Effect of Thermal Pretreatment on the Fracture Behavior of Polycarbonate in Medium Strain Rate Tensile Tests

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SYNOPSIS

The fracture properties of as-received and annealed (48 h at 403 K) commercial polycarbonates (PC) were examined in tensile tests with an average strain rate of $\dot{\epsilon} = 2\ s^{-1}$. Both materials were subjected to tensile tests at temperatures ranging from 223 to 423 K. The results were processed by a computer interfaced to the testing machine. The tensile strength of the annealed (pretreated) PC was superior to that of the as-received (untreated) material. The elongation at break and the fracture energy, then, decreased due to annealing at all temperatures, yet followed impact strength curves. Fracture analysis and fracture morphology revealed clear differences in the behavior of the materials. Fracture nucleation occurred commonly at several points in the pretreated specimens, whereas only one nucleation point was found in the untreated specimens. Shear yielding morphology, which indicated plastic deformation, started to appear at a lower temperature in the pretreated specimens than in the untreated ones.

INTRODUCTION

Much attention has over the last few years been paid to the deformation and fracture mechanisms of polycarbonate because of its considerable strength and ductility. A number of extensive studies on the behavior of PC under tensile stress have been carried out,[1-10] the main conclusion being that deformation behavior and fracture are affected by several different factors. One of the most important factors would seem to be the internal structure of the polymer, which is affected by different kinds of heat treatment.[5-10] Annealing runs performed below the glass transition temperature (T_g) 423 K have been found to improve the yield strength and to reduce the elongation at break as measured at room temperature (RT). Our research group has earlier studied the effect of heat treatment on the behavior of PC in high strain rate compression tests ($\dot{\epsilon} \sim 10^3/s$)[11,12] and found growth in strength only in experiments carried out at higher temperatures (over 403 K). The effect of heat treatment has been most evident in impact tests, where we have earlier found a drastic decrease in the impact toughness (Fig. 1), and the embrittlement temperature has climbed up to 353 K.[13] Similar results have been found in a number of publications.[6,9,14-16]

Previous research has also focused on the effect of temperature and molecular relaxations on the fracture of PC in tensile tests.[17,18] The results have been presented by the term K_{IC} (fracture toughness), and the values for K_{IC} have been calculated by the stress-causing crack initiation in prenotched specimens. The results at temperatures of 100–373 K[18] and at 153–293 K[17] showed that the K_{IC} values follow the loss modulus or the damping factor tan δ.

This study differs from those just discussed in several respects. The experiments were carried out with unnotched specimens and using a relatively high strain rate; the results are presented in the form of fracture energy (referring here to the energy required to break the bar transversely, i.e., the strain integral of the stress–strain curve). All experiments were carried out at temperatures above the secondary transition temperature, which is located at 173–193 K, and concentrated on revealing the effect of test temperature on the fracturing of PC and annealed PC.

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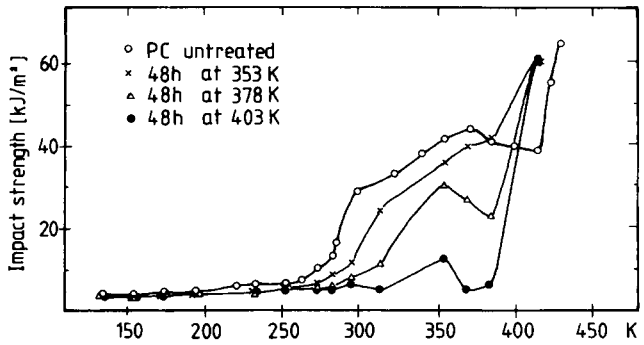

Figure 1 Notched impact strength curves of untreated PC and PC annealed at different temperatures by DIN 53453 method as presented in Ref. 13.

