EFFECT OF GAS DIFFUSION ON CREEP BEHAVIOR OF POLYCARBONATE

H. HOJO and W. N. FINDLEY

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Effect of Gas Diffusion on Creep Behavior of Polycarbonate

Hidemitsu Hojo* and William N. Findley

Division of Engineering,
Brown University,
Providence, R.I.

Summary

Biaxial tension-tension creep experiments were performed to study the effect of gas diffusion on creep behavior of polycarbonate. Experiments were conducted on a thin-walled tubular specimen by applying both gas pressure and axial tension at room temperature, and measuring axial strain and gas absorption. It was found that the creep deformation was highly affected by the solubility controlled gas, carbon dioxide. The absorption measurements showed that the gas absorption behavior was clearly affected by the creep deformation of the material. Also an anomalous diffusion type behavior appeared even in permanent gas-polymer systems under creep conditions. The modified superposition principle satisfactorily predicted the recovery following creep. The axial creep for the biaxial tension-tension experiments were also computed from data previously reported for creep under combined tension and torsion of a different sample of polycarbonate.

*Present address: Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan.
Introduction

A number of papers and data concerning the permeation of gases through plastic membranes [1-4] and the penetration of organic vapors into polymers [1,5,6] have been published, but little information is available on the effect on creep of diffusing gases or vapors other than water vapor [7]. The permeation of gases and vapors through plastic materials is regarded as a combination of three processes, that is, as a process in which the gas first dissolves on one side of the material then diffuses through the material to the other side, and there evaporates out. For permanent gases, in general, their solubility is proportional to the partial pressure of the gas above the material, that is Henry's law, and the diffusion process obeys Fick's law. According to Fick's law, the rate of transfer of a diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section. The proportionality constant is called the diffusion coefficient.

Therefore, the permeation of gases depends on both the diffusivity and the solubility of gases for the material. Thus the permeability equation is given by

\[ Q = DS \frac{p_1 - p_2}{a} \]

where \( Q \) is the amount of gas passing through unit area per sec., \( D \) is the diffusion coefficient, \( S \) is the solubility coefficient and \( p_1 \) and \( p_2 \) are the partial pressures of the permeating gas at the two sides of the material of thickness \( a \). It is known that the size of a gas molecule determines the diffusion rate. The solubility of the following gases is generally in the order of \( CO_2 > O_2 > N_2 > H_2 > He \) for rubbers and plastics. But, gases such

Numbers in square brackets refer to the references at the end of the paper.
as carbon dioxide do not always behave ideally in their dependence of solubility on pressure [8]. On the influence of straining [9,10], it was found that a considerable increase in permeability was effected by straining for polystyrene, polyethylene and polypropylene films, while polyethylene terephthalate and rubber films did not show this effect. However, there is no known information on the simultaneous behavior of both the creep of solid plastics and the diffusion of permanent gas into the material under relatively high pressure.

The objective of the present investigation is to obtain information on how an absorbed gas affects the creep behavior of plastics and how absorption is affected by creep deformation. For this purpose, biaxial creep testing was conducted on a thin-walled polycarbonate tube by applying both internal gas pressure and axial tensile load at room temperature and 50 per cent R.H.

Materials and Specimen

The polycarbonate employed in this investigation was from the same lot of material as that used in a previous study [11]. However, it was taken from an extruded plate instead of a rod and annealed in air instead of oil. This material, called Zelux, was produced by Westlake Plastics, and supplied by the Lawrence Radiation Laboratory. The intrinsic viscosities measured in methylene chloride for this material were about 0.50, implying a molecular weight of 25 to 30 x 10^3. The material was extruded as 2 by 10 inch bars. The specimen was cut parallel to the direction of extrusion and before final machining it was annealed in air. The annealing cycle was 9 hr. heating from 80°F to 260°F, held at 260°F for approximately 5 hr. and returned to 80°F over a 9 hr. period. Tensile strength of this type of material is about 8600 psi. Except for one test with Freon* all tests reported were performed on the same specimen. The

*The test with Freon was performed on the same specimen employed in [11].
specimen was machined and finished to the shape of a thin-walled tube with
enlarged threaded ends. The overall length of the specimen was 8.0 in. and
the gage length was 3.98 in. The average outside diameter of the test section
was 0.9987 in. and the average wall thickness was 0.03929 in. The maximum
device from the average thickness was 2 per cent. The specimen used in a
preliminary test with Freon had an average wall thickness of 0.05975 in. The
ends of the tube were sealed by end plugs and O-rings.

