



DEFINITION OF THE COMPOSITIONS OF MICROPHASES DURING FORMATION OF POLY(EPOXY URETHANE ISOCYANURATE) NETWORKS

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Abstract

The principles of application of some experimental and computational methods for description of the processes of formation of network poly(epoxy urethane isocyanurates) are presented. The compositions of microphases that are formed during microphase separation of the components of networks based on poly(propylene glycol) or poly(tetramethylene oxide), 2,4-toluene diisocyanate and ED-20 epoxy resin based on bisphenol A are analyzed by the theoretical approach. The latter shows that the oligomeric products at the initial step of synthesis can be either incompatible or compatible with the resulting oligomeric system. This suggests the presence of several microphases with different compositions. The microphase based on poly(propylene glycol) contains from 6.6% to 29.0% of the epoxy oligomer, while the microphase based on poly(tetramethylene oxide) is almost completely formed by a mixture of this component and the cured epoxy oligomer.

Key words: microphase separation, poly(epoxy isocyanurate) polymer networks, dynamic mechanical analysis, poly(propylene glycol), poly(tetramethylene glycol), 2,4-toluene diisocyanate, epoxy resin.

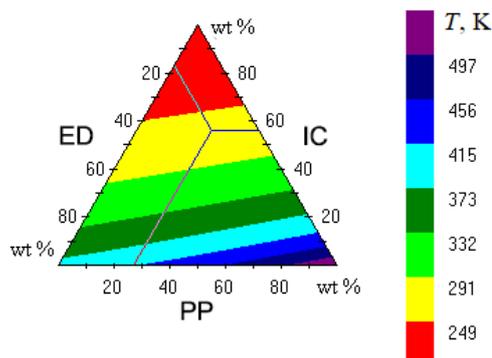
Introduction

The main goal of this work is to define the compositions of microphases of network poly(epoxy isocyanurates) that undergo microphase separation due to a large difference in the surface energies of cross-links and connecting linear polymer chains, which significantly affects their properties. According to the results of dynamic mechanical analysis, it is necessary to estimate the relaxation transitions, which are associated, in particular, with the glass-transition temperatures of the polymer networks, and to establish the compositions of microphases by comparing the calculated and experimental glass-transition temperatures.

The resulting polymers were obtained using the following compositions: a mixture of poly(propylene glycol) ($M = 2000$) or poly(tetramethylene oxide) ($M = 1000$) with 2,4-toluene diisocyanate and an epoxy oligomer (ED-20 epoxy resin based on bisphenol A) cured with 2,4-toluene diisocyanate.

To analyze the compositions of microphases, dynamic mechanical analysis (DMA) was combined with the calculation of glass-transition temperatures of the samples obtained. Based on the results of DMA studies, we determined the experimental glass-transition temperatures, which were used to estimate chemical compositions of the microphases using the resulting relations.

Let us briefly consider a computational scheme for prediction of the compatibility of polymers [1, 2] that enables



definition of the compositions of microphases which result during microphase separation. Let us introduce the following notions.

$$\beta_1 = \Phi \left(\Phi - \sqrt{\Phi^2 + \gamma_{p,1}/\gamma_{p,2} - 2\Phi \left(\gamma_{p,1}/\gamma_{p,2} \right)^{0.5}} \right), \quad (1)$$

$$\beta_2 = \Phi \left(\Phi - \sqrt{\Phi^2 + \gamma_{p,2}/\gamma_{p,1} - 2\Phi \left(\gamma_{p,2}/\gamma_{p,1} \right)^{0.5}} \right), \quad (2)$$

where $\gamma_{p,1}$ and $\gamma_{p,2}$ are the surface energies of polymers **1** and **2**, respectively;

$$\Phi = \frac{4(V_{p,1} \cdot V_{p,2})^{1/3}}{\left(V_{p,1}^{1/3} + V_{p,2}^{1/3} \right)^2}, \quad (3)$$

where $V_{p,1}$ and $V_{p,2}$ are the molar volumes of polymers **1** and **2**, respectively.

The following situations may arise.

