

# Correlation between the Mechanical Behavior and Relaxation Processes in the Plastically Deformed Polycarbonate

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## Synopsis

The low-temperature  $\beta$  relaxation has been studied via thermally stimulated depolarization current (TSD) method for polycarbonate that had been cold-rolled and subsequently undergone the  $\alpha'$  relaxation at 70°C as a function of time. It has been found that the intensity of the  $\beta$  process increased as the annealing at 70°C increased. The analysis of the activation energy spectrum associated with the  $\beta$  relaxation indicated that the enhancement in the  $\beta$  intensity was due to the liberation of local dipoles from their aligned orientation as a result of undergoing the  $\alpha'$  relaxation process. Tensile flow curves have also been determined for the same set of specimens. Similar enhancement was also observed in the yield stress behavior. In view of the good correlation between the mechanical property and the structural change revealed by the relaxation study, it was concluded that the variation of the yield stress and the work-hardening in the rolled polymer was primarily associated with those parts of the chain that had been disoriented from their frozen-in conformations.

## INTRODUCTION

The mechanical behavior of polymers has long been associated with the molecular relaxation transition, in particular, the secondary ( $\beta$  mode) relaxation. In many cases, high impact strength is ascribed to the existence of a secondary transition<sup>1-5</sup> which, during the fracture process, is presumed to dissipate a large amount of energy. In the case of ductile-brittle transition brought about by thermal pretreatment below  $T_g$ , however, the accompanied change in the secondary relaxation as measured by conventional dynamic-mechanical or dielectric methods, if any, is too small to account for the macroscopic difference in the impact strength.<sup>6-8</sup> The relaxation transition also manifests itself in the behavior of yield stress. The temperature and/or strain rate dependence of yield stress has been ascribed to Eyring's rate theory<sup>9-12</sup> and the molecular motion occurring momentarily at the yield point is dominated by the relevant processes.<sup>13-17</sup> In addition, rate theory has also been applied to the time dependent fracture of polymeric materials.<sup>18</sup> In the light of these findings, a change in the relaxation process is expected to result in a corresponding change in the yield stress or vice versa.

In the previous paper,<sup>19</sup> we reported a  $\alpha'$  relaxation process at ca. 70°C for cold-rolled polycarbonate measured by thermally stimulated depolarization current (TSD) technique. In this work, the mechanical behavior and the local mode  $\beta$  relaxation have been studied in parallel for the rolled specimens that have undergone the  $\alpha'$  process and the correlation between the  $\beta$  relaxation and the mechanical behavior, in particular the yield stress, as influenced by the  $\alpha'$  relaxation process was investigated.

## EXPERIMENTAL

The material and its treatment are as previously described.<sup>19</sup>

In this work, one set of the rolled specimens with thickness reduction of 24% were placed in the oven maintained at 70°C, i.e.,  $\alpha'$  peak temperature, and annealed for various periods of time. Their tensile flow curves and  $\beta$  relaxation were then determined as a function of the 70°C annealing process, respectively.

For TSD measurements of the  $\beta$  relaxation, specimens were first poled at room temperature with an electric field of 30 kV/cm for 10 min. The specimen was then rapidly cooled down to liquid nitrogen temperature with the field sustained. After short-circuiting the specimen for 15 min following the removal of the field, the temperature was raised linearly at 3°/min and the TSD current was registered. Again, as in the previous work,<sup>19</sup> partial heating method was used to determine the activation energy spectra associated with the  $\beta$  relaxation processes.

Tensile specimens were cut in dumbbell shape with a  $\frac{3}{4}$  in. gauge length and  $\frac{1}{8}$  in. width. An Instron Tensile Tester was used with a head speed of 0.05 in./min. Measurements were conducted at room temperature. The error in the value of  $\sigma_y$  as a result of variation in the specimen's thickness and width was estimated to be less than 7%.

