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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Statistical Analysis of the Microstructure and Mechanical Properties of Rolivsans in the Course of Thermal Curing

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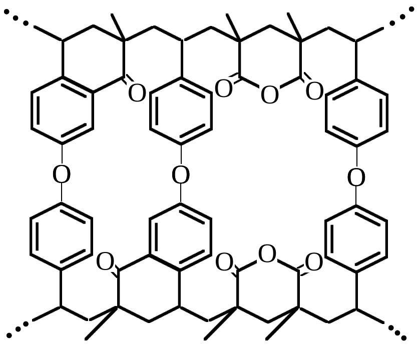
Abstract—The reversible aggregation model was applied to analyze the electron-microscopic data for statistical ensembles of Rolivsan microdomains in the course of thermal curing. The experimentally established correlation between the average size of the microdomains in the ensembles and the dynamic Young modulus of the Rolivsan samples cured at different temperatures was interpreted in terms of the kinetic strength concept.

Rolivsans are polyfunctional monomeric–oligomeric systems whose molecules contain styrene-like and/or methacrylate terminal groups [1, 2]. In the course of curing, they form thermally stable cross-linked polymers of a new type, which find various engineering applications [3, 4].

As known [5–7], the polymer network yielded by three-dimensional copolymerization of the monomeric and oligomeric components of Rolivsan at 100–170°C is converted upon further heating (≥180°C) to a network with a much greater thermal stability. It fundamentally differs from the original (essentially, trivial) network both chemically and topologically; also, their supramolecular structure is different. The main structural unit of the new network of exhaustively cured Rolivsans can be represented as follows:



Naturally, rearrangement of such specific densely cross-linked methacrylates under the action of 4,4'-divinyldiphenyl oxide (analogue of *n*-divinylbenzene) into cross-linked polyether-ketones of the Tetralone type affects the properties of new thermosetting binders. In particular, cured Rolivsans surpass the known binders in thermal (softening point 270–330°C and over) and thermooxidative stability.

EXPERIMENTAL

Samples for studies were prepared by open pouring of MV-1 commercial Rolivsan [1–5] into 50 × 50 × 10 mm metallic or Teflon molds, followed by heating at a rate of 5 deg $\min^{-1}$ to the end curing temperatures T_0 (150, 160, 180, 200, and 250°C) in the following modes, °C/h: 150/5, 160/5, 170/5, 180/4, 200/4, and 250/9.

Prior to microstructural studies, the Rolivsan samples were cleaved at liquid nitrogen temperature to minimize the plastic deformation at failure. Then, the surfaces of low-temperature chips were etched in a high-frequency oxygen discharge plasma for 15–40 min, depending on T_0. Next, two-stage replicas were prepared by alternately depositing at an angle of 45° to the chip surface (oblique shadow-casting) [8] platinum (Pt) and carbon (C) layers. The Pt/C replicas were detached from the sample surface with an aqueous solution of polyacrylic acid, which was subsequently removed by placing the replicas in distilled water. Next, the Pt/C replicas in the form of thin (30–40 nm) films were deposited onto a copper grid, dried, and examined in a Tesla (Czech Republic) BS-500 transmission electron microscope at the ×20 000 magnification.

The dynamic Young modulus of the cured Rolivsan samples in the form of 34 × 20 × 8-mm parallel-