Experimental Apparatus

The creep testing machine employed for this investigation was the same
as described in [12] except that no provision was made for torsion. It was
equipped to subject a tubular specimen to combinations of tension and internal
pressure as shown in Fig. 1. Crossed knife edge shackles were used at both
d ends of the specimen to achieve axial alignment. The knife edges were adjusted
to minimize bending by using a special bending detector described in [12]. Axial
strain was measured over a 4-inch gage length by means of an instrument employ-
ing a one-inch differential transformer and a matched transformer for refer-
ence [12]. The core of the reference transformer was adjusted to null balance
by means of a micrometer screw which served as the strain read-out device. The
sensitivity of strain measurement was \( 2.5 \times 10^{-6} \) in/in.

The tests were performed in a room maintained at a temperature of
75 ± 0.5°F and 50 ± 1 per cent R.H. [13]. A thermal shield was placed around
the specimen area to further reduce the temperature fluctuation.

Figure 2 shows the apparatus for gas pressure supply and control.
The internal pressure was supplied from a gas cylinder A Fig. 2 to the inside of
a specimen H through copper tubing F with connections of Sewagelok. Gas pres-
sure was maintained constant with an accuracy of ± 0.2 psi. by means of a
pressure controller B during the test periods, and measured by use of a
Heise gage $P_3$ Fig. 2. The gas flow volume was determined by using a U-tube
c with a glass capillary D filled with machine oil.

Experimental Procedure

Gases used in this experiment were helium, air, nitrogen, carbon
dioxide and Freon-22. Some properties of these gases are listed in Table I.
The upper level of test pressure was chosen to be about 10 atm. This choice
was consistent with industrial application and the properties of gases used.

The experimental procedure was as follows:

1. Before testing the air inside the tubing and specimen was replaced by the
testing gas.

2. All valves were then closed and the gas pressure was regulated to a value
nearly as high as the test pressure by a valve $V_1$.

3. Then $V_2$ was opened, gas was supplied to the system and then $V_2$ was closed
again. The pressure was then maintained by controller B for 15 minutes or
so before loading the specimen.

4. The internal pressure and tensile load were applied simultaneously, by
opening $V_4$ and applying the required weights to a scale pan on the loading
lever.

5. Immediately after loading the strain measurement was initiated and continu-
ed for two hours.

6. At 4.5 minutes after loading $V_4$ was closed and both $V_5$ and $V_6$ were opened
to measure the gas flow volume.

7. After two hours under load the tensile load and the internal pressure were
removed simultaneously. The pressure was released by closing $V_5$ and $V_6$
and then opening $V_3$ and $V_4$. 
8. Strain readings were recorded during recovery at least until the strain approached the strain prior to the test within $20 \times 10^{-6}$ in./in. for most tests.

It was observed that the final strain during recovery was often less then the final strain in the previous test. In some tests a positive strain greater than $20 \times 10^{-6}$ in./in. remained. The positive strain remaining prior to the following tests was 60, 50, 80, 90, 35, 35, $40 \times 10^{-6}$ in./in. for tests 4, 5, 17, 18, 20, 21, 23 respectively. Over the entire series of tests the specimen showed a shrinkage of $180 \times 10^{-6}$ in./in..

In a preliminary experiment, a check was made of the effect on the axial strain of the heat generated by compressing the gas. The axial strain increased immediately after pressurization and then decreased gradually. It took about 30 to 40 minutes for the thermally induced strain to stabilize.

For this reason, an aluminum cylinder with a diameter nearly equal to the bore of the specimen was inserted inside the specimen to quickly absorb the heat generated and reduce the volume of gas compressed, and hence the amount of heat generated.

Two overlapping series of tests were made. In one the circumferential principal stress $\sigma_2$ was constant at $\sigma_2 = 1000$ psi. while the axial principal stress $\sigma_1$ was changed so that $\sigma_1/\sigma_2 = 1, 2, 3$ respectively. In the other $\sigma_1$ was constant at $\sigma_1 = 3000$ psi. while $\sigma_2$ was changed such that $\sigma_1/\sigma_2 = 1, 2, 3$ respectively. The radial principal stress in all cases varied from a compression equal to the internal pressure at the inner surface to zero (atmospheric pressure) at the outer surface. The radial principal stress $\sigma_3$ at the inner surface for the first series was constant, $\sigma_3 = -85.4$ psi. In the second series the internal pressure (= $-\sigma_3$) was 85.4, 128.1 and 256.2 psi.
for $\sigma_1/\sigma_2 = 1, 2, 3$ respectively (see Table II).

