PHYSICAL CHEMISTRY

S. A. ARZHAKOV, E. E. RYLOV, G. L. SLONIMSKII, and B. P. SHTARKMAN

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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE QUESTION OF THE ROLE OF THERMAL DESTRUCTION IN THE PROCESSES OF PRESSING MONOLITHIC SOLIDS FROM POWDERED POLYMETHYL METHACRYLATE

(Presented by Academician V. A. Kargin, March 17, 1962)

1. Regularities in the Preparation of Transparent Specimens

In processing polymeric materials, the usual task is to obtain monolithic articles that retain their dimensions and shape under service conditions. Of great importance is the case of obtaining transparent articles from powders. Earlier ([1,2]) it was shown that, when powdered and granulated amorphous polymers are pressed, there exists a region of temperatures and pressures in which it is possible to obtain transparent specimens that do not lose transparency upon subsequent annealing above the glass-transition temperature of the polymer (the so-called region of true pressing). Specimens pressed outside this region become opaque upon annealing. On passing into the region of true pressing (for example, at constant pressing pressure), a decrease in the loss of transparency as a result of annealing is observed, up to the preservation of complete transparency. In Fig. 1, curve 1 shows the change in transparency of specimens before and after annealing. The specimens were pressed by the procedure described in ([1]).

Fig. 1. Dependence of the loss of transparency (1) and of the change in molecular weight (2) on the pressing temperature. $P_{\text{pr}} = 50$ kg/cm^2, annealing time 1 hour. Annealing temperature $= T_g + 30°$. $\Delta S/S$ –loss of transparency, $\Delta M/M$ –change in molecular weight, t_{pr} –pressing temperature.

It is evident that the loss of transparency of specimens during annealing is a measure of the relaxation of stresses in the deformed grains of the polymer dur-

Fig. 2. Dependence of the molecular weight of specimens on pressing temperature. M —mol. wt.; t_{pr} —pressing temperature

Figure 2: Fig. 2. Dependence of the molecular weight of specimens on pressing temperature. M —mol. wt.; t_{pr} —pressing temperature

ing pressing. If this relaxation has proceeded completely, no loss of transparency is observed during subsequent annealing. If, however, relaxation of the stresses under pressure has proceeded only partially, then the stresses remaining in the polymer grains relax during annealing with partial restoration of the original shape of the grains, and the specimen correspondingly loses transparency. With an increase in pressing pressure, the rate of the relaxation processes decreases, and therefore the curve of transparency loss, as the experiments showed, shifts toward higher temperatures.

Consequently, the formation of a monolithic solid from powdered polymethyl methacrylate under the action of pressure and temperature is determined, first of all, by relaxation processes in the deformed polymer grains under pressure. The region of true pressing proves to be the region of temperatures and pressures in which the pressing process is accompanied by complete relaxation of the stresses that have arisen.

2. Mechanism of Relaxation Processes and Monolithization during Pressing of Polymethyl Methacrylate

The data shown in Fig. 2 on the dependence of the molecular weight (by viscosity) of pressed specimens on the pressing temperature at a pressure of 50 kg/cm^2 show that above 130° the molecular weight of the polymer begins to decrease as a result of thermal-destruction processes. However, because of the high viscosity of the polymer under pressure at temperatures below the interval of transition to the visco-fluid state, the process of combination of macroradicals formed during thermal destruction is impeded. In the visco-fluid state (above temperatures of 170–180°), the macroradicals formed acquire comparatively high mobility and, consequently, can combine with one another. As a result, at temperatures of 190–230° the molecular weight increases. Above 230° the destruction process proceeds mainly by chain scission of macromolecules with the formation of gaseous monomer ([3]), which is readily observed during pressing by the formation of bubbles in the specimens. From the data of Fig. 2, the change in the molecular weight of the polymer as a function of the pressing temperature of the specimens was calculated.

Fig. 2. Dependence of the molecular weight of specimens on pressing temperature. M —mol. wt.; t_{pr} —pressing temperature

The difference between the initial molecular weight and the molecular weight at 190° was taken as 100%, and from this value the relative change in molecular weight at the corresponding temperature was calculated. This dependence of

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

the relative change in molecular weight on pressing temperature is shown in Fig. 1 (curve 2). This curve practically coincides, over the entire compared temperature interval, with the curve

$$\frac{\Delta S}{S} = f(T_{\text{pr}}),$$

which determines the dependence of the loss of transparency on pressing temperature. In our opinion, this indicates that relaxation of the stresses arising during pressing is accompanied by rupture of the C–C bond.

Figure 3 gives curves of the relative change in specimen height during annealing (the so-called annealing curves) for different constant residence times of the polymer under the experimental conditions. The specimens were pressed from polymethyl methacrylate (mol. wt. 420000) at a pressure of 125 kg/cm^2. The annealing curves run parallel over a considerable temperature range. It was found that the dependence of the logarithm of the pressing time on the reciprocal temperature corresponding to the transition of the curve to the horizontal section is linear over the entire range of times compared. Calculation of the activation energy from the given dependence yielded a value of 75 kcal/mole, which agrees well with the value of the C–C bond energy. This unexpectedly high activation energy of the process once again confirms that relaxation of stresses during pressing of polymethyl methacrylate proceeds with rupture of the C–C bond. The same value of the activation energy was obtained by calculating it from data on the dependence of the loss of transparency on pressing temperature for different residence times of the polymer under the experimental conditions. From the parallelism of the annealing curves up to their transition to the horizontal section, it follows that any degree of monolithization of this polymer is characterized by the above value of activation energy, which confirms the active role of destruc-

tion in the mechanism of stress relaxation during the formation of a solid monolith from polymethyl methacrylate.

It could be assumed that the processes leading to deterioration of macroradical recombination in the polymer should also affect the position of the annealing curve. Indeed, the addition of a small amount of inhibitor (0.22% diphenylpicrylhydrazine) to the polymethyl methacrylate powder shifts the annealing curve into the region of higher temperatures (Fig. 4). Hence

Fig. 3. Dependence of the change in specimen thickness during annealing on the pressing temperature (annealing curves). Holding time at the experimental

temperature: **1** –360; **2** –120; **3** –15; **4** –5 min. $\Delta h/h$ –change in specimen thickness, t_{pr} –pressing temperature

Fig. 4. Dependence of the change in specimen thickness during annealing of pure polymethyl methacrylate (**1**) and with the addition of diphenylpicrylhydrazine (**2**) on the pressing temperature. $\Delta h/h$ –change in specimen thickness, t_{pr} –pressing temperature

it follows that the addition of an inhibitor, which leads to the destruction of macroradicals formed during thermal degradation, hinders the process of forming a monolith from powdered polymethyl methacrylate. Apparently, the recombination of macroradicals at the points of contact between polymer particles plays an essential role in the monolithization process of the specimen.

Thus, in the formation of transparent monoliths from powdered polymethyl methacrylate by pressing, the decisive role is played by thermal degradation of the polymer under conditions of elevated pressures and temperatures.

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