EFFECT OF THE NETWORK DENSITY ON THE DEFORMATION BEHAVIOUR OF VARIOUS TYPES OF NETWORK

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The deformation behaviour of polymer networks in the case of unidirectional tension in the region of mean deformations (at a relative elongation $\alpha = 1$ to 2) is described with sufficient accuracy by the Mooney-Rivlin equation[1] $f = (C_1 + C_2/\alpha)(\alpha - \alpha^{-2})$, where f is the stress related to a non-deformed cross-section of a dry sample and C_1 and C_2 are elastic parameters whose molecular meaning is not yet clear. It has been established, in the case of networks obtained by additional crosslinking of linear macromolecules (*e.g.*, natural rubber[2,3]), that the parameter C_1 increases with the content of the crosslinking agent in principle similarly to the equilibrium modulus of elasticity; the parameter C_2, too, first increases and then passes through a maximum. On the other hand, in the case of networks prepared by copolymerization of a bi- and tetrafunctional monomer (for instance, 2-hydroxyethyl methacrylate with ethylene dimethacrylate[4-6]) it has been established that the parameter C_1 depends on the content of the crosslinking agent similarly to the former case, whereas the parameter C_2 rapidly decreases over the whole concentration range of the crosslinking agent and approaches zero roughly in the same region of C_1

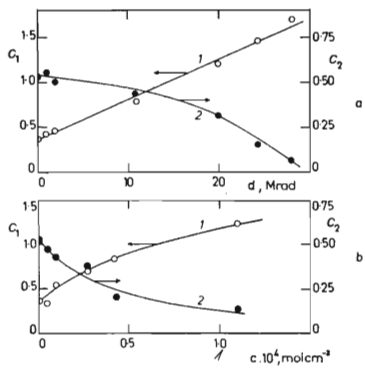

FIG. 1

Dependence of the Parameters C_1 and C_2 (kg cm^{-2}) on the Radiation Dose (*a*) or the Content of the Crosslinking Agent (*b*)

Parameter: ○ C_1, ● C_2.

values in which in the case of rubbers there is a maximum in the dependence of C_2 on C_1. It has been an aim of the present communication to demonstrate that different dependences of the parameters C_2 on C_1 (or the content of the crosslinking agent) for the above network types are probably connected with different mechanisms of the network structure formation. This is why we studied the poly(butyl acrylate) networks prepared by radiation crosslinking of the macromolecules already in existence and by copolymerization of butyl acrylate with ethylene dimethacrylate.

Poly(butyl acrylate) was obtained by polymerization during 48 hours, initiated with isopropyl percarbonate at 45°C; the polymer was insoluble in all common solvents. The samples of the series A were prepared by irradiation of poly(butyl acrylate) in a nitrogen atmosphere with γ-rays from a Co^{60} source, using doses from 0 to 30 Mrad. The samples of the series B were prepared by copolymerization of butyl acrylate with various amounts of ethylene dimethacrylate ($c = 0$ to $1 . 10^{-4}$ mol cm^{-3}) under the same conditions as samples of the series A. Prior to measurements, the samples were extracted with the mixture methanol–benzene(1 : 1) at 25°C for three days. The deformation of samples, $60 \times 10 \times 2$ mm in size, was determined optically at 25°C on a simple apparatus by applying a load to the sample for five minutes; the procedure used has been described elsewhere[4]. From the experimental deformation curves, the parameters C_1 and C_2 were determined by the least squares method[5,6].

The parameter C_1 increases with both increasing radiation doses (Fig. 1*a*) and an increasing content of the crosslinking agent (Fig. 1*b*), whereas the parameter C_2 decreases in both cases. The course of the dependence differs in both cases (Fig. 2): at the same C_1 C_2 is always lower in the case of a network prepared by copolymerization (the point with the lowest C_1 value corresponds to an uncrosslinked sample and is common for both dependences). Viscoelastic effects (the deformation values were read each time in five minutes' intervals), which affect the magnitude of the parameters C_1 and C_2 mainly in the case of a lightly crosslinked network, will probably have the same effect with both networks, and will prevailingly affect the magnitude of the parameter C_1, so that the course of the dependence of C_2 on C_1 for both networks would probably remain unchanged also for the equilibrium values of the parameters C_1 and C_2.

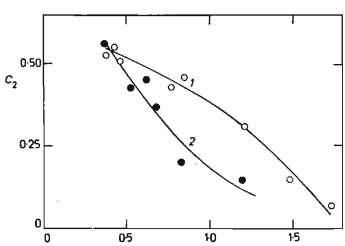

FIG. 2

Correlation of the Parameters C_2 *vs* C_1 (kg cm^{-2}) for a Network Based on Butyl Acrylate Crosslinking: ○ by radiation, ● with ethylene dimethacrylate.

The different course of the dependences of the parameter C_2 on C_1 for both networks is probably determined by a different mechanism of formation, leading to different topology of the network formed. The network prepared by radiation crosslinking contains a certain concentration of entanglements, which is determined by the initial distribution of molecular weights before crosslinking and does not change during crosslinking. In a network obtained by copolymerization the entanglements and crosslinks arise during the network formation, with the monomers present at the same time. It is known[7-9] that the content of the diluent, *e.g.* unreacted monomer, reduces both the effectivity of the crosslinking reaction and the content of entanglements; the latter decreases quicker than the concentration of the active chains in the network[10]. It can be assumed, therefore, that the radiation-pretreated network has a higher content of entanglements at the same concentration of the active chains than a network prepared by copolymerization. Since the parameter C_2 (ref.[11]) increases with increasing amount of entanglements in the network, the lower concentration of entanglements in the copolymerization network can explain the lower value of C_2 in comparison with the radiation network, as well as the total course of the dependence of the parameter C_2 on C_1 for both networks.

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