ELSEVIER

Polymer 43 (2002) 5651–5659

polymer

www.elsevier.com/locate/polymer

‘Non-solvent’ heat resistant binders: rheology of blends of oligoimides with liquid oligomers

Semion M. Mezhikovskii, Boris I. Zapadinskii*

Department of Polymers & Composites, N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, P.O. Box 119991, ul. Kosygina, 4, Moscow, Russian Federation

Received 7 December 2001; received in revised form 12 June 2002; accepted 17 June 2002

Abstract

The rheology of binders based on blends of powdery oligoimides with liquid epoxy and acrylic oligomers was studied for a broad interval of concentrations, temperatures and shear rates. It was shown, that prehistory of blends, phase organization of a system and the extent of approaching the equilibrium state determine the rheological behavior of blends. At equilibrium, depending on the state variables, the investigated blends can be single-phase or two-phase. Furthermore, the coexisted phases are not uniform and are characterized by a complex supermolecular structure of composites. In some cases the original blends have not sufficient time to reach the equilibrium state by the beginning of the rheological test, and the system structure evolution to the equilibrium occurs during the experiment. In terms of rheology some structural transformations act in the same direction and the others act in the opposite direction promoting simultaneously both an increase and a decrease in viscosity, affecting the rheological behavior of the system. The experimental dependence of rheological parameters can be explained within the framework of the following conception: structural transformations have thermodynamic nature, they are kinetically controlled and, depending on external factors, can proceed sequentially and/or simultaneously, at the molecular, supermolecular, phase and morphological levels.

The resulting data allowed determination of the most perspective compositions of binders based on oligoimides and liquid ‘temporary’ plasticizers as well as the optimal processing conditions.

Keywords: Polymer blends; Rheology; Binders

1. Introduction

Blends of solid oligoimides with liquid reactive oligomers are interesting prospective binders for heat resistant reinforced plastics [1]. Their physicochemical properties have been investigated recently in detail [2–4]. In the work presented here the rheological behavior of blends of an oligoimide with liquid oligomers was studied. The temperature–concentration dependence of viscosity of oligomer blends along with the dependences of rheological parameters of intermixtures determine both the processing behavior of oligomer–oligomer blends and mechanical characteristics of the cured plastics. Representatives of the two most widespread classes of oligomers—acrylic and epoxy oligomers—were selected as liquid components of compositions. The selected oligomers possess close rheological properties, but at the same time demonstrate different physicochemical behavior in intermixtures. For instance, a network of hydrogen bonds is realized in epoxy oligomers, while in N-phenyl-substituted oligourethane methacrylate the formation of so strong intermolecular bonds may be excluded. Besides, the preliminary examinations have shown that in the investigated range of temperatures acrylic oligomers are chemically stable in the absence of initiators, whereas the epoxy oligomers interact with oligoimide at temperatures above 100 °C.

2. Experimental

2.1. Materials

As a basis for the study we used blends of a powdery oligoimide (unless otherwise specified, the reaction product of N,N'-bisfurfuryliden-4,4′-diaminodiphenyloxide and *m*-phenylenedimaleimide [5], molecular weight 3500) with two types of liquid oligomers—commercial diglycidyl ether of bisphenol A (ED-20™, epoxy number 20) and

---

* Corresponding author. Tel. +7-095-939-7472; Fax: +7-095-137-8284.
E-mail address: zapadi@polymer.chph.ras.ru (B.I. Zapadinskii).

PII: S0032-3861(02)00375-0

oligourethane methacrylate [6] (OUM-2P)—the reaction product of bis-chloroformate of diethylene glycol with 2-phenylaminoethyl methacrylate. Oligoimide concentrations in blends ranged from 0 up to 90% (hereinafter by weight).

2.2. Methods

The blends were prepared by mechanical mixing of components with short-term heating at 60 °C (up to 30 min) until obtaining visually homogeneous blends. The storage time of blends after preparation and before testing did not exceed 48 h.

Dynamic viscosity of blends was determined by use of a rotary viscosimeter ‘Reotest™-2.1’ with application of a cone-plane measuring device. Viscosity, $\eta = \tau/\gamma$, where τ and γ are the shear stress and the shear rate correspondingly, was calculated via the known procedure [7].

3. Results and discussion

The starting liquid oligomers are rather close in their rheological behavior (Fig. 1), so the discussed below regularities of the flow of their intermixtures with the oligoimide may be considered valid for both the oligomers, unless otherwise specified.

The attempts of obtaining flow curves for the starting oligoimide were not successful under any of the test conditions. Nevertheless, note, that in a closed mould the oligoimide do form rather low viscous melts even at small pressures (3–10 kg cm^{-2}) and temperatures higher than 80 °C. The temperatures and pressures realized by the used device probably do not provide a specimen conversion to the viscous-flow state.

In the operating conditions of the specimens preparation, initial oligoimide blends with ≤30% of liquid oligomers at ambient temperature are powders, stable for 10 days from the moment of their preparation. However, even at a small shear stress during the test these blends transform into fluid systems. The intermixtures with 35–45% of a liquid oligomer are heterogeneous colloidal systems, composed of the oligoimide particles swelled in the oligomer, which in turn are dispersed in the liquid solution of the oligoimide in the oligomer. In such systems strong interphase interactions are developed resulting in the formation of complex supermolecular structures with dominance of the physical network. The intermixtures are gradually structured within 3–4 days and after 5–6 days blends become rubber-like.

