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1963

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

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ON A THERMOMECHANICAL CHARACTERISTIC OF THE MOLECULAR WEIGHT OF LINEAR POLYMERS, USING NATURAL RUBBER AS AN EXAMPLE

(Presented by Academician B. A. Arbuzov, January 2, 1963)

Already in the works of Kargin and Slonimsky, and of Kargin and Sogolova ([1,2]), which initiated the investigation of polymers over a wide temperature interval by the method of thermomechanical curves, a dependence was shown of the form of these curves on the magnitude of the molecular weight. As a result of a theoretical consideration of the question, and also of an experimental investigation carried out for polyisobutylene, the possibility was shown of estimating the molecular weight of polymers on the basis of studying its thermomechanical properties. An equation was proposed that relates the magnitude of the molecular weight M to the glass-transition and flow temperatures, T_c and T_t, found under definite conditions. For practical use of this equation it is necessary to know the magnitude of the segment and two empirical constants. These quantities can be found by calculation for three different fractions of the polymer, the molecular weight of which must be determined experimentally by some independent method.

Since these quantities are determined, in order to calculate the molecular weight of any sample of the same polymer it is necessary to find, from the thermomechanical curve, the values of T_c and T_t. It should be noted that, with the low accuracy of determining these quantities, and especially their difference, the accuracy of calculating the molecular weight cannot be high, all the more so because the equation contains not the molecular weight itself, but its logarithm. Apparently, a graphical solution is simpler than an analytical one: from the data of thermomechanical investigations for different fractions of known molecular weight, one can construct a graph of the dependence of M or $\lg M$ on $T_t - T_c$.

From what has been said it is clear that the method considered is applicable only to polymers possessing high elasticity, and only to those fractions for which $T_t - T_c > 0$.

Thus, the experimentally determined quantities are T_c and T_t. Whereas finding the first of these usually presents no difficulties, determining the second is often

Fig. 1

Figure 1: Fig. 1

difficult, which is due to the very nature of the viscous flow of polymers. Plastic deformations often begin along with high-elastic deformations, and the latter may accompany viscous flow right up to the completion of penetration. The difficulty of delimiting the temperature boundaries of high-elastic and plastic deformations has led some investigators to the conclusion that it is inexpedient to introduce such a characteristic at all as the flow temperature ([3]).

At the same time, there is no doubt as to the desirability of characterizing the flow of a polymer, which is one of its most important properties, connected with the magnitude, structure, and interaction of macromolecules, from the data of ordinary thermomechanical investigations. This purpose may, to a certain extent, be served by determining the point of the end of penetration, T_k, which can easily be found from the thermomechanical curve. When the constant-load method is used, it can be determined by extrapolating the as-

branch of the curve (corresponding to viscous flow) to the level of 100% penetration. The values found in this way are usually readily reproducible. Although T_k, naturally, differs considerably from the conventionally found flow temperature T_t, it is not difficult to see that it characterizes the plastic properties of the polymer. In order for the punch to reach the base of the specimen (the bottom of the cup), it is necessary that the polymer pass into the flowing state at T_t and undergo plastic deformation during a time corresponding to the temperature interval $T_k - T_t$. The higher the viscosity of the flowing polymer, the larger this interval will be.

In any case, under unchanged experimental conditions (the shape and dimensions of the specimen cup and punch, the heating rate, and the atmospheric medium), the magnitude T_k can in a definite way characterize the viscosity of the polymer and even its molecular weight.

What has been said is confirmed by our investigations of natural rubber. By milling for different lengths of time, rubber specimens with different molecular-weight values were prepared. The thermomechanical curves of the specimens obtained, recorded under a constant load of 3.2 kg/cm^2 on an automatic recording apparatus ([4]), are presented in Fig. 1.

Fig. 1. Thermomechanical curves of natural rubber of different molecular weight; constant load 3.2 kg/cm^2.
1 –706,000; 2 –577,000; 3 –449,000; 4 –296,000; 5 –162,000; 6 –134,000.

As can be seen from Fig. 1, determination of the flow points T_t for the fractions investigated is extremely difficult. This makes it practically impossible to estimate the molecular weight from the difference $T_t - T_c$. At the same time, differences in the values of T_k for each of the specimens are quite clearly

Fig. 2

Figure 2: Fig. 2

revealed.

Special experiments showed that the value of T_k obtained is the same when the thermomechanical curve is recorded from temperatures below the glass-transition point and from room temperature. When recording from temperatures below T_c, it likewise does not change depending on the cooling regime, which affects the possibilities for crystallization of the rubber. Thus, the value of T_k characterizes the specimen quite unambiguously. As a result, it proves possible to determine the dependence of T_k on the magnitude of the molecular weight. Such a dependence is presented in Fig. 2. The values of T_k for curve 1 were found from the data of Fig. 1, and for curve 2 from an analogous series of TM curves recorded under a load of 0.64 kg/cm^2; the molecular weight was determined by the viscometric method (^{5}).

Fig. 2. Dependence of the temperature at the end of penetration T_k on the viscosity-average molecular weight.
1 —under a load of 3.2 kg/cm^2; 2 —under a load of 0.64 kg/cm^2.

These results show that from the data of thermomechanical investigations, using the value of T_k and the graph presented, one can easily determine the viscosity-average molecular weight of rubber. Thus,

the method of thermomechanical curves can be applied to the study of the efficiency of rubber rolling.

We have investigated several rubber samples from different batches, some of which had been preheated in order to carry out thermal destruction. It turned out that the values of the molecular weights found by the viscosimetric method and determined from the thermomechanical curves by the indicated method differ by no more than 5%.

The proposed method can apparently also be used for other amorphous linear polymers, provided that, when heated to the temperature of the end of penetration T_k, no substantial changes in molecular weight occur in them as a result of thermal destruction or structuring. By increasing the load on the sample one can reduce the value of T_k. In this way it is sometimes possible to avoid the temperature region where the indicated processes begin. In this case the thermomechanical curves rise more steeply, and the value of T_k can be found with greater accuracy. It should be borne in mind, however, that in this case the same differences in molecular weight will produce smaller differences in T_k, and as a result there will hardly be any gain in the accuracy of the molecular weight being determined.

We note that this method may also be applicable to crystallizing polymers, provided that the melting temperature of the crystalline phase is lower than the yield point.

Constancy of the experimental conditions is of substantial importance for the accuracy and reproducibility of the results. Especially important is strict observance of the specified dimensions of the sample, at which it tightly (although without effort) fills the cavity of the cup.

Objectivity and accuracy are ensured by recording the thermomechanical curve on an automatic apparatus directly in the coordinates deformation (penetration) —temperature.

We see the advantages of the proposed method in the fact that it has no limitations with respect to low-molecular fractions, for which the high-elastic state is not observed. It is not associated with the need to determine the glass-transition points and, in particular, the yield points, which could be a source of large errors. As a result, an accuracy is achieved that is not inferior to determinations of molecular weight from the viscosity of a solution. It should be noted that the determinations are relatively rapid: an experiment requires no more than 1–2 hours. The use of a calibration graph eliminates the need to carry out laborious calculations and constructions.

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Academy of Sciences of the USSR

Received
27 XII 1962

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