(1) Upon introduction of the first polymer into the second one

$$\mu_1 = \frac{\delta_{p,1}^2}{\delta_{p,2}^2} > 1.374 \beta_1, \quad (4)$$

and upon introduction of the second polymer into the first one

$$\mu_2 = \frac{\delta_{p,2}^2}{\delta_{p,1}^2} > 1.374 \beta_2, \quad (5)$$

Here $\delta_{p,1}$ and $\delta_{p,2}$ are the solubility parameters of polymers **1** and **2**, respectively. These inequalities describe the situation when the polymers are incompatible.

(2) Upon introduction of small amounts of the first polymer into the second one, the following inequality is fulfilled

$$\mu_1 = \frac{\delta_{p,1}^2}{\delta_{p,2}^2} < 1.374 \beta_1, \quad (6)$$

i.e., the polymers are compatible.

However, upon introduction of the second polymer into the first one, the left part of the criterion may exceed the right one, i.e., there is not observed any compatibility

$$\mu_2 = \frac{\delta_{p,2}^2}{\delta_{p,1}^2} > 1.374 \beta_2, \quad (7)$$

This case leads to a specific shape of the curve of the dependence of a glass-transition temperature on the mixture composition [1, 2].

(3) Upon introduction of the first polymer into the second one and the second polymer into the first one, the following inequalities are fulfilled

$$\mu_1 = \frac{\delta_{p,1}^2}{\delta_{p,2}^2} < 1.374 \beta_1, \quad (8)$$

$$\mu_2 = \frac{\delta_{p,2}^2}{\delta_{p,1}^2} < 1.374 \beta_2, \quad (9)$$

This case corresponds to the full compatibility of the polymers.

The process of microphase separation was observed many times for block copolymers [3–7]. For example, Potemkin and Bodrova [3] studied the microphase separation in block copolymers of poly(ethylene oxide) (PEO) and poly(vinylpyridine) (PVP). Let us analyze the compatibility of PEO and PVP blocks. For PEO $\delta = 18.9$ (J/cm³)^{0.5}, $\gamma = 28.0$ mN/m², $V_m = 40.7$ cm³/mol. For PVP $\delta = 16.9$ (J/cm³)^{0.5}, $\gamma = 42.5$ mN/m², $V_m = 94.7$ cm³/mol. In all cases, relations (4) and (5) are valid. Therefore, the clearly expressed microphase separation takes place [3].

Dolgov *et al.* [4] studied self-organization of the molecules of linear diblock PEO–polylactide (PL) copolymer and triblock PL–PEO–PL copolymer by dissipative particle dynamics and compared quantitatively the results obtained with the experimental data. The microphase separation for the triple copolymer was manifested even in solution. Let us analyze the compatibility of PEO and PL blocks. For PEO $\delta = 18.9$ (J/cm³)^{0.5}, $\gamma = 28.0$ mN/m², $V_m = 40.7$ cm³/mol. For PL $\delta = 20.5$ (J/cm³)^{0.5}, $\gamma = 36.1$ mN/m², $V_m = 55.1$ cm³/mol. For these examples, relations (4) and (5) are also valid, which predicts the realization of microphase separation.

Finally, Papadakis, Potemkin and coworkers [5–7] studied block copolymers of polystyrene (PS) and polybutadiene (PB). For PS $\delta = 18.7$ (J/cm³)^{0.5}, $\gamma = 40.4$ mN/m², $V_m = 97.1$ cm³/mol. For PB $\delta = 15.3$ (J/cm³)^{0.5}, $\gamma = 33.5$ mN/m², $V_m = 60.6$ cm³/mol. Relations (4) and (5) are also valid for these cases, which predicts the microphase separation.

All the calculations were carried out using the Cascade computer program (INEOS RAS).

Let us proceed to the analysis of microphase separation of the polymers considered in this work.

Experimental

System with the low PPG concentration. The concentration of 2,4-TDI in the system was 20 wt %. The

resulting network structure featured the high content of chains based on oligo(urethane isocyanurates) (composition **I**). The reaction was carried out with the following amounts of the components: PPG 5 g, epoxy resin 1.267 g, 2,4-TDI 1.09 g (used in the beginning of the reaction) and 1.522 g (introduced additionally).

