Reokinetics of urethane epoxy oligomers hardening and formation of cold curing adhesive compositions based on them

E R Volkova¹, A I Slobodinuk¹,², A I Savchuk¹, E V Pogoreltsev¹ and V N Strelnikov¹

¹Federal State Budgetary Institution of Science Perm Federal Research Center, Ural Branch of the Russian Academy of Sciences, ul. Akademika Koroleva, 3 614013 Perm, Russia

²E-mail: slobodinyuk.aleksey.ktn@mail.ru

Abstract. In order to obtain polymeric binders for cold cure structural adhesives based on urethane epoxy oligomers, cycloaliphatic amines such as aminoethyl piperazine and isophorone diamine are used as hardeners. The reokinetic features of the curing process of polytetraurethanhydroxyl compositions at temperature of 25 ± 1 °C were investigated, and influence regularities of the reactive oligomers composition on the dynamics of viscosity increase and the viability time of the compositions were established. The rheological parameters of the hardening process of the investigated compositions were determined. The assessment of adhesion strength for detachment of cold-curing adhesive joints formed on the basis of EUO is presented. The proposed compositions can be used for bonding ceramic linings operating under extreme conditions of the Arctic.

1. Introduction

When forming cold-resistant polymer composites and cold-curing structural adhesives, the choice of components used in the synthesis is of fundamental importance. Analysis of scientific literature showed that when forming composites that are operated in harsh climatic conditions, it is advisable to use epoxyurethane oligomers (EUO) [1–3]. An important difference in EUO is that, with the correct combination of epoxy and urethane fragments in the polymer structure, the final products of their curing -polytetraurethanhydroxyl compositions (PUHX) are high-strength elastic materials [4–8] that are out of brittle state and at low temperatures.

An important part in the development of polymer compositions based on reactive EUO is changes kinetics studying in the rheological properties of reaction mixtures (reokinetic) during their curing. The viscometric method is the most accessible for studying the rheokinetics of curing, which allows to register the change in viscosity at different stages of structuring [9]. According to the results of the reaction mixture viscosity measurements, one determines the kinetic characteristics of the curing process: reaction rate constants and the composition viability.

In this paper, the laws governing the reaction mixture viscosity changes based on EUO and the speed of their curing when interacting with amines are studied in order to form a cold-curing adhesive composition. For the first time, the adhesive strength of compositions based on EUO to ceramics was studied.
2. Experiment description
2.1. Research material
As subjects of study, polymer compositions based on EUO are considered, which are cured with amines at the temperature 25 ± 1 °C. The original EUO were synthesized in two stages [3, 10]. In the first stage, the interaction of oligotetramethylene oxydiol with MM~1400 (pF 1400) with isophorone diisocyanate (IPDI) by the reaction of urethane formation results in oligomeric urethane diisocyanate (OUDI) having active isocyanate groups. In the second stage, as a result of the reaction of OUDI with epoxypropanol (glycidol), the epoxy urethane oligomer EUO is formed.

It is shown in researches [3, 10] that with the ratio of the reactive groups NCO: OH> 2 (at the first stage of EUO synthesis), the final reaction product is a mixture of two types of oligomers: EUO(I) with long and EUO(II) with short oligomeric blocks, hereinafter – long and short oligomers.

![Epoxyurethane oligomer I](image1)

![Epoxyurethane oligomer II](image2)

The molar ratio of the NCO groups of the isocyanate and the OH groups of the oligodiol (NCO:OH) in the reaction mixture EUO was 2.0; 2.4; 2.7; 3.0 and 4.0.
As hardeners in the synthesis of PUHX, amine-type hardeners are selected:
- aminoethylpiperazine (AEP) with primary nitrogen atoms

![Aminoethylpiperazine](image3)

- isophorone diamine (IPDA), containing both primary, secondary and tertiary nitrogen atoms

![Isophorone diamine](image4)

The molar ratio of EUO to AEP and IPDA was 1:0.87 and 1:0.75, respectively. Synthesis of PUHX was carried out under vacuum at a temperature 25 ± 1 °C for 5 minutes. Marking and composition of polymer samples are presented in table 1.
Table 1. Marking and composition of PUHX samples.

