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'-divinylidiphenyl 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 ×20000 magnification.

The dynamic Young modulus of the cured Rolivsan samples in the form of 34 × 20 × 8-mm parallel-
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 $T_0$.

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. 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.

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.