The equations used to determine the stresses were as follows:

$$\sigma_1 = \sigma_z + F/A \quad (2a)$$

$$\sigma_z = p(\pi d_i^2/4)/A \quad (2b)$$

$$\sigma_2 = \sigma_\theta = p d_i/2a \quad (2c)$$

$$A = \pi(d_o^2 - d_i^2)/4 \quad (2d)$$

where

- $A = \text{Sectional area, in.}^2$
- $d_i = \text{Inside diameter, in.}$
- $d_o = \text{Outside diameter, in.}$
- $p = \text{Internal pressure, psi.}$
- $a = \text{Thickness, in.}$
- $F = \text{Axial load added, lb.}$
- $\sigma_z = \text{Axial stress due to internal pressure, psi.}$
- $\sigma_\theta = \text{Circumferential stress due to internal pressure, psi.}$
- $\sigma_1 = \text{Principal stress in axial direction, psi.}$
- $\sigma_2 = \text{Principal stress in circumferential direction, psi.}$

The maximum stress level chosen, 3000 psi., corresponds to about 40% of the tensile strength of this material.

**Results**

Rectangular plots of axial creep strain versus time for different stress ratios and different gases are shown in Figs. 3 to 6.

In some curves such as Tests 2 and 11 in Fig. 3, Tests 12 and 21 in Fig. 4 and Tests 8, 9 and 10 in Fig. 5, the effect induced by the small
temperature spike resulting from compressing the gas is seen at just the initial stage of creep.

The creep was small in every case except that for carbon dioxide which was much greater than the creep for the other gases. Two tests were repeated after many intervening tests as shown in Figs. 3 and 5. The agreement was excellent, especially for the last test number 22 as compared with the second test, see Fig. 3.

Discussion

In earlier work [14,15] it was shown that the creep behavior of many plastics under constant stress could be described quite well even for extended time periods by a power function of time such as

\[ \epsilon_{11} = \epsilon_{11}^0 + \epsilon_{11}^+ t^n, \]  \hspace{1cm} (3)

where \( \epsilon_{11} \) is the total strain, \( \epsilon_{11}^0 \) is the instantaneous strain, \( t \) is the time, \( \epsilon_{11}^0 \) and \( \epsilon_{11}^+ \) are stress dependent functions, and \( n \) is a constant under isothermal conditions. Equation 3 may be written as follows:

\[ \log (\epsilon_{11} - \epsilon_{11}^0) = \log \epsilon_{11}^+ + n \log t. \]  \hspace{1cm} (4)

This is an equation of a straight line in the variables \( \log(\epsilon_{11} - \epsilon_{11}^0) \) and \( \log t \).

Some of the plots of \( \log(\epsilon_{11} - \epsilon_{11}^0) \) versus \( \log t \) for the present experiments are shown in Fig. 7. Values of \( \epsilon_{11}^0 \), \( \epsilon_{11}^+ \) and \( n \) determined from such straight line plots are listed in Table II for various gases and stress ratios. The results of the calculation using Eq. 3 are also shown as solid lines in Figs. 3 to 6.
Effect of Gas on Creep Behavior

Figure 8 shows the effect of gas on creep (total strain plotted) at a stress ratio $\sigma_1/\sigma_2$ of 3 ($\sigma_2 = 1000$ psi.). Also shown are data obtained from a test with Freon in a preliminary experiment using a different specimen. Figure 8 shows that the strains resulting from use of carbon dioxide and Freon are remarkably larger than those of the other gases. Also the strains for helium, air and nitrogen are nearly the same. Therefore, the creep behavior is highly affected by the solubility controlled gases, carbon dioxide and Freon, because of the plasticizing action of their dissolved gases. On the contrary, diffusion controlled gases like helium seem apparently to have little or no effect on the creep behavior. Concerning air and nitrogen, it is assumed that the diffusivity is far smaller than that of helium and the solubility is smaller than that of carbon dioxide [3]. In the case of Freon, it was observed that some of the pressurized Freon gas appeared to liquefy inside the tubular specimen.

Effect of Axial Stresses on Creep Behavior

In Fig. 9 the values of $\varepsilon_{11}^0$, $\varepsilon_{11}^+$ and $n$ are presented as a function of axial stress under a constant circumferential stress $\sigma_2 = 1000$ psi. (constant pressure). The instantaneous strain $\varepsilon_{11}^0$ is almost the same level for different gases, but the lowest in helium gas. As expected it has a negative value at $\sigma_1 = 0$ because $\sigma_2 = 1000$ psi., not zero. Values of $\varepsilon_{11}^+$ increase with increasing stress and show about the same level (except the highest stress point) for air, nitrogen and helium gases; but, they show much greater values for carbon dioxide. The values of $n$ are different from gas to gas, especially at lower stresses, but again the value for carbon dioxide was markedly higher than for the other gases.
Effect of Internal Pressure on Creep Behavior

The effect of internal pressure, or circumferential stress $\sigma_2$, on values of $\epsilon_{11}^0$, $\epsilon_{11}^+$ and $n$ at a constant axial stress of $\sigma_1 = 3000$ psi. is given by Fig. 10. The values of $\epsilon_{11}^+$ increase with increasing pressure for both helium and carbon dioxide, but the value is much greater for carbon dioxide. The time exponent $n$ shows different behaviors between dissolution controlled and diffusion controlled gases; $n$ is much larger for carbon dioxide, a dissolution controlled gas.