| Oligodiol Designation | Diisocyanate Designation | Ratio NCO:OH | Hardener | Sample Code |
|-----------------------|--------------------------|--------------|----------|-------------|
| PF 1400               | IPDI                     | 2.0:1        | AEP      | PF1400-2.0IPDI-3A-0.87AEP |
|                       |                          | 2.4:1        | AEP      | PF1400-2.4IPDI-3A-0.87AEP |
|                       |                          | 2.7:1        | AEP      | PF1400-2.7IPDI-3A-0.87AEP |
|                       |                          | 3.0:1        | AEP      | PF1400-3.0IPDI-3A-0.87AEP |
|                       |                          | 4.0:1        | AEP      | PF1400-4.0IPDI-3A-0.87AEP |
| PF 1400               | IPDI                     | 2.0:1        | IPDA     | PF1400-2.0IPDI-3A-0.75IPDA |
|                       |                          | 2.4:1        | IPDA     | PF1400-2.4IPDI-3A-0.75IPDA |
|                       |                          | 2.7:1        | IPDA     | PF1400-2.7IPDI-3A-0.75IPDA |
|                       |                          | 3.0:1        | IPDA     | PF1400-3.0IPDI-3A-0.75IPDA |
|                       |                          | 4.0:1        | IPDA     | PF1400-4.0IPDI-3A-0.75IPDA |

*3A is an epoxy fragment in the oligomeric block of EUO.

2.2. Research methods

Rheological studies were performed on a rotational viscometer RHEOTEST 2.1 (Germany) with a working cone-plate unit. The kinetics of curing polymer compositions was investigated at the temperature 25 ± 1 °C and shear rates of 180 s⁻¹. According to the test results, the kinetic curves η(t) were constructed, which characterize the change in the dynamic viscosity of the reaction mass over time, the constants of the viscosity growth rate kη and the viability time were determined. During the time of viability of the compositions during the curing process, a time to reach the viscosity of 100 Pa·s has been adopted.

Tensile strength (adhesion strength) σtensile for adhesive joints of compositions based on EUO with ceramics based on aluminum oxide was determined at the temperature 23 ± 1 °C according to Russian National State Standard 14760-69 on samples "fungi" with a thickness of polymer layer (2 ± 0.1) mm and stretch speeds of 20 mm / min.

3. Results and discussion

Figure 1 shows the kinetic curves of compositions viscosity changes based on PF1400 nIPDI–3A during the curing of their AEP at the temperature 25 ± 1 °C.

It is seen that rheokinetic curves have 2 characteristic areas of viscosity change, corresponding to certain structural transformations occurring in the polymer mass during its curing [11]. At the initial stage, a rapid and significant increase in viscosity is observed, which is associated with an increase in the molecular weight of oligomeric chains and the formation of a fluctuation network as a result of intermolecular interactions leading to the formation of an internal spatial structure in the volume of the oligomer [12, 13]. At the same time, the intensity of the viscosity increase does not depend on the type of initial EUO, as evidenced by the same angle of inclination of the initial portion of the dependence η(t) for all five compositions. At the second stage of curing, associated with the formation of branched and cross-linked structure [14], the viscosity increase rate slows down. When describing the kinetics of the process, the second, final stage of curing of the EUO, when the reaction mass loses its fluidity (η → ∞) is decisive. The dependence η(t) at the final stage of curing (figure 1) can be described by the exponential equation

\[ η = η_0 \exp(k_η t), \]

where η₀ is the initial viscosity, k_η is the viscosity increase constant, t is the curing time.
Figure 1. The dependence of the dynamic viscosity on the curing time at a temperature of 25 ± 1 °C for compositions: 1 – PF1400-2.0IPDA-3A-0.87AEP; 2 – PF1400-2.4IPDA-3A-0.87AEP; 3 – PF1400-2.7IPDA-3A-0.87AEP; 4 – PF1400-3.0IPDA-3A-0.87AEP; 5 – PF1400-4.0IPDA-3A-0.87AEP.

Equation (1) presented in semi-logarithmic coordinates makes it possible to determine the viscosity increase constants $k_\eta$ graphically from the dependence slope $\ln \eta(t)$ [9, 11] shown in figure 2.

Figure 2. The dependence of $\ln \eta$ on the curing time at a temperature of 25 ± 1 °C for compositions: 1 – PF1400-2.0IPDA-3A-0.87AEP; 2 – PF1400-2.4IPDA-3A-0.87AEP; 3 – PF1400-2.7IPDA-3A-0.87AEP; 4 – PF1400-3.0IPDA-3A-0.87AEP; 5 – PF1400-4.0IPDA-3A-0.87AEP.