No significant thickness change in the specimen was observed as a result of annealing treatment at 70°C, in agreement with a previous report.<sup>20</sup>

## RESULTS

### $\beta$ Relaxation

When the cold-rolled specimens were annealed at 70°C, it was found that, as a result of the  $\alpha'$  relaxation process, both the yield stress and the low-temperature  $\beta$  mode relaxation change accordingly. Figures 1(a) and 1(b) depict the evolution of  $\beta$  relaxation with annealing time at 70°C of up to 161 hr. It is seen that the peak broadens and generally increases in height as the annealing time increases. The activation energy associated with the  $\beta$  relaxation processes for several of the specimens is plotted against temperature in Figures 2(a) and 2(b). The activation energy spectrum for the cold-rolled LEXAN can be compared with that for solution-cast polycarbonate<sup>21</sup> [Fig. 2(a)]. Unpublished data<sup>22</sup> also showed a significant increase in the activation energy at ca. 190°K upon cold-rolling. For annealing times up to 18 hr, the activation energy data falls on a single curve with 4 steps of constant energy: 0.20, 0.28, 0.36, and 0.83 eV [Fig. 2(a)]. However, long-time annealing, e.g., 161 hr, results in a reduction in the activation energy from 0.83 to 0.70 eV in the fourth step [Fig. 2(b)].

### Tensile Stress

An as-rolled specimen generates two different engineering stress-strain curves depending on the relative orientation of the rolling direction and the tensile test direction as shown in Figures 3(a) and 3(b). The tensile specimen oriented with the tensile axis perpendicular to the rolling direction is seen to exhibit higher ductility than the one oriented parallel to the rolling direction. Also plotted in

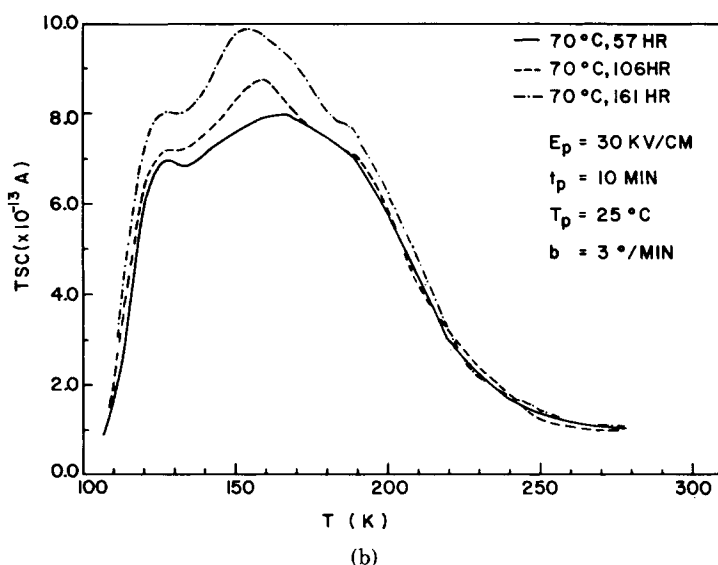
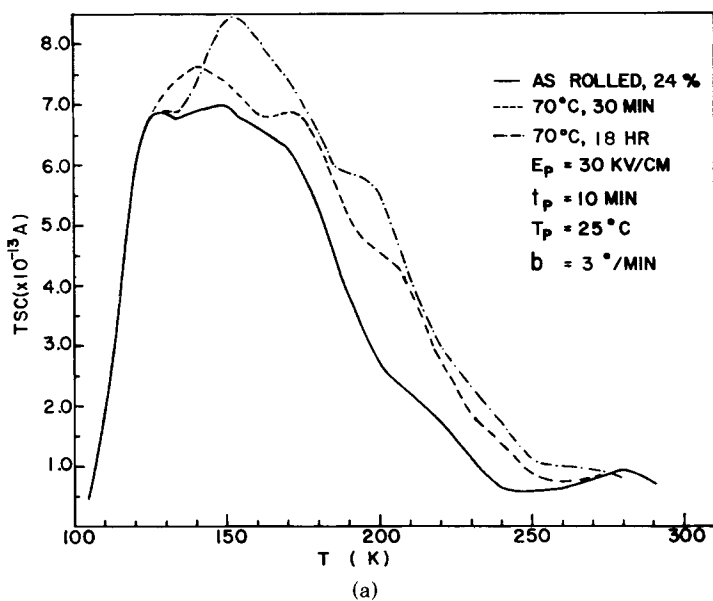


Fig. 1. Evolution of the  $\beta$  relaxation in TSD measurements with the annealing time at  $70^{\circ}\text{C}$  for one set of polycarbonate cold-rolled to 24% reduction in thickness. The experimental conditions and the annealing times are indicated.