MATERIAL AND SPECIMENS

The specimens were machined from commercial 4-mm PC sheet Sunloid EC 100, manufactured by Tsutsunaka Plastic Industry Co. Ltd. All specimens were machined in the same direction to avoid differences in orientation. The dimensions and shape of the specimens are shown in Figure 2. The short gauge length is due to the limited free space for the fixing jaws in the heating chamber. Part of the specimens were annealed by keeping them at a heating chamber at 493 K for 48 h. They were cooled down at room temperature. To eliminate the effect of surface quality as a cause of crack nucleation as far as possible, all machined sides of the bars were finished by water grinding paper (grit 800) before testing.

EXPERIMENTAL

All tensile tests were carried out on an electrohydraulic Fiskars material testing unit at a strain rate of 2 s^{-1}, which can be considered a medium strain rate. The specimens were tested at ten different temperatures within the range of 223–423 K. A heating chamber was used to generate the temperatures required. For each specimen the temperature was allowed to settle for 15 min, and at each temperature three or four parallel experiments were performed.

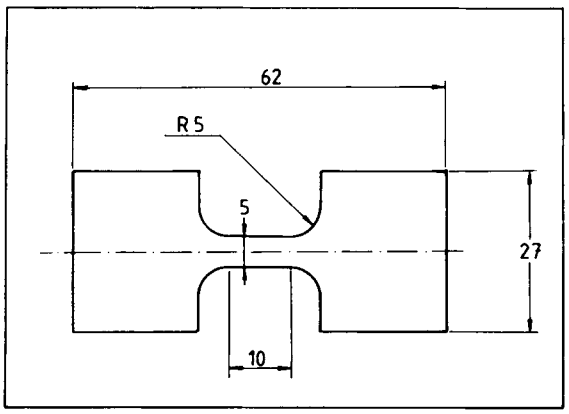

Figure 2 Shape and dimensions of tensile specimens. Thickness 4 mm.

Load measurement was arranged by a load cell attached to the upper jaw, while elongation was measured by a sensor in the working cylinder. The measured data were fed to a minicomputer, which calculated the stress–strain curve and the fracture energy in accordance with the program introduced in the previous report.[27] The computer started the tensile test by giving a trigger pulse to the function generator of the material testing machine and then read force and elongation values for a preset period via an A/D converter. On the basis of these values the computer calculated strain and stress values using the generally known equations:

$$e = \frac{\Delta l}{l_0} \quad \text{and} \quad \sigma = \frac{F(1+e)}{A_0}$$

where l_0 = original gauge length of the specimen
Δl = measured length increase
A_0 = original cross-sectional area of the specimen
F = measured force

The program printed out the values of the yield strength and elongation at break and plotted a stress–strain curve for each test.

Fracture energy was calculated by integrating the stress–strain curve up to the fracture point, i.e.,

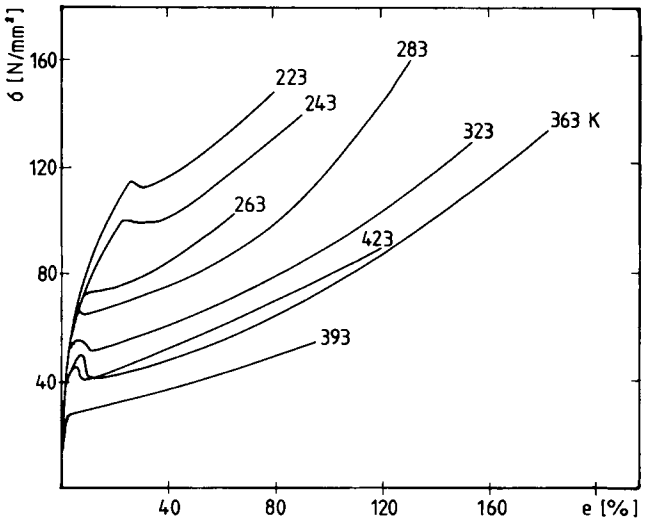

Figure 3 Stress–strain curves of untreated PC at different temperatures.

$$W = \int_{e}^{e_F} \sigma(e)\, de$$

In practice integration was performed by determining the area between the stress–strain curve and the elongation axis using a simple trapezium formula. The details have been presented in previous work.[27]

The cracked bars were first analyzed by an optical stereomicroscope to examine the fracture processes, and the fracture surfaces were then examined by a scanning electron microscope.