Similar rheokinetic studies were conducted for compositions based on oligomer PF1400‒n IPDI‒3A, curable with IFDA at a temperature of 25 ± 1 °C. The values of the curing parameters $k_\eta$ and $t^*$, determined from the rheological curves (figures 1, 2) and the adhesive strength characteristics of the adhesive joint are presented in table 2.

Table 2 shows that the constant $k_\eta$ monotonously increases with growth in the isocyanate component in the ratio of the reactive groups NCO:OH during the synthesis of EUO and reaches its maximum value at NCO:OH = 4.0:1. So replacing PF1400–2.0 IPDI–3A with PF1400–4.0 IPDI 3A when curing their AEP, allows to increase $k_\eta$ by ~5.5 times, and reduce $t^*$ composition by more than 4 times, which inevitably leads to a reduction in the curing time of the finished material.
Table 2. Rheokinetic parameters of compositions curing process at a temperature of 25 ± 1 °C and adhesive strength of adhesive bonding indicators.

| No | Compositions Code       | $k_\eta \times 10^3$ min⁻¹ | $t^*$ min | $\sigma_{\text{tensile}}$ MPa |
|----|-------------------------|-----------------------------|-----------|-------------------------------|
| 1  | PF1400-2.0IPDI-3A-0.87AEP | 8.7                         | >90       | 6.2                           |
| 2  | PF1400-2.4IPDI-3A-0.87AEP | 13.9                        | 89        | 7.2                           |
| 3  | PF1400-2.7IPDI-3A-0.87AEP | 17.3                        | 51        | 8.1                           |
| 4  | PF1400-3.0IPDI-3A-0.87AEP | 29.7                        | 33        | 10.1                          |
| 5  | PF1400-4.0IPDI-3A-0.87AEP | 47.8                        | 23        | 12.4                          |
| 6  | PF1400-2.0IPDI-3A-0.75IPDA | 3.2                        | >150      | 7.5                           |
| 7  | PF1400-2.4IPDI-3A-0.75IPDA | 11.2                        | 135       | 8.2                           |
| 8  | PF1400-2.7IPDI-3A-0.75IPDA | 13.3                        | 90        | 10.1                          |
| 9  | PF1400-3.0IPDI-3A-0.75IPDA | 14.5                        | 79        | 11.4                          |
| 10 | PF1400-4.0IPDI-3A-0.75IPDA | 16.7                        | 52        | 12.9                          |

As mentioned above, the oligomer PF1400–nIFDI – 3A, is a mixture of EUO of two types: “long” and “short”. The higher the concentration of the “short” EUO, the greater the content of oligomeric fragments with terminal epoxy groups in the reaction mixture, which are capable of entering into chemical interaction with the amine hardener. It is obvious that the change in the rheokinetic parameters of curing is associated with different mobility of the "oligomer-polymer" segments formed during the epoxyurethane polymer formation. The presence in the reaction system of short oligoester segments, leads to a restriction of the mobility of long macromolecular chains, and, as a result, to an increase in the viscosity of the composition and a decrease in its viability.

From table 2 it can be seen that the highest rate of the EUO curing is observed when using AEP as a hardener. This is probably due to the presence of a tertiary nitrogen atom in the AEP, and the tertiary amines, being Lewis bases, work as catalysts, initiating the polymerization process. Thus, AEP performs two functions simultaneously: a hardener and a catalyst, which affects the curing reaction kinetics.

The adhesion strength $\sigma_{\text{tensile}}$ of adhesive joints based on EUO and hardeners (aminoethylpiperazine and isophorone diisocyanate) was evaluated. The results are presented in Table 2. It can be seen that the composites synthesized on the basis of PF1400-4.0 IPDI-3A have higher adhesion strength values compared to other materials. The use of PF1400-4.0 IPDI-3A as an oligomeric base instead of PF1400-2.0 IPDI-3A contributes to an increase $\sigma_{\text{tensile}}$ by 1.72 times during the IFDA curing, and 2.0 times when the AEP is cured.

4. Conclusion

The study of the curing epoxyurethane oligomer kinetics with amino ethyl piperazine and isophorone diamine at a temperature of 25 ± 1 °C showed that with an increase in the isocyanate component during the synthesis of the initial EUO, a noticeable increase in the viscosity increase constant and a decrease in the pot life of the polymer composition are observed.