According to the previous findings [8], curing of an epoxy resin with diisocyanates consumes two molecules of the epoxy resin per a molecule of the isocyanate (Fig. 1).

1 mole of the epoxy resin weighs 482 g; 1 mole of 2,4-TDI weighs 174 g; 2 moles of the epoxy resin (ED) weigh 965 g; since 1 mole of the diisocyanate requires the consumption of 2 moles of ED, then 1 g of ED requires the consumption of $174/965 = 0.180$ g of 2,4-TDI. The reaction was carried out with 1.267 g of ED, which required the use of $0.180 \times 1.267 = 0.228$ g of 2,4-TDI; the total mass of ED with 2,4-TDI composed 1.267 g + 0.228 g = 1.495 g. This is the mass of the cured ED structure.

The isocyanurate cycle (IC) has the structure depicted in Fig. 2.

Since a part of 2,4-TDI is consumed for curing of the epoxy resin, the rest part of it is consumed for the formation of isocyanurate cycles. The mass of 2,4-TDI consumed for the formation of these cycles composed $1.09 + 1.522 - 0.228 = 2.384$ g. Then, the mass fractions of each component of the network have the following values: PPG 56.3%, IC 26.9%, cured ED 16.8%.

Using the Cascade software, we found that for the isocyanurate cycle $\delta = 25.4$ (J/cm³)^{0.5}, $\gamma = 56.8$ mN/m², $V_m = 392$ cm³/mol. For PPG $\delta = 18.2$ (J/cm³)^{0.5}, $\gamma = 27.3$ mN/m², $V_m = 56.2$ cm³/mol. In all cases, relations (4) and (5) are satisfied. Therefore, there occurs the microphase separation. The existence of microphase separation in the system is substantiated by the appearance of two and more peaks on the temperature dependences of loss modulus and mechanical loss tangent. It is also supported by a reduction of the storage modulus in the

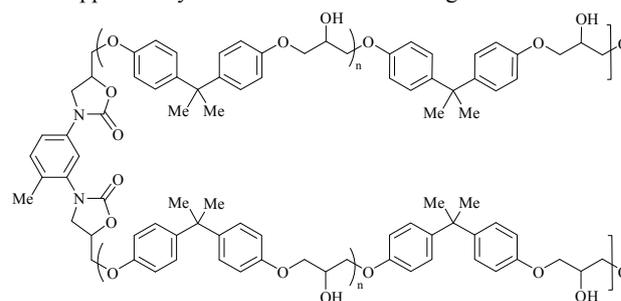


Figure 1. Structure of epoxy resin cured by isocyanate.

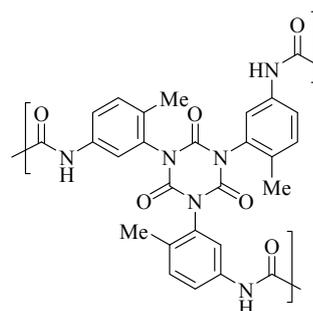


Figure 2. Structure of isocyanurate cycle.

vicinity of peak temperatures. The peak temperatures are associated with the glass-transition points of the microphases, which compositions were determined by comparing the experimental and calculated data. The microphase compositions are chosen from the network polymer components in such a manner that the calculated glass-transition temperature coincides with the experimental one. The glass-transition temperature of the system (T_g) was also calculated. The value of T_g composed 283 K; this is typical for an absolutely uniform system that does not undergo any segregation into microphases. Figure 3 shows a triangular diagram which reflects the dependence of the glass-transition temperature on the composition of a three-component system.

In our case, the dynamic mechanical analysis of the system, performed on a DuPont DMA-983 unit, revealed the following dependence of $\text{tg}\delta$ (Fig. 4).

It is obvious that the low-temperature maximum appears at 234 K. Since the maximum temperature is close to the glass-transition point of neat PPG (according to the literature data, it composes 228 K) and only slightly exceeds it, the microphase formed by PPG is enriched with a small amount of components which have the higher glass-transition temperatures than T_g of PPG. This evidences that the analyzed system is not uniform and reveals the microphase separation, which was observed earlier by our research group for analogous systems [9–15].

