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ON TWO TYPES OF PLASTICIZATION OF RIGID-CHAIN POLYMERS

Plasticization of polymers is usually regarded as a technological method for increasing the elastic and plastic properties of a material, i.e., for reducing its brittleness as a result of introducing specially selected low-molecular-weight substances—plasticizers. In this process, as is known, the transition points of the polymer from one physical state to another are shifted toward lower temperatures, or the temperature interval of its highly elastic state is broadened (^{1}). In the first case, intermolecular bonds are weakened as a result of the blocking, by plasticizer molecules, of the active groups of the polymer chains responsible for these bonds; in the second case, the active groups of the links of the polymer chain responsible for imparting rigidity to the chains as a whole are blocked. Therefore such plasticization increases the flexibility of polymer macromolecules without changing the transition point from the highly elastic to the viscous-flow state.

The two mechanisms of plasticization set forth above follow from modern concepts of the model of a polymer macromolecule and its behavior under deformation (^{2}). It is not difficult to see that the indicated explanations of the plasticizing action of plasticizers are based on the molecular interaction of the components of the system: the polymer macromolecule—the plasticizer molecule. The molecular mechanism of this action is described by the rule of moles (^{3}) or, in generalized form, by the rule of volume fractions (^{4}). This interpretation of the phenomenon of plasticization is valid in all those cases where there is unlimited compatibility of the plasticizer with the polymer, i.e., when the plasticizer is soluble in the polymer. However, for rigid-chain polymers in particular, numerous cases are known of poor or even complete incompatibility of the plasticizer with the polymer. At the same time, even in such cases, by introducing low-molecular-weight substances into the polymer it is possible to reduce the brittleness of the polymeric material, which is manifested to the greatest extent at reduced temperatures and under impact loading.

One of us (^{1}) proposed that the mechanism of this third type of plasticization is due to an increase in the looseness of the packing of the chain molecules of the

Fig. 1. Thermomechanical curves of cellulose samples plasticized with guanidine thiocyanate. Amount of plasticizer by weight of the mixture: 1 –8%; 2 –10%; 3 –12%; 4 –15%; 5 –17%; 6 –18%; 7 –20%; 8 –30%; 9 –40%; 10 –50%; 11 –60%.

Figure 1: Fig. 1. Thermomechanical curves of cellulose samples plasticized with guanidine thiocyanate. Amount of plasticizer by weight of the mixture: 1 –8%; 2 –10%; 3 –12%; 4 –15%; 5 –17%; 6 –18%; 7 –20%; 8 –30%; 9 –40%; 10 –50%; 11 –60%.

polymer as a result of the introduction of low-molecular-weight substances, the improvement in the mechanical properties of the material under such plasticization being due to the manifestation of the Hookean elasticity of macromolecules. However, even these views, which are close to the truth, concerning the mechanism of action of plasticizers that are only limitedly miscible or not at all miscible with the polymer, were also based on the nature of the behavior of the chain molecules of the polymer and the molecules of the plasticizer. At the same time, in all the concepts set forth, questions of the structure of the polymeric material were ignored, although they apparently play a rather important role in the manifestation of the plasticization effect, especially in cases of plasticizers only limitedly miscible with a given polymer.

It was of interest to examine the mechanism of the plasticizing action of plasticizers in the light of modern ideas about the structure of amorphous polymers, using as an example the most rigid-chain natur—

···of a high-molecular-weight substance, such as cellulose. For this purpose an industrial sample of sulfite cellulose with an average molecular weight of about 200,000 was used. The cellulose was first converted to a powdery state by dissolving it in triethylphenylammonium oxide, followed by precipitation with a 2% solution of acetic acid. The precipitate obtained was thoroughly washed with water, then with acetone and, finally, with ethyl alcohol, and dried in a drying oven at $t = 80^\circ$ to constant weight. Low-molecular-weight compounds that mix with cellulose only to a limited extent were chosen as plasticizers; one of them (guanidine thiocyanate) mixes with cellulose somewhat better than the other (urea).

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Plasticizers were introduced into the cellulose after first dissolving them in ethyl alcohol; the cellulose impregnated with alcoholic solutions of the plasticizers of specified concentrations was kept for 2–3 days at room temperature to improve the distribution of the plasticizer in the cellulose. The samples were then dried at 60° to an air-dry state, and tablets were pressed from them at 130–140° and at a

Fig. 2. Dependence of the glass-transition temperatures T_c of cellulose on the amount of plasticizer introduced, determined from thermomechanical curves by the point at which bending begins (odd numbers) and by the point of inflection (even numbers): 1, 2—triethylphenylammonium oxide; 3, 4—rhodanide guanidine; 5, 6—urea.

Figure 2: Fig. 2. Dependence of the glass-transition temperatures T_c of cellulose on the amount of plasticizer introduced, determined from thermomechanical curves by the point at which bending begins (odd numbers) and by the point of inflection (even numbers): 1, 2—triethylphenylammonium oxide; 3, 4—rhodanide guanidine; 5, 6—urea.

pressure of 75 atm. The pressed tablets were held for 30 min under the specified temperature and pressure conditions, and then cooled. The thermomechanical curves were obtained on dynamometric balances with a variable load (^{5}). The temperature rise was regulated at a rate of 1°C per minute. The magnitude of the load on samples with large amounts of plasticizer (from 20% and above) reached 200 g/mm^2, while with small amounts of plasticizer (up to 20%) it reached 300 g/mm^2. The thermomechanical curves of cellulose plasticized with various amounts of guanidine thiocyanate (8-60% by weight) are shown in Fig. 1. The presence of polar groups in guanidine thiocyanate makes possible a certain interaction of it with cellulose, leading to limited compatibility. The existence of a plasticizing action may be judged from a certain lowering of the glass-transition temperature (T_c) of cellulose. However, this lowering of T_c is comparatively small and does not characterize the direct dependence typical of plasticizers that mix with the polymer only to a limited extent. A simple calculation showed that the plasticization effect for this plasticizer does not obey the rules of molar or volume fractions.

