

Influence of History on the Gas Sorption, Thermal, and Mechanical Properties of Glassy Polycarbonate

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Synopsis

Glassy polycarbonate has been subjected to sub-glass-transition annealing and exposure to high-pressure CO₂. The subsequently measured solubilities of nitrogen, argon, and CO₂ in these specimens were found to be decreased by the former and increased by the latter. Annealing decreases the enthalpy of polycarbonate and mechanically embrittles it, whereas subsequent exposure to CO₂ erases these effects of annealing, can make the polymer even more ductile than the untreated material, and can apparently give it a higher enthalpy. Annealing densifies the glass, whereas the CO₂ treatment dilates it. The gas sorption observations are in accord with the dual-sorption model, and the effects of prior history are apparently the result of changes in the Langmuir capacity, which evidently is a sorption mechanism that exists as a result of the nonequilibrium nature, or excess volume, of the glassy state.

INTRODUCTION

The distribution of molecular segments and their kinetic motions in amorphous, rubbery polymers are closely similar to those of the molecules in a normal liquid and are thus independent of any prior sample history. In contrast, the glassy state of the polymer possesses "excess" volume and enthalpy relative to the extrapolated equilibrium liquid state and has a tendency to minimize these excess quantities at a rate commensurate with existing segmental mobility. It is now well known that thermal annealing just below the T_g is an effective way of *reducing* these excess quantities.¹⁻²⁰ It is somewhat less well known that these excess quantities can be *increased* by exposure to certain chemical environments which swell the glassy polymer but are subsequently removed from it.²¹⁻²⁵

Volumetric and thermal measurements are most often used to define the current state of a glassy polymer. However, other properties—e.g., mechanical behavior or sorptive capacity for gases or vapors—are also sensitive to the state of the glass and hence to its prior history. In recent papers, we have shown that the apparent equilibrium sorption of CO₂ in polycarbonate (PC) at 35°C ($T_g \sim 145^\circ\text{C}$) is *reduced* by sub- T_g annealing²⁰ and *increased* by previous exposure to higher pressures of CO₂.²⁵ The purpose of this paper is to further elaborate on how these two means of altering the state of a glassy polymer affect the sorption, thermal, and mechanical behavior of PC. Their effects on transport behavior have been dealt with elsewhere.²⁵⁻²⁷

The materials, equipment, and procedures employed here have all been described previously.^{20,25-30} Annealing of the thin PC film was done in a forced-air oven in which the air temperature was set at the temperature of interest.

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RESULTS

Sorption

Figure 1 shows, in a somewhat uncontrolled fashion, the two history effects on the apparent equilibrium sorption of CO_2 in PC at 35°C (above the T_c of CO_2). In the first, the as-received, melt-extruded, and quenched PC film was exposed to CO_2 at successively higher pressures up to 25 atm (open circles). After complete degassing, a different isotherm (solid circles) is observed on re-exposure to CO_2 . The last isotherm obtained is reproducible over periods of months, regardless of subsequent CO_2 exposure, provided this does not exceed the previously established limit of 25 atm. In the second, the as-received PC film was given a sub- T_g annealing and the above-mentioned sequence repeated. The "initial" isotherm and the one after exposure to 25 atm of CO_2 exhibit less CO_2 sorption for the annealed specimen than the respective isotherms for the as-received PC.

Clearly, care must be exercised to assess properly the various history effects when, in fact, the property measurement itself, CO_2 sorption, affects the state of the glassy polymer. In the past it was found expedient to expose the sample first to the highest gas pressure to be used in the sorption isotherm determination, say 20 to 25 atm, and thus to achieve subsequent results with a standardized conditioning.^{20,25-30} This practice was also followed here, and hereafter none of the results shown will correspond to the "initial" isotherms shown in Figure 1, which can only be observed on initial pressurization. The CO_2 conditioning effect results from the swelling caused by CO_2 sorption and the failure of the glass to collapse back to its original state on removal of the CO_2 .²⁵ Gases like argon and nitrogen have much lower solubilities²⁹ in PC than does CO_2 and, consequently, do not alter the state of the glass to nearly the extent that CO_2 does. Thus these gases should make useful probes to determine changes in the glassy state produced by previous history without appreciably perturbing that state by the very act of characterizing it.

