

The Effect of Thermal Pretreatment on the Strength of Polycarbonate

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Synopsis

The effect of preheat treatment at temperatures below the glass transition for various periods of time on selected properties of molded polycarbonate has been studied. Changes in tensile and flexural strength as functions of time and preheat temperature (80–140°C.) were determined and these are discussed in relation to changes in the nature of the β -transition region and the influence of the glass transition region. It is suggested that the preheat treatment produces a greater degree of order within the amorphous region of the polymer, resulting in an increase in strength at temperatures up to 132°C. The strength of the polycarbonate before and after heat treatment appears to be independent of the presence of the equilibrium water content.

Introduction

Peilstocker has shown^{1,2} that molded polycarbonate parts held at 100–130°C., i.e., below the glass transition temperature (142°C.)³ undergo gradual changes in mechanical properties. Thus increases occur in the Martens deflection temperature, flexural strength, and ultimate tensile strength and a reduction in notched impact strength is apparent. The explanation advanced for these changes was in terms of a rearrangement of existing ordered regions of the polymer.

As part of another study we required the mechanical properties of polycarbonate specimens to be in a thermally stable condition and unchanged by subsequent heat treatment in the range 80–110°C. Therefore it was of interest to investigate in more detail the rates of change in strength brought about in polycarbonate specimens by heat treatment at temperatures below the glass transition temperature, and if possible to explain it. Accordingly, we have studied the effects of time and temperature (in the range 80–140°C.) of heating on the flexural and tensile-yield strength and various other properties of polycarbonate specimens. At the same time we have briefly examined the effect of water content on the tensile properties of specimens before and after heat treatment.

Experimental

Preparation of Specimens. Makrolon Grade S (Farbenfabriken Bayer) poly[2,2-propanebis(4-phenylcarbonate)], was employed throughout.

Bars ($4 \times 0.5 \times 0.125$ in.) were machined from extruded sheet; dumbbells, of a type previously described,⁴ were injection molded.

Thermal Treatment. Specimens, contained in stoppered tubes, were immersed in an oil bath at the required temperature ($\pm 0.2^\circ\text{C}$.) for appropriate periods.

Test Methods. Unless otherwise stated specimens were tested after preconditioning at $20 \pm 1^\circ\text{C}/70\%$ R. H. for 24 hr.

Tensile Measurements. Tensile yield strength σ_T was measured using a Hounsfield Tensometer at crosshead speed of 0.1 in. min.⁻¹.

Fracture Energy. The fracture energy of specimens in tensile impact was determined by the method previously described⁴ at a velocity of impact of 320 in. sec.⁻¹.

Flexural Strength. Flexural strength at yield was measured by three-point loading. The method used was in general accordance with A.S.T.M. Designation D 790-58T, Procedure B, except that the samples were conditioned and tested at $20 \pm 1^\circ\text{C}/70 \pm 2\%$ R.H. at a crosshead speed of 0.5 in. min.⁻¹. The maximum yield strength was calculated.

Density. The densities of specimens were determined using a Techné density gradient column maintained at 23°C .

X-Ray Crystallography. X-ray diffraction photographs were taken of thin sections (~ 0.004 in.) of specimens.

Dynamic Mechanical Measurements. Logarithmic decrement δ was measured on specimens with freshly machined surfaces using a torsion pendulum. Measurements were carried out on specimens before and after heating for 24 hr. at 132°C ., at a series of temperatures in the range -175 to $+175^\circ\text{C}$.

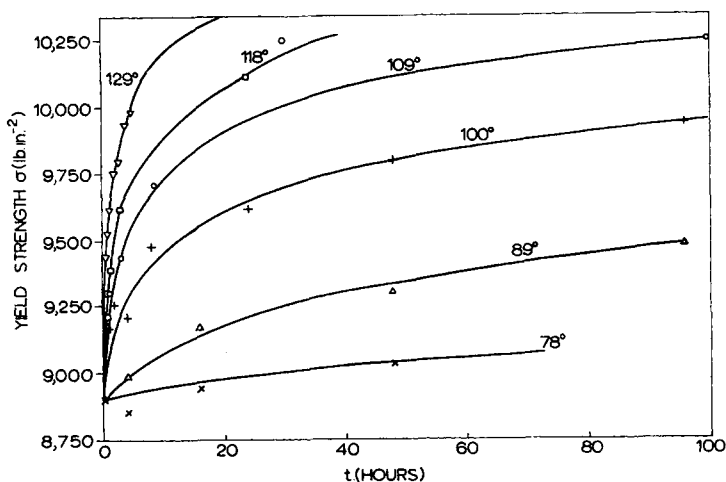


Fig. 1. Tensile yield strength (σ) vs. time of heating (t) at various temperatures ($^\circ\text{C}$.): (\times) 78; (Δ) 89; ($+$) 100; (O) 109; (\square) 118; (∇) 129.