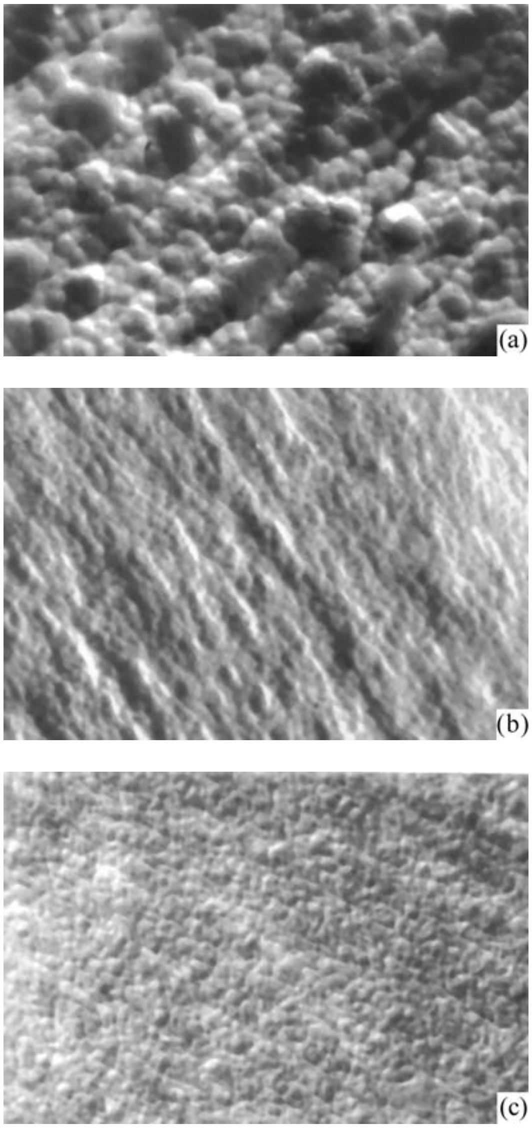


Fig. 1. Electron micrographs of the platinum-carbon replicas from the surface of the Rolivsan samples heated to (a) 150, (b) 190, and (c) 250°C.

epipeds was determined on a facility described in [9] at 20°C at the exciting vibration frequency of 72 Hz.

Figure 1 shows the electron micrographs of the Pt/C replicas from the etched surface of the low-temperature chips of the Rolivsan sample cured at T_0 = 150, 190, and 250°C. It is seen that, like for other cross-linked polymers [5, 6, 10], the surface microstructure of the samples is formed by a set of densely cross-linked microdomains (polymer grains, globules, microdomains) and intergranular layers characterized by a looser polymer network [11–13]. The domains have a close-to-spherical shape, and their linear size (diameter) varies with T_0.

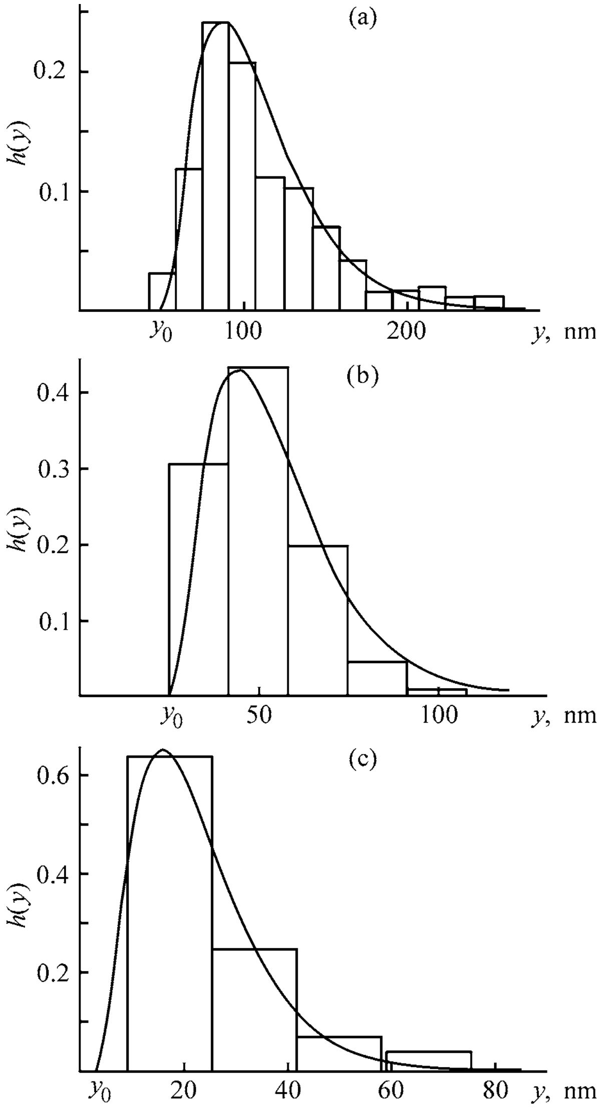


Fig. 2. Statistical distribution $h(y)$ of microdomains over the diameter y, on the surface of Rolivsan samples heated to (a) 150, (b) 190, and (c) 250°C.

Figure 2 shows the histograms derived from a statistical analysis of the microdomain diameters. From 500 to 4500 microdomains were analyzed in each micrograph. It is seen that, for each T_0, the statistical size distribution patterns for microdomains form common statistical ensembles. For analytical description of these ensembles, we used the reversible aggregation model.

