The Influence of Diluents on the Kinetics of Volume Shrinkage and Stress upon Curing of Epoxy Oligomers

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It is known that for decrease in viscosity polymeric binding on the basis of epoxy oligomers in their composition injecting solvents of the different nature and thermodynamic compatibility. In this paper the dependences describing influence on shrinkage, kinetics of increase and maximum level of strains from diluents content and temperature of curing of epoxy oligomers are established. Introduction about 20 % of the reactive diluents (DEG-1 and SO-3) in system on the basis of epoxy oligomers leads to decrease in viscosity in ~ 3 times, to improvement of imbibition quality of fibrous fillers, increase of volume contraction (on ~ 2.5. %) and decrease in residual stresses in ~ 6 times as a result of increase of mobility of pieces of a polymeric chain in a three-dimensional grid, and also to decrease in glass transition temperature no more than~ 20°C.

***Keywords**: residual stresses, volume shrinkage, composite materials, matrix, epoxy resin, diluters, generalized structure parameters.*

Introduction

In order to decrease the viscosity of plastic binders based on epoxy oligomers, solvents of different nature and thermodynamic compatibility are introduced into their structure [1].

Introducing reactive and inactive solvents can result in changes in the hardened epoxy polymer structure. This affects the volume contraction and the residual stresses arising upon hardening.

Work [2] provides data on the effect of the molecular characteristics, initial and secondary heterogeneity, as well as the conversion of functional groups and shrinkage kinetics upon epoxy-dian oligomers (EDO) hardening on the level and kinetics of residual stresses growth. It was established before that falloff of shrinkage level and of residual stresses is observed when the content of associates (φ_{as}) is increased from 5 to 20% vol. due to the start of the formation of a quasicontinuous "framework" of associates in EDO volume with $MM_{av} \approx 450$ g/mol at $\varphi_{as} \sim 25.5\%$ vol. (for cubic packing).

In order to study the effect of thinners on the kinetics of change in volume contraction and stresses upon hardening it is expedient to use EDO with MM_{av} not less than 400 – 450 g/mol. This oligomer is characterized by the highest stability of properties.

Experimental

Compositions based on EDO of ED-20 brand (GOST 10587-84, MM_{av} ~ 405 g/mol) and a liquid aliphatic hardener of the amine type – triethylenetetramine (TETA) (Dow Chemical) – were selected as research objects. The quantity of the introduced hardener was calculated on the basis that the epoxy and amine equivalents are equal. Inactive (toluene, GOST 5789-78) and reactive (diethylene glycol diglycidyl ester of DEG-1 brand, technical specifications 2225-027-00203306-97 brand) and SO-3 (modified DEG-1) thinners were used to regulate the viscosity of the composition based on EDO.

The kinetics of volume contraction upon EO hardening was studied by dilatometry with the use of a dismountable glass dilatometer with a graduated capillary. The study was conducted at the step mode of EO hardening by the technique described in [3], where each step was an isothermal process with a preset temperature and process time. In this work, the following mode was used: 25 °C – 24 h, 50 °C – 6 h and 80 °C – 4 h. This allowed obtaining samples based on EO with amine hardeners with conversion degree up to 98%.

In order to study the kinetics of residual stresses (σ) increase and to determine them we used the console method (GOST 13036-67). The kinetics of stress increase upon EDO hardening was studied by the method of bending through an angle with the use of substrates made of 100×15×0.35 mm alumina-borosilicate glass in the isothermal EDO hardening mode at 25 °C during 24 h. The glass plates modelled systems based on glass fibers and plastic binders.

Results and Discussion

One of the main operational characteristics of shaping products made of polymeric composite materials (PCM) is the binder viscosity. It determines the technological effectiveness of the process, the quality of fibrous fillers impregnation, the choice of processing method and the properties of PCM [4].

It can be seen from Table 1 that the inactive thinner (toluene) reduces EDO viscosity more than the other thinners (almost 8-fold). The reactive thinners – DEG-1 and SO-3 – reduce the system viscosity approximately with the same efficiency (almost 3-fold) despite the difference in their initial viscosity.