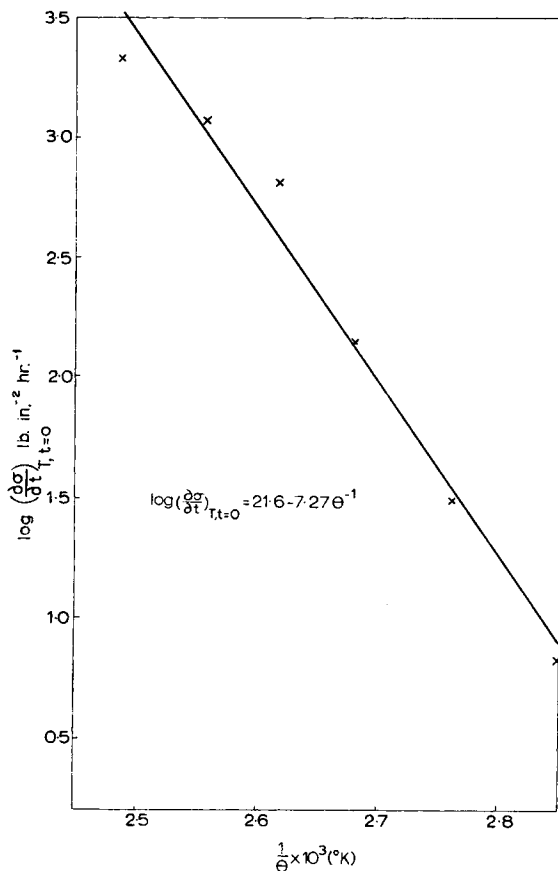


Fig. 2. Log initial rate of increase of strength with time, $\log (d\sigma/dt)_{t \rightarrow 0}$ vs. reciprocal of temperature (θ).

Results

Tensile Properties. The effect of thermal treatment on the tensile strength of polycarbonate dumbbells is illustrated in Figure 1. The initial rates of increase of strength with time ($\text{lb. in.}^{-2} \text{ hr.}^{-1}$) plotted against reciprocal temperature, $^{\circ}\text{K.}$, are shown in Figure 2, the straight line thus obtained yielded a temperature coefficient of 29 kcal./mole for the process.

The increases in tensile-yield strength resulting from heat treatment were accompanied by decreases in extension to yield and energy to yield, e.g., heating for 48 hr. at 100°C. led to changes in extension to yield (-10.6%) energy to yield (-5.3%) and strength ($+11.1\%$).

The relatively small effect of the normal (equilibrium) water content on the tensile strength of both untreated and heat-treated dumbbells is shown in Table I.

TABLE I
Average Tensile Strength and Moisture Content of Specimens
Tested Immediately After Specified Treatment

Treatment	Moisture content	Tensile strength, lb. in. ⁻²
20°C./70 R.H. for 21 days	0.22%	8,900
Heated 100°C./28 days	nil	10,600
Heated 100°C./28 days, stored 20°C./70 R.H. for 15 days	0.22%	10,500
Dried over P ₂ O ₅ for 21 days	nil	8,640
Dried over P ₂ O ₅ for 21 days stored 20° C./70 R.H. for 56 days	0.22%	8,640

Fracture Energy and Extension to Break. The results obtained from impact experiments at 320 in. sec.⁻¹ for a range of specimens are given in Figure 3.

The energy to fracture was reduced by heat treatment but as shown in Figure 4 the draw energy per unit length was unchanged.

Flexural Strength. The effect of thermal treatment of polycarbonate bars on flexural yield strength is shown in Figure 4. The initial rates of increase in strength with time, compare tensile strength results, yielded a temperature coefficient of 29 kcal./mole.