Extensive evidence^{20,25-32} has demonstrated that gas and vapor sorption in

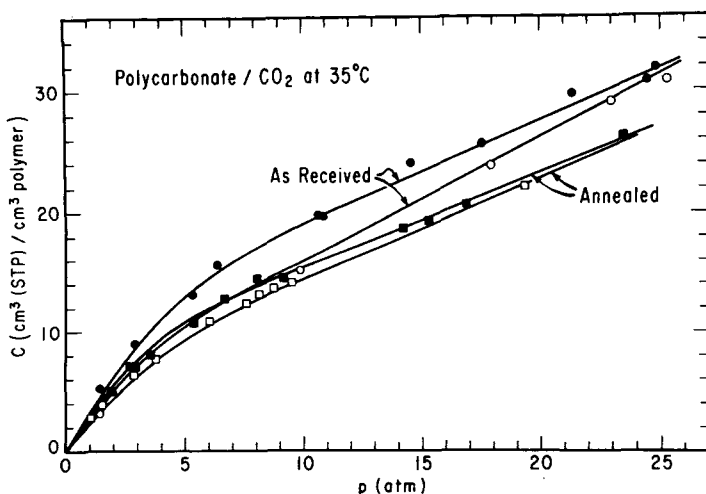


Fig. 1. Comparison of the "initial" sorption isotherms (\square) for CO_2 in as-received and annealed polycarbonate with that observed after exposure to 25 atm of CO_2 (\bullet).

glassy polymers is well described by the so-called dual-mode sorption isotherm:

$$C = k_D p + C'_H b p / (1 + b p) \quad (1)$$

This implies that both Henry's law and Langmuir mechanisms are simultaneously operative. The isotherms for CO₂ in PC shown in Figure 2 are well described by eq. (1). Recently it has been shown^{20,25,30,33,34} that the Langmuir part of this equation is related to the nonequilibrium character of the glass, and the capacity term C'_H appears to be directly proportional to the "excess" volume of the glass. By curve fitting, it can be shown that the observed decrease in CO₂ sorption caused by annealing, and the increase caused by higher-pressure CO₂ exposure is well described in terms of eq. (1) by, respectively, decreases or increases in C'_H , while the other two parameters, k_D and b , are effectively unchanged by this history. In turn, the changes in C'_H appear to be directly connected to the volume of the glass and the densification that occurs on sub- T_g annealing²⁰ or the dilation that results from high-pressure CO₂ exposure.²⁵

Figures 3 and 4 show the effects of sub- T_g annealing and CO₂ exposure on the sorption of argon and nitrogen in PC. Results for untreated, or as-received, PC are also shown for comparison. Neither of these gases shows any difference between the "initial" and subsequent determinations of the sorption isotherm, which is in contrast to the conditioning effect illustrated in Figure 1 for CO₂. Prior exposure to CO₂ causes a significant increase in the sorption of both argon and nitrogen compared to the as-received PC. Sub- T_g annealing decreases the sorption of either gas compared to the untreated control, but interestingly, this effect is considerably smaller than that seen for CO₂ conditioning.

As an aside, it is important to note that all isotherms for argon and nitrogen show less curvature, which is characteristic of dual-mode sorption, than those for CO₂. Earlier, the parameters k_D , b , and C'_H were determined for a series of

