EFFECT OF HYDROGEN-BOND NETWORK ON THE THERMOMECHANICAL AND RELAXATION PROPERTIES OF BLOCK COPOLYMERS


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The thermomechanical and relaxation properties of methyl methacrylate-methacrylic acid block copolymers have been investigated to study the effect of the controlled hydrogen-bond network due to the presence of carboxyl groups on the mechanical behavior of these copolymers. It has been established that the hydrogen-bond network exerts an influence even at temperatures above the glass transition point, slowing the rate of development of deformation under certain conditions in tests performed in the thermodeformation heating regime, affecting the height and location of the temperature maxima in isometric heating experiments, and reducing the initial compliance and the intensity of the relaxation process at constant temperature and load.

It has previously been shown in connection with solutions of methyl methacrylate (MM) methacrylic acid (MA) copolymers in a binary solvent capable of selective reactions that amorphous fluctuational hydrogen-bond networks actually exist even in relatively dilute solutions [1] and determine the structural-mechanical characteristics of those solutions [2]. By varying the solvent it is easy to convert such solutions either into stable rubberlike gels [3] or into low-viscosity systems. In some cases the transition from one state to the other is extremely sharp. It is all the more probable that networks of this kind affect the properties of block copolymers in the high-elastic and glassy states. In fact, copolymers capable of forming hydrogen bonds may be regarded as quasi-vulcanized. In this case the experimental data can be interpreted in terms of a superposition of two networks: the ordinary van der Waals network and the hydrogen-bond network. As a continuation of the research on solutions [1, 2] we have made a comparative study of the thermomechanical characteristics of MM + MA copolymers and pure PMM.

For investigation we selected MM + MA copolymers (20 molar %) and pure PMM with degree of polymerization $5 \cdot 10^4$. The MM was subjected to radical polymerization at 60°C in a benzene solution to obtain the most probable molecular-weight distribution ($\langle M_w / M_n \rangle = 2$). Copolymers were obtained from the starting PMM by acid hydrolysis [4]. The degree of polymerization was estimated from the intrinsic viscosity of PMM in benzene [5] and the MA content by indicator titration with alcoholic alkali against phenolphthalein.

The test films were prepared by slow evaporation of 3% solutions of the polymer in acetone. Specimens with a cross section $1.6 \times 0.06 \text{ mm}^2$ were dried in a vacuum at 60°C to constant weight and annealed at 150°C for 5 hr with subsequent slow cooling. The films were oriented by double drawing at a temperature exceeding the glass transition temperature ($T_g$) by 25°C.

The thermomechanical characteristics were investigated in the thermodeformation and isometric regimes [6]. Moreover, we investigated the deformation properties of the specimens at 20°C under constant tensile load.

The thermodeformation method makes possible a standard determination of $T_g$ from the intersection of the tangents to the temperature-deformation curve. The heating rate was 3 deg/min. The results of the measurements were recorded on the chart of an EPP-09 automatic electronic recorder. From the curves obtained at different stresses we constructed a graph showing the increase of strain rate as a function of stress.

In the isometric heating regime [7] we registered the development of internal stresses in rigidly clamped, i.e., constant-length, oriented films. These stresses are due to "defreezing" of the high-elastic strains that remains after orientation.

To study the relaxation properties we evaluated the time dependence of deformation under constant tensile load. The tests were conducted at a temperature of 20 ± 1°C on a Melentiev instrument [8, 9]. The strain measuring base (distance between instrument grips) was 50 mm, and the range of tensile deformation investigated was 0-2%.

In view of the smallness of the strains the true stress was taken equal to the value based on the initial cross-sectional area of the specimen. Before testing, each specimen was subjected to a cycle of so-called mechanical conditioning consisting of stretching under load (exceeding the load in the subsequent "working" cycles) for 1 min with subsequent recuperation until almost complete equilibrium was established. The working cycles—10 min under load followed by extended recuperation—were carried out at successively decreasing loads.

EXPERIMENTAL RESULTS AND DISCUSSIONS

The dependence of $T_g$ on copolymer composition, studied by the thermodeformation method to characterize the specimens, is presented in Fig. 1a. It can be described by the expression $T_g = 107 + 1.35 n$, where $n$ is the MA content of the copolymer in molar %, which is in agreement with the data obtained by other authors (for example, [10]) for analogous systems in a narrow range of copolymer composition.

As may be seen from Fig. 1b, the rate at which the deformation increases (at a temperature above $T_g$) for different loads and the same rate of temperature variation decreases linearly with increase in the MA content of the copolymer, since the continuous three-dimensional network due to the presence of MAA links prevents the development of deformation.

We now have sufficient information to characterize in general form the metamorphoses of the network for the MM + MA copolymer system. The fact that a network exists scarcely requires proof, such proof has already been presented in [3] (experiments on the "disappearance" of rubberlike gels on addition of DMP). At high dilutions in moderately polar media the intermolecular network has a well-expressed fluctuational character. Reducing the polarity of the solvent or increasing the concentration of polymer leads to strengthening the network and to a transition from fluctuational to real. Conversely, raising the temperature of the block copolymer promotes a transition to the fluctuational network. For a given copolymer composition the range of intermediate states can be simulated by the
Fig. 1. Thermomechanical and relaxation characteristics of block copolymers as functions of MA concentration: a) glass transition temperature; b) rate of deformation increase in the thermodeformation regime, i.e., slope of the straight line characterizing the variation of relative deformation at constant rate of temperature change as a function of the load; c) values of maximum temperature stresses in the isometric regime; d) parameter L.