A different situation occurs at high (≥50%) content of liquid oligomers in blends. In this case intermixtures initially are in the viscous-flow state and the flow regularities of such intermixtures are typical for physically structured fluids [8]. This is evident from the dependence of rheological parameters on temperature and shear rate. On the other hand, the essential peculiarities are exhibited in the rheological behavior of intermixtures, associated with structural transformations depending on the components ratio and the temperature–time pre-history of blends.

The flow curves of blends of the oligoimide with 90 and 50% of ED-20 at 20–90 °C are depicted in Figs. 2 and 3. It is evident, that the non-Newtonian flow regime is characteristic for the majority of intermixtures. As the test temperature (T) is increased the dependence of viscosity on shear rate is partially degenerated (Fig. 1, curves 1,3–6) for blends with high content of the liquid component. For intermixtures with the approximately equal content of components there are some intervals of temperatures and shear rates, where η is independent of γ (Fig. 2, curves 4 and 5). At the same time the oligomer ED-20 behaves as a Newtonian liquid at the test temperatures below 50 °C and

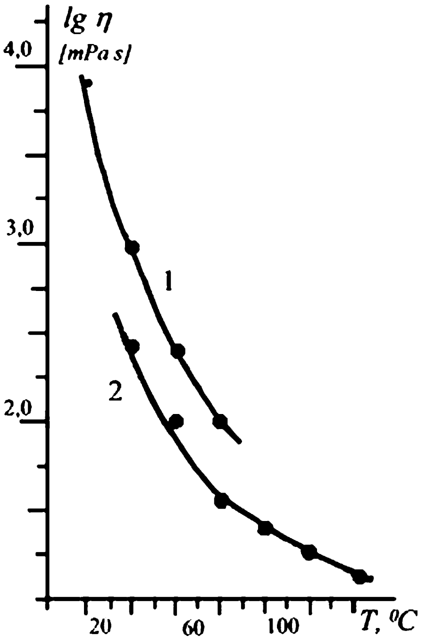

Fig. 1. The temperature dependences of viscosity of ED-20 (1) and OUM-2P (2).

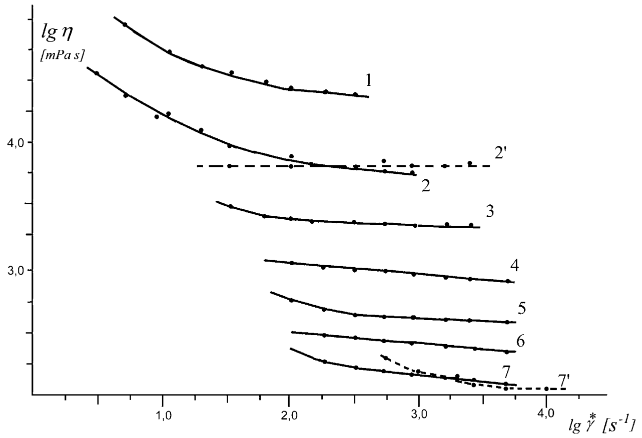

Fig. 2. The flow curves of the oligomer ED-20 (2′, 7′) and its blend with 10% oligoimide at the temperatures of 20, 30, 40, 50, 60, 70 and 80 °C (curves 1–7, respectively).

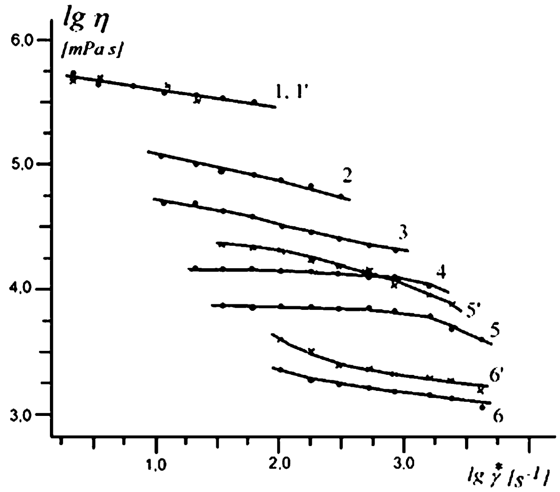

Fig. 3. The flow curves of the oligoimide blends with ED-20 in the ratio of 1:1 at the temperatures of 60, 65, 70, 75, 80 and 90 °C (curves 1–6, respectively), $1'$, $5'$ and $6'$—re-testing.

the dependence of η on γ is exhibited only at the temperatures ≥50 °C (Fig. 1).