Figure 3 are the tensile flow curves after 30 min of annealing at  $70^{\circ}\text{C}$ . In either orientation, annealing tended to promote a yield point (heterogeneous yielding) and decreased the rate of work-hardening. Because the parallel orientation gives no clear yield points in the as-rolled specimens, only those values obtained in the perpendicular orientation are reported here. Figure 4(a) depicts the evolution of the stress at the upper yield point with annealing time at  $70^{\circ}\text{C}$  for the same set of cold-rolled specimens as those depicted in Figures 1(a) and 1(b).

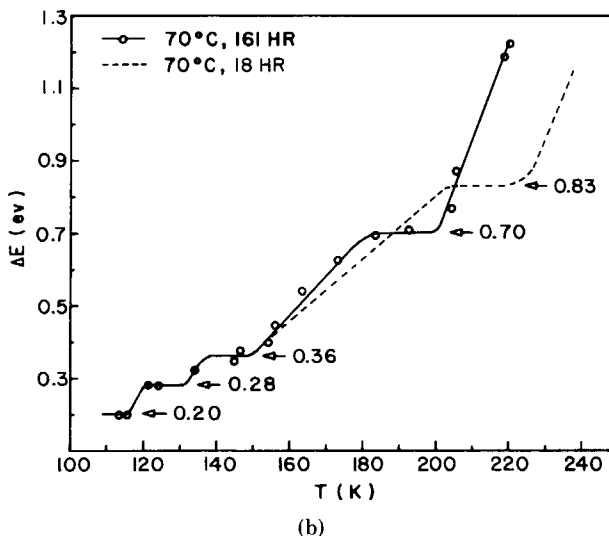
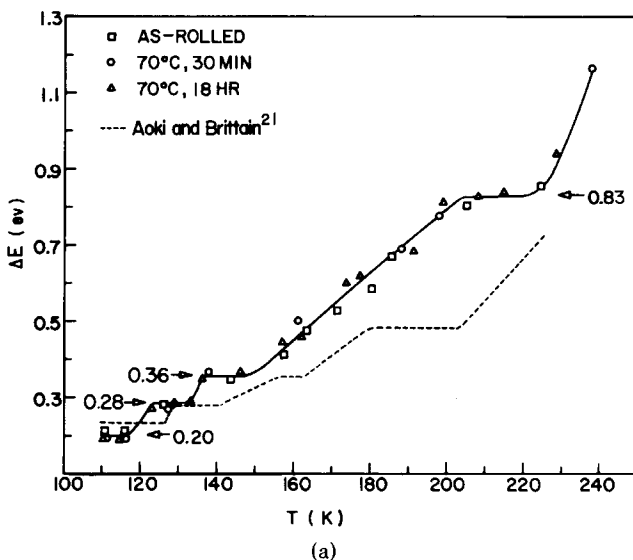


Fig. 2. (a) Temperature dependence of the activation energy for the  $\beta$  relaxation processes in the rolled polycarbonates annealed at 70°C for the times indicated (—), as well as that for the solution-cast undeformed polycarbonate reported by Aoki and Brittain (ref. 21) (---). (b) Activation energy spectrum for the rolled specimen annealed for 161 hr at 70°C (—○—) compared to the activation energy spectrum depicted in (a) for rolled specimens annealed 18 hr (---).