Therefore, it is concluded that the dissolution controlled gases have a striking influence on the creep behavior of polycarbonate, but the creep behavior is not much influenced by the diffusion controlled gases. Also there is a pronounced effect of pressure on creep for carbon dioxide.

On the Absorbed Gas Volume

The absorption volumes of gases were observed instead of the permeation because of the experimental apparatus available. The results are shown in Figs. 11 and 12. The change in gas volume is given by the following relation:

$$ W = W_1 + W_2 + W_3 + W_4 $$

(5)

where

- $W_1 =$ Volume change due to creep deformation, in.$^3$
- $W_2 =$ Volume absorbed into polymer, in.$^3$
- $W_3 =$ Volume permeated through polymer, in.$^3$
- $W_4 =$ Leakage gas volume, in.$^3$

Before and during creep testing, the leakage was checked by a detecting agent (detergent), and no leakage was found in any test, thus $W_4 = 0$. 
Although $W_2$ and $W_3$ cannot be separated in our experiment, $W_3$ is assumed to be quite a small quantity or negligible for the short time of testing. The volume change due to creep $W_1$ can be calculated for two of the stress states $\sigma_1 = \sigma_2 = 1000$ psi. and $\sigma_1 = \sigma_2 = 3000$ psi. by assuming that the material behavior is isotropic and using the axial strain data $\varepsilon_{11}$ for both axial and circumferential strain. For this case $W_1$ is given by the following,

$$W_1 = \frac{\pi}{4} (d + \Delta d)^2 (l + \Delta l) - \frac{\pi}{4} d^2 l = \frac{3}{4} \pi d^2 l \varepsilon_{11},$$

where $d$ and $l$ are the inside diameter and length of the specimen tube respectively, $\Delta d$ and $\Delta l$ are the change in diameter and length of the tube due to creep respectively and $\varepsilon_{11}$ is the axial strain in a biaxial stress state for which $\varepsilon_{11} = \varepsilon_{22}$. The change in volume from the time of the first reading of gas volume ($t = 4.5$ min.) to two hours yields the following examples: for $\sigma_1 = \sigma_2 = 3000$ psi. $W_1/W$ is 9.5, 2.4, 16.8 per cent for carbon dioxide, helium and air respectively; for $\sigma_1 = \sigma_2 = 1000$ psi. the corresponding values are 1.0, 1.0 and 11.8 per cent. For cases where the flow volume is small, but creep still important $W_1/W$ may be larger. Since it is not possible to calculate $W_1$ for other stress states, since the above values of $W_1/W$ are small and since the trends are clear without accounting for $W_1$, no correction has been made in the value of gas flow shown in Figs. 11 to 15 and identified as "apparent absorbed gas volume".

As described before, almost the same creep occurred in air, nitrogen and helium (see Fig. 8), but a clear difference was found among the absorbed volumes of those gases (see Figs. 11 and 12). The order of increasing absorption corresponds to the inverse of increasing molecular size (except for carbon dioxide). Helium with the smallest molecular diameter diffuses through
the intermolecular space of the polymer easily, so it shows a large amount of
absorbed volume. Owing to the inclusion of oxygen in air, the absorbed volume
of air is larger than that of nitrogen, since the molecular diameter of oxygen
is less than nitrogen.

The effect of stress state is shown in Fig. 13, where the apparent gas
volume absorbed at two hours versus axial stress $\sigma_1$ at constant pressure for
various gases is given. For this comparison all volumes have been adjusted to
0°C and one atmosphere of pressure. At constant pressure, though the effect of
axial stress $\sigma_1$ on the gas absorption is not great, the volumes of helium and
air show an increasing tendency and those of carbon dioxide and nitrogen show a
decreasing tendency with increasing axial stress $\sigma_1$. Those tendencies are
similar to those of the time exponent $n$, except for air, as shown in Fig. 9.

The strong effect of pressure (or circumferential stress) on absorbed gas
is evident in Fig. 14. For this comparison all volumes have been adjusted to 0°C
and one atmosphere of pressure. The absorption increases with increasing pressure
for all gases but the tendency is opposite between carbon dioxide versus helium
or air or nitrogen.