The maximum value of flexural strength (15,500 lb. in.⁻²) recorded was obtained after 280 hr. at 130°C.; this represented an increase of 18% over the initial value. Specimens heated at 120°C. for 280 hr. (flexural strength 15,260 lb. in.⁻²) and then postheated at 136°C. showed decreases in strength (Table II).

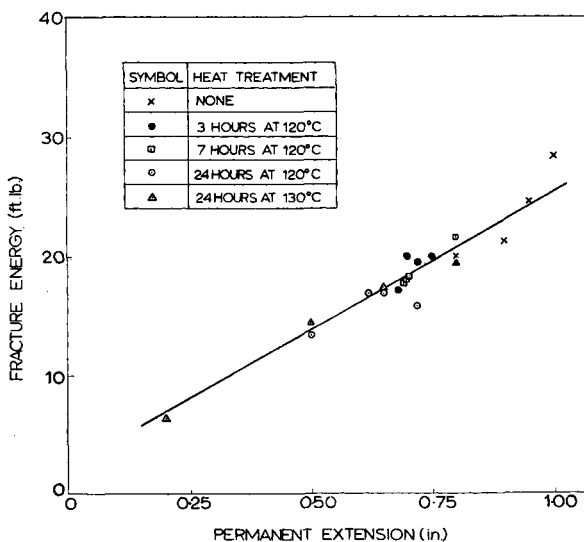


Fig. 3. Fracture energy (ft.-lb.) vs. permanent strain (in.) for polycarbonate dumbbells (ref. 4) tested at 320 in.-sec.⁻¹ after various heat treatments.

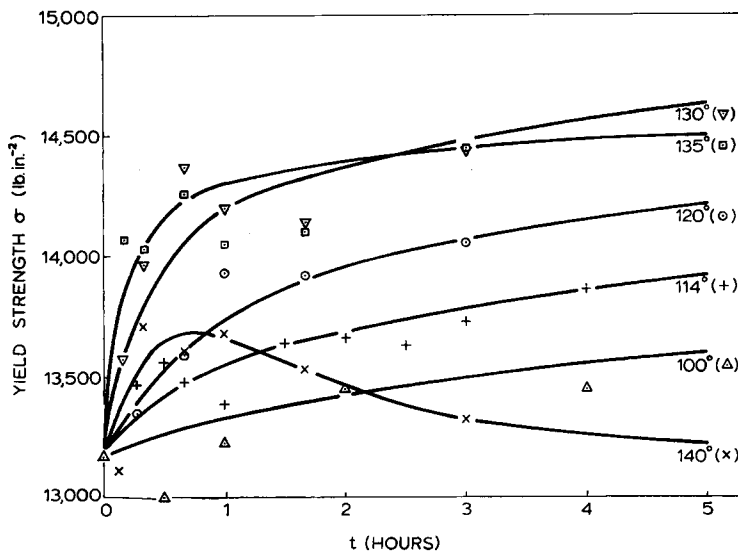


Fig. 4. Flexural yield strength vs. time of heating at various temperatures ($^{\circ}\text{C}.$): (Δ) 100; (+) 113; (\circ) 120; (∇) 130; (\square) 135; (\times) 140.

TABLE II
Post-Treatment, at $135^{\circ}\text{C}.$, of Specimens After Heating at $120^{\circ}\text{C}.$ for 280 hr.

Time of heating, min.	Flexural strength
0	15,260
20	15,000
40	14,620
60	14,640
90	14,700
120	14,680

Isochronal plots showing the relationships between flexural strength and temperature after various times of heating are given in Figure 5.

Density. Table III shows that the densities of heat-treated bar specimens are only slightly different from that of untreated material.

TABLE III
Density of Polycarbonate Specimens at $23^{\circ}\text{C}.$

Pretreatment, $^{\circ}\text{C}.$	Time, hr.	Density, g. cm. ⁻³
—	—	1.2010 (control)
120	2	1.1983
120	560	1.2012
129	0.5	1.1990
129	1	1.1990
129	2	1.1990

