The effect of external pressure on the amount of carbon dioxide sorbed by specimens of polymethyl methacrylate and on the strength of the specimens after removal of the pressure during the initial period of desorption has been experimentally investigated. The experiments were conducted at 20°C, the pressure varied from 20 to 56 bar.

When an attempt was made to use Plexiglas windows in a chamber containing boiling carbon dioxide [1] it was noted that numerous bubbles of the order of a millimeter or less in diameter appeared in the unloaded material after an extended period of operation. These were distributed over a layer several millimeters thick on the inside face. The pressure in the experiments was 63-73 bar.* The formation of the bubbles is associated with the high degree of supersaturation of the polymethyl methacrylate (PMMA) with gas after removal of the pressure and proceeds at a specimen temperature of about 40°C.

The excess of sorbed gas may gradually escape from the PMMA without disturbing the macroscopic homogeneity of the specimen. The growth of existing microscopic cavities associated with loose molecular packing and fluctuations requires satisfaction of certain conditions. Firstly, the excess gas pressure \( \Delta p \) must exceed the compressive force of the surface tension. In the simple case of a spherical cavity of radius \( r_0 \) this condition takes the form

\[
\Delta p > 2\sigma/r_0.
\]

Here, \( \sigma \) is the surface tension at the solid phase–gas boundary. Secondly, the medium must possess sufficient fluidity for a bubble satisfying condition (1) to be able to grow to macroscopic size during the observation time \( t \). The radius of the bubble \( r \) at time \( t \) is given approximately by the expression

\[
\ln \frac{r}{r_0} = \frac{\Delta p t}{4\eta},
\]

obtained in a particular case from the differential equation of bubble dynamics [2]. Here, the viscosity \( \eta \) is assumed to be the only factor restraining bubble growth under the influence of the excess internal pressure. Taking \( r_0 = 10^{-6} \text{ cm} \), \( r/r_0 \approx 10^4 \), \( \Delta p \approx 10^2 \text{ bar} \), and \( t \approx 10^4 \text{ sec} \), from Eq. (2) we obtain \( \eta \approx 3 \cdot 10^{15} \text{ P} \). At greater viscosities the bubbles cannot grow to visible size in the time indicated.

The supersaturation of the unloaded specimen is gradually relieved as a result of desorption of the gas; accordingly, the appearance of bubbles cannot be anticipated at substantially high values of \( t \). However, a rise in temperature may considerably accelerate bubble growth by reducing the viscosity \( \eta \).

The fact that bubbles are detected in saturated PMMA at 40°C is evidence of the plasticizing effect of the sorbed gas and a lowering of the glass transition temperature \( T_g \) of the specimens (for PMMA [3] \( T_g \approx 100^\circ \text{C} \), \( \eta_g \approx 10^{15} \text{ P} \)).

*We recall that 1 bar = 10^8 dyn/cm^2 = 1.019 kgf/cm^2.
TABLE 1. Density of Carbon Dioxide (g/cm³) Sorbed at 20°C and Various Gas Pressures $p_1$ in the Chamber

<table>
<thead>
<tr>
<th>$p_1$ bar</th>
<th>$\rho$</th>
<th>$\rho^*$</th>
<th>$\rho_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.041</td>
<td>0.042</td>
<td>0.120</td>
</tr>
<tr>
<td>30</td>
<td>0.068</td>
<td>0.097</td>
<td>0.277</td>
</tr>
<tr>
<td>40</td>
<td>0.097</td>
<td>0.170</td>
<td>0.485</td>
</tr>
<tr>
<td>50</td>
<td>0.140</td>
<td>0.211</td>
<td>0.603</td>
</tr>
</tbody>
</table>

Note: $\rho$ is the density of the CO₂ outside the specimen; $\rho^*$ is the partial density calculated for the entire volume of the specimen; $\rho_e$ is the effective density in the "free volume" of the PMMA, which is assumed equal to 0.35 of the total volume [3]. The density of CO₂ at the liquid–vapor critical point is 0.468 g/cm³.

The liberation in the polymer of a gas phase recalls the behavior of an ordinary aerated liquid. There is also an analogy with the effervescing of a pure superheated liquid [4, 5]. In all these cases an important consideration is the nature of the nucleating centers of the new phase. Apparently, in polymers below the glass transition point, the largest of the micropores associated with loose packing of the molecules serve as nuclei. The pores have a complex configuration. Their subsequent evolution is determined by several factors—the partial pressure of the gas, the viscoelastic stresses in the medium, surface tension, and intermolecular and intramolecular forces. The development of gas cavities in the specimen is facilitated if a tensile stress $\sigma_n$ is applied.

Since the cavities, which usually grow in the form of cracks, weaken the material, the presence of a high degree of supersaturation with gas should reduce the breaking stress for a given test duration.

We have conducted experiments on PMMA. The starting sheet material was factory-made. The object of the first series of experiments was to estimate the amount of dissolved carbon dioxide at different gas pressures on the specimens and to investigate the desorption kinetics after removal of the excess pressure.

From a sheet of polymethyl methacrylate 3 mm thick we cut plates measuring $4 \times 5 \text{ cm}$. These were weighed and placed in a steel chamber. Then carbon dioxide was admitted from a cylinder. The specimens were held for three days at room temperature (20°C) and constant pressure $p_1$. After releasing the pressure, we removed the plates from the chamber and weighed one of them systematically on an analytical balance. At $p_1 = 40$ bar the specimen lost 25% of the sorbed gas in 7.5 h and 50% in 60 h. Desorption is not described by a diffusion equation with a constant diffusion coefficient. If in the above example we take the weight loss in the first 1.5 h of the process, then the effective diffusion coefficient $D^*$ is $18 \cdot 10^{-7}$ cm²/sec. Increasing the interval to 89 h leads to a value $D^* = 0.7 \cdot 10^{-7}$/cm². This may indicate the existence of different physical conditions for the carbon dioxide molecules in the polymer (occupation of large and small pores, penetration of the polymer network).

Under pressure the PMMA absorbs a great deal of carbon dioxide from the gas phase without an appreciable change in the volume of the specimen. For example, at $p_1 = 50$ bar the weight of the plate increased

Fig. 1. Shape of specimens.

Fig. 2. Strength of PMMA as a function of the carbon dioxide pressure for gas-saturated specimens. The specimens were tested at atmospheric pressure.