Fig. 4 gives the dependences of viscosity on the component ratio for blends of the oligoimide with the oligoepoxide at $\gamma = 100\ \mathrm{s}^{-1}$ and the temperatures of 20–90 °C. In all the cases the regular increase of viscosity with the high-viscous component content is exhibited. The rate of η change essentially depends on T, that influences the shape of the curves $\eta = f(c_{\mathrm{oi}})$, where c_{oi} is the oligoimide concentration. While at the temperatures ≤50 °C the rate of viscosity rising begins to increase noticeably for intermixtures with $c_{\mathrm{ou}} = 30$–40%, on the contrary, at temperatures ≥50 °C and the same oligoimide contents the viscosity rising slows down, that, in some cases, results in the inverse of the curves (Fig. 4, curves 5–8). We discuss these data later. Let us mark here, that such a character of dependences results in a paradoxical situation: the viscosity of the blend of the oligoimide and ED-20 (1:1), measured at 70 and 80 °C, appears to be higher, than at 60 °C. At first glance, this experimental result is inconsistent not only with all the known temperature dependences of viscosity for polymers, colloids and other physically structured liquids, but also with the universally accepted grounds interpreting these dependences, for example Ref. [9].

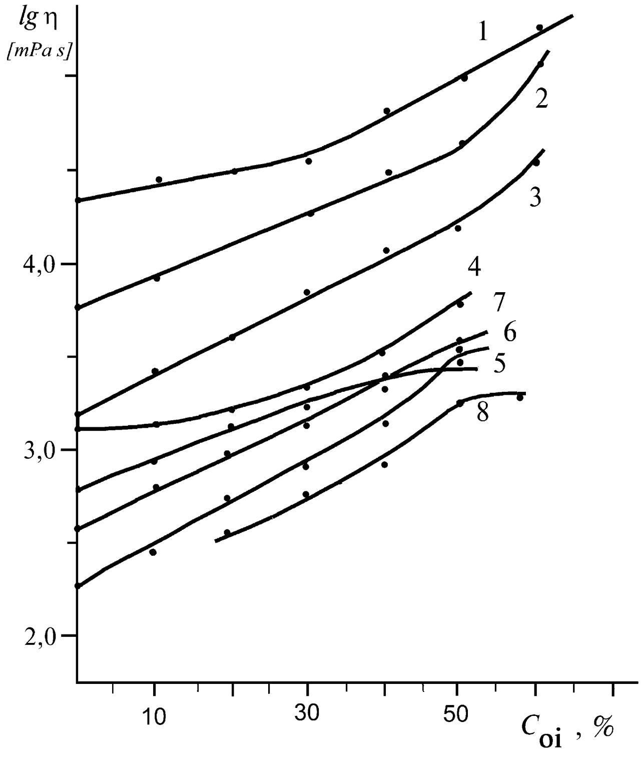

Fig. 4. The dependence of the oligoimide–ED-20 mixtures viscosity on composition at 20, 30, 40, 50, 60, 70, 80 and 90 °C (curves 1–8, respectively); $\gamma = 100\ \mathrm{s}^{-1}$.

The rheological behavior of intermixtures at high temperatures (100–130 °C) was studied by the example of oligoimide–oligourethane methacrylate blends (Figs. 5 and 6). The viscosity of the given blends, as well as of the oligoimide–epoxy oligomer blends, regularly rises with the increase in the less viscous component dosage, but (and is essential) some viscosity growth is also observed by increasing the duration of blends heating. It is reasonable to suggest that the increase of viscosity is caused by some chemical transformations of oligomers, resulting in chains propagation and (or) curing reactions. However, this explanation does not agree with some experimental data. For instance, the GPC data show that at these temperatures all the blend components are practically stable. Further, the detailed study of the kinetics of the intermixtures viscosity changes has revealed more complex picture of the dependence of viscosity on the time of experiment (t)

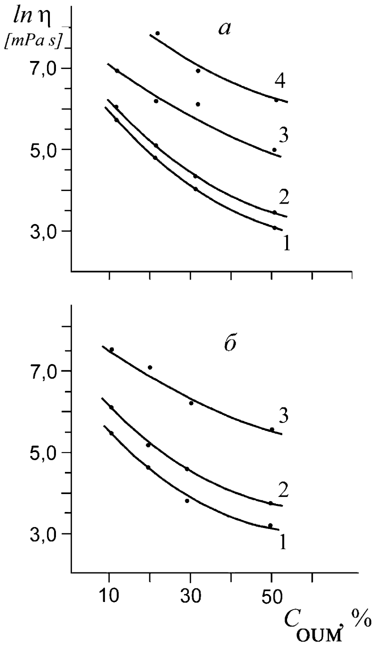

Fig. 5. The concentration dependences of the oligoimide–OUM-2P blend viscosity within 5, 10, 20, 30 and 60 min (curves 1–4, respectively) after starting the test at 110 °C (a) and 120 °C (b).

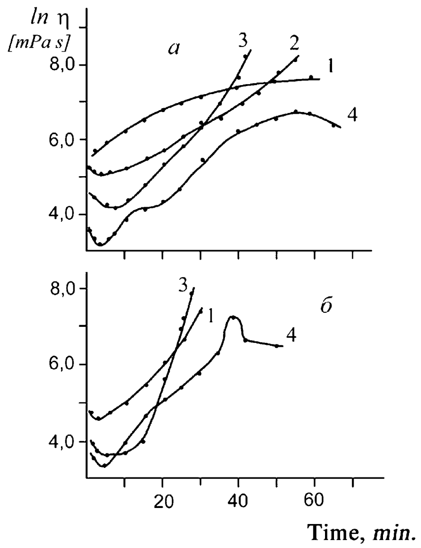

Fig. 6. The kinetics of viscosity change for the oligoimide–OUM-2P blends at 110 °C (a) and 120 °C (b) and at the content of OUM-2P: 10, 20, 30 and 50% (curves 1–4, respectively).