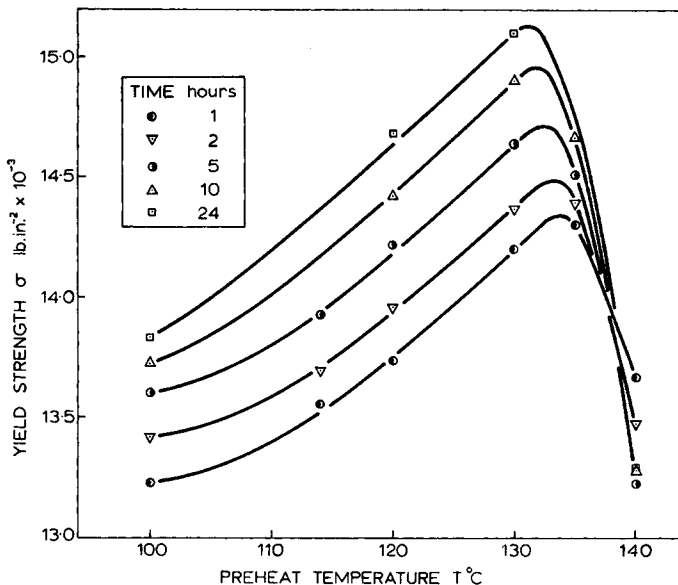


Fig. 5. Flexural yield strength vs. temperature ($^{\circ}\text{C}.$) T at various times of heating (hr.).

X-Ray Crystallography. X-ray powder photographs exhibited very little crystallinity and did not differentiate between control and heat-treated specimens.

Dynamic Mechanical Properties. Comparative results for logarithmic decrement obtained on two specimens, one untreated and the other previously heated at $130^{\circ}\text{C}.$ for 24 hr., are shown in Figure 6.

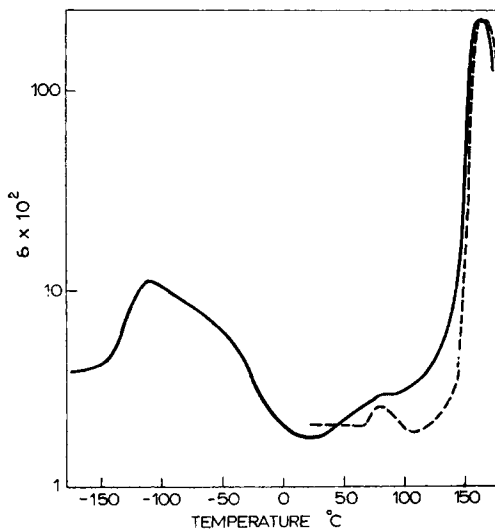


Fig. 6. Change in logarithmic decrement ($\delta \times 10^{-2}$) with increasing temperature ($^{\circ}\text{C}.$): (—) untreated, (---) preheated for 24 hr. at $132^{\circ}\text{C}.$

Infrared Analysis. No significant changes in the frequency, intensity, or breadth of the methyl C—H deformation and stretching bands were observed over the temperature range 20–200°C.

Differential Thermal Analysis. No exotherm or endotherm was observed when an untreated polycarbonate specimen was examined in the temperature range 40–130°C. using a Perkin-Elmer differential scanning calorimeter at heating rates from 2 to 64 deg./min.

Discussion

Thermal treatment of polycarbonate in the region 80–130°C. produced a marked increase in both tensile and flexural-yield strength (Figs. 1 and 4). The rates of increase of strength with time (e.g., Fig. 2) led to temperature coefficients for the process in the initial region of 29 kcal./mole in tension and in flexure. However, the strength appeared to approach a limiting value (Figs. 1 and 4) which increased with temperature up to approximately 130°C.² and then fell slightly (Fig. 4 and Table II). The isochronal plots (Fig. 5) of the flexural-strength results also clearly illustrate this increase up to 130°C. and the subsequent decrease at higher temperatures.

The increased strength observed after heat treatment of specimens was accompanied by decreases in extension and energy to yield.

The fracture energy of specimens tested in tensile impact at high speed was markedly reduced (Fig. 3), although the draw energy per unit length was unchanged. The effects of heat treatment on strength, extension, energy to yield, and fracture energy are consistent with a stiffening of the material due to internal rearrangements. Observation of specimens under polarized light did not however suggest any alleviation of internal (molding) stresses. Changes in the appearance of the surfaces of specimens heated at 130°C. have been reported by Kampf⁵ but removal of the surface of heated specimens before testing did not affect the increase in strength observed. This effect is therefore characteristic of the bulk of the specimen and not just of the surface.