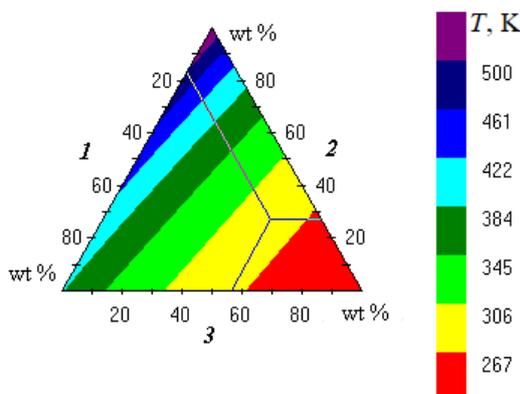


Figure 3. Dependence of the glass-transition temperature of the flexible three-component system on the component compositions: ED (**1**), IC (**2**), PPG (**3**).

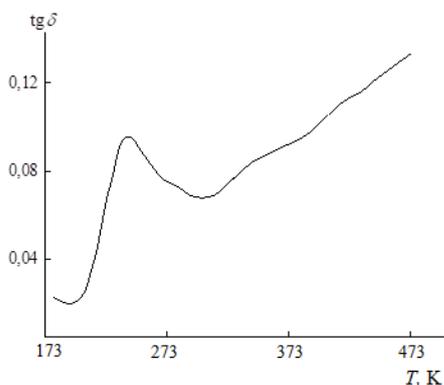


Figure 4. Temperature dependence of $\text{tg}\delta$ for the material under consideration.

In order to elucidate which component is included in the PPG microphase in a small amount, the surface energies of all three components, comprising the network, were calculated. The calculations showed that the surface energy of PPG composes 27.3 mN/m, that of cured ED 31.8 mN/m, and that of IC 56.2 mN/m. Hence, the PPG microphase is likely to be enriched with the cured epoxy resin rather than the isocyanurate cycle, for which a difference of the surface energy from that of PPG composes a considerable magnitude.

To estimate the composition of the microphase, let us use the relation for a glass-transition temperature (T_g) of a two-component system

$$T_g = \frac{(\sum_i \Delta V_i)_1 + \alpha_2 [(\sum_i \Delta V_i)_2 - (\sum_i \Delta V_i)_1]}{\frac{(\sum_i \Delta V_i)_1}{T_{g,1}} + \alpha_2 \left[\frac{(\sum_i \Delta V_i)_2}{T_{g,2}} - \frac{(\sum_i \Delta V_i)_1}{T_{g,1}} \right]} \quad (10)$$

where α_2 is the molar fraction of polymer **2**; $T_{g,1}$ and $T_{g,2}$ are the glass-transition temperatures of polymers **1** and **2**, respectively; $(\sum_i \Delta V_i)_1$ and $(\sum_i \Delta V_i)_2$ are the van der Waals volumes of repeating units of polymers **1** and **2**, respectively.

In our case, polymer **1** is PPG and polymer **2** is ED cured with the diisocyanate. For polymer **1** $T_{g,1} = 228$ K, for polymer **2** $T_{g,2} = 387$ K (according to the previous experimental data [14]); $(\sum_i \Delta V_i)_1 = 60.7 \text{ \AA}^3$, $(\sum_i \Delta V_i)_2 = 1100 \text{ \AA}^3$.

Taking into account that molar fraction α_m is connected with the weight (mass) fraction α_w by the following relation

$$\alpha_m = \frac{1}{1 + \frac{M_2}{M_1} (1/\alpha_w - 1)}, \quad (11)$$

we obtain the following dependence of the glass-transition temperature on the weight fraction of polymer **2** in the mixture

$$T_g = \frac{(\sum_i \Delta V_i)_1 + \frac{[(\sum_i \Delta V_i)_2 - (\sum_i \Delta V_i)_1]}{1 + \frac{M_2}{M_1} (1/\alpha_w - 1)}}{\frac{(\sum_i \Delta V_i)_1}{T_{g,1}} + \frac{[(\sum_i \Delta V_i)_2 - (\sum_i \Delta V_i)_1]}{T_{g,2} + \frac{(\sum_i \Delta V_i)_1}{T_{g,1}} \left[\frac{M_2}{M_1} (1/\alpha_w - 1) \right]}} \quad (12)$$

Here M_1 and M_2 are the molecular masses of components **1** and **2**, respectively.