In the case of dissolution controlled gas, the absorption is considered
to take place by ordinary dissolution and "hole-filling" processes [8].
Increasing the axial stress from $\sigma_1 = 1000$ psi toward 3000 psi while holding
the circumferential stress constant at $\sigma_2 = 1000$ psi as in Fig. 13 would
change the shape of strain induced molecular spacing from circular to elongated-
slit type while reducing the minimum width of the hole. In such circumstances,
therefore, the pre-existing holes large enough to accommodate and to disperse
the penetrant molecules would reduce, so the effect of the change in the shape
of strain alone would result in a decrease in absorption with increase in axial
stress as shown for carbon dioxide and nitrogen in Fig. 13 but not for helium
and air. The change in absorbed volume shown in Fig. 13 for nitrogen, air and
Increasing the circumferential stress for $\sigma_2 = 1000$ toward 3000 psi, holding the axial stress constant as in Fig. 14 would change the shape of the strain induced molecular spacing from an elongated-slit to a circular shape while increasing the minimum dimension. Thus the absorption would increase as shown in Fig. 14. However, in Fig. 14 there is another factor which is much more important in increasing the absorption, that is, the pressure also increased. Although Henry's law is obeyed only over the pressure range 0 - 1.0 atm for various gases [8], the dissolution process strongly depends on pressure and the permeation process also depends on pressure.

The diffusion coefficient is known to react exponentially to change in the apparent free volume, and Yasuda et al. [10] proposed the following relationship between diffusion coefficient $D$ and strain $\varepsilon$:

$$D(\varepsilon) = D(0) \exp \left( \frac{\psi^*}{V_f(0)} \left[ \frac{V_f(\varepsilon)}{V_f(0)} - 1 \right] \right), \quad (7)$$

where $V_f = V - V_o$, $V_f$ is the free volume in the material, $\psi^*$ the characteristic volume required to accommodate the diffusing gas molecule in the material, $V$ the specific volume, and $V_o$ the extrapolated value of $V$ at 0 K. Therefore, the increase in absorbed volume for the diffusion controlled helium may be explained by an increase in free volume in the material due to the creep deformation.

Filled circles in Figs. 13 and 14 indicate corrections for volume increase due to creep deformation, assuming that the axial strain and circumferential strain take the same value when the stress ratio is unity.
To check the behavior of gas absorption in the polymer, a further analysis was made. In organic vapor penetrant-polymer systems, when the diffusion is of the Fickian type, the absorption of the penetrant is initially proportional to the square root of the time, provided that a steady surface equilibrium is established immediately and that the diffusion coefficient is a constant. In this case, the equation for absorption is given by the following:

\[
\frac{M_t}{M_\infty} = \frac{4}{\pi} \left( \frac{D}{\pi d^2} \right)^{1/2} t^{1/2},
\]

where
- \( M_t \) = Amount of diffusing gas taken up by the material in a time \( t \),
- \( M_\infty \) = Equilibrium absorption,
- \( D \) = Diffusion coefficient,
- \( a \) = Thickness of the material.

Plots of the apparent absorbed volume versus \( \sqrt{t} \) are shown in Fig. 15. The data for carbon dioxide is a straight line on Fig. 15. Thus it is in very good agreement with (8). This indicates that the diffusion of carbon dioxide is of the Fickian type. Helium is nearly straight but shows a slight sigmoid character -- so nearly Fickian. However, nitrogen and air have an irregular, roughly sigmoidal shape, characteristic of anomalous or non-Fickian diffusion. Non-Fickian diffusion is found in organic vapor-polymer systems under the glass transition temperature. Generally, the anomalous behavior is explained as the combined effects of time or history, molecular orientation and internal stress on both the diffusion coefficient and on the surface concentration. In the first stage of two-stage absorption, vapor is absorbed until quasi-equilibrium is established at the surface of the polymer, then the equilibrium spreads throughout the polymer. Absorption in the second stage proceeds by a slow increase of the quasi-equilibrium throughout the material.
Thus anomalous-diffusion like behavior appears even in the permanent gas-polymer system under creep conditions when subjected to relatively high gas pressure.

Creep Recovery

Creep recovery was measured after the two hour loading period. In air, nitrogen, and helium, the deformation due to creep was fully recovered within twenty or thirty hours, while for carbon dioxide there remained a large amount of strain induced by the dissolution of the gas. It turned out, however, that this permanent set was only apparent, because it recovered completely by applying air pressure for a long duration of time.

When the pressure was released after the creep test using Freon in the preliminary experiment the specimen was found to have a clouded appearance and an inner layer of material a few thousands in. thick was completely separated from the specimen. This action presumably resulted from the following causes. The plasticizing action of the dissolved Freon reduced the van der Waals forces and hence reduced the strength of the polymer where the concentration of Freon was the highest. On release of pressure the large size of the Freon molecule impeded its diffusion out of the polymer. Thus the vapor pressure of Freon at 1 atm apparently exceeded the reduced strength of the polymer.