To allow analysis of the changes in the microstructure of the specimens caused by annealing, the specimens were subjected to chemical etching—as in the literature—by NaOH aqueous solutions[5,8,19] and by KOH aqueous solutions.[20] Also, the specimens were subjected to ionic bombardment, where the polished surface of the samples was bombed by argon ions (4 kV, 40 mA) on a JEOL MIM.

RESULTS

Stress–Strain Curves

Examples of stress–strain curves obtained on untreated PC are given in Figure 3, and those on annealed PC are shown in Figure 4. These examples are selected so as to represent a typical case for each temperature.

All curves of untreated PC show a sharp yield peak except those for 393 K, which, in addition, kept below other curves. The curves obtained on annealed materials were irregular, and no constant or typical pattern can be found here. An outstanding case was curves for 393 K, which all remained clearly below the others.

Yield Strength and Elongation at Break

Yield strength was obtained from the curves as the value of the yield, or, where no yield point appeared,

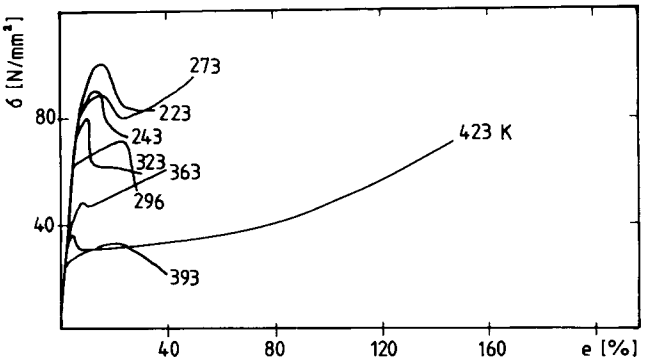

Figure 4 Stress–strain curves of annealed PC at different temperatures.

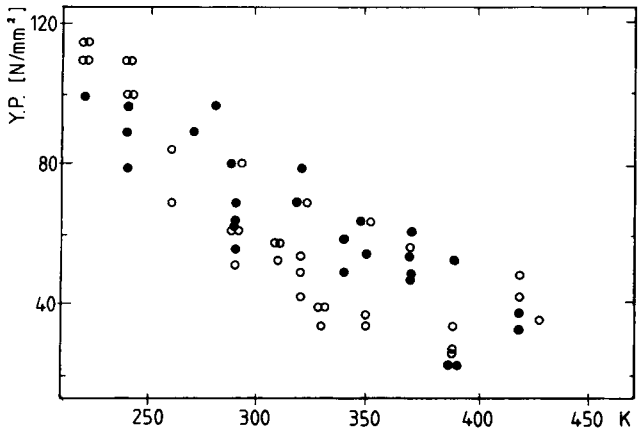

Figure 5 Yield strength of PC (○) and annealed PC (●).

the stress value was taken from the point of ~ 5% of strain. All yield strength values are given in Figure 5. Here, we can clearly see that the yield strength of the annealed PC is higher than that of the untreated material at almost every temperature; and, further, the yield strength of the former decreases less in relation to the temperature than that of the latter.

Figure 6, illustrating elongations at break, shows that the elongations of PC have reduced approximately by one-half due to heat treatment. The elongation at break of untreated PC shows a broad peak between 223 and 393 K, whereas that of the annealed material shows no distinct maximum. The scatter of elongation values is disturbingly large in both materials.

Fracture Energy

The fracture energy values versus temperature as printed by the computer are given in Figure 7. Due to the considerable variations in the elongation at break, the energy values are also widely scattered. Untreated PC shows a clear peak between 223 and 393 K, and its energy values are some ten times higher than those for the heat-treated material.

Microscopic Analysis of the Fracture Surfaces

The photographs of the cracked specimens are shown in a series in Figure 8. The fracture surfaces of the specimens were also examined and photographed by an electron microscope. Because of the large size of the surfaces, at least four partial pictures had to be taken of each fracture surface. The fracture surfaces are shown in a series in Figure 9.