Comparative evaluation of adhesion strength of adhesive joints showed that an increase in the ratio of reactive NCO:OH groups during the EUO synthesis leads to an increase in the adhesion strength of polytetraurethanhydroxyl composites, which is probably due to an increase in the effective density of the mesh due to an increase in the proportion of hard hydroxyurethane segments and intermolecular hydrogen bonds.

It was found that the most promising when forming cold-curing adhesive compositions with high curing speed and level of adhesive strength is a model composition based on EUO synthesized at the ratio NCO:OH = 4:1 and containing aminoethy1piperazine as a hardener.
Acknowledgments
This work was supported by the Ministry of Education and Science of the Russian Federation project number 14.604.21.0192 (UI PNI RFMEFI60417X0192).

References
[1] Hepburn C 1992 Polyurethane elastomers (London New York: Elsevier appl. Science) p 441
[2] Cornille A, Serres J, Michaud G, Simon F, Fouquay S, Boutevin B and Caillol S 2016 Syntheses of epoxyurethane polymers from isocyanate free oligo-polyhydroxyurethane European Polymer Journal 75 175–189
[3] Strel’nikov V N, Senichev V Yu, Slobodinyuk A I, Savchuk A V, Volkova E R, Makarova M A, Nechaev A I, Krasnosel’skikh S F and Ukhin K O 2018 Preparation and Properties of Frost-Resistant Room-Temperature-Curable Compounds Based on Oligoetherurethane Diepoxides of Various Chemical Structures Russian Journal of Applied Chemistry 91(3) 463–468
[4] Jin H, Zhang Yu, Wang Ch, Sun Yi, Yuan Z, Pan Yo, Xie H and Cheng R 2014 Thermal, mechanical, and morphological properties of soybean oil-based polyurethane/epoxy resin interpenetrating polymer networks (IPNs) Journal of Thermal Analysis and Calorimetry 117(2) 773–781
[5] Ghozali M, Triwulandari E and Haryono A 2015 Preparation and characterization of polyurethane-modified epoxy with various types of polyol Macromolecular Symposia 353(1) 154–160
[6] Prokopchuk N R, Krutsko E T and Morev F V 2015 Modification of epoxy resins by polyisocyanates Journal of Nature Science and Sustainable Technology 9(1) 121–127
[7] Nuraini L, Triwulandari E, Ghozali M, Hanafi M and Jumina J 2017 Synthesis of Polyurethane/Silica Modified Epoxy Polymer Based on 1,3-Propanediol for Coating Application Indonesian Journal of Chemistry 17(3) 477–484
[8] Kausar A 2018 An investigation on epoxy/poly(urethane-amide)-based interpenetrating polymer network reinforced with an organic nanoparticle Materials Research Innovations 22(2) 58–68
[9] Volkova E R, Strel’nikov V N, Borisova I A, Slobodinyuk A I and Savchuk A V 2018 The Effect of the Isocyanate-Hydroxyl Ratio on the Structure and Properties of Hard Polyurethanes Polymer Science Series D 11(3) 292–296
[10] Strel’nikov V N, Senichev V Yu, Slobodinyuk A I, Savchuk A V, Volkova E R, Makarova M A, Belov Yu L, Derzhavinskaya L F and Selivanova D G 2018 Preparation and Properties of Frost-Resistant Materials Based on Compounds of Oligoether Urethane Epoxides and Diglycidyl Urethane Russian Journal of Applied Chemistry 91(12) 1937–44
[11] Malkin A Ya and Kulichikhin S G 2008 Rheokinetics: Rheological Transformations in Synthesis and Reactions of Oligomers and Polymers (John Wiley & Sons Inc) p 326
[12] Pierre-Gilles de Gennes 1979 Scaling concepts in polymer physics (London: Cornell University Press) p 368
[13] Ianniruberto G and Marrucci G 2014 Convective constraint release (CCR) revisited Journal of Rheology 58(1) 89–102
[14] Hu Y Th 2014 Mechanisms of shear thickening in transient guar network Journal of Rheology 58(6) 1789–1807
[15] Mezhikovskiy S M and Irzhak V I 2008 Chemical Physics of Oligomers Curing (Moscow: Science) p 269 (in Russ.)