The dependence of T_g on the mass fraction of ED in PPG and ED copolymer is depicted in Fig. 5.

The dynamic mechanical analysis showed that the low-temperature transition, connected with the devitrification of a rubbery microphase, occurs at 234 K (Fig. 4). Introducing this value into formula (12), we receive $\alpha_w = 0.066$. Hence, the microphase based on PPG contains a small amount of ED. This value can be calculated from the diagram of a two-component system obtained with the Cascade program (Fig. 6).

System with the high PPG content. The concentration of the diisocyanate component in the system was 60 wt %; naturally, at the high concentration of 2,4-TDI, the resulting structure contains predominantly the cycles which consist of TDI trimerization products (composition **II**). The reaction was carried out with 1.754 g of the epoxy resin. Its curing consumed $0.180 \times 1.754 = 0.315$ g of 2,4-TDI (for the calculation principle *vide supra*). Therefore, the mass of the epoxy resin with the diisocyanate composed $1.754 + 0.315 = 2.069$ g. The mass of 2,4-TDI consumed for the formation of the isocyanurate cycles

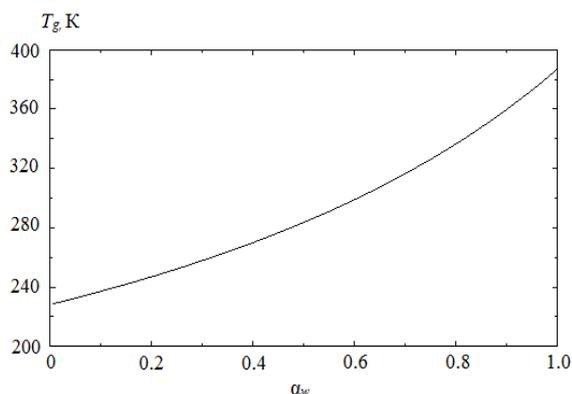


Figure 5. Dependence of T_g on the mass fraction of the epoxy oligomer α_w .

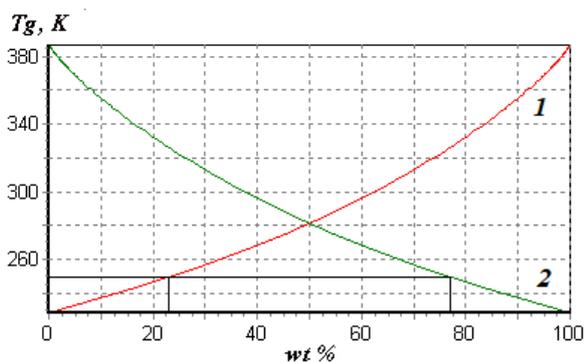


Figure 6. Two-component system (composition I): ED (1), PPG (2).

composed $1.09 + 9.135 - 0.315 = 9.91$ g. Then, the mass fractions of each component of the network have the following values: PPG 29.4%, IC 58.4%, cured ED 12.2%. According to the calculations performed using the Cascade computer program, the value of the glass-transition temperature for the uniform system composes 350 K. Figure 7 represents a triangular diagram for composition II.

As a result, the system under consideration features T_g equal to 350 K.

The dynamic mechanical analysis of the system showed the following temperature dependences of G'' and $\text{tg}\delta$ (Figs. 8 and 9).

The low-temperature maximum of G'' appears at 251 K. It was mentioned above that the microphase can be formed predominantly by a mixture of PPG with ED. The analysis performed using relation (12) showed that if all the epoxy resin was included in the low-temperature microphase, the maximum temperature would compose 256 K. Then the composition of the low-temperature phase would include 29% of ED. This value can be calculated from the diagram of a two-component system using the Cascade software (Fig. 10).