Using the terminology presented in literature,[1,13,14,21,22] cracking in the specimens can be characterized as follows. The necking line of the untreated specimens was always perpendicular to the stress axis, whereas that of pretreated specimens was at an angle of 45° to the stress axis. In untreated

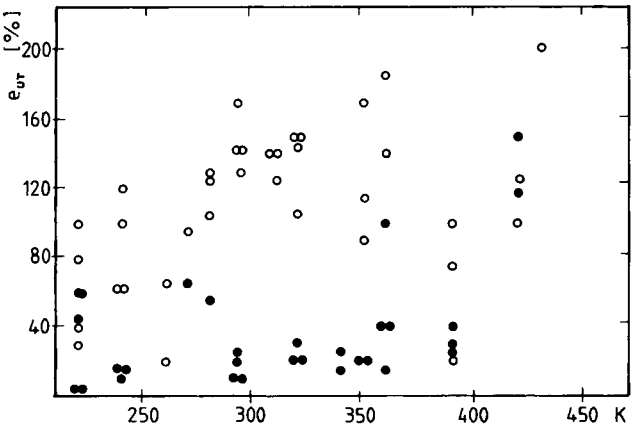

Figure 6 Elongation at break of PC (○) and annealed PC (●).

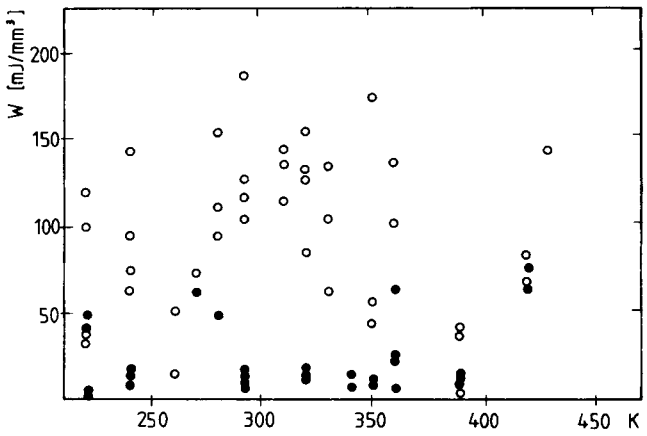

Figure 7 Fracture energy computed from the stress–strain curves of Figures 3 and 4, PC (○) and annealed PC (●).

specimens, the crack had nucleated at one point. The cracks in annealed specimens were rough and irregular, and nucleation had occurred at several points on the side of the bar. In addition to a 45° necking line, slip bands[1] were also found in many specimens. No logical explanation was found for the