In [16] it was shown that the superposition principle was useful in predicting recovery following creep at constant stress even after long time. For recovery strain $\varepsilon_R$, after removal of load at time $t_R$, the following equation is obtained from (3) by using superposition,

$$\varepsilon_R = \varepsilon_{11}^+ [t^n - (t - t_R)^n]$$

$$t > t_R$$

$$t_R = 2 \text{ hours}$$
The recovery strain following creep was calculated from the creep constants in Table II with this equation as shown in Fig. 16, together with the test data. The agreement between theory and data is excellent for helium, air and nitrogen, and rather good for carbon dioxide.

**Prediction from Combined Tension-Torsion Creep**

From the results of combined tension-torsion creep of polycarbonate by Ni and Findley [11] it is possible to calculate the creep behavior under tension and internal pressure, assuming the material is isotropic. The general equation is given in [17]. From the general equation the expression for axial strain \( \varepsilon_{11} \) in tubes subjected to axial stress \( \sigma_1 \), and circumferential stress \( \sigma_2 \) can be expressed as follows.

\[
\varepsilon_{11} = \pi_1 (\sigma_1 + \sigma_2) + \pi_2 (\sigma_1^2 + \sigma_2^2) + \pi_3 (\sigma_1 + \sigma_2)^2 + \pi_4 (\sigma_1 + \sigma_2) (\sigma_1^2 + \sigma_2^2) \\
+ \pi_5 (\sigma_1 + \sigma_2)^3 + \sigma_1 [\nu_0 + \nu_1 (\sigma_1 + \sigma_2) + \nu_2 (\sigma_1^2 + \sigma_2^2)] \\
+ \nu_3 (\sigma_1 + \sigma_2)^2 \\
\]  

(10)

where the coefficients \( \pi_1 \), \( \nu_0 \) are functions of time and properties of material. Values of \( \pi_1 \), \( \nu_0 \) determined from a different specimen of polycarbonate as reported in [11] are shown in Table III.

Using (10) and the constants in Table III obtained from combined tension-torsion creep of a different sample of polycarbonate equations for creep corresponding to the present series of creep tests using air pressure were calculated. The constants for the resulting equations are shown in Table IV together with the constants for the corresponding equation for axial creep determined from the present series of creep experiments using air pressure. The strain at one hour in the present tests was substantially greater than the predicted strain.
This was generally true of $\varepsilon^0_{11}$ and $n$ also, but for $\varepsilon^+_{11}$ the predicted values were usually larger than the results of the present experiments. However, when $\sigma_2$ was increasing with constant $\sigma_1$ the trend of $\varepsilon^+_{11}$ from the present tests was opposite to the predicted trend as shown in Table IV. These differences may result from the difference in the extrusion and heat treatment of the two samples.

Acknowledgment

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References


Table I: Properties of Gases Used

<table>
<thead>
<tr>
<th>Type of gas</th>
<th>Molecular Weight</th>
<th>Molecular Diameter ā Å</th>
<th>Polarity</th>
<th>Density 0°C, 1 atm (g/L)</th>
<th>Boiling Point (°C)</th>
<th>Viscosity 20°C, 1 atm (poise)</th>
</tr>
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<tbody>
<tr>
<td>Freon-22 (CHClF₂)</td>
<td>86.48</td>
<td>-</td>
<td>Polar</td>
<td>1.4909 (-69°C)</td>
<td>-39.8</td>
<td><strong>1.28 x 10⁻⁴</strong></td>
</tr>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>44.01</td>
<td>3.34</td>
<td>Polar</td>
<td>1.977</td>
<td>-78.5</td>
<td>1.48 x 10⁻⁴</td>
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<td>Air</td>
<td><strong>28.97</strong></td>
<td>2.98(O₂)</td>
<td>Non-Polar</td>
<td>1.2929</td>
<td>-194.5</td>
<td>1.83 x 10⁻⁴ (18°C)</td>
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<tr>
<td>Nitrogen (N₂)</td>
<td>28.01</td>
<td>3.15</td>
<td>Non-Polar</td>
<td>1.2506</td>
<td>-195.8</td>
<td>1.78 x 10⁻⁴ (27.4°C)</td>
</tr>
<tr>
<td>Helium (He)</td>
<td>4.0026</td>
<td>1.90</td>
<td>Non-Polar</td>
<td>0.1785</td>
<td>-268.9</td>
<td>1.94 x 10⁻⁴</td>
</tr>
</tbody>
</table>

