ESA-15	100.0	21.0	-	-	2.0	-
ESA-16	100.0	21.0	-	-	-	2.0

The dependences of the change in the viscosity of the epoxy compositions at the time of their curing are shown in fig. 1.



a



b

Fig. 1. The dependence of the increase in viscosity during the curing of the epoxy-amine compositions at 100°C. where: (a) – compositions with a ratio of ED-20: “Amikrost-1” = 100.0:21.0 wt.p.; (b) – compositions with a ratio ED-20: “Amikrost-1” = 100.0:30.0 wt.p.

Figure 2 shows dependency graphs in the coordinates $1/\eta=f(t)$, which allow you to graphically determine the time when the system reaches the gel point (time to reach the gel point).

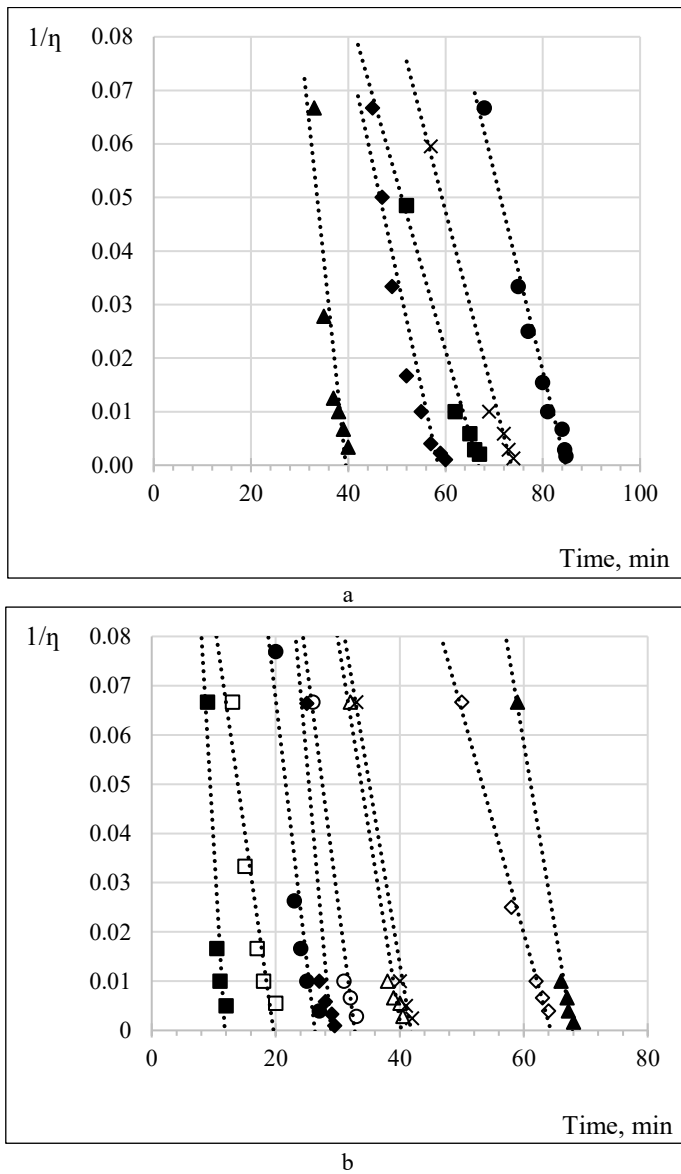


Fig. 2. The dependence of the reduced viscosity on the curing time of the epoxy-amine compositions at 100°C. where: (a) – compositions with a ratio of ED-20: Amikrost-1=100.0: 21.0 wt.p.; (b) – compositions with a ratio of ED-20: Amikrost-1= 100.0: 30.0 wt.p.

Table 3 shows the values of the time to reach the gel point, determined by extrapolation of the dependencies shown in Figure 2 to the x-axis.

Table 3. Gel dots of studied the epoxy-amine compositions.