Hence, this microphase is practically formed by a mixture of PPG with ED. Then an increase on the temperature dependences of G'' and $\text{tg}\delta$ is connected only with the isocyanurate cycle.

System with the high PP content. The reaction was carried out with the following amounts of the components: PP 5 g, ED 1.267 g, 2,4-TDI 1.09 g (used in the reaction beginning) and 1.522 g (added in the course of the reaction) (composition IIa).

The mass fractions of each of the components of the network have the following values: PP 56.3%, IC 26.9%, cured

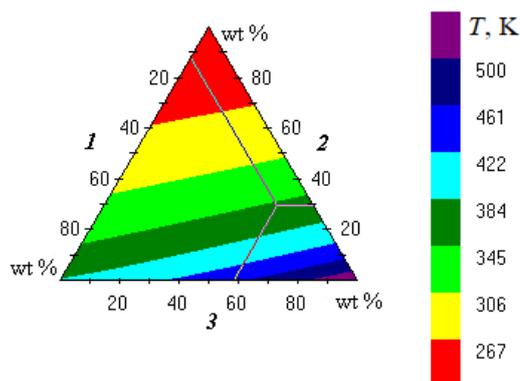


Figure 7. Dependence of the glass-transition temperature of the rigid three-component system on the component compositions: ED (1), IC (2), PPG (3).

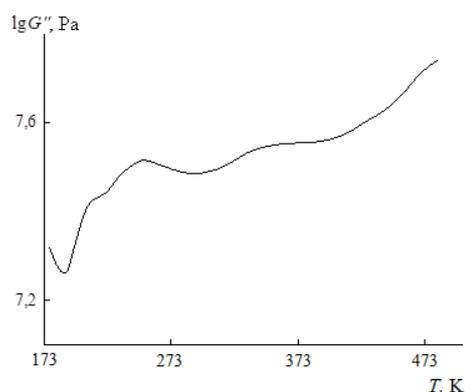


Figure 8. Temperature dependence of loss modulus G'' .

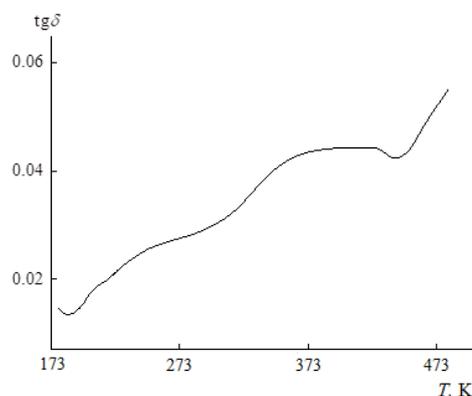


Figure 9. Temperature dependence of $\text{tg}\delta$ for the material containing 12.2 wt % of ED, 58.4 wt % of IC, and 29.4 wt % of PPG.

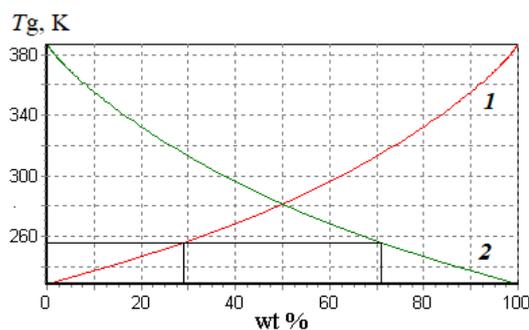


Figure 10. Two-component system (composition II): ED (1), PPG (2).

ED 16.8%. The calculation carried out using the Cascade computer program afforded the value of a glass-transition temperature for the uniform system equal to 262 K. A triangular diagram that depicts the dependence of the glass-transition temperature on the composition of a three-component system is presented in Fig. 11.

For the material consisting of 16.8 wt % of ED, 26.9 wt % of IC, and 56.3 wt % of PP, the glass-transition temperature is equal to 262 K.

In our case, the dynamic mechanical analysis of the system showed the following temperature dependence of the loss modulus (Fig. 12).