## DISCUSSION

The molecular mechanism associated with the  $\alpha'$  process discussed previously,<sup>19</sup> namely, local disorientational motion of aligned molecular groups, can also be perceived from the behavior of low temperature  $\beta$  relaxation in the rolled specimens. It is seen in Figures 1(a) and 1(b) that  $\beta$  process is enhanced by annealing the rolled specimen at  $\alpha'$  peak temperature. Since the area under the

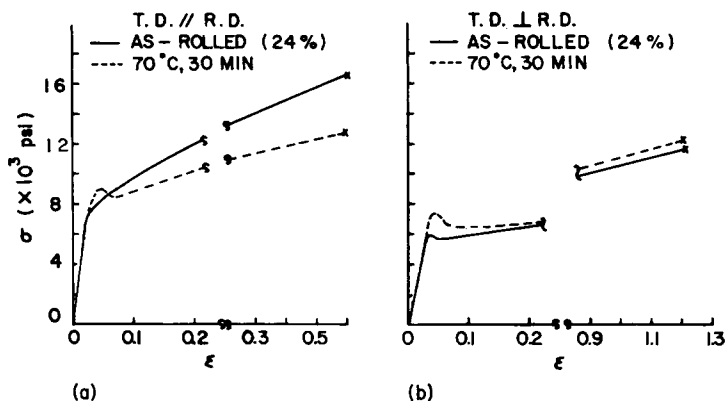


Fig. 3. Engineering tensile flow curves for the rolled polycarbonate: (a) the specimen oriented with its rolling direction parallel to the tensile test direction; (b) the specimen oriented with its rolling direction perpendicular to the test direction.

$\beta$  curve is the total charge released, we have

$$Q = \int_{T_0}^{T=\infty} I(T) dT$$

where  $I(T)$  is the TSD current, this means that more charges are released as a result of the annealing process. On the molecular level, this could arise from a decrease in the activation energy associated with this  $\beta$  process and/or an increase in the number of dipoles available for alignment under the given poling field. It appears that the former is immediately ruled out by the single activation energy curve in Figure 2(a) for annealing time under 18 hr and the enhancement of the  $\beta$  peak is thus mainly due to the progressive liberation, upon annealing, of more dipoles that had been frozen in during the cold-work. Furthermore, the lack of change in the local environment to each particular constituent group for

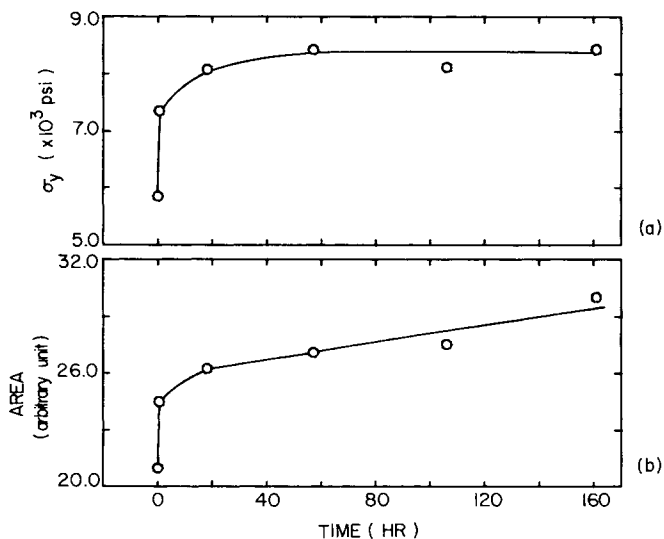


Fig. 4. Property changes as a function of annealing time at 70°C: (a) stress at the upper yield point; (b) area under the  $\beta$  relaxation curve (in arbitrary units).

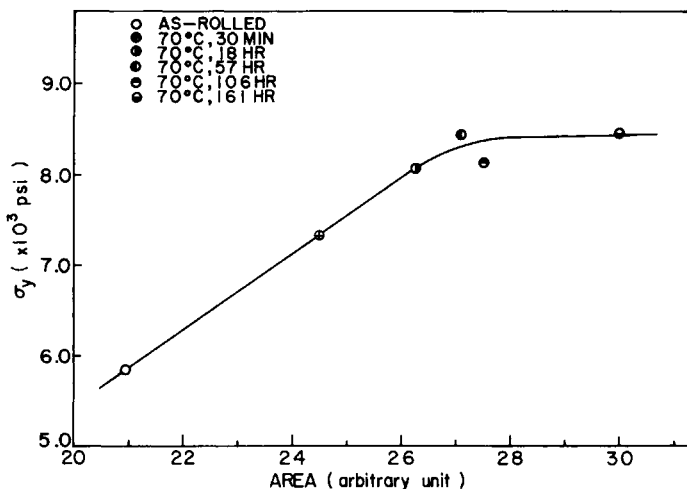


Fig. 5. Correlation between the stress at the yield point and the area under the  $\beta$  relaxation curve for the cold-rolled polycarbonates annealed at 70°C for various periods of time.