(Fig. 6). Indeed, except for one case (small dosages of OUM-2P at 110 °C, Fig. 6a, curve 1) in all the other experiments the increase of viscosity is preceded by its reduction. Moreover, for blends with large content of OUM-2P the extremal dependence of viscosity on t is observed—a stage of the gradual (Fig. 6a, curve 4) or sharp (Fig. 6b, curve 4) decrease of viscosity follows the initial increase of η. The occurrence of the extremum on the curves $\eta = f(t)$ may be attributed to proceeding of at least one more (in addition to the chemical transformations) process of the structure reorganization, exerting some opposite influence on the character of the blends flow.

Let us consider in general some probable explanations for the set of the unusual results presented above. The analysis of our experimental results is based on the theoretical aspect that all the observed changes in the rheological behavior of our systems arise from structural transformations resulted from both the thermal (temperature) and mechanical (deformation) effects. These transformations are thermodynamic by nature, are controlled by kinetic rules, and are realized simultaneously and/or consistently (depending on external factors) on the molecular, supermolecular, phase and morphological levels of structure. From this point of view, for the systems under study the following positions are valid:

- At the equilibrium, the blends, in accordance with the state parameters, may be single-phase or two-phase. Two-phase blends represent dispersions of the oligoimide particles, swollen in a liquid oligomer, which dispersed in the oligoimide solution in a liquid oligomer. Each of the coexisted phases of two-phase systems, as well as single-phase solutions, is non-uniform and has complex supermolecular structure.
- In some cases starting blends do not reach the thermodynamic equilibrium to the beginning of the rheological test under the conditions of samples preparation. So, the evolution of the system structure to the equilibrium proceeds during the experiment.
- Under rheological tests at high temperatures chemical transformations of binder components are possible, that gives rise to the reorganization of not only molecular, but also other (for example, phase) levels of the structure of a system.
- A set of structural transformations in the intermixtures may be unidirectional (for example, promoting the viscosity increase only). More common, however, is the situation when the transformations act in the opposite directions in respect to the rheological behavior of a system.

From this standpoint the change of the flow character of the epoxy oligomer with the rise in temperature (Fig. 2, curves $2'$,$7'$) is determined by the changes of the oligomer structure at the supermolecular level. Such a conclusion is confirmed by the data of the pulse NMR method [3]: a temperature increase results in destruction of the physical network of hydrogen bonds in the epoxy oligomer and to the formation of stronger and less mobile associative structure of another type. It is destruction of this new structure that leads to the dependence η vs. γ. It should be noted, that the temperatures of structural reorganization in ED-20 fixed by the rheological method are 30–40 °C lower than those determined by the NMR relaxation method. It is apparent, that the shear deformations arising in a specimen under the conditions of a rheological test take part in the processes of structure reorganization, sensitive to the changes in the sizes of kinetic units involved in the transfer processes (the macroviscosity level). The changes in a blend structure observed in the NMR relaxation method at the microviscosity level are initiated by temperature only and therefore appear at higher temperatures than in the case of rheological tests.

The character of the blends flow is determined by the structural transformations occurring on both the supermolecular and the phase levels, and, in addition, is complicated by a very low rate of the phase equilibrium establishment. For example, the blend of ED-20 and 10% of the oligoimide is single-phase at the equilibrium state, but the relaxation data show [3,4], that under the conditions of the specimen preparation (temperature, time) our systems do not equilibrate to the beginning of rheological tests. The given mixture remains two-phase during rheological experiments at temperatures <50 °C. The system flows as a typical non-Newtonian liquid with essential colloidal character.

As the temperature increases, under the condition of intensive shear deformation the process of interdiffusion controlling the rate of the components intersolubility and, hence, the rate of the equilibrium establishment, is accelerated [10]. As a result, at temperatures >50 °C the system has sufficient time to approach the equilibrium during the test, and a thermodynamically allowed single-phase intermixture is formed. Therefore, the dependence of η vs. γ appears in a less extent than in two-phase systems, and this assumption is confirmed by our experiment (Fig. 2, curves 4–7).

For the blends with high content of the oligoimide (Fig. 3) it should be pointed out that, first, the system even at the equilibrium state remains two-phase [4] and, second, the duration of experiment is not enough for achievement of the equilibrium intersolubility between components in coexisted phases. Therefore the dependence of viscosity on γ is indicated at all the studied temperatures. However, in a very narrow range of temperatures (75–80 °C) the energy of interphase interaction apparently compensates the mechanical energy of shift that is absorbed in the course of destruction of supermolecular structure of system. As a result, the upper limit of the Newtonian mode of flow (the greatest Newtonian viscosity) is exhibited. Only at very high speeds of shift ($>10^3\ \mathrm{s}^{-1}$) these strong bonds are disrupted, and the dependence η vs. γ is restored. The thermal energy has a similar influence on the blends rheology: at temperatures >80 °C the supermolecular structures providing existence of the above-mentioned upper limit are collapsed due to activation of the thermal motion, and the system flows in the non-Newtonian mode within all the investigated interval of shift rates (Fig. 3, curve 6). It is possible that at temperatures >80 °C some chemical transformations in the blend components influence the flow of the systems. There is good indirect evidence that this assumption is true: under the re-test conditions at the temperatures >80 °C the blend viscosity is greater than that under the initial tests, in contrast to the re-test at temperatures <80 °C. Therefore, viscosity of oligoimide–ED-20 intermixtures at temperatures >80 °C are found to be lower than viscosity of the same blend under the re-test at the same temperature, whereas at 60 °C the flow curves under the initial and re-test conditions are identical.