It is obvious that the low-temperature maximum for the flexible material appears at 219 K. Since the maximum temperature is close to the glass-transition point of neat PP (208 K) and only slightly exceeds it, the microphase formed by PP contains a small amount of the components which have the higher glass-transition temperatures than T_g of PP. This testifies that the system under consideration is not uniform and displays the microphase separation.

In order to elucidate which component can be predominantly included into the microphase in a small amount, let us compare the surface energies of all the components which take part in the network formation. The results of calculations are presented above. In this case, the PP microphase is likely to be enriched with the cured epoxy resin rather than the isocyanurate cycle, for which a difference of the surface energy from that of PP composes a considerable magnitude.

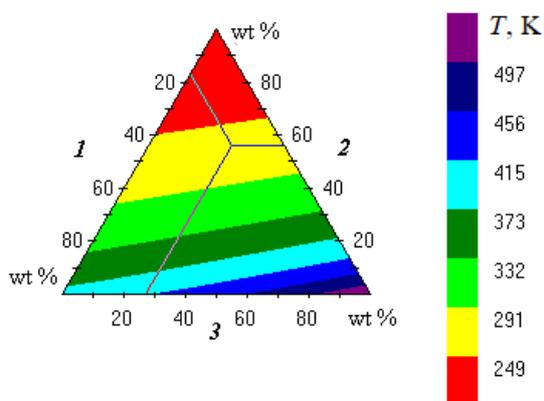


Figure 11. Three-component system (composition **1a**): ED (1), IC (2), PP (3).

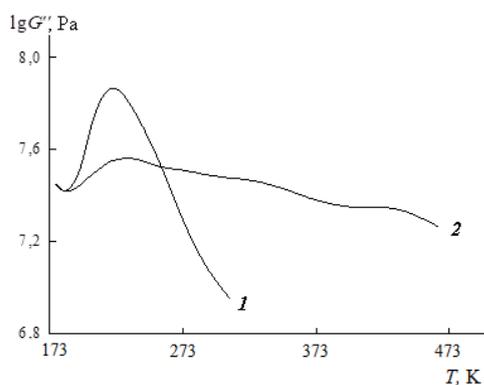


Figure 12. Temperature dependence of the loss modulus for the materials based on PP: flexible material (1), rigid material (2).

To evaluate the composition of the microphase, let us use relation (12). The dependence of T_g on the mass fraction of ED for the material based on PP is depicted in Fig. 13.

The dynamic mechanical analysis showed that the low-temperature transition occurs at 219 K (Fig. 12). Introducing this value into formula (12), we obtain $\alpha_w = 0.12$. Hence, the microphase based on PP contains a small amount of ED, but the higher one than in the case of PPG. This value can be calculated by the diagram for a two-component system obtained with the Cascade software (Fig. 14).

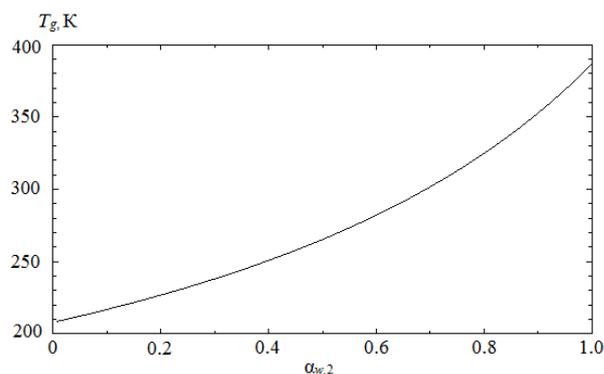


Figure 13. Dependence of T_g on the mass fraction of ED for the material based on PP.

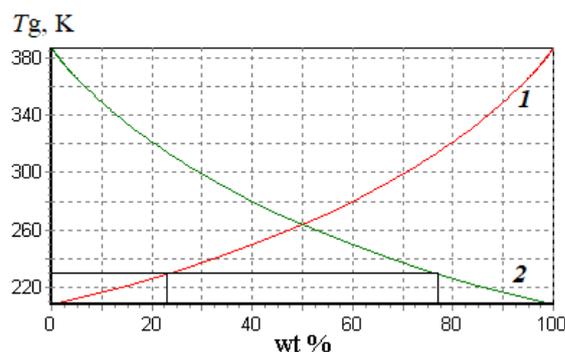


Figure 14. Two-component system based on ED (1) and PP (2) which represents the flexible (low-modulus) material.