Table 1. Viscosity of ED-20 (Pas · s) with various thinners

Thinner	Thinner content, % vol.					
	0	5	10	15	20	100
Toluene	16.0	9.60	5.76	3.46	2.07	0.0006
DEG-1	16.0	12.2	9.3	7.1	5.40	0.07
SO-3	16.0	12.10	9.15	6.9	5.24	0.06

Because the thinners are thermodynamically compatible with EDO, the compositions do not undergo phase separation and do not show opalescence. However, their introduction into the composition decreases the complex of the physicomechanical characteristics of the hardened systems by more than 20% vol. This should be considered when creating low-viscous compounds based on EDO.

Note that introducing thinners into EDO changes the hardened polymer structure. Thus, inactive thinners change its physical structure without interacting with it chemically. In contrast, introducing the reactive thinners rearranges the molecular structure of EDO and changes its van der Waals volume. The reduction of the latter upon hardening causes shrinkage of the composition based on EDO [5].

Shrinkage is an important operational characteristic affecting the formation of the complex of properties of products made of polymeric composite materials based on epoxy binders. However, there are not enough data in the scientific and technical literature on the kinetics of volume shrinkage upon hardening.

Figure 1 shows dependences of kinetics of ED-20 shrinkage (Sh) upon hardening by the amine hardener and introducing the inactive solvent (toluene) in various concentrations.

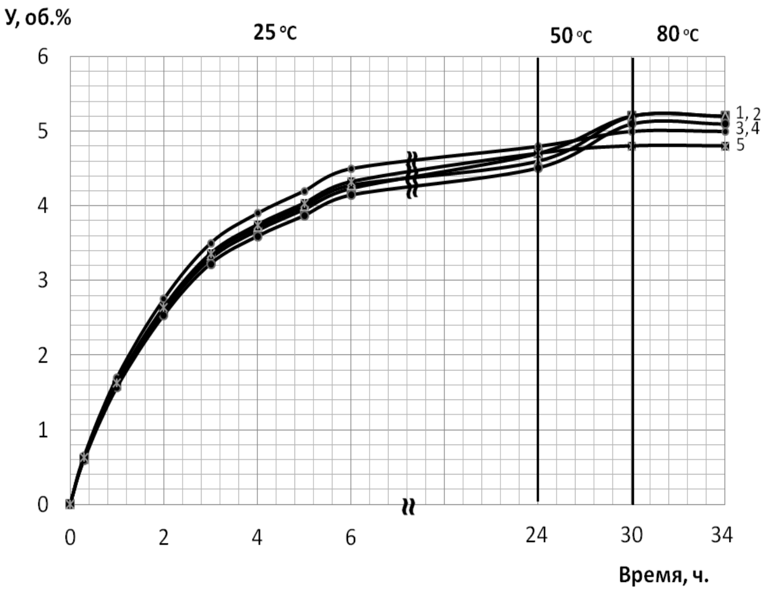


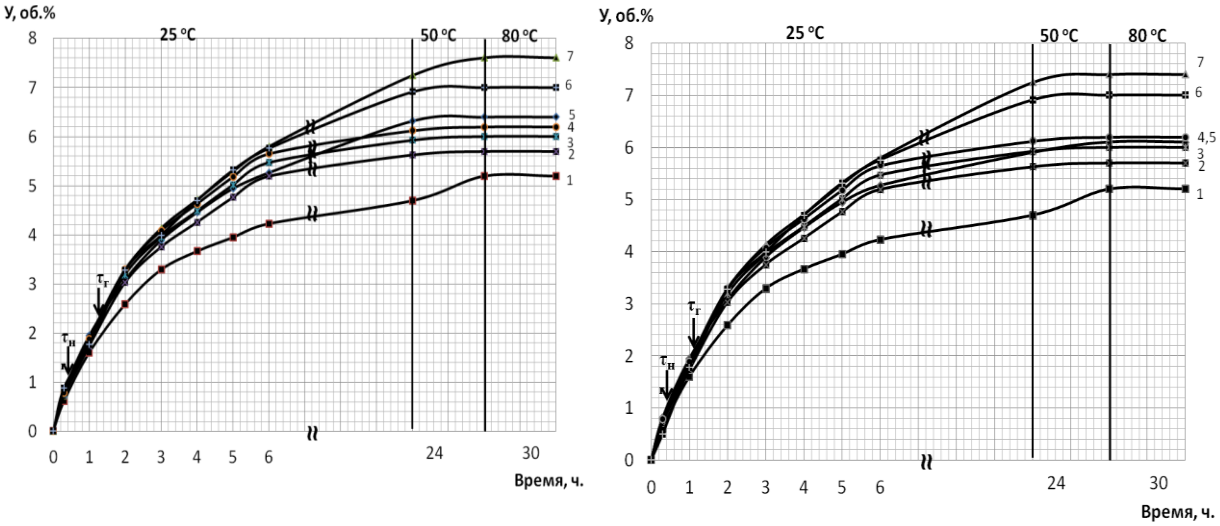
Figure 1. Kinetic curves of ED-20 + TETA composition shrinkage with different content of the inactive thinner – toluene (% vol.): *1* – 0; *2* – 5; *3* – 10; *4* – 15, *5* – 20.