Code	Temperature, °C	Gel dot, min
ESA-2	100	85
ESA-2	150	12
ESA -3	100	58
ESA -4	100	40
ESA -5	100	33
ESA -6	100	42
ESA -7	100	26
ESA -8	100	12
ESA -9	100	20
ESA -10	100	40
ESA -11	100	64
ESA -13	100	68
ESA -14	100	29
ESA -15	100	67
ESA -16	100	73

4 Conclusion

1. A comparison of the results obtained for the ESA-2 and ESA-13 compositions shows that an increase in the content of the Amikrost-1 amine hardener (within the calculated interval) leads to a noticeable increase in the epoxy resin curing rate at the same temperature (time reaching the gel point decreases from 85 to 68 minutes).
2. All studied accelerators (Agidol-53, TEA, TEAT, KatAB) are active accelerators of the curing process of the studied epoxy-amine compositions. Moreover, with the same mass ratio, Agidol-53 is the most effective process accelerator in comparison with other accelerators studied in the work. When the content in the compositions of the accelerator in the amount of 2.0 wt.p. the time to reach the gel point decreases in the sequence CatAB (ESA-16, 73 min), TEAT (ESA-15, 67 min), TEA (ESA-3, 58 min), Agidol-53 (ESA-10, 40 min).
3. Increasing the amount of accelerator Agidol-53 from 1.0 to 5.0 wt.p. in the epoxy-amine composition leads to a significant increase in the speed of the curing process (the time to reach the gel point decreases from 42 to 12 minutes).
4. The simultaneous introduction of two accelerators (Agidol-53 and TEA) into the epoxy-amine composition leads to a noticeable increase in the curing rate compared to their separate introduction into the composition (the time to reach the gel point is 20 min for the ESA-9 composition containing 1, 5 mass parts Agidol-53 and 1.5 mass parts TEA, and for the compositions ESA-7 and ESA-14 containing 3.0 mass parts AG-53 or TEA, the times to reach the gel point are 26 and 29 min, respectively).
5. An increase in the temperature of the process leads to a significant increase in the curing rate of the epoxy-amine composition (for the ESA-2 composition, the time to reach the gel point at a curing temperature of 100°C is 85 min, and at a curing temperature of 150°C it is 12 min).

Acknowledgments

This project was carried out by Bauman Moscow State Technical University with the financial support of the Ministry of Science and Higher Education of the Russian Federation on the basis of an Agreement on granting dated June 24, 2021 No. 075-11-2021-056.

References

1. I.V. Bessonov, A.V. Polezhaev, M.N. Kuznetsova et al, *Polymer Science - Series D* **6(4)**, 308-311 (2013)
2. V.A. Nelyub, A.S. Borodulin, *Polymer Science - Series D* **11(2)**, 147-153 (2018)
3. P.A. Belov, L.P. Kobets, A.S. Borodulin, *Applied Research* **5(4)**, 403-406 (2014)
4. A.S. Borodulin, *Polymer Science - Series D* **6(1)**, 59-62 (2013)
5. I.V. Bessonov, M.N. Kopitsyna, V.A. Nelyub, *Russian Journal of General Chemistry* **84(12)**, 2439-2444 (2014)
6. Y. Chen', M.A. Gorodetskii, V.A. Nelyub, G.V. Malysheva, *Russian Metallurgy (Metally)* **2019(13)**, 1369-1372 (2019)
7. L.V. Chursova, A.N. Babin, N.N. Panina, A.I. Tkachuk, I.V. Terekhov, *PCM Proceedings of VIAM* **6(42)**, 24-37 (2016)
8. L.P. Kobets, I.S. Deev, *Russian Chemical Journal* **1(44)**, 67-78 (2010)
9. D.V. Grashchenkov, L.V. Chursova, *Aviation materials and technologies* **5**, 231-242 (2012)
10. V.S. Osipchik, I.Yu. Gorbunova, N.V. Kostromina et al, *Chemistry and chemical industry* **3(57)**, 19-22 (2014)
11. L.Kh. Nguyen, Yu.V. Olikhova, A.I. Kochetkov et al, *Advances in chemistry and chemical technology* **10(29)**, 35-37 (2015)
12. I.D. Simonov-Emelyanov, A.N. Trofimov, P.V. Surikov, L.K. Shcheulova, *Bulletin of MITHT* **3(5)**, 102-107 (2010)
13. A.Ya. Malkin, S.G. Kulichikhin, *Rheology in the processes of the formation and transformation of the polymers* (Chemistry, M., 1985)
14. A.Ya. Malkin, A.I. Isaev, *Rheology. Concepts, methods, applications* (CSP Profession, St. Petersburg, 2010)
15. *ASTM D2471-71 Gel Time and Peak Exothermic Temperature of Reaction Thermosetting Resins* (1971)
16. A.Ya. Malkin, S.G. Kulichikhin, M.L. Kerber et al, *Polymer Engineering and Science* **8(37)**, 1322-1330 (1997)
17. S.G. Kulichikhin, A.S. Reutov, M.S. Surova et al, *Plastic* **5**, 43-44 (1988)
18. E.V. Taranenko, L.B. Kandyrin, *Bulletin of MITHT* **1(3)**, 79-85 (2008)