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Abstract

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ON THE GLASS-TRANSITION TEMPERATURE OF CELLULOSE

It is known that cellulose, which is the most rigid polymer, does not exhibit temperature transitions from one physical state to another. We suppose that this is connected with the fact that the indicated temperature points lie above the temperature of thermal decomposition of cellulose. At the same time, it is of great theoretical interest to establish by some indirect methods, if not both temperature transition points, i.e., the glass-transition temperature T_c and the flow temperature T_t, then at least the point of its transition from the glassy to the highly elastic state, T_c.

It is also known that a lowering of T_c for any amorphous polymers can be achieved by introducing plasticizing additives into the polymer. This has been shown for nitrocellulose (^{1}) and for such a synthetic polymer as polymochevina, whose molecular chains have a very rigid conformation (^{2}). Using the possibility of introducing various amounts of plasticizing additives into a polymer and constructing a graphical dependence of the change in T_c on the amount of such additives, it would seem justified to extrapolate the experimental straight line to zero concentration of plasticizer and thereby determine T_c of the polymer itself. We chose this path for determining the glass-transition temperature of cellulose.

For this purpose, ordinary sulfite cellulose, used for the manufacture of viscose fiber, with an average molecular weight equal to 210426, was used. First it was purified of resinous impurities and fats with dichloroethane in a Soxhlet apparatus for 24 hours, dried, and, to convert it into a powdery state, dissolved in a 36.5% aqueous solution of triethylphenylammonium oxide. From this solution the cellulose was precipitated with a 10% solution of hydrochloric acid, filtered off, thoroughly washed first with water, then with ethyl alcohol and diethyl ether, treated with acetone, and dried. The molecular weight of the reprecipitated cellulose was not determined by us, since it is known that the intrinsic viscosity of different types of cellulose in aqueous solutions of triethylphenylammonium oxide practically does not change during two days of standing (^{3}).

Measured amounts of triethylphenylammonium oxide were introduced into weighed portions of cellulose powder as a plasticizer in the form of its aqueous solutions. Then acetone was added to the system in amounts of 10 ml per 1 g of cellulose powder, and the samples were dried at 75° to the air-dry state.

Fig. 1. Thermomechanical curves of cellulose samples plasticized with triethylphenylammonium hydroxide. Amount of plasticizer by weight of the mixture: 1 –37%; 2 –35%; 3 –32%; 4 –30%; 5 –28%; 6 –25%; 7 –20%; 8 –10%

Figure 1: Fig. 1. Thermomechanical curves of cellulose samples plasticized with triethylphenylammonium hydroxide. Amount of plasticizer by weight of the mixture: 1 –37%; 2 –35%; 3 –32%; 4 –30%; 5 –28%; 6 –25%; 7 –20%; 8 –10%

From the mixture of powder with plasticizer, at a pressure of 100 atm/cm^2 and at a temperature of 160°, tablets were pressed, which were used to determine the thermomechanical properties of the products on dynamometric balances with variable load (^{4}). The temperature was raised at a rate of 1° over 1 min.

The results of the thermomechanical tests are shown in Fig. 1. From the bend in the thermomechanical curves, the temperature points of the glass transition of cellulose plasticized with various quan-

by triethylphenylammonium hydroxide. These points were plotted on a graph characterizing the dependence of the change in the glass-transition temperature on the amount of plasticizer (see Figs. 2, 2). By extrapolating this curve to zero plasticizer concentration, it was possible to determine the glass-transition temperature of cellulose, which is approximately 370° for this sample. However, determining T_c as the temperature at the bend of the thermomechanical curve gives us the value of those temperatures that constitute the boundary for the onset of highly elastic deformation at the given rate of application of the load. In practice, this means the beginning of the appearance of highly elastic, rubber-like properties of the polymer, and one may say that rubber-like properties in cellulose could arise only at temperatures above 370°.

Fig. 1. Thermomechanical curves of cellulose samples plasticized with triethylphenylammonium hydroxide. Amount of plasticizer by weight of the mixture: 1 –37%; 2 –35%; 3 –32%; 4 –30%; 5 –28%; 6 –25%; 7 –20%; 8 –10%

On the other hand, we are also entitled to estimate the temperature at which minimal chain mobility arises, characterizing the first signs of highly elastic deformation. This temperature correspondingly reflects the rate of relaxation processes at which any structural changes associated with chain mobility can occur. This value of T_c is determined from the bend of the thermomechanical curve, which corresponds to the classical definition of T_c for low-molecular-weight substances. For clarity, in Fig. 1, for thermomechanical curve 3, both temperature points (T_1, T_2) are indicated as an example.

Figure 2 gives both the values of T_c, determined from the beginning of the bend of the thermomechanical curves (T_1), and the temperature values corresponding

Fig. 2. Dependences of the glass-transition temperatures of cellulose T_c on the amount of introduced plasticizer (triethylphenylammonium oxide), determined from thermomechanical curves: 1—by the point of inflection; 2—by the point of bend

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to the emergence of rubber-like elasticity (T_2).

It follows from these data that rubber-like properties can arise in cellulose at temperatures above 370°, while the glass-transition temperature, below which neither manifestations of highly elastic properties nor spontaneous structural changes are possible, is 220°.

For reasons mainly of a historical nature, cellulose has always been assigned a special place among high-molecular-weight compounds in general. At the same time, cellulose, as is known, is a polymer with linear and regularly constructed molecular chains, and we pre-

it seemed very important to us to assess correctly its position among other polymers—as we would do with a newly obtained synthetic polymer product. In this case, determination of the temperatures of transitions from one physical state to another is the first initial characteristic of the properties of a polymer, and therefore determination of the glass-transition temperature seemed to us very important for understanding the properties of cellulose.

As a result of obtaining the experimental data presented above, we became convinced that the glass-transition temperature of cellulose lies approximately 40° above the temperature of its chemical decomposition, since, as is known, sufficiently intensive chemical decomposition of cellulose begins already at 180° (5). Consequently, pure cellulose itself always exists only in the glassy state. Connected with this is that complex of properties which distinguishes cellulose from the whole series of synthetic polymers, deliberately synthesized so that the transition temperatures in them are always below the temperatures of chemical decomposition. First of all, cellulose forms nonequilibrium structures with extraordinary ease, since the mobility of molecular chains in polymer glasses is negligibly small, and any action on cellulose will, naturally, change the mutual arrangement of the chains and hence the structure of the material. The circumstance that the creation of one structure or another, and especially of oriented highly ordered structures, requires the action of external forces is also connected with the glassy state.

Fig. 2. Dependences of the glass-transition temperatures of cellulose T_c on the amount of introduced plasticizer (triethylphenylammonium oxide), determined from thermomechanical curves:

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Finally, the reason for the amorphousness of cellulose also becomes elementarily clear, since no substance can crystallize at all if it is in the glassy state. When low-molecular substances capable of lowering the glass-transition temperature of the polymer are introduced, the geometrical order in the arrangement of the chain molecules that existed in pure linear polymers and that is necessary for crystallization of a polymeric substance is disrupted.

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Note: Figure translations are in progress. See original paper for figures.