[У, об.% means Sh, % vol.; Время, ч means Time, h]

Introducing toluene into ED-20 results in a slight decrease in post-shrinkage (no more than by 0.5% ob.) and practically does not affect the process kinetics. An essential fault of using inactive thinners is the necessity of removing them from the binder volume in the course of EDO drying and hardening with the formation of microdefects and pores reducing the composite material durability [6].

The reactive thinners are well compatible with EDO and contain epoxy groups in the chemical structure. This allows them, in contrast to the inactive thinners, to be incorporated in the hardened polymer structure by forming chemical bonds. Note that ED-20 + DEG-1 and ED-20 + SO-3 systems undergo phase separation neither before nor in the course of hardening. This indicates that the initial components have good thermodynamic compatibility, and the thinner molecules are incorporated in the chemical three-dimensional structure of the polymeric matrix.

Figure 2 shows dependences of ED-20 shrinkage kinetics at different content of the reactive diluents – DEG-1 and SO-3.



a) b)

Figure 2. Kinetic curves of ED-20 + TETA composition shrinkage with DEG-1 (A) and SO-3 (b) thinners at their different content (% vol.):

1 – 0; *2* – 5; *3* – 10; *4* – 15; *5* – 20; *6* – 50, *7* – 100.

[У, об.% means Sh, % vol.; Время, ч means Time, h]

The rate of increase and the value of post-shrinkage (PS) for all the studied systems with the introduction of the reactive diluents DEG-1 and SO-3 increase by 15–30% as compared to initial ED-20 (Figure 3).

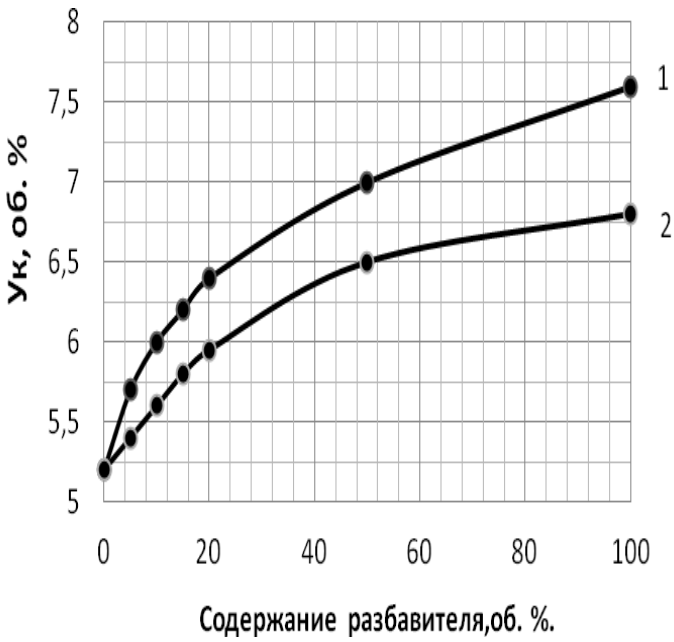


Figure 3. Dependence of post-shrinkage (PS) upon ED-20 hardening with reactive diluents – DEG-1 (*1*) and SO-3 (*2*) – on their content.

[Ук, об.% means PS, % vol.; Содержание разбавителя,об.% means Thinner content, % vol.]