System with the low PP content. Let us proceed to the analysis of the rigid composition that exhibits the high elasticity modulus. The reaction was carried out with 1.754 g of the epoxy resin. Its curing consumed $0.180 \times 1.754 = 0.315$ g of 2,4-TDI (for the calculation principle *vide supra*). Hence, the mass of the epoxy resin along with 2,4-TDI consumed for its curing composed $1.754 + 0.315 = 2.069$ g. The mass of 2,4-TDI consumed for the formation of the isocyanurate cycles composed $1.09 + 9.135 - 0.315 = 9.91$ g. Then, the mass fractions of the components have the following values: PP 29.4%, IC 59.0%, cured ED 11.6%. The calculation performed using the Cascade software showed that the glass-transition temperature of a uniform system is equal to 331 K. A triangular diagram that demonstrates the dependence of the glass-transition temperature on the composition of this three-component system is shown in Fig. 15.

For the material consisting of 16.8 wt % of ED, 26.9 wt % of IC, and 56.3 wt % of PP, the glass-transition temperature composes 331 K.

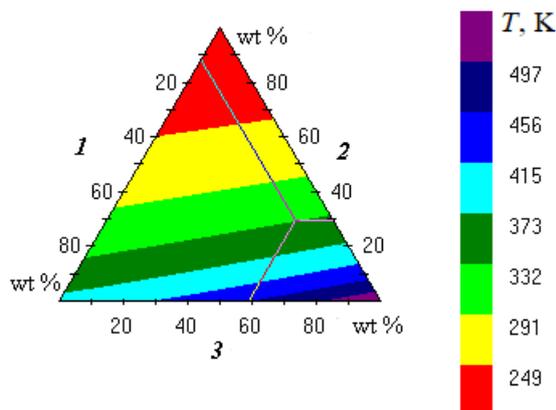


Figure 15. Three-component system (composition Ia): ED (1), PP (2), IC (3).

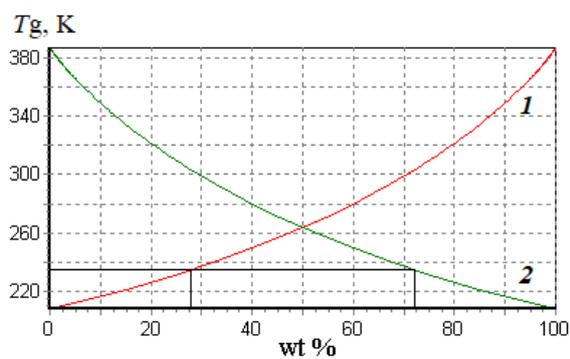


Figure 16. Two-component system (composition Ia): ED (1), PP (2).

The dynamic mechanical analysis of the system under consideration afforded the temperature dependences of G'' which are depicted in Fig. 12. A weak low-temperature maximum of G'' appears at 235 K. It was mentioned above that the microphase can be formed predominantly by a mixture of PP with ED. The analysis performed using relation (12) showed that if all the epoxy resin was included in the low-temperature microphase, then the maximum temperature would compose exactly 235 K. Hence, this microphase is almost fully formed by a mixture of PP and ED. This can be seen also from the diagram of a two-component system obtained using the Cascade program (Fig. 16).

Conclusions

To sum up the results presented, we showed the possibility of definition of the microphase compositions during microphase separation of three-component systems that consist of the structures, which strongly differ in the surface energies and other characteristics. It was found that the microphase, which features a low-temperature transition upon heating, is formed in all cases by PPG or PP with some content of ED. In the case when the system contains PP, this microphase has somewhat higher content of ED. This is the computer-processed analysis which allows one to rapidly determine the compositions of microphases based on the experimentally measured transition temperatures.

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