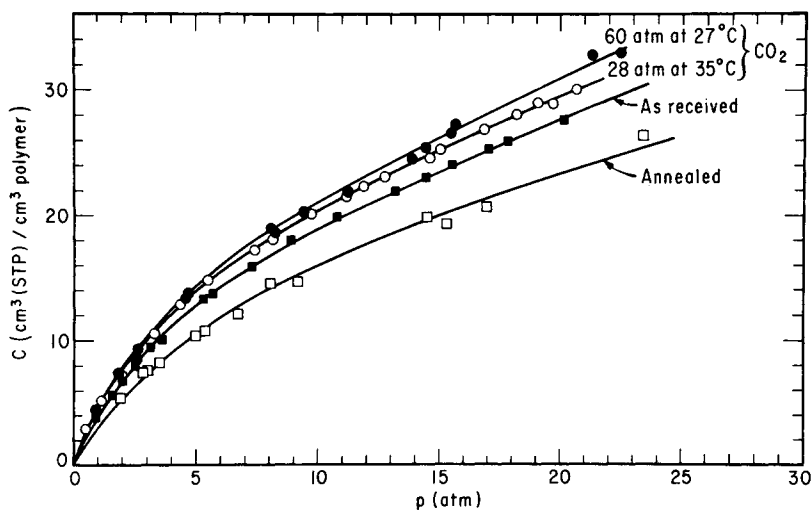


Fig. 2. Effect of history on the CO₂ sorption in polycarbonate. The as-received specimen was conditioned at 25 atm of CO₂ at 35°C prior to determination of the isotherm. The upper two curves are for specimens exposed to the higher CO₂ pressures shown at the temperatures indicated for a period of 1 day. The lower curve is for a specimen annealed at 135°C for 1 day and then exposed to 25 atm of CO₂.

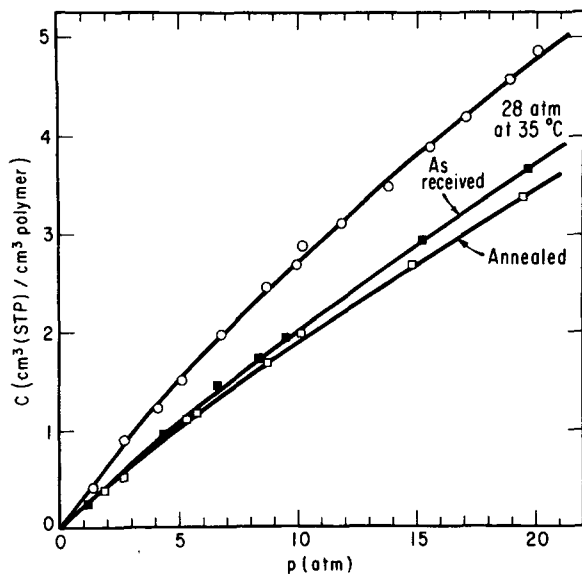


Fig. 3. Argon sorption in polycarbonate. The upper curve is for a specimen exposed to 25 atm of CO_2 for 1 day at 35°C , while the lower curve is for a specimen which had been annealed at 135°C for 1.5 days. The as-received specimen was neither annealed nor exposed to CO_2 . All specimens were conditioned to 20 atm of argon prior to determination of the sorption isotherms.

gases in PC,²⁹ and all three parameters were found to increase as the Leonard-Jones force constant (a measure of the strength of the intermolecular forces or propensity to condense), ϵ/k , increased. Thus less curvature for the less condensible argon and nitrogen than for the more condensible CO_2 is reasonable.

Figure 5 provides a way of examining how the nature of the sorbed gas influences the effect that the prior history of the glass has on its sorption behavior. Here the ratio of the solubilities of a particular gas at 15 atm in the treated to the untreated PC is plotted versus the Leonard-Jones force constant for that