An increase in the degree of crystallinity of the polymer can be discounted in view of negligible changes in density and the lack of change in x-ray diffraction pattern after heating. Both of these techniques have been successfully employed^{1,6} to demonstrate changes in crystallinity brought about at higher temperatures. The result obtained is to be expected, however, as the present work was carried out well below the glass transition temperature and crystallization, in the absence of solvents,⁷ is slow at temperatures below 175°C.⁸

It would therefore appear probable that the increased strength is due to changes within the amorphous region. This is supported by the dynamic mechanical results (Fig. 6). There are three maxima⁹ in the log decrement curve, α (glass transition) at about 160, β at about 80, and γ at about -110°C. The β peak, which is not detectable by differential thermal analysis, appears to be associated with the amorphous region as in poly-

ethylene.¹⁰ It undergoes significant changes on heating, initially a diffuse peak, it is reduced in intensity and sharpened. Stern¹¹ has obtained similar results and the appearance of this peak when the polymer is stretched has been reported by Krum and Muller.¹² These results now suggest rotation of a segment of the chain leading to the possibility of increased order in the amorphous region and higher strength of the specimen.

Murakami et al., have deduced¹³ from broadline nuclear magnetic-resonance spectra that free rotation of the methyl groups in polycarbonate becomes perfect at approximately 90°C. and have linked this tentatively with the temperature for crack formation in the polymer. However Mattes and Rochow¹⁴ have found that free rotation of the methyl groups in various methyl-substituted aromatic polymers can occur at temperatures down to -196°C. and the present infrared studies have revealed no change in the appearance of the methyl absorption in the temperature range 20-200°C. It is not therefore likely that the observed changes in strength and associated properties can be attributed directly to enhanced mobility of the methyl groups in the polymer.

It appears that the relatively rapid cooling, during molding, of the specimens examined, freezes the chains into position. The bulky nature of the chains leads to difficulties in segmental alignment and results in poor packing and unoccupied volume in the glassy state.^{15,16} On the application of heat some motion of the chains presumably becomes possible and they move into more favored (and more ordered) positions without affecting the degree of crystallinity; since the existence of a relatively high degree of order has been suggested¹⁷ (from density considerations) to exist even in the amorphous region.

Further evidence for some degree of freedom has been adduced by Kampf⁵ from electron microscopic studies of the polymer surface after heat treatment at 130°C.

At temperatures above 130°C. this ordering appears to enter into competition with a disordering effect (Fig. 5) which increases markedly from 135 to 140°C. This disorder is due to the onset of the glass transition which results in free rotation of the polymer chains and would oppose the low temperature effect.

It is likely, therefore, that the increased strength and related effects observed after heat treatment of polycarbonate in the temperature range 80-130°C. are due to further ordering of the amorphous regions although the precise nature of this ordering is uncertain.

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Résumé

L'effet d'un traitement à des températures inférieures à la transition vitreuse au cours de différentes périodes de temps, sur certaines propriétés des polycarbonates moulés a été étudié. Les changements dans la force de tension et la flexion en fonction du temps et de la température de préchauffage (80–140°C) ont été déterminés et ils ont été discutés en fonction des mouvements de la nature de la région de transition- β et de l'influence de la région de transition vitreuse. On suggère que le traitement préthermique produit un ordre plus élevé au sein de la région amorphe du polymère, avec comme conséquence une augmentation de la force à des températures allant jusque 132°C. La force du polycarbonate avant et après le traitement thermique apparaît indépendante de la présence de la teneur en eau à l'équilibre.

Zusammenfassung

Der Einfluss der Wärmevorbehandlung bei Temperaturen unterhalb der Glasumwandlung für verschiedene Dauern auf ausgewählte Eigenschaften von geformtem Polycarbonat wurde untersucht. Die Änderung der Zug- und Biegefestigkeit wurde als Funktion der Dauer und der Temperatur (80–140°C) der Wärmevorbehandlung bestimmt und in Beziehung zu Änderungen der Natur des β -Umwandlungsbereiches und zum Einfluss des Glasumwandlungsbereiches diskutiert. Es wird angenommen, dass die Wärmevorbehandlung zu einem höheren Ordnungsgrad im amorphen Bereich des Polymeren und damit zu einer Erhöhung der Festigkeit bei Temperaturen bis zu 132°C führt. Die Festigkeit von Polycarbonat vor und nach der Wärmebehandlung scheint von der Gegenwart des Gleichgewichtsgehaltes an Wasser unabhängig zu sein.

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