up to 18 hr of annealing as implied by the single solid curve in Figure 2(a) requires this liberating motion to be localized, e.g., wagging or torsional motion of phenylene and/or carbonate groups. Thus, the conclusion arrived here on the mechanism of  $\alpha'$  process is seen to justify the one described previously.<sup>19</sup> The reduction in the fourth energy step in Figure 2(b) suggests, in combination with Figure 1(b), that long-time annealing eventually lead to the weakening in intermolecular interaction as the number of the disoriented molecular groups increases to certain extent. This seems to be consistent with the observation illustrated in Figure 2(a) that the isotropic solution-cast polymer<sup>21</sup> has a considerably lower value in its fourth energy step as compared to the rolled polymer in this work.

Annealing at  $\alpha'$  peak temperature causes the yield stress to increase sharply first followed by leveling off, as shown in Figure 4(a). This type of behavior is somewhat similar to that of undeformed polycarbonate annealed at temperatures above 80°C.<sup>23,24</sup> The interpretation, however, is rather different. In the present case, it can be better appreciated if the concurrent structural change is also taken into consideration. This is done in Figure 4(b) where the area under the  $\beta$  peaks determined from Figures 1(a) and 1(b) is plotted as a function of annealing time at 70°C. A behavior in close resemblance to that of the yield stress is observed, indicating a coherent relationship between the evolution of the yield stress and that of the  $\beta$  relaxation. The latter can be better perceived if one combines Figures 4(a) and 4(b) into a plot of the yield stress versus the area shown in Figure 5. It is interesting to see that for the annealing time under 18 hr,  $\sigma_y$  increases linearly with the area, suggesting that it is those parts of the chain which have been disoriented from the frozen-in configuration that cause and predominate the promotion of the stress at the yield point. This is, perhaps, due to the greater degree of freedom enjoyed by these parts than the rest of the chain. Figure 5 further illustrates that as the annealing time progresses, more chain segments are liberated, causing the area to increase continuously. The enhancement of the stress at the yield point, however, suffering from the weakening in intermolecular interaction which sets in at this stage, begins to level off, even though more

regions of the material are becoming capable of carrying the load. Similar argument can also explain the suppression of the work-hardening (Fig. 3) as a result of annealing. It has been proposed that work-hardening is prompted by the lining up of the molecular chain along the tensile axis.<sup>25</sup> As the alignment proceeds increasingly, more stress is required to cause the molecular chains to slide over each other. Consequently, a liberation of the local chain segments from their aligned orientation as a result of annealing at 70°C would reduce the stress required to deform the material. Thus, it is seen that the mechanical behavior of the rolled polymer can be well correlated with its structural change revealed by the relaxation study. Finally, it is to be noted that a similar curve was used by Boyer<sup>2</sup> to correlate the impact strength of plasticized PVC with its  $\beta$  relaxation height and a linear relationship between toughness and the mechanical dissipation factor was observed by Sacher<sup>26</sup> for several untreated films.

### CONCLUSIONS

(i) Low-temperature ( $\beta$  mode) relaxation study has further confirmed the nature of localized motion associated with  $\alpha'$  process at 70°C reported previously.<sup>19</sup>

(ii) Cold-work has modified polycarbonate in its tensile property at room temperature as well as its  $\beta$  mode relaxation: both the stress at the yield point and the relaxation intensity are suppressed.

(iii) The yield stress and  $\beta$  relaxation tend to vary in a coherent way in deformed PC undergoing the  $\alpha'$  process.

(iv) Yield stress in the rolled polymer is primarily associated with those parts of the chain that have been disoriented from their frozen-in conformations resulting from cold-work.

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