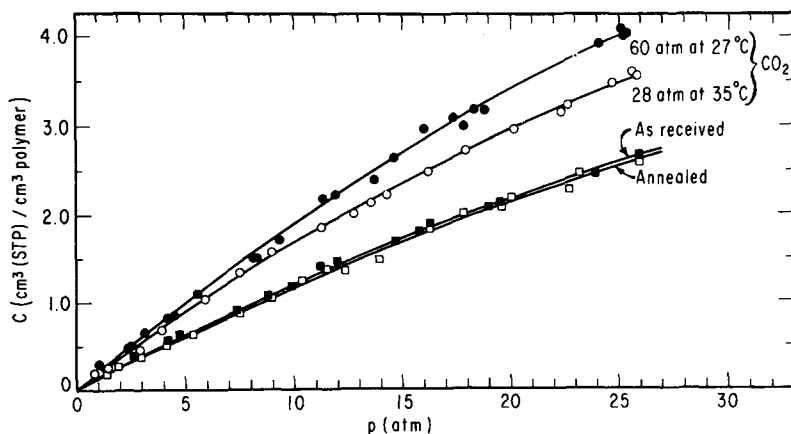


Fig. 4. Nitrogen sorption in polycarbonate. The specimens for the upper two curves were exposed to CO_2 for 1 day at the conditions shown, while the specimen for the lower curve was annealed at 135°C for 1.5 days. All specimens were conditioned to 25 atm of nitrogen prior to determination of the isotherms.

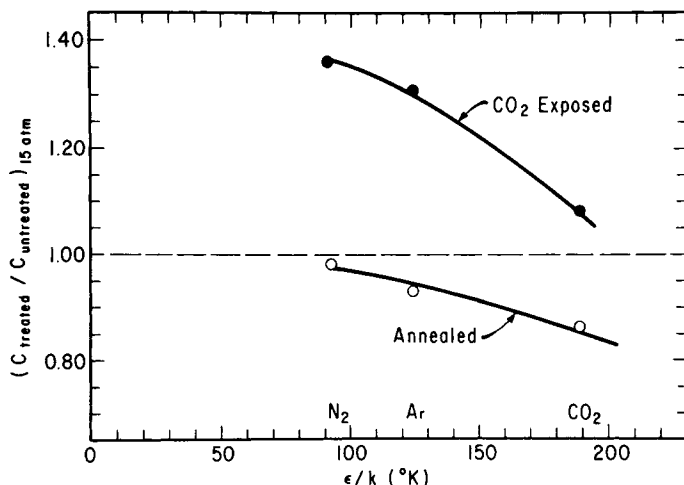


Fig. 5. Effect of gas type on the magnitude of the changes in solubility following annealing (1.5 days at 135°C) and CO₂ exposure (28 atm at 35°C for 1 day). The untreated controls were exposed only to the gas indicated.

gas. The reduction in solubility caused by annealing, lower curve, appears to become smaller as ϵ/k decreases, whereas the increase in solubility resulting from prior CO₂ conditioning seems to become larger as ϵ/k decreases. Superficially one might offer explanations of these trends in terms of changes in the distribution of free-volume elements affecting the solubility of the various gases; however, such speculations ought to be reserved until information is available for a wider range of sorbant molecules.

Enthalpy

It is well known that sub- T_g annealing at a temperature T_a for a time t causes both a reduction in volume and enthalpy of a quenched glass, as Figure 6 schematically illustrates.²⁰ Thermal analysis of the annealed glass results in a heat-capacity "overshoot" (dotted line in Fig. 6) on heating above T_g , which gives rise to an apparent endotherm in the thermal scan, as schematically shown in Figure 7. The area of this endotherm when properly constructed³⁵ is a measure of the extent of enthalpy relaxation on annealing. Earlier, it was shown²⁵ that CO₂ conditioning of PC caused a dilation of the specimen volume, which is in contrast to the densification that occurs on annealing.²⁰ Thus CO₂ exposure appears to be the antithesis of annealing, and so it is of interest to examine the changes in the glassy state on samples which have first been annealed and then exposed to CO₂ using the endotherm area defined in Figure 7 as a monitor. We were prompted to make this study because it became apparent to us that by attempting to follow the changes in the glassy state caused by annealing through observations of CO₂ sorption and transport, we might, in fact, erase a portion of the annealing effect because of the "de-annealing" effect CO₂ appears to produce. From the present results, one can establish some feeling for the amount of erasure that occurs for given CO₂ exposures.