** These values are from another source.
Table II: Evaluation of $\epsilon_{11}^o$, $\epsilon_{11}^+$ and $n$ in Eq. 3

<table>
<thead>
<tr>
<th>$\sigma_1$ psi</th>
<th>$\sigma_2$ psi</th>
<th>Gas</th>
<th>Test No.</th>
<th>$\epsilon_{11}^o = \epsilon_{11}^o + \epsilon_{11}^+ t^n$ Percent</th>
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<tbody>
<tr>
<td>3000</td>
<td>0</td>
<td>-</td>
<td>1</td>
<td>0.8700 + 0.0655 $t^{0.102}$</td>
</tr>
<tr>
<td>1000</td>
<td>1000</td>
<td>He</td>
<td>8</td>
<td>0.1830 + 0.0094 $t^{0.142}$</td>
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<tr>
<td></td>
<td></td>
<td>Air</td>
<td>6</td>
<td>0.1840 + 0.00975 $t^{0.213}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N$_2$</td>
<td>21</td>
<td>0.1855 + 0.0083 $t^{0.340}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO$_2$</td>
<td>17</td>
<td>0.1875 + 0.0408 $t^{0.451}$</td>
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<tr>
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<td>1000</td>
<td>He</td>
<td>18</td>
<td>0.4740 + 0.0226 $t^{0.145}$</td>
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<tr>
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<td></td>
<td>Air</td>
<td>11</td>
<td>0.4760 + 0.0205 $t^{0.199}$</td>
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<td>N$_2$</td>
<td>12</td>
<td>0.4770 + 0.0194 $t^{0.242}$</td>
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<td>CO$_2$</td>
<td>13</td>
<td>0.4800 + 0.0560 $t^{0.437}$</td>
</tr>
<tr>
<td>3000</td>
<td>1000</td>
<td>He</td>
<td>9</td>
<td>0.7750 + 0.0400 $t^{0.153}$</td>
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<tr>
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<td></td>
<td>Air</td>
<td>22</td>
<td>0.7760 + 0.0415 $t^{0.176}$</td>
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<td></td>
<td>N$_2$</td>
<td>20</td>
<td>0.7650 + 0.0540 $t^{0.126}$</td>
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<tr>
<td></td>
<td></td>
<td>CO$_2$</td>
<td>15</td>
<td>0.7920 + 0.0792 $t^{0.398}$</td>
</tr>
<tr>
<td>3000</td>
<td>1500</td>
<td>He</td>
<td>19</td>
<td>0.7230 + 0.0406 $t^{0.145}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Air</td>
<td>14</td>
<td>0.7230 + 0.0437 $t^{0.163}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N$_2$</td>
<td></td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td>CO$_2$</td>
<td>23</td>
<td>0.7300 + 0.0996 $t^{0.397}$</td>
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<tr>
<td>3000</td>
<td>3000</td>
<td>He</td>
<td>5</td>
<td>0.5300 + 0.0620 $t^{0.0597}$</td>
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<tr>
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<td>Air</td>
<td>4</td>
<td>0.5570 + 0.0356 $t^{0.202}$</td>
</tr>
<tr>
<td></td>
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<td>N$_2$</td>
<td>7</td>
<td>0.5550 + 0.0353 $t^{0.163}$</td>
</tr>
<tr>
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<td></td>
<td>CO$_2$</td>
<td>16</td>
<td>0.5685 + 0.1335 $t^{0.450}$</td>
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</table>
Table III: Time and Material Functions from Reference [11] for Eq. 10

\[
\begin{align*}
\pi_1 &= -1.225 \times 10^{-6} - 0.074 \times 10^{-6} t^{0.15} \\
\pi_2 &= +0.015 \times 10^{-9} \\
\pi_3 &= -0.031 \times 10^{-9} + 0.04 \times 10^{-9} t^{0.15} \\
\pi_4 &= -0.004 \times 10^{-12} - 0.009 \times 10^{-12} t^{0.15} \\
\pi_5 &= -0.0005 \times 10^{-12} - 0.002 \times 10^{-12} t^{0.15} \\

\nu_0 &= 4.03 \times 10^{-6} + 0.21 \times 10^{-6} t^{0.15} \\
\nu_1 &= 0.016 \times 10^{-9} - 0.04 \times 10^{-9} t^{0.15} \\
\nu_2 &= 0.013 \times 10^{-12} + 0.013 \times 10^{-12} t^{0.15} \\
\nu_3 &= -0.0025 \times 10^{-12} + 0.005 \times 10^{-12} t^{0.15}
\end{align*}
\]
Table IV: Prediction from Combined Tension - Torsion Creep in Air

