PHYSICAL CHEMISTRY

B. P. SHTARKMAN, S. S. VOYUTSKII, Academician V. A. KARGIN

1963

SovietRxiv

Fig. 1. Dependence of the work of autohesion on time for polyvinyl chloride plasticized with dibutyl sebacate. 1—50°, 2—60°, 3—75°, 4—100°, 5—125°, 6—150°

Figure 1: Fig. 1. Dependence of the work of autohesion on time for polyvinyl chloride plasticized with dibutyl sebacate. 1—50°, 2—60°, 3—75°, 4—100°, 5—125°, 6—150°

Abstract

Full Text

PHYSICAL CHEMISTRY

B. P. SHTARKMAN, S. S. VOYUTSKII, Academician V. A. KARGIN

ON THE MOLECULAR MECHANISM OF AUTOGHESION OF POLYMERS WITH AN ORDERED STRUCTURE

The phenomenon of autohesion (self-adhesion), which underlies the welding of polymeric materials, has been widely studied by a number of authors. A review of these studies is given in (^{1}). Studies by Voyutskii and co-workers (^{2}) showed that the process of autohesion of polymers is diffusional in nature and is connected with the chain structure and flexibility of polymer molecules. The principal objects in the study of autohesion were, in the overwhelming majority of cases, elastomers, chiefly rubbers. It was found that with increasing duration of contact the autohesion first increases rapidly, and then ever more slowly, tending toward a certain limiting value, and that with increasing contact temperature the autohesion increases according to an exponential law. These facts indicate the diffusional character of the process. The dependence of autohesion on polarity, molecular weight, polydispersity, branching of molecules, and the presence of spatial structures in the polymer was also studied. The influence of these factors on autohesion can be explained on the basis of the diffusional character of the formation of an autohesive joint.

Fig. 1. Dependence of the work of autohesion on time for polyvinyl chloride plasticized with dibutyl sebacate. 1—50°, 2—60°, 3—75°, 4—100°, 5—125°, 6—150°

At the same time, the question of the role of diffusion processes in autohesion is considerably complicated in connection with modern views on the structure of polymers. The concepts of the bundle-like structure of polymers, developed by Kargin, Kitaigorodskii, and Slonimskii (^{3}), are now confirmed by numerous experimental data relating to the most varied properties of polymers. The

Figure 2

Figure 2: Figure 2

concept of an ordered structure of polymers must inevitably lead to a refinement of the mechanism of adhesion and autohesion. It was of great interest to investigate the main features of autohesion of polymers possessing various supramolecular structures in order to elucidate the influence of these structures on the conditions of formation of an autohesive bond. On the other hand, it was of interest to establish the possibility of using autohesion to study the mobility of macromolecules entering into these structures.

For the investigation, polyethylene (PE) and polyvinyl chloride (PVC) were used, the latter containing different amounts of dibutyl sebacate (DBS) as plasticizer. PE specimens were prepared from film obtained by the extrusion method, followed by doubling with fabric (percale) at a temperature of 140°. PVC specimens were prepared by rolling, followed by doubling the film with fabric at a temperature of 160°. Before the determination of adhesion, the specimens were pressed together in pairs between na-

heating plates under a pressure of 0.5 kg/cm^2 and held for a specified time at the prescribed temperature. Separate experiments showed that applying a pressure above 0.2 kg/cm^2 does not lead to a further increase in the work of delamination. The work of autohesion was determined by the delamination method (1). Delamination was carried out on a tensile-testing machine at a rate of 100 mm/min at room temperature. We investigated the dependence of the work of autohesion during delamination on the duration of contact, on temperature, on the amount of plasticizer introduced, on heat treatment, etc.

The effect of the duration of contact on the work of autohesion was studied at different temperatures. In Fig. 1, as an example, semilogarithmic curves are given for the dependence of the work of autohesion (A) on time (τ) for plasticized PVC. An interesting feature of this dependence is the fact that, at temperatures below 60°, it is described by an equation of the form

$$A = A_0(1 - e^{-\kappa\tau}), \tag{1}$$

where A_0 and k are constants for the given polymer and the given temperature. Above 60° for PVC plasticized with DBS, this regularity is violated. For polyethylene the same dependence holds up to a temperature of 100°.

Fig. 2. Dependence of the work of autohesion on temperature for polyvinyl chloride plasticized with various amounts of dibutyl sebacate (in parts by weight per 100 parts PVC).
1—10 h; 2—20 h; 3—30 h; 4—40 h; 5—50 h; 6—60 h.

For polyisobutylene it was found (4) that the dependence of the work of autohesion on temperature follows an exponential law, the activation energy of the process having a value characteristic of diffusion processes in this polymer —about 2800 cal/mol. In studying the temperature dependence of the work of autohesion for polyethylene and plasticized polyvinyl chloride, we obtained the curves shown in Figs. 2 and 3. It is evident from the graphs that the dependence in the coordinates $\lg A - 1/T$ is expressed by curves having two rectilinear sections. For PVC plasticized with DBS, the transition section on the curves lies at approximately 60°. The activation energy at temperatures below 60° is 50-90 kcal/mol (depending on the plasticizer content), while at temperatures above 60° it ranges from 12.1 to 14.8 kcal/mol.