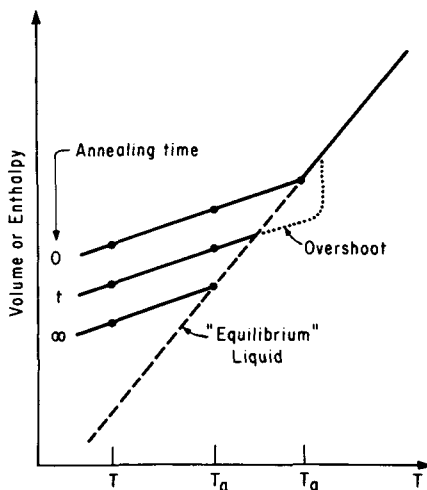


Fig. 6. Schematic representation of volume and enthalpy near the T_g of a polymer showing the effect of annealing at T_a .

A PC specimen which had been annealed at 135°C for 1.5 days (a high degree of annealing) was selected for these experiments. Figure 8 shows the effect of CO_2 exposure time at 27°C for various CO_2 pressures on the endotherm area observed after removing the CO_2 from the specimen. The area decreases with exposure time and appears to plateau at a level which decreases with increasing CO_2 pressure. For high enough pressures, the endotherm area eventually disappears altogether, i.e., the thermal trace has the appearance of a quenched glass in the T_g region. Separate experiments on the kinetics of CO_2 uptake by the PC specimen showed that this process ought to be effectively complete in less than 2 hr. Hence the time scale of the changes in Figure 8 must reflect that of

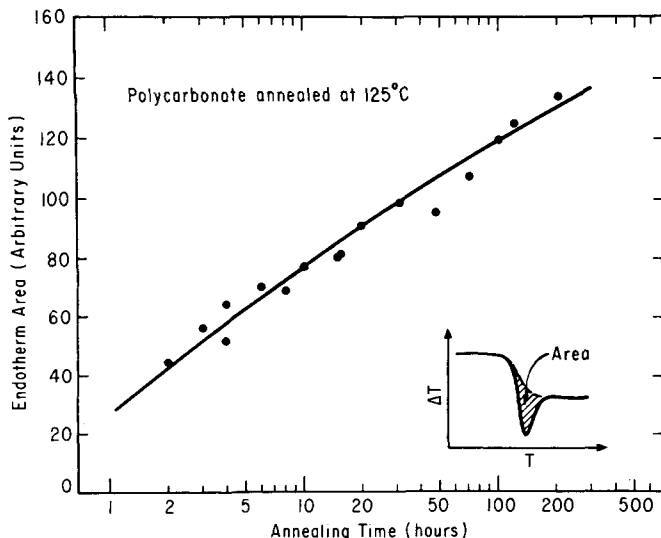


Fig. 7. The inset illustrates the apparent endotherm observed in DTA traces after sub- T_g annealing. The data show the increase in its area (100 units ≈ 0.26 cal/g) with annealing time.

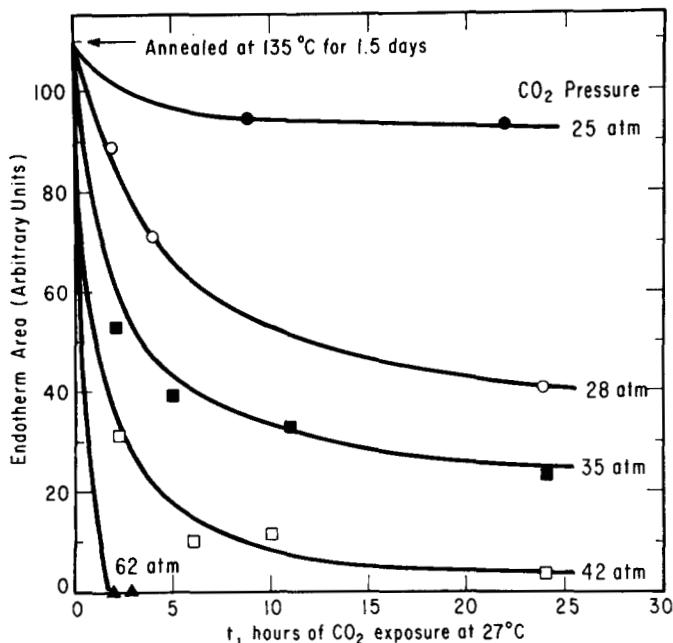


Fig. 8. Effect of CO₂ exposure at 27°C on the endotherm area. All CO₂ was removed from the specimen prior to these and all similar observations shown in subsequent figures.