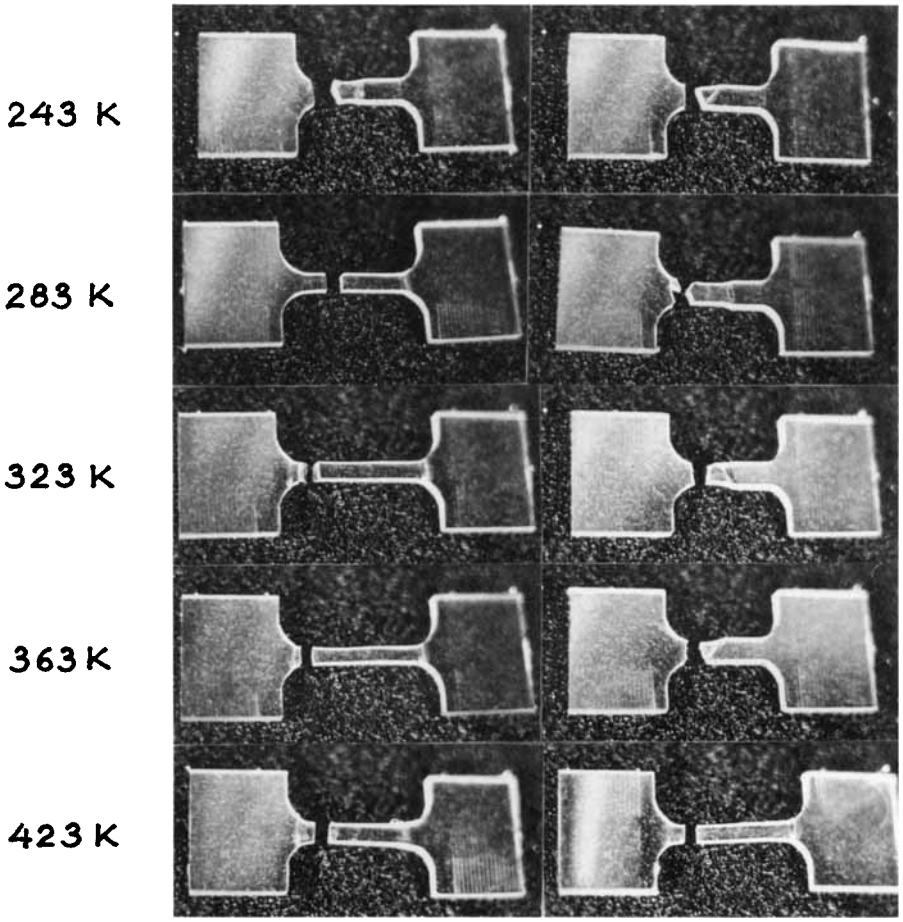

Figure 8 Comparison of tensile specimens fractured at different temperatures; annealed PC on the right.