The non-trivial concentration dependences of viscosity of the oligoimide–oligoepoxide blends at different temperatures, given in Fig. 4, may also be explained quite logically within the framework of the considered scheme. Indeed, at a constant temperature viscosity of an intermixture increases with increasing concentration of the high-viscous component (oligoimide). On one hand, viscosity of the disperse medium grows as a result of an increase of the high-viscous component concentration in the phase of the oligoimide solution in the oligoepoxide. On the other hand, the number of particles of the dispersed phase rises. Both these factors operate in the direction of increasing viscosity of the system, but in a different extent, and their ratio determines the rheological behavior of blends. At room temperature and at the oligoimide concentration $<30\%$ viscosity of blends depends on c_{oi} only (the limiting solubility of oligoimide in ED-20 is 25–28% at 20 °C, 43–45% at 60 °C and ~50% at 80 °C), i.e. the first factor controls rheology. At $c_{\mathrm{oi}} > 30\%$ phase separation of the system occurs, and the flow of these blends up to the coalescence threshold and the subsequent inversion of phases, should follow Einstein's law [11]

$$\eta = \eta_0(1 + 2.5\varphi) \tag{1}$$

where η_0 is the viscosity of the disperse medium, and φ is the volume fraction of the disperse phase. Therefore in two-phase systems at $c_{\mathrm{oi}} > 30\%$ increasing c_{oi} leads to growth of the number of particles of the disperse phase in a volume unit, at a constant concentration of components in the disperse medium (the second factor).

As the temperature rises, mobility of the kinetic units determining viscosity in each of the coexisted phases grows and, all other conditions being equal, viscosity of the system as a whole is reduced, as it is shown in the experiment: for single-phase systems the viscosity drop obeys the Arrhenius equation (Fig. 4).

For two-phase systems the enhancement of the mobility of kinetic units stimulated by elevation of temperature results not only in decrease of viscosity, but also in increase of the rate of interphase diffusion and therefore of the rate of intersolubility of components. As a result of these processes, first, increasing the oligoimide concentration in disperse medium leads to growth of viscosity of this medium and of the system as a whole. Second, elevation of temperature at $c_{\mathrm{oi}} = \mathrm{const.}$ results in reduction of the oligoimide concentration in the disperse phase and, thus, of the volume fraction of this phase in the system, that must lead to decrease of viscosity according to Eq. (1). At temperatures >80 °C the oligoimide–oligoepoxide systems come close to the critical region where regularities of the blends flow may be differentiated from those discussed above. In addition, as it is stated above, chemical transformations of the components are possible at elevated temperatures.

Thus, in the temperature range from 20 to 80 °C the dependence of viscosity on temperature must be controlled by simultaneous action of three factors:

- a viscosity drop due to increase in mobility of kinetic units of flow from the Arrhenius equation;
- growth of viscosity because of thickening of the disperse medium;
- reduction of viscosity owing to decrease of the volume fraction of the disperse phase.

If this is the case, inevitably there must be threshold values of both concentration and temperatures at which the mechanism of blends flow must change. The experiments have confirmed this conclusion (Fig. 7). For the oligoimide–oligoepoxide blends the temperature dependence of viscosity is characterized by a change in the rate of viscosity reduction (an inflection on the curve η vs. T) as distinct from the individual oligoepoxide having a monotonically decreasing viscosity (Fig. 1).

Processing of these data with use of values of the greatest

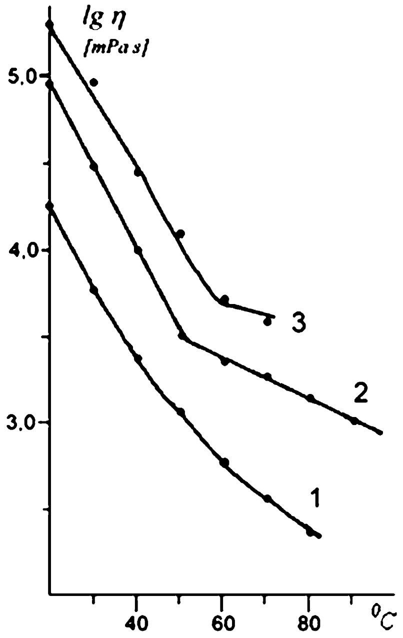

Fig. 7. The temperature dependences of the oligoimide–ED-20 blends viscosity at the oligoimide content of 20, 40 and 60% (curves 1–3, respectively).

Newtonian viscosity (η_n), obtained by extrapolation to the zero shift rate [12], discloses (Fig. 8) that dependences of log η_n vs. $1/T$ can be approximated by two straight lines over the temperature intervals of 20–40 and 50–80 °C with the point of intersection close to 45 °C (the change of the mechanism of blend flow).