The dependence presented in Figure 3 (curve 1) illustrates the change of ED-20 post-shrinkage with increasing DEG-1 content. DEG-1 practically does not affect the kinetics of the composition hardening at the initial stages. Introducing 20% vol. of DEG-1 into ED-20 increases post-shrinkage 1.34-fold as compared to ED-20 shrinkage without thinner. This will affect the structure parameters upon hardening.

The reactive diluent of SO-3 brand is a modified DEG-1 product, and its effect on shrinkage and post-shrinkage kinetics is almost identical to the effect of DEG-1 (Figure 3, curve 2). Introducing 20% vol. of SO-3 increases ED-20 post-shrinkage 1:31-fold. Note that the sample of hardened SO-3 was more elastic than in case of DEG-1.

It may be concluded on the basis of the experimental data that it is inexpedient to use high concentrations (more than 20% vol.) of reactive thinners such as DEG-1 and SO-3 in order to adjust EDO viscosity. While they reduce viscosity approximately 3-fold, they increase shrinkage 1.30-fold as compared to initial shrinkage. This can be followed by residual stress growth and decrease in the indicators of the complex of physicomechanical characteristics. However, the chosen thinners are also elasticizers. As a result, using them increases molecular mobility, which accelerates relaxation processes in the chemical grid of intermolecular bonds formed upon hardening, and residual stress decreases.

Figure 4 shows dependences illustrating the increase of residual stress upon hardening ED-20 + TETA system with different content of DEG-1 at 25 °C. Dependences obtained at other temperatures (50, 70 and 100 °C) are similar.

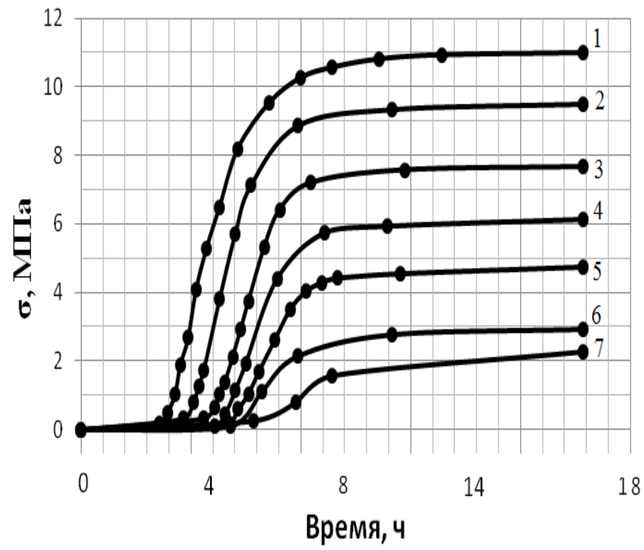


Figure 4. Kinetics of stress increase at 25 °C in ED-20 + TETA system (1) and ED-20 + TETA + DEG-1 system (2–7) upon hardening vs DEG-1 content (% vol.): 2 – 0; 3 – 5; 4 – 10; 5 – 15; 6 – 20; 7 – 40.

[МПа means MPa; Время, ч means Time, h]

Kinetic dependences of the increase of residual stress for ED-20 mixtures with DEG-1 are S-shaped, and their nature does not differ from that of the curves obtained for unmodified EDO. Depending on the thinner content in the system hardening results in the emergence of stress from 2.0 to 12.4 MPa (at 25 °C), which ranges from 1.0 to 11.0% of the epoxyamine polymer durability.

Increasing temperature increases stress, as in case of unmodified EDO. However, in this case as well DEG-1 elasticizer efficiently reduces residual stress in EDO. Thus, when hardening temperature is 100 °C, stress decreases from 42 to 2.3 MPa.

Figure 5 presents generalized dependences of maximum residual stress in ED-20 + TETA + DEG-1 composition on the DEG-1 thinner content at different temperatures.