structural rearrangements within the glass caused by the CO₂ swelling. Direct evidence has shown that the presence of CO₂ in PC causes a significant reduction in its T_g stemming from plasticization.²⁵

In these early experiments, the PC was conditioned in CO₂ at a convenient ambient temperature. Afterwards, it was decided that the sorption temperature might be a significant factor, and the results shown in Figure 9 show this to be

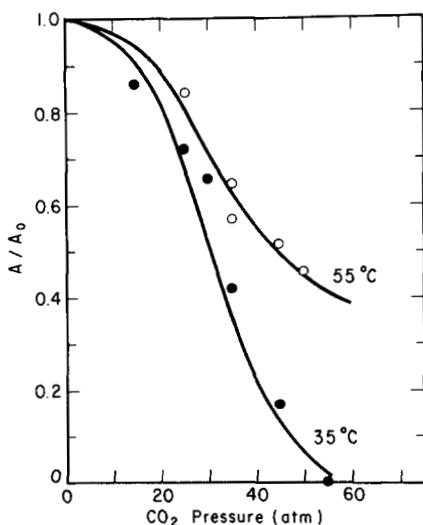


Fig. 9. Effect of CO₂ exposure for 4 hr at 35 and 55°C on the endotherm area, A . A_0 = area after annealing at 135°C for 1.5 days prior to any CO₂ treatment.

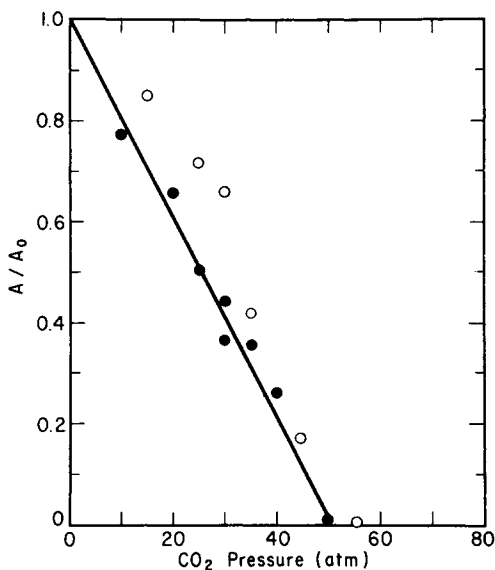


Fig. 10. Further examples of the reduction in the endotherm area for annealed polycarbonate caused by exposure to CO₂ at 35°C for 4 hr (○) and 10 hr (●).

the case. The change in area is greater, for a given CO₂ exposure time and pressure, the lower the exposure temperature, evidently because of the larger CO₂ sorption.²⁰ Figure 10 shows similar data at 35°C for two different exposure times. For these conditions the endotherm area is completely erased when exposed to 50 atm or more of CO₂.

Earlier,²⁰ it was shown that the apparent T_g (defined by the onset of the DTA base-line shift using the usual intersection construction employed in thermal analysis) for PC increased with annealing time—unannealed PC has a $T_g \sim 145^\circ\text{C}$. Figure 11 shows that these elevated T_g 's produced by annealing are reduced following CO₂ exposure. The T_g returns to the unannealed value at

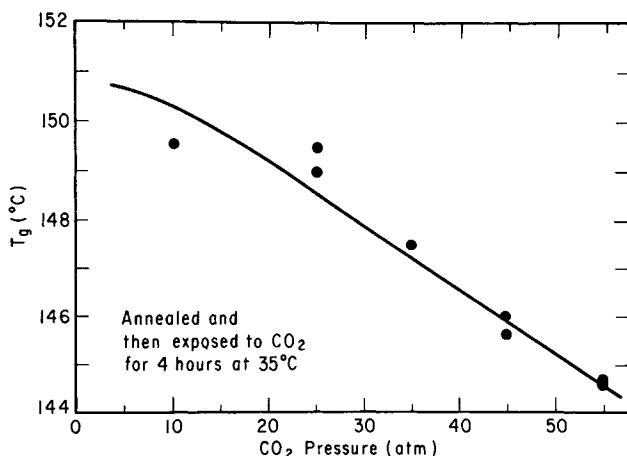


Fig. 11. Effect of CO₂ exposure on the apparent T_g , determined by the onset of the DTA base-line shift, for previously annealed polycarbonate. All CO₂ had been removed prior to this determination.