Existence of the two temperature intervals manifests itself also in the dependence of the effective energy of activation (the temperature factor of viscous flow, E_{ef}) on the composition of blends (Fig. 9). E_{ef} is calculated by the following equation [12]

$$E_{ef} = 2.3R\Delta \log \eta_n/\Delta(1/T) \tag{2}$$

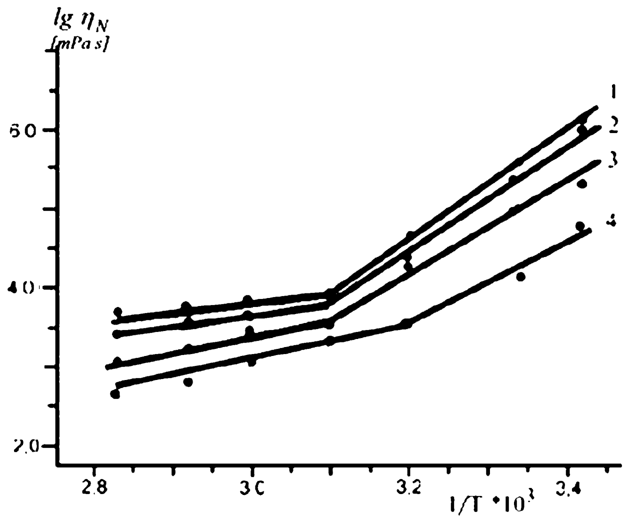

Fig. 8. The plot of the greatest Newtonian viscosity of blends vs. $1/T$ at the oligoimide content of 10, 30, 40 and 50% (curves 1–4, respectively).

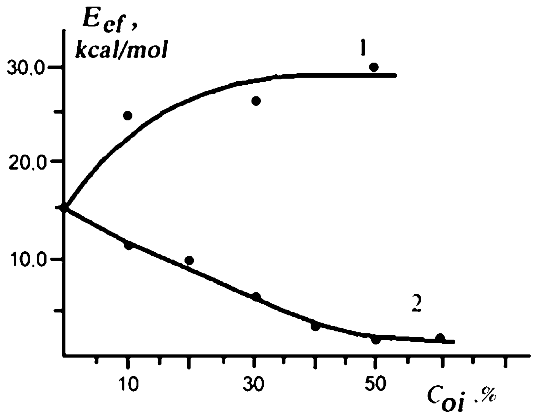

Fig. 9. The influence of the oligoimide concentration on the effective activation energy of viscous flow of the blends in the regions of 20–40 °C (1) and 50–80 °C (2).

where R is the universal gas constant and $\Delta \log \eta_n$ is the change in viscosity in the temperature interval ΔT. Over the interval of 20–40 °C the value of E_{ef} grows with increasing the oligoimide concentration up to $\sim 30\%$ that corresponds to the position of the coexistence curve (binodal) under these conditions, and then E_{ef} practically does not depend on the blends composition. At the same time in the range from 50 to 80 °C the value of E_{ef} monotonically diminishes with increasing oligoimide concentration up to $\sim 50\%$, that also corresponds to the position of the binodal for this temperature interval.

The revealed atypical character of the change of E_{ef} with c_{oi} proves our assumptions stated above. First, for single-phase systems at low temperatures an additional consumption of energy is necessary to disrupt supermolecular structures. As the oligoimide concentration increases, the stability as well as E_{ef} of such structures rise. At high temperatures the thermal energy is sufficient to break intermolecular bonds and consequently E_{ef} is naturally reduced. Second, for two-phase systems these two factors (thermal and mechanical) are compensated to some extent. This compensation leads, in particular, to independence of E_{ef} from c_{oi} as it is detected by the experiments at c_{oi} above the threshold concentration.

At the test temperatures much higher than 80 °C the flow of the systems under study is complicated by some additional structural transformations besides those considered above. It is our intention to focus on the basic transformations and to analyze their influence on the blends viscosity. As the temperature increases the thermal movement of both molecules and more complex kinetic units are always activated resulting in decrease of viscosity. Simultaneously, the mass transfer rate is raised that in turn results in increasing the rate of the components interdiffusion [2]. As shown above, a change in the components concentration in coexisted phases of two-phase systems may result both in increasing and decreasing viscosity.

Furthermore, during heating some desorption of groups of molecules of a low-viscous component (LVC) from the surface of the oligoimide particles in the dispersion medium takes place that must inevitably result in a significant decrease of the system viscosity because of the sharp increase of the LVC concentration in the continuous phase. This statement is based on the conception of aggregative sorption [11] and on our experimental data [3,4]. It was shown, that in the case of low-temperature mixing of the oligoimide with LVC, i.e. under the conditions used in the present work, formation of complex two-phase blends precedes the process of the components intersolution. The blends are thermodynamically non-equilibrium and kinetically unstable. At first, some part of molecules of LVC is sorbed at the surface of the oligoimide powder (at its active sites) in the form of immobilized clusters. Subsequently, LVC slowly diffuses in the volume of the oligoimide particles in parallel with fast intersolution of other components.

As a result of the aggregative sorption at a constant temperature, quasi-equilibrate structures are formed. With the temperature elevation, weak sorption bonds are collapsed and the oligomer molecules constituting clusters not dissolved in oligoimide are desorbed in the phase of the oligoimide solution in the oligomer. This experimental fact mostly explains the down-tending branch of the curves $\eta = f(t)$ at high temperatures (Fig. 6): increase of the concentration of LVC in the continuous phase resulting from the aggregative desorption is evident in a rheological experiment in the form of a drop in viscosity.