<table>
<thead>
<tr>
<th>Stress (psi)</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>$\varepsilon_{11}$ (^0) (%)</th>
<th>$\varepsilon_{11}$ (^+) (%)</th>
<th>$\varepsilon_{11} = \varepsilon_{11}^0 + \varepsilon_{11}^+ t^n$ at $t = /hr.$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>0</td>
<td>Predicted</td>
<td>0.8577</td>
<td>0.0597</td>
<td>0.9174</td>
<td>0.15</td>
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<td></td>
<td></td>
<td>Tested</td>
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<td>0.9355</td>
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<tr>
<td>3000</td>
<td>1000</td>
<td>Predicted</td>
<td>0.7114</td>
<td>0.0636</td>
<td>0.7750</td>
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<td></td>
<td>Tested</td>
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<td>0.0415</td>
<td>0.8175</td>
<td>0.176</td>
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<tr>
<td>3000</td>
<td>1500</td>
<td>Predicted</td>
<td>0.6373</td>
<td>0.0672</td>
<td>0.7045</td>
<td>0.15</td>
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<td></td>
<td></td>
<td>Tested</td>
<td>0.7230</td>
<td>0.0437</td>
<td>0.7667</td>
<td>0.163</td>
</tr>
<tr>
<td>3000</td>
<td>3000</td>
<td>Predicted</td>
<td>0.4074</td>
<td>0.0744</td>
<td>0.4818</td>
<td>0.15</td>
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<td>Tested</td>
<td>0.5570</td>
<td>0.0356</td>
<td>0.5926</td>
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<tr>
<td>2000</td>
<td>1000</td>
<td>Predicted</td>
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<td>0.0349</td>
<td>0.4638</td>
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<td></td>
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<td>Tested</td>
<td>0.4760</td>
<td>0.0205</td>
<td>0.4965</td>
<td>0.199</td>
</tr>
<tr>
<td>1000</td>
<td>1000</td>
<td>Predicted</td>
<td>0.1514</td>
<td>0.0136</td>
<td>0.1650</td>
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<tr>
<td></td>
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<td>Tested</td>
<td>0.1840</td>
<td>0.00975</td>
<td>0.1938</td>
<td>0.213</td>
</tr>
</tbody>
</table>
Fig. 1. Apparatus for Creep of Tubular Specimens under Tension and Internal Pressure
Fig. 2. Apparatus for Gas Pressure Supply and Control

A. Gas container
B. Pressure controller
C. U-tube
D. Glass capillary
E. Scale
F. Copper tubing
G₁, G₂. Gage section of tubular test specimen
H. Tubular specimen
I₁, V₃. Gas purging valves
P₁, P₂, P₃. Bourdon gages
V₁. Pressure regulating valve
V₂-V₆. Valves
Fig. 4. Creep Curves for Polycarbonate Tubes Pressurized by Nitrogen at Various Stresses, 75°F and 50 per cent Relative Humidity.
Fig. 5. Creep Curves for Polycarbonate Tubes Pressurized by Helium at Various Stresses, 75°F and 50 per cent Relative Humidity
Fig. 6. Creep Curves for Polycarbonate Tubes Pressurized by Carbon Dioxide at Various Stresses, 75°F and 50 per cent Relative Humidity
Fig. 7. Log-log Plots of Strain Difference vs. Time for Axial Tensile Creep at $\sigma_1/\sigma_2 = 2$ ($\sigma_1 = 2000$ psi, $\sigma_2 = 1000$ psi)
Fig. 8. Effect of Gases on Creep at $\sigma_1/\sigma_2 = 3$ ($\sigma_1 = 3000$ psi, $\sigma_2 = 1000$ psi)
Fig. 9. Relationship between $\varepsilon_{11}^0$, $\varepsilon_{11}^+$, and $n$ in Eq. 3 and Axial Stress $\sigma_1$ for a Constant Value of $\sigma_2 = 1000$ psi
Fig. 10. Relationship Between $\varepsilon_{11}^0, \varepsilon_{11}^+$ and $n$ in Eq. 3 and Circumferential Stress $\sigma_2$ (or internal pressure) at Constant Axial Stress $\sigma_1 = 3000$ psi
Fig. 11. Apparent Absorption Curves for Various Gases and Stress Ratios at $\sigma_2 = 1000$ psi = constant. (Constant Internal Pressure)
Fig. 12. Apparent Absorption Curves for Various Gases at $\sigma_1/\sigma_2 = 1$ and 3 for $\sigma_1 = 3000$ psi
Fig. 13. Apparent Absorbed Gas Volume versus Axial Stress $\sigma_1$ at $\sigma_2 = 1000$ psi = constant (Constant Internal Pressure). Volumes adjusted to 0°C and 1 atmosphere.
Fig. 14. Apparent Absorbed Gas Volume versus Internal Pressure ($\sigma_2 = 3000$ psi $= \text{constant}$). Volumes adjusted to $0^\circ\text{C}$ and 1 atmosphere.
Fig. 15. Apparent Absorption Curves for Various Gases under Creep Conditions at $\sigma_1/\sigma_2 = 1$ ($\sigma_1 = \sigma_2 = 3000$ psi)
Fig. 16. Recovery Curves Following Creep for Two Hours at $\sigma_2 = 1000$ psi and Various Values of $\sigma_1$