A similar picture is also observed in the case of plasticization of cellulose with urea, whose interaction with cellulose is still weaker.

and as a result of this the lowering of T_c of cellulose plasticized with urea is still less significant than for rhodanide guanidine. The foregoing is illustrated by Fig. 2, which shows the change in T_c of cellulose plasticized with various amounts of rhodanide guanidine and urea, in comparison with the change in T_c of cellulose plasticized with various amounts of triethylphenylammonium oxide, which we studied earlier (^{6}). As in work (^{6}), Fig. 2 gives curves for the change in T_c of plasticized cellulose as a function of the amount of plasticizer, according to the beginning of the bend on the thermomechanical curves T_{c1} (curves 1, 3, 5) and according to the point of inflection on these curves T_{c2} (curves 2, 4, 6). As was discussed in work (^{6}), the first series of curves characterizes the onset, in plasticized celluloses, of minimal chain mobility, determining the first signs of high-elastic deformation. The second series gives the values of the glass-transition temperatures of plasticized celluloses at which, at a given rate of action of the deforming forces, rubber-like elasticity of the material arises.

Fig. 2. Dependence of the glass-transition temperatures T_c of cellulose on the amount of plasticizer introduced, determined from thermomechanical curves by the point at which bending begins (odd numbers) and by the point of inflection (even numbers): 1, 2—triethylphenylammonium oxide; 3, 4—rhodanide guanidine; 5, 6—urea.

Thus, the data obtained in the present study and in the earlier work (^{6}) show that we are dealing with two sharply different types of plasticization of cellulose. In one case, introduction of the plasticizer leads to a regular lowering of T_c of cellulose, and the molecular mechanism of plasticization, as the calculations performed show, fully reflects the validity of the rules of molar and volume fractions. Such plasticization occurs in all cases of unlimited mixing of the plasticizer with the polymer, i.e., in our example, in the plasticization of cellulose with triethylphenylammonium oxide. In the other case, introduction of the plasticizer does not lead to the regularities set forth above, and the effect of plasticization cannot be explained as the result of interaction of plasticizer molecules with polymer macromolecules. Such plasticization occurs when the plasticizer does not mix without limit with the polymer, i.e., in our example, in the plasticization of cellulose with rhodanide guanidine and urea.

The effect of the plasticizing action of this kind of plasticizer seems to us fruitfully interpreted on the basis of modern ideas about the structure of amorphous polymers (^{7}). Indeed, if one accepts as correct the fact that amorphous polymers in the condensed phase consist of highly ordered secondary structural forma-

formations—bundles of highly oriented chains, then we have the right to consider two possible types of plasticization. One of these types—**intramicellar plasticization**—is realized in the case where the interaction of plasticizer molecules with the active groups of the polymer chains is greater than the intermolecular interaction in the polymer itself. The plasticizing action of such plasticizers, which mix without limitation with the polymer, leads to the destruction of any secondary structural formations in the polymer, and we are dealing essentially with a solid solution of polymer and plasticizer. The picture changes sharply if the effect of interaction of the plasticizer molecules with the active groups of the polymer chains is substantially weaker than the intermolecular interaction in the polymer itself. Then the plasticizer can interact only with molecules located on the surface of the secondary structural formations in the polymer, and such a type of plasticization should be called **intermicellar plasticization**.

The mechanical properties of polymer materials obtained as a result of intra- and intermicellar plasticization apparently also differ substantially. In intramicellar plasticization, when deforming forces are applied, we may expect a decrease in the mechanical strength of the material and a substantial increase in elongations, based on the manifestation of the highly elastic properties of the polymer, whose glass-transition point will decrease in proportion to the amount of plasticizer introduced. With such plasticization, consequently, all relaxation processes that are determined by changes in the conformations of the molecular chains will appear in the material. An increase in temperature will also lead to the realization of viscous flow, since with intramicellar plasticization the temperature of transition of the polymer from the highly elastic to the viscous-flow state is also substantially reduced. For rigid-chain polymers such as, for example, cellulose, this is the only way to bring about its transition temperatures, since these points, as is known, in the pure polymer lie above the temperature of chemical decomposition of the product (^6).

A different picture of the manifestation of the mechanical properties of the polymer will probably be obtained with intermicellar plasticization. In the ideal case of such plasticization, the glass-transition temperature of the polymer should not decrease at all in the presence of the plasticizer. Then, consequently, the mechanical strength determined by bundles of highly oriented polymer chains will remain high. At the same time, the elasticity of the plasticized polymer is determined by the Hookean elasticity of bundles possessing very high asymmetry of their shape, i.e., it will be determined by the elasticity of shape of such secondary structural formations. The indicated plasticization is apparently most advantageous for obtaining frost-resistant polymer materials possessing increased resistance to impact, i.e., for such conditions of practical use of polymer materials when the material is required to exhibit high elastic properties determined by the elasticity of shape of the structural elements of the material.

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