Finally the rise of temperature (> 80 °C) considerably activates the chemical processes resulting in lengthening and crosslinking of molecular chains. In the presented study we do not consider reaction mechanisms and structures of formed products. Within the framework of the problem discussed here it is important that practically all the processes of chemical curing result in increasing viscosity of the system. This circumstance can be clearly recognized from the data of Fig. 6 (the middle part of the kinetic curves of viscosity). Under the isothermal conditions at temperatures > 110 °C and $c_{\mathrm{oi}} > 10\%$, the initial drop in viscosity of OI-OUM-2P blends is followed by a fast rise of viscosity by 2–4 order of magnitude up to the values restricted only by the device capability.

The viscosity drop revealed for the blends with 50% concentration of OUM-2P after 40 min (Fig. 6), is probably connected with specificity of three-dimensional polymerization of acrylic oligomers. According to the present point of view [13], at the deep stages of acrylic esters polymerization microsyneresis [14] of unreacted oligomers molecules (as well as of liquid impurities) occurs from the network aggregates. The release of these low-viscous compounds to the dispersion medium must result (and do result at the sufficiently high concentrations (peaks on curve 4 Fig. 6a,b)) in some decrease of viscosity at the final stage of the curing process.

Naturally, the kinetic curves of viscosity, depicted in Fig. 6, reflect the integrated contribution to viscosity of all the processes leading to evolution of a blend structure. At this stage of our investigation, we do not quantitatively estimate the differentiated contribution of every individual process. Taking into account that all these processes have the activation nature and their rates are determined by temperature and phase organization of system, it is apparent that a relative contribution of any process depends both on blend compositions and on the test conditions (temperature, time). Nevertheless, some qualitative relations may be found. For example, for the intermixture of the oligoimide with 10% OUM-2P at 110 °C (Fig. 6a, curve 1) the contribution of aggregative desorption of the LVC to the blend viscosity is negligible. So the monotonic increase in viscosity is determined by slow curing of the oligoimide in the solution of oligourethane methacrylate stable under these conditions. At the temperature of 120 °C viscosity of this intermixture (Fig. 6b, curve 1) already 'feels' increase of mobility of kinetic segments of the flow resulting from increase of the LVC concentration (desorption) or from activation of the heat motion. Therefore, at the early stage of the test the system viscosity is slightly lowered and then sharply rises as a result of chemical reactions accelerated at 120 °C. With increasing the LVC concentration above 10% the dependence of the blends viscosity on the processes of aggregative desorption becomes more essential, so the initial drop of viscosity is exhibited not only at 120, but also at 110 °C (Fig. 6a,b).

It is clear from the above discussion that the studied systems are characterized by low rates of establishment of the concentration and phase equilibrium. This fact, in turn, results in the dependence of macroscopic properties (in our case viscosity) on the remoteness of the system from the equilibrium state at the moment of the test beginning. In other words, the temperature–time pre-history of a system, as well as the test conditions, must affect a relative contribution of a certain process to the blend viscosity.

Fig. 10 demonstrates the kinetics of viscosity change for

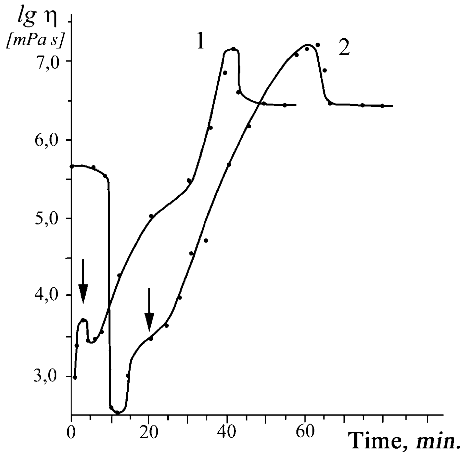

Fig. 10. The kinetics of viscosity change of the oligoimide–OUM-2P blends in the ratio of 1:1 at 120 °C. The mixtures were placed on the device plate pre-heated up to 120 °C (1) or 40 °C (2). Arrows specify the time taken to achieve the test temperature (120 °C).

Table 1
Processing properties of oligoimide–ED-20 blends and strength of the cured materials

Oligoimide/ED-20 ratio	Blending conditions		Melt lifetime (min)	σ_t^a (kg cm^{-2})	σ_t^b (kg mm^{-2})
	Temperature (°?)	Time (min)			
50:50	90	35	>240	690	168
	130	15	23		
70:30	130	25	25	1030	183
	150	17	15		
80:20	130	24	15	1255	185

[a] Tension strength of cured binders (220 °C h^{-1}).

[b] Tension strength of unidirectional glass–fibre-reinforced plastics.

the oligoimide–OUM-2P blend with the components ratio of 1:1 at the temperature of 120 °C, for two methods of conducting the test: in one case the blend was placed on the 'cold' plate of the device with subsequent specimen heating to the test temperature at the rate of 5 °C/min, and in the other case the blend was placed on the plate pre-heated up to 120 °C. The time of the test temperature attainment is indicated in Fig. 10 by arrows and approximates to 20 and 2–3 min under the 'cold' and 'hot' conditions, respectively. The distinctions in the intensity of heating between the two discussed procedures determine the dissimilar nature of the dominant process on the way to the isothermal state.