Based on the general principles of chemical kinetics and equilibrium thermodynamics of irreversible processes, we obtained in terms of the reversible aggregation model an expression describing the statistical size distribution $h(y)$ of the structural formations, aggregates [14, 15]:

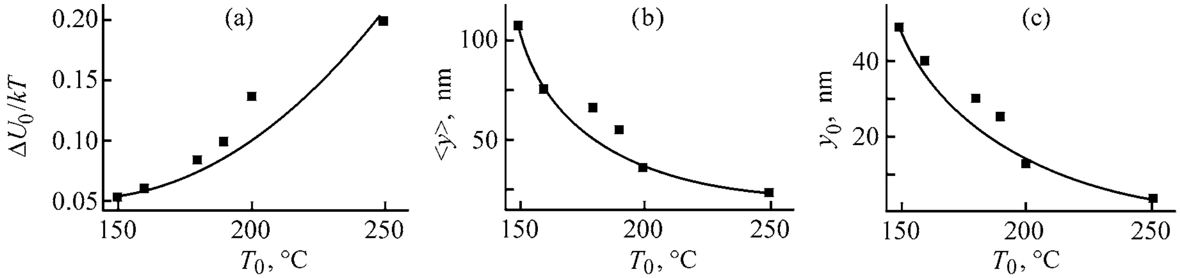


Fig. 3. (a) Reduced aggregation energy $\Delta U_0/kT$ and (b) average $<y>$ and (c) nucleation y_0 diameters of microdomains in the Rolivsan samples vs. the heating temperature T_0.

$$h(y - y_0) = A(y - y_0)^m \exp\left[-\frac{(y - y_0)\Delta U}{kT}\right]. \quad (1)$$

Here, A is the normalizing coefficient; $(y - y_0)\Delta U_0$, J, aggregation energy which is a product of the reduced size of an aggregate in the ensemble $(y - y_0)$ by the standard aggregation energy ΔU_0, J m^{-1}; y_0, size of the smallest aggregate; k, Boltzmann constant; T, absolute temperature; and m, dimensionality of the space in which the aggregate grows (for the surface, $m = 2$).

The key role in expression (1) is played by the ΔU_0 parameter determining the equilibrium size distribution of the aggregates.

The lines in Fig. 2 represent the experimental statistical data obtained using Eq. (1). Our results suggest the applicability of the reversible aggregation model to the objects of study. Notably, this model has been successfully applied earlier to derive statistical size distributions for microdomains yielded by solid-phase intramolecular chemical transformations of polyamido acids of various chemical structures to polyimides [16–19]. Our results suggest that this model is suitable for describing the kinetics of various solid-state chemical reactions.

A practically important characteristic of the statistical distribution is the average size of an aggregate in the ensemble, which is defined as the normalized expectancy:

$$<y> - y_0 = \frac{\int_0^\infty (y - y_0)\, h(y - y_0) dy}{\int_0^\infty h(y - y_0) dy} = \frac{(m + 1)kT}{\Delta U_0} = \frac{3kT}{\Delta U_0}. \quad (2)$$

Figure 3 shows how the reduced standard aggregation energy $\Delta U_0/kT$, as well as the average ($<y>$) and nucleation (y_0) diameters of the microdomains, vary with T_0. It is seen that, upon high-temperature heating, the supramolecular structure of cured Rolivsan gets more uniform: $\Delta U_0/kT$ increases approximately fivefold with temperature raized from 150 to 250°C, which means that the statistical distribution of the diameters of the microdomains narrows, and $<y>$ and y_0 decrease ten- and fivefold, respectively.

The fact that the size of the polymer grains diminishes in the course of high-temperature curing of Rolivsans is evidently due to chemical and topological rearrangements in the polymer networks constituting these grains. These rearrangements involve scission of polymer chains and cross-links, accompanied by (poly)cyclization, cross-linking, and degradation reactions [5–7]. These processes are responsible for decreased size and denser packing of the polymer grains and forthe resulting optimization of the supramolecular structure.

The optimization of the structure of Rolivsan in the course of thermal curing is confirmed by the results of dynamic mechanical measurements, shown in Fig. 4. It is seen that, with rising T_0, the dynamic Young modulus E' of the Rolivsan samples tends to increase, most steeply at temperatures corresponding to formation of the primary network (T_0 = 150–170°C). To establish the practically important correlation between the microstructure and the macroscopic characteristics, we examined the $<y>(T_0)$ and $E'(T_0)$ dependences.