the pressure where the endotherm area disappears. It is important to note that the T_g observed in this manner differs from that computed in other ways,³⁶ and the main significance of Figure 11 is the demonstration of the opposite trend observed earlier for annealing.²⁰

The evidence discussed above clearly demonstrates that exposure of PC to high-pressure CO₂ may erase a part or all of the enthalpy relaxation that occurs on sub- T_g annealing. Preliminary experiments showed a similar effect of CO₂ on polystyrene. Therefore, conditioning in CO₂ prior to measuring the CO₂ sorption or transport properties as practiced in earlier studies²⁵⁻³⁰ erases a portion of the annealing effect that might otherwise be observed. The use of 20 atm of CO₂ at 35°C for PC erases about 20-25% of the endotherm area, and a comparable effect on the sorption might be anticipated. Interestingly, exposure of annealed PC to 60 atm of argon or nitrogen did not result in a distinguishable change in the endotherm area. Thus from this point of view, these gases seem to be better probes of the state of glassy polymers; however, because of their lower solubility than CO₂, the measurement error is greater. In addition, one cannot apply the dual-sorption model with the same confidence for parameter estimation²⁹; hence this potentially useful interpretive tool is sacrificed. In the end, there is a compromise in selecting the best molecular probe for studying the glassy state of polymers.

The increase in the endotherm area on annealing implies a reduction in enthalpy, as might be visualized in terms of the change from line $t = 0$ to line t in Figure 6. The reduction in the endotherm area following CO₂ exposure implies that the enthalpy is increased. Since this area can be reduced to zero for certain CO₂ exposure conditions, the further implication is that the enthalpy has been returned to the line $t = 0$, or the quenched state. If the CO₂ treatment is made more severe than this or applied to an unannealed specimen, one might expect the enthalpy to be raised to a higher level than observed for the quenched state, (line $t = 0$ in Fig. 6). The observed changes in volume and sorption imply that this occurs; however, we saw no direct evidence for this in the thermal analysis of samples treated in this manner. We feel that elevation of the enthalpy does occur, but that this extra excess enthalpy is lost in a less dramatic manner prior to the T_g owing to the higher mobility that exists in such dilated glasses.

Mechanical Properties

It is well known that sub- T_g annealing embrittles glassy polymers.¹¹ Therefore, we thought that it would be an interesting adjunct to the present studies to examine the mechanical properties of the PC films employed here and, especially, to see whether CO₂ conditioning also produced the opposite effect of annealing in these properties as the observations on sorption and enthalpy presented above would lead one to anticipate.

The PC films were cut into dog-bone shapes and tested mechanically with a table-model Instron at a crosshead speed of 1 in/min. The gage length of the specimens was approximately 0.7 in. The results from 10 specimens were averaged, and the error bars in Figure 12 denote the standard deviation among these different observations.

