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Abstract

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THE EFFECT OF LOW-MOLECULAR SUBSTANCES SORBED BY SUPRAMOLECULAR STRUCTURES ON THE MECHANICAL PROPERTIES OF RIGID-CHAIN POLYMERS

Ideas about the structure of amorphous polymers in the condensed state as a system of entangled chain molecules led to the development of molecular mechanisms for the plasticizing action of additives of low-molecular substances introduced into such polymers, expressed by the rules of molar (^{1}) or volume (^{2}) fractions. The influence of low-molecular substances on the mechanical properties of polymers was considered in these cases at the molecular level of characterization of the phenomenon of plasticization. However, in recent times these ideas have undergone substantial changes. It has turned out that polymers are a system of highly ordered secondary structural formations (^{3}), in some cases having a strict geometric faceting similar to crystalline forms ($^{4-7}$). New data obtained on the characterization of the structure of amorphous polymers have proved very fruitful for understanding the phenomenon of plasticization of polymers by low-molecular substances that are only limitedly compatible with polymers. It was shown that the influence of precisely such low-molecular substances on the mechanical properties of polymers, which determines their plasticizing effect, is connected with the degree of disintegration of supramolecular structures in polymers. It may be supposed that the processes of disintegration of supramolecular structures in polymers have the same stepwise character as the processes of structure formation themselves. Complete destruction of all secondary structural formations is characterized by the formation of a thermodynamically stable solution (^{8}). A reduction in the brittle properties of the material in this case leads to the so-called intrapack plasticization of the polymer (^{9}). The introduction into a polymer of low-molecular substances that are limitedly compatible with it and cause destruction of secondary supramolecular formations leads to the formation of a system of molecules of such substances uniformly distributed between the primary supramolecular formations—bundles of chains. If, in this process, the brittle properties of the polymer material decrease, then the so-called interpack plasticization of the polymer takes place (^{9}). Finally, one may also envisage the existence of an initial act of disintegration, which must be characterized by disruption of contacts between secondary supramolecular structural formations. In this case the mobility of such complex formations must increase, while the amount of low-molecular substance sorbed at the contact sites must apparently be very small. The considerations set forth above were the subject of the present investigation.

The objects of the investigation were two cellulose complex esters—cellulose triacetate and cellulose nitrate. Industrial samples of cellulose esters were used, without any purification or fractionation. The cellulose triacetate contained 61.97% bound acetic acid, and the cellulose nitrate 12.16% nitrogen. As low-molecular compounds, butyl stearate was chosen for cellulose triacetate, and castor oil for cellulose nitrate. These low-molecular compounds are incompatible with cellulose esters and at the same time, as is known, substantially reduce the brittle properties of the materials.

At the same time, the mechanism of the plasticizing action of such low-molecular-weight substances with respect to polymers remained unclear. For comparison, low-molecular-weight substances that are readily compatible with cellulose esters were also used (for cellulose triacetate—1-nitro-2-methyl-2-propanol, and for nitrocellulose—dibutyl phthalate). In addition, for cellulose triacetate, tri-monochloroethyl phosphate was also used; it is only limitedly compatible with the indicated cellulose ester and the latter swells well in it. The effect of the above-listed low-molecular-weight substances on the mechanical properties of cellulose esters was determined by the thermomechanical method, widely used for investigations of this kind (10).

Solutions of low-molecular-weight substances in solvents inert with respect to the polymers under study were introduced by thorough mixing of these solutions with the polymers. The solvent for the low-molecular-weight substances used for mixing with nitrocellulose was methylene chloride, and for mixing with cellulose triacetate—diethyl ether. After removal of the solvents by heating the mixtures and subsequent vacuum treatment, tablets 10 mm in diameter and 3 mm high were pressed from the polymers themselves and from their mixtures with low-molecular-weight substances. Pressing was carried out at a pressure of 50 kg/cm^2 and at a temperature close to the glass-transition temperature of the polymer. Samples in the form of such tablets were tested on dynamometric balances under a constant load of 160 g/mm^2 over a wide temperature range. The temperature was raised at a constant rate of 2° per 1 min. As a result of the tests carried out, five series of thermomechanical curves were obtained. The glass-transition temperatures (T_c) of cellulose triacetate and of mixtures of both cellulose esters with low-molecular-weight substances were determined from the onset of bending of the thermomechanical curves (11). The glass-transition temperature of nitrocellulose itself was determined by extrapolating the linear dependence on the concentration of dibutyl phthalate in it to the ordinate axis, i.e., to zero concentration of dibutyl phthalate (12). Knowing the concentration of low-molecular-weight substances in the mixture with cellulose esters and having obtained the values of T_c for each such mixture, graphical dependences were constructed for the change in T_c of the mixtures on the concentration of low-molecular-weight products in them. These dependences for mixtures with nitrocellulose are shown in Fig. 1, and for mixtures with cellu-

