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Abstract

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DEPENDENCE OF CERTAIN PHYSICAL PROPERTIES ON THE COMPOSITION OF POLYMERIZATION PRODUCTS IN A TERNARY SYSTEM OF VINYL MONOMERS

(Presented by Academician P. A. Rehbinder, January 26, 1963)

In connection with the problem of obtaining polymeric materials with prescribed properties, suitable for the photoelasticity method, pure and copolymers of three vinyl monomers were investigated: methyl methacrylate, styrene, and benzyl methacrylate. The synthesis was carried out by the method of induced polymerization in the presence of benzoyl peroxide. A prepolymer was first obtained at $t = 60$–$80°$C. Polymerization was then carried out by stepwise raising of the temperature to 35, 45, 55, 80, and 100°, until the product acquired stable properties.

Massive specimens in the form of parallelepipeds of average dimensions $5 \times 10 \times 80$ mm^3 were investigated. The composition of the polymers studied is presented in Table 1. The thermomechanical, mechanical, and optical properties of the polymer system were determined. Thermomechanical curves were recorded on a Polanyi-type dynamometer under various tensile loads. The glass-transition temperature was recorded as the result of extrapolation to zero stress. The longitudinal elastic moduli were determined using a strain-gauge clamp (^{1}). Measurement of the optical coefficients under stress was carried out on a coordinate-synchronous polarimeter KSP-5. The results obtained are presented in Table 1.

Table 1

MMA	ST	BMA	T_{st}, °C	$C_\sigma \cdot 10^7$, cm^2/kg	$E^5_{20°}$, kg/cm^2	$C_\varepsilon \cdot 10^{-3}$
100	–	–	121	−4.9	35300	−1.73
–	100	–	103	9.6	31700	3.40
–	–	100	57	66.3	1360	0.90
–	75	25	83	24.3	28100	6.84
–	50	50	75	28.7	15300	4.35
–	25	75	62	31.5	5400	1.70
33.3	33.3	33.3	75	27.5	30700	8.45

Fig. 1. "Composition–property" diagram for transition temperatures T_{st} ($\sigma = 0$)

Figure 1: Fig. 1. "Composition–property" diagram for transition temperatures T_{st} ($\sigma = 0$)

MMA	ST	BMA	T_{st}, °C	$C_\sigma \cdot 10^7$, cm^2/kg	$E^5_{20^\circ}$, kg/cm^2	$C_\varepsilon \cdot 10^{-3}$
20	60	20	83	19.1	30600	5.85
20	20	60	75	37.2	11500	4.28
60	20	20	102	12.4	26800	3.32
50	50	–	109	0.0	29100	0.0
80	20	–	119	−2.7	28000	−0.76
20	80	–	105	3.9	31200	1.22
94.6	–	5.4	–	0.0	–	0.0
89.0	–	11.0	–	2.5	–	0.56
76.6	–	23.4	95	14.5	12400	1.80
60.0	–	40.0	62	31.6	1870	0.74
30.0	–	70.0	–	44.7	–	–

It is of definite interest to characterize materials by means of the quantity C_ε, which is obtained from equality (1)

$$C_\varepsilon = C_\sigma \cdot E. \tag{1}$$

The quantity C_ε is the optical coefficient with respect to deformation, or the "quality index" of the material, since C_ε more fully characterizes the combination of mechanical and optical properties. The calculated values of C_ε are also given in Table 1. The results obtained were processed using the methods of physicochemical analysis according to N. S. Kurnakov, which makes possible a better survey of the data and analysis of the internal relationships in the system. The "composition–property" diagrams are given in Figs. 1-3. These diagrams above all give an idea of the properties of the pure polymers PMMA, PST, and PBMA.

Pure PMMA is a high-modulus polymer with a fairly high glass-transition temperature and a small negative optical sensitivity. Pure PS also has a high modulus, but the sign of the optical constant is positive. Pure PBMA is low-modulus, with a low glass-transition temperature, but with a large positive optical constant. The presence of such a difference in the properties of the pure polymers makes it possible to reveal clearly the character of the relationship between the properties and the composition of copolymers in a ternary system.

Fig. 1. "Composition–property" diagram for transition temperatures T_{st} ($\sigma = 0$)

Fig. 2. “Composition—property” diagram for E, kg/cm^2, $t = 20^\circ$

Figure 2: Fig. 2. “Composition—property” diagram for E, kg/cm^2, $t = 20^\circ$

Fig. 3. “Composition—property” diagram for $C_\varepsilon \cdot 10^{-7}$ (cm^2/kg)

Figure 3: Fig. 3. “Composition—property” diagram for $C_\varepsilon \cdot 10^{-7}$ (cm^2/kg)

Fig. 2. “Composition—property” diagram for E, kg/cm^2, $t = 20^\circ$

Fig. 3. “Composition—property” diagram for $C_\varepsilon \cdot 10^{-7}$ (cm^2/kg)

Fig. 4. Types of dependences of some physical properties of copolymers on composition

Comparing the character of the curves for the dependence of the properties studied on the composition of binary copolymers (and also of ternary copolymers when sections of the volume diagram are considered), one can see four main types of dependences (Fig. 4).

Complete or approximate additivity (curve I), as, for example, the dependence of C_ε (cm^2/kg) on the composition of MMA and ST copolymers.

A dependence showing the influence of small additions of the second component (curves IIa, b). For example, the dependence of the moduli on the composition of BMA and MMA copolymers. An S-shaped course of the curve, in which the maximum change in the property occurs in the middle part of the diagram (small additions do not exert a large influence) (curve III). For example, the dependence of C_ε (cm^2/kg)

on the composition of BMA and ST copolymers. Passage through an extremum (curve IV). For example, in the diagram for C_ε. This case is the most specific and, probably, reflects the combination of two kinds of influences, different in direction.

It follows from the foregoing that, by varying the composition of copolymers based on a multicomponent mixture of monomers, and taking into account information on the nature of the influence of the individual components, we obtain the possibility of systematically creating serial materials with the required set of mechanical and optical properties.

Fig. 4. Types of dependences of some physical properties of copolymers on composition

Figure 4: Fig. 4. Types of dependences of some physical properties of copolymers on composition

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1. N. A. Shegolevskaya, S. I. Sokolov et al., *Izv. vyssh. uch. zav.*, Machine Building, 3-4, 72 (1958).

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