In the 'hot' alternative activation of the heat motion has a dramatic impact on viscosity: within 1 min of heating the blend viscosity drops by ~2.5 decimal orders of magnitude. Heating stimulates intersolubility of the components accompanied by some viscosity increase. However, aggregative desorption of the LVC molecules preceding chemical curing concurrently leads to some decrease of the blend viscosity. Influence of these two processes results in appearance of the first inflection on the curve $\eta = f(t)$. Then the processes evolve in accordance with the mechanism proposed above from the examination of the data of Fig. 6.

At the initial stage of the 'cold' test aggregative desorption is primarily responsible for the magnitude of viscosity. Thus, after heating for 10 min the η values drop by more than three decimal orders of magnitude, i.e. below the initial viscosity in the 'hot' alternative. Then the processes of chemical curing of oligomers play the dominant role, and the kinetic curves of viscosity for the both tests become similar with a shift in time defined by the difference in the duration of heating.

The results of our study have allowed determination of the compositions of blends of the oligoimide with liquid 'temporary' plasticizers, which are the most perspective from the practical point of view, and also development of the optimal conditions of processing the blends into composites.

It should be particularly emphasized that low-molecular oligoimides prepared under the strictly controlled conditions form true molecular solutions—melts with epoxy oligomers of different structures. Therefore, it is possible to use our blends as binders in the production of composite materials or in the processes of injection molding of thermosets [1].

The processing properties of some blends listed in Table 1 allow producing laminates by the winding method with application of a heated impregnating bath. It was revealed as a result of the study of the kinetics of blends curing by torsion braid analysis, that oligoimides contain active sites capable to react with epoxy groups [15]. The concentration of these sites is rather high, and at the oligoimide contents >50% the epoxy oligoimide blends cure completely without introduction of any hardener. At first fast thermal polymerization of maleimide groups of the oligoimide proceeds, and then an epoxy oligomer is inserted into the network in the course of relatively slow reactions.

Similarly, blends of the oligoimide with high-molecular epoxy resins based on bisphenol A or alloys of cycloaliphatic epoxyimide with epoxynovolak form melts stable for 500–1000 s at 120 °C. Curing of these melts filled by chopped glass fibers at 220 °C for 90 s gives rise to formation of composites characterized [16] by very high compressive strength 295–305 MPa and by a high level of retention of dielectric properties up to 250 °C. Martens temperature of these materials is in the range of 230–250 °C, the oxygen index is 48–50.

Acknowledgments

We thank Dr Nina Varlamova and Dr Oleg Stankevich for synthesis of the oligomers and Mrs Eugenia Vasilchenko for assistance in the study. The financial support from the Russian Foundation for Basic Research (grant no. 01-03-32991) is gratefully acknowledged.

References

[1] Zapadinsky BI. The base trends in the synthesis of heat resistant polymers by the oligomer method. Preprints of the IV conference on the chemistry and physicochemistry of oligomers, Nal'chik, Chernogolovka; 1990.

[2] Kotova AV, Stankevich AO, Varlamova NV, Shashkova VT, Kuznetsov YuL, Zapadinsky BI. Plastmassy 1997;1:25.

[3] Kotova AV, Stankevich AO, Shashkova VT, Varlamova NV, Kuznetsov YuL, Zapadinsky BI. Plastmassy 1997;7:7.

[4] Vasilchenko EI, Mezhikovskii SM, Stankevich AO, Kuznetsov YuL, Varlamova NV, Zapadinsky BI. Plastmassy 1999;3:19.

[5] Liogon'ky BI, Zapadinsky BI, Stankevich AO, Kuznetsov YuL, Berlin AA. Doklady AN SSSR 1979;24:920.

[6] Berlin AA, Varlamova NV, Korshunov MA, Kefeli TYa, Mikhlin VS, Abdusalamov VA. Vysokomol Soed 1980;22A:683.

[7] Belkin IM, Vinigradov GV, Popov AI. Rotary devices. Moscow: Mashinostroenie; 1968.

[8] Vasilchenko EI, Mezhikovskii SM. Vysokomol Soed 1989;31A:1362.

[9] Malkin AYa, Kulychikhin SG. The rheology in processes of formation and transformation of polymers. Moscow: Khimia; 1985.

[10] Chalykh AE. Diffusion in polymer systems. Moscow: Khimiya; 1987.

[11] Lipatov YuS. Colloidal chemistry of polymers. Kiev: Naukova Dumka; 1987.

[12] Tager AA. Physical chemistry of polymers. Moscow: Khimia; 1968.

[13] Berlin AA, Korolev GV, Kefely TYa. Acrylic oligomers. Moscow: Khimia; 1983.

[14] Dusek K, Sedlacek B. Eur Polym J 1971;7:1275.

[15] Kuznetsov YuL, Stankevich AO, Zapadinskii BI. Preprints of the III conference on the chemistry and physicochemistry of oligomers, Odessa; 1979. p. 148.

[16] Prilepskaya TI, Zadontzev BG, Doljikova LA, Zapadinskii BI. USSR Patent 1,246,579; 1989.