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

lose triacetate—in Fig. 2. As follows from the figures presented, low-molecular-weight substances that are unlimitedly miscible with the polymer lower the T_c of the mixture to a greater extent, the higher the concentration introduced into these mixtures. Such substances are, for nitrocellulose, butyl phthalate, widely used as a plasticizer for the indicated cellulose ester, and for cellulose triacetate —1-nitro-2-methyl-2-propanol (straight lines 1 in Figs. 1 and 2). For these examples of plasticizing action the molecular mechanism is well known (1,2). Here it should only be emphasized that when such low-molecular-weight substances are introduced into the polymer, apparently, any supramolecular structures in it break down, and that in this case there is there occurs a uniform distribution of molecules of the low-molecular-weight substance among the macromolecules of the polymer.

Fig. 1. Dependence of the glass-transition temperature (T_c) of nitrocellulose on the weight content in the mixture of low-molecular-weight substances (C%). 1—dibutyl phthalate; 2 and 2′—castor oil.

Another case of the action of a low-molecular-weight substance on a polymer product is illustrated by the behavior of a mixture of cellulose triacetate and triethyl phosphate. The latter is only limitedly miscible with the indicated cellulose ester. Here, apparently, we are dealing with a mixed case of distribution of the low-molecular-weight substance both among part of the polymer macromolecules and among secondary structural formations, i.e., a real case of partial intrachain and interchain plasticization, analyzed in sufficient detail in (9). Finally, of greatest interest is the third case of action on polymers of such low-molecular-weight substances as castor oil with respect to nitrocellulose and butyl stearate with respect to cellulose triacetate, i.e., substances that are not at all compatible with the polymer. This is illustrated by curves 2 in Fig. 1 and 3 in Fig. 2. The influence of small concentrations of the indicated substances on the lowering of the T_c of cellulose esters is shown, respectively, by curves 2′ and 3′ in the same figures. In fact, the introduction into the polymer of insignificant amounts of these substances (0.05–0.1% of the weight of the polymer) sharply lowers the temperature of its vitrification. As little as 0.1% of castor oil introduced into nitrocellulose lowers the T_c of nitrocellulose by 82°, and 0.05% of butyl stearate lowers the T_c of cellulose triacetate by 60°.

Fig. 2. Dependence of the vitrification temperature (T_c) of cellulose triacetate on the weight content in the mixture of low-molecular-weight substances (C, %). 1—trimonitro-2-methyl-2-propanol; 2—trimono-chloroethyl phosphate; 3 and 3′

—butyl stearate

A further increase in the concentration of castor oil in nitrocellulose or of butyl stearate in cellulose triacetate does not affect the lowering of the vitrification temperature of the polymers. It is difficult to imagine that such amounts of low-molecular-weight substances increase the segmental mobility of chain molecules of cellulose esters, i.e., that the observed phenomenon is due to the molecular mechanism of the process of interaction of low-molecular-weight substances with the polymer. At the same time, it is most plausible to consider the processes occurring at the structural level as characteristic of this phenomenon. Probably, insignificant amounts of the low-molecular-weight substances investigated are sufficient to ensure the initial act of disintegration in polymers of large supramolecular structures, to disrupt contacts between such supramolecular formations, and thereby to increase their thermal mobility. In light of the foregoing, it is also necessary to reconsider our usual notions about the nature of the temperature point of vitrification, or, what is the same thing, softening. It is known that by this temperature point—or, more precisely, region—is meant the temperature interval in which segmental mobility of the macromolecules of a polymer arises, if it is heated, or this mobility is lost, if the heated polymer is cooled. Apparently, these notions should also be extended to the secondary structural elements of the polymer substance. Consequently, the temperature region of vitrification or softening of a polymer should be understood as that temperature region in which the mobility of the entire variety of structural elements of the polymer substance arises or disappears, beginning with the macromolecules themselves (segmental-

chain mobility) and ending with a set of secondary structural formations of the fibrillar type (mobility of chain bundles and the larger secondary supramolecular structures composed of them).

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