Comparison of the time and temperature dependences permits some conclusions to be drawn about the nature of the autohesion process for polymers with an ordered structure. First of all, attention is drawn to the fact that autohesion begins to appear only at temperatures far exceeding the glass-transition temperature as determined by the thermomechanical method. Thus, for example, for PVC plasticized with DBS, the glass-transition temperatures lie in the range from −40° to +30°, depending on the plasticizer content, while autohesion begins to appear to a noticeable extent only at 45°. For polyethylene this interval is even larger. The only reason for this phenomenon may be the presence of strong supramolecular structures that hinder the free diffusion of macromolecules, or even of their segments. At the same time, the assumption that autohesion can occur through dif-

fusion of entire supramolecular formations, is unlikely, since such a process would require enormous activation energies. Hence it follows that, in order for an autohesive bond to form between two layers of polymer, preliminary detachment of macromolecules from the supramolecular structures is required.

From the data we have obtained it follows that above the glass-transition temperature, i.e., in the highly elastic state, ordered structures are still retained; noticeable destruction of these structures begins only at a higher temperature. This fact leads one to suggest that at the glass-transition temperature the kinetic energy of thermal motion is already sufficient for the individual flexibility of molecules to begin to manifest itself, which also affects the flexibility of supramolecular formations (collective flexibility). At the same time, it is still insufficient for the destruction of the primary supramolecular formations (bundles), accompanied by the detachment of individual macromolecules. This proposition helps to refine the concept of the glass-transition temperature (more precisely, interval) as a temperature region in which segmental mobility of polymer macromolecules arises. The presence of segmental motion, apparently, up to a certain limit is not necessarily associated with the exit of a molecule, or at least of a significant part of it, beyond the limits of the bundle. The process of detachment of macromolecules proceeds with a high activation energy, far exceeding the activation energy of diffusion processes in the polymer. Up to a certain temperature limit (in the case of PVC plasticized with DBS—up to 60°), the rate of this process determines the course of the process of formation of the autohesive bond.

Figure 3. Dependence of the work of autohesion on temperature for polyethylene. 1—low-pressure polyethylene, 2—high-pressure polyethylene.

Figure 3: Figure 3. Dependence of the work of autohesion on temperature for polyethylene. 1—low-pressure polyethylene, 2—high-pressure polyethylene.

Fig. 3. Dependence of the work of autohesion on temperature for polyethylene. 1—low-pressure polyethylene, 2—high-pressure polyethylene.

In this connection, the fact becomes understandable that the dependence of A on τ up to this temperature limit is expressed by equation (1), which is an equation of a monomolecular reaction, i.e., analogous, for example, to the equation of radioactive decay. In the present case it is easily derived if one assumes that the rate of formation of the "nodes" of the bond between the layers is proportional to the number of free molecules, i.e., molecules that have detached from the bundle. Using this dependence, one can estimate the half-life period of the structure. In the case of PVC containing 60 parts of DBS per 100 parts of PVC, the half-life period, for example at 60°, is 32 minutes, which, incidentally, is of the same order as the duration of the experiment.

On the basis of the facts presented, some conclusions may also be drawn concerning the mechanism of autohesion of polymers with an ordered structure. Apparently, in the contact zone of two polymer layers there occurs a restoration of its structure characteristic of any region in the bulk. This restoration takes place through the diffusional transition of macromolecules from bundles located in one layer to bundles located in the other layer. The transition is accomplished during thermal fluctuations of the bundle. A bundle is a fluctuational formation with a very long lifetime; however, upon reaching a certain temperature (above the glass-transition temperature), the lifetime of the bundle, or, more precisely, the duration of the "sedentary life" of a molecule in the bundle, becomes comparable with the observation time. Thus, a necessary condition for the formation of an autohesive bond is the occurrence of structural decay. The bond is effected by···

through the local restoration of the structure in the plane of contact. In the limiting case, with complete restoration of the structure, cohesive strength should be attained.

On the basis of the considerations presented, one can explain the temperature of the "second softening," which was found on the thermomechanical curves of plasticized PVC (^{5}), as the temperature at which the lifetime of supramolecular structures becomes commensurate with the duration of the experiment. The temperature dependence of A for PE also agrees with the data of an X-ray study (^{6}), which showed that in the temperature range of 100–120° a sharp increase is observed in certain unit-cell parameters, associated with the onset of the breakdown of structures proceeding by a stepwise mechanism. First, monocrystalline formations disintegrate into ribbons, which then break down into simpler, primary forms of supramolecular formations (bundles). The data we have obtained make it possible to trace the stepwise breakdown of structures all the way to the detachment of individual macromolecules.

It is important to note that determining the work of autohesion and its dependences on temperature and time may, in a number of cases, become a convenient method for studying the mobility of macromolecules and the stability of supramolecular structures.

Received
13 V 1963

LITERATURE CITED

[1] S. S. Voyutskii, *Autohesion and Adhesion of Polymers*, 1960.
[2] S. S. Voyutskii, Yu. L. Margolina, *Uspekhi khim.*, **18**, 449 (1949).
[3] V. A. Kargin, A. I. Kitaygorodskii, G. L. Slonimskii, *Koll. zhurn.*, **19**, 131 (1957).
[4] S. S. Voyutskii, V. M. Zamazii, *Koll. zhurn.*, **15**, 407 (1953).
[5] V. A. Kargin, G. L. Slonimskii, L. Z. Rogovina, *Koll. zhurn.*, **19**, 124 (1957).
[6] Li Li-shen, N. S. Andreeva, V. A. Kargin, *Vysokomolek. soed.*, **3**, 1238 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.