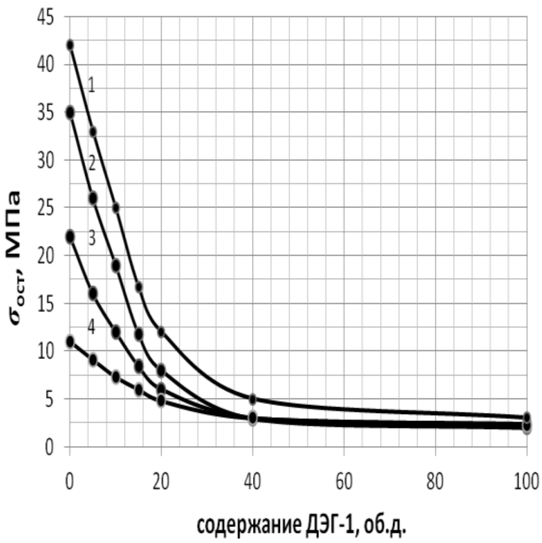


Figure 5. Curves of residual stress change (σ_{res}) in ED-20 + TETA + DEG-1 system at various hardening temperatures, °C: *1* – 100; *2* – 70; *3* – 50; *4* – 25.

[ост means res (residual); МПа means MPa; содержание ДЭГ-1, об.д. means DEG-1 content, vol. fr.]

Post-shrinkage (PS) upon hardening of ED-20 + TETA + DEG-1 compositions at 30 °C changes within 24 hours from 5.1 to 7.0% vol., and stress decreases from 11.0 to 2.0 MPa.

At all temperatures, the dependences of maximum residual stress of ED-20 compositions with a reactive diluent have a curve bend in the region of its content about 20% vol., and then they are essentially stabilized at a value about 2 MPa.

However, note that increasing the thinner content up to 40% vol. and more decreases glass transition point (heat resistance) by 30 °C as evidenced by DSC (Figure 6).

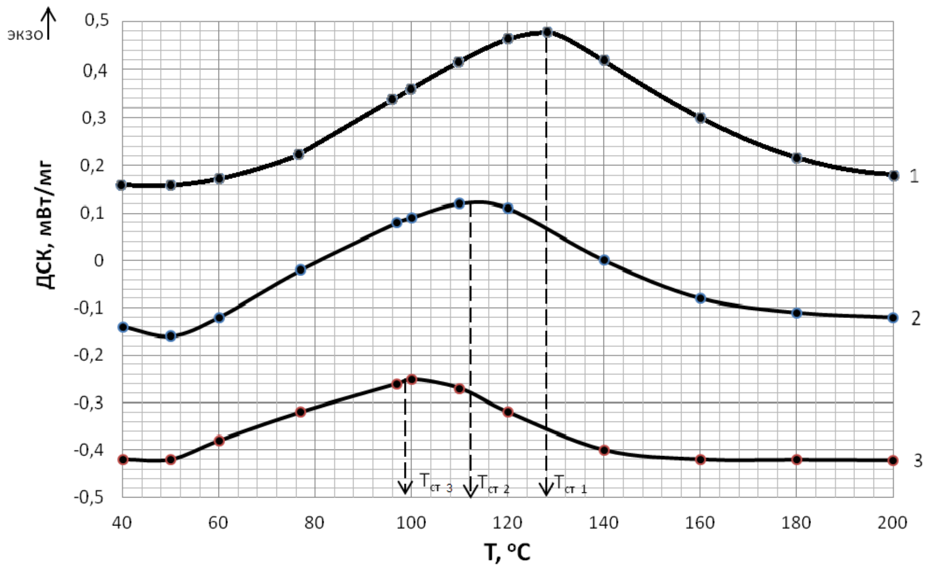


Figure 6. DSC thermograms for ED-20 + TETA + DEG-1 thinner systems hardened at 130 °C. DEG-1 content, % vol.: 0 (*1*), 10 (*2*) and 40 (*3*).
[ДСК, мВт/мг means DSC, Mw/mg; ст means gt]

Introducing up to 20% vol. of the reactive diluents (DEG-1 and SO-3) into the system based on EDO decreases viscosity up to 3-fold, improves the quality of fibrous fillers impregnation, increases volume shrinkage by no more than 2.5% vol. and decreases residual stress up to 5-fold as a result of increasing molecular mobility. At the same time T_{gt} decreases by less than 20 °C.

Conclusion

It may be concluded on the basis of the thermomechanical analysis data, as well as of the study of the kinetics of shrinkage and residual stress arising upon hardening that the optimal concentration of the DEG-1 reactive diluent in the composition based on EDO with the amine hardener is ~ 10–20% vol.

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