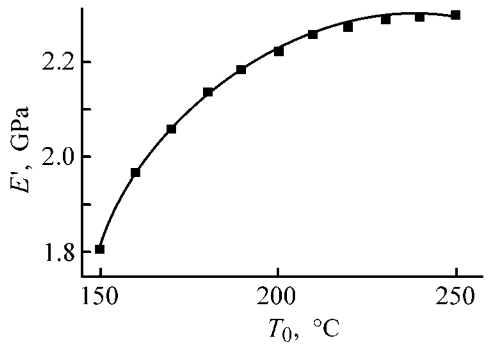


Fig. 4. Dynamic Young modulus E' of the Rolivsan samples vs. the heating temperature T_0.

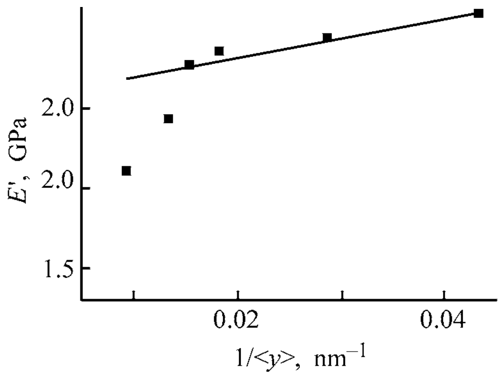


Fig. 5. Dynamic Young modulus E' of Rolivsan samples vs. the inverse average diameter $1/\langle y\rangle$ of microdomains in the course of curing.

In terms of the kinetic failure concept, the strength of a solid, σ, is determined by the characteristics of the interatomic bonds (elasticity E, equilibrium length r_0, and ultimate strain ε^*), free path length of phonons Λ, failure activation energy ΔU_0, and the time before failure τ [20–22]:

$$\sigma = \frac{Er_0\varepsilon^*}{\Lambda}\left(1 - \frac{kT}{U_0}\ln\frac{\tau}{\tau_0}\right), \qquad (3)$$

where $\tau_0 \approx 10^{-13}$ s. It can be suggested that, in amorphous substances, including polymers, phonons are scattered at the boundaries of structural (supramolecular) formations, i.e., that the parameter Λ is determined by the average diameter of the microdomains $\langle y\rangle$:

$$\Lambda \cong \langle y\rangle. \qquad (4)$$

Vettegren' *et al.* [23, 24] found that the failure and the relaxation of stresses have a common thermal-fluctuation nature, which is manifested in identical kinetic equations describing the temperature and time dependences of the strength and the Young modulus. The common nature of the processes of interest is reflected by the known empirical equation, which relates the dynamic Young modulus E' and the strength [25]:

$$E' = A\sigma + C, \qquad (5)$$

where $A \cong 0.1$ and C are empirical parameters. Taking into account Eqs. (3) and (4), we write Eq.(5) as

$$E' = \frac{0.1Er_0\varepsilon^*}{\langle y\rangle}\left(1 - \frac{kT}{U_0}\ln\frac{\tau}{\tau_0}\right) + C = \frac{B}{\langle y\rangle} + C, \qquad (6)$$

where

$$B = 0.1Er_0\varepsilon^*\left(1 - \frac{kT}{U_0}\ln\frac{\tau}{\tau_0}\right).$$

Equation (6) was tested in the E'–$1/\langle y\rangle$ coordinates, as illustrated by Fig. 5. It is seen that the experimental data can be fitted with a linear dependence represented by Eq. (6). The fact that the first two points (corresponding to T_0 150 and 160°C) fall out of this dependence is evidently due to the lower ductility (Er_0 parameter) of the polymer chain in the primary network of a weakly cured Rolivsan, compared to that in the final stage of high-temperature curing (densely cross-linked network).

CONCLUSIONS

(1) In the course of thermal curing, microdoamins in Rolivsan form statistical ensembles which can be described in terms of the reversible aggregation model.

(2) With increasing curing temperature, the statistical size distribution parameters of the domains in Rolivsan exhibit the following trends: The aggregation energy tends to grow, and the average and nucleation sizes of the microdomains, to decrease.

(3) A weak inverse proportionality was revealed between the average size of the microdomains and the dynamic Young modulus of thermally cured Rolivsan samples; it was explained in terms of the kinetic strength concept.

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