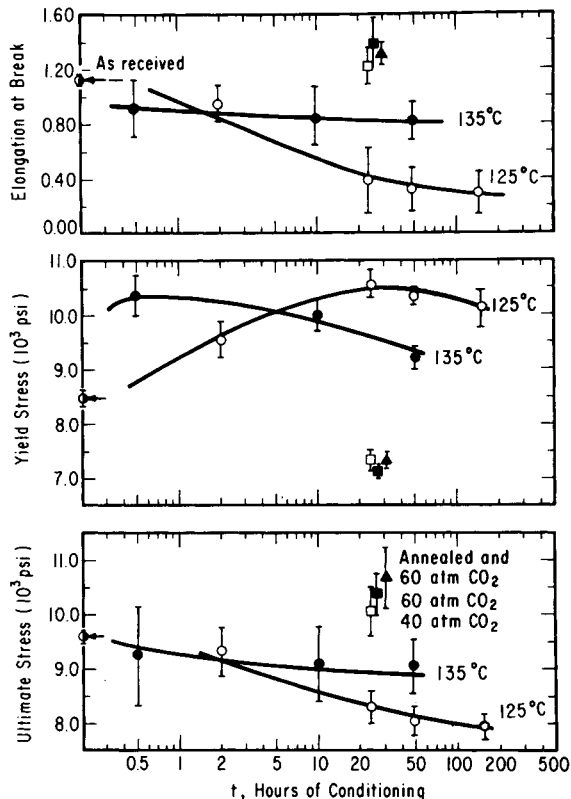


Fig. 12. Effect of annealing and CO_2 exposure on the mechanical properties of polycarbonate. Note that elongation at break is not expressed as a percent. CO_2 exposure was at 35°C for 1 day at 40 (\square), 60 (\blacksquare), and 60 atm (\blacktriangle); however, this latter specimen had been annealed at 125°C for 1 week prior to the CO_2 treatment.

Figure 12 shows various parameters obtained from the Instron test for the treated PC specimens—values for the untreated, or as-received, control are shown as points on the left-hand scale marked by arrows. Modulus values are not shown, since none of these treatments produced a significant variation from the control.³⁷ The yield stress is higher than that of the as-received specimen for all annealing conditions. Generally the yield stress first increases with annealing time and then appears to decline slightly with prolonged annealing.¹¹ The CO_2 -exposed specimens had a lower yield stress than the control. Annealing lowered the elongation at break, whereas CO_2 exposure increased it. The reduction in ductility or the embrittlement caused by 125°C annealing is quite large. The ultimate failure stress is reduced by annealing and increased by CO_2 exposure. Thus we see that CO_2 exposure does in fact have a toughening effect on PC, which is opposite that of sub- T_g annealing.

The area under the stress-strain curve, or energy to break, is a particularly useful measure of toughness, and Figure 13 shows a rather good correlation of this quantity with the observed Langmuir sorption capacity of PC for CO_2 , C'_H , which previous work has shown to be a good indicator of the excess volume of the glass.^{20,25,30} Thus, as one might expect, the toughness of a glass is strongly related to its "free volume."

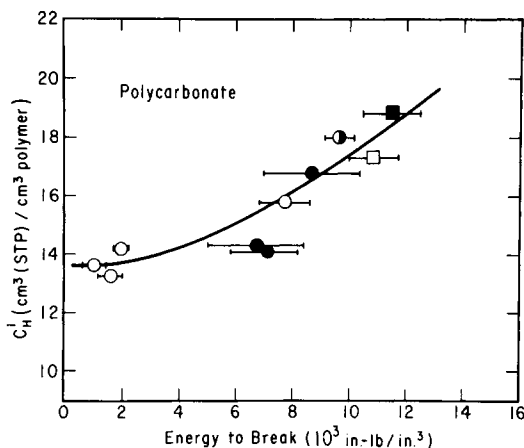


Fig. 13. Correlation of the energy to break polycarbonate with its Langmuir sorption capacity for CO_2 at 35°C : (●) as received; (○) 125°C annealed; (●) 135°C annealed; (□) 40 atm CO_2 ; (■) 60 atm CO_2 .

SUMMARY

The state of a glassy polymer is not an equilibrium one and, consequently, is affected by prior history. As is well known, sub- T_g annealing densifies the glass, reduces its enthalpy, and makes the material mechanically less tough. As seen here, annealing also reduces the solubility of gases in the glassy polymer. On the other hand, exposure of the glass to a penetrant which swells it causes a dilation of the glass which is not immediately reversible on removing this penetrant. As a consequence, the glass has a higher sorptive capacity for gases, is mechanically toughened, and presumably has a higher enthalpy compared to the untreated specimen. Such treatments, then, act in the opposite manner of sub- T_g annealing. With proper precautions, gas molecules can be used as effective probes for characterizing the physical state of glassy polymers.

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