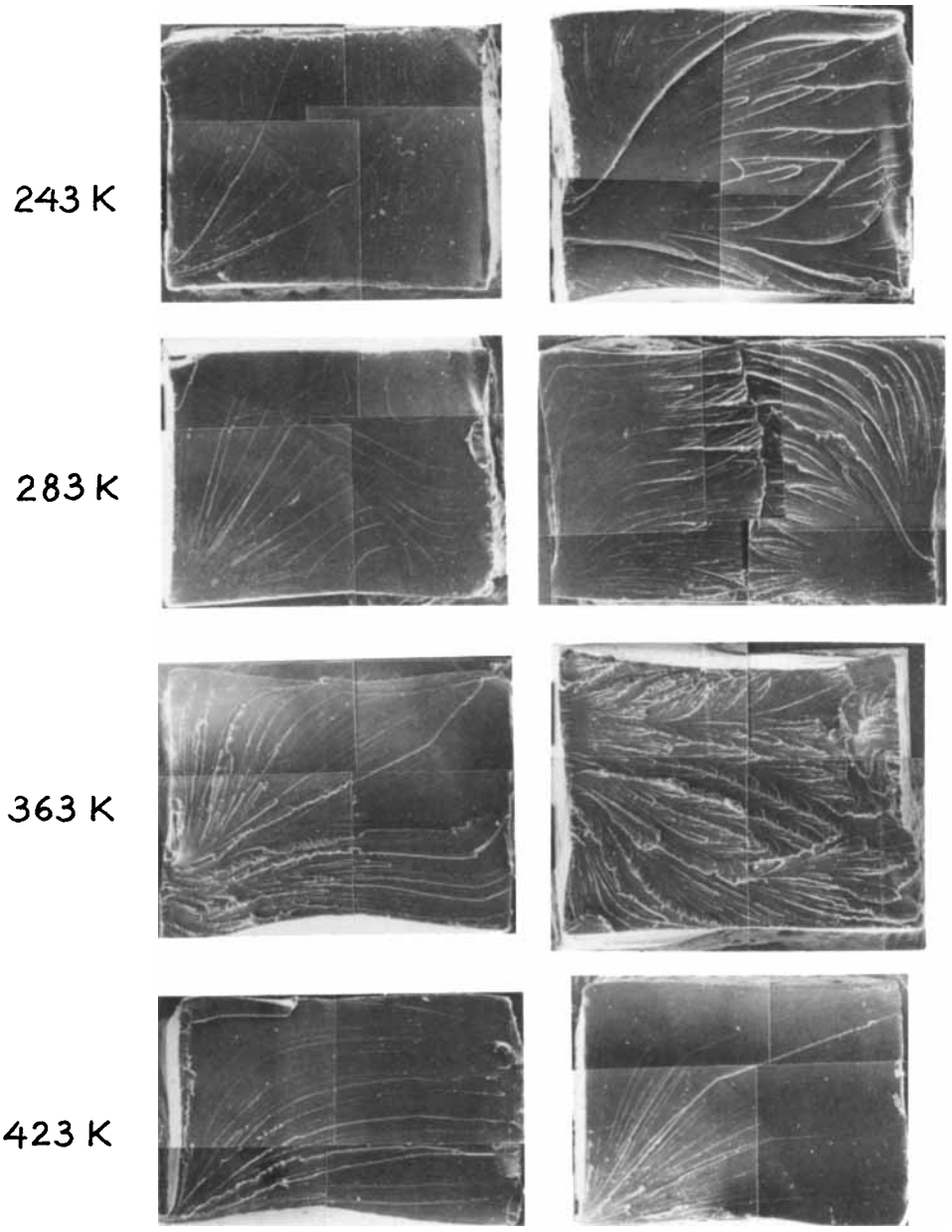

Figure 9 SEM microphotographs of fracture surfaces; annealed PC on the right.

regular necking and considerable elongation of annealed specimens at 223 and 423 K.

Scanning electron microscopy (Figure 9) revealed that cracking in PC had up to 353 K occurred by the crazing mechanism and from 363 upward by shear yielding. The surface found at 433 K was very smooth.

Cracking advanced in the annealed specimens by crazing up to 243 K, where shear yielding appeared in the fracture surface. The fracture surface found at 423 K was very smooth.

Changes in the Microstructure

Neither the chemical method nor ionic bombardment revealed the microstructural differences in the specimens caused by heat treatment. Some sources introduce nodular structures, which have been called forth by oxygen ion bombardment[23] or by chemical etching.[5,19,20] Nodular structures have been found in relatively thin specimens (< 1 mm), whereas attempts with thicker specimens have in this respect been unsuccessful.[8]

DISCUSSION

The present experiments clearly revealed the effect of the surface in cracking. Although the specimen surfaces had been carefully finished, even small scratches easily led to crack nucleation, causing considerable scatter in the results. The specimen surfaces had become scratched during machining and other handling. Prenotching as done in literature[17,18] would, of course, have eliminated the surface quality problem. Besides the important role of the surface, another factor that caused some scatter in the calculation of fracture energy was that the necking of the specimens was not taken into account, but the original cross-sectional area was used instead.

Heat treatment had caused embrittlement, which was manifested by the drastic decrease in the elongation at break and in the fracture energy. An interesting finding is that, although previous works have obtained the same effect in impact experiments, the fracture morphology differs radically between the two cases.[13] This can most likely be explained by the different stress geometry and strain rate. Figures 8 and 9 reveal annealed specimens to have very low elongation in comparison with untreated specimens. On the other hand, the fracture surfaces shown in Figure 9 for the temperatures 243, 283, and 363 K indicated that the propagation of the fracture was obstructed in particular in the annealed specimens. This implies that the annealing of PC affects both plastic deformation and the fracture mechanism.

Explanations offered for annealing embrittlement are not quite established. Most commonly, it is argued that the phenomenon is a result of the internal arrangement of the material,[7,14,24,26] whereby the possibilities for molecular motions decrease with the decreasing entropy. This theory receives support from earlier results,[6,13] according to which the density of PC increased by 0.1% in the same heat treatment.

Another interesting result is the peak that was found in the curves of both fracture energy and elongation at break as shown in Figures 6 and 7. Annealing seems to remove this peak almost entirely. The same peak (at 293–393 K) was earlier found by our research group in impact tests, as Figure 1 shows. It is claimed in the literature that this peak is caused by intermediate relaxation, which arises in PC deformation or in rapid heating and cooling. This relaxation has earlier been noted in mechanical[5,14] and dielectric[7,24] measurements. An extensive account of these results is given in the literature.[25] A closer look at the fracture surfaces in Figure 9 also shows that in untreated PC a shear yielding-type ductile fracture surface appears exactly at the peak temperature of this relaxation, 363 K. In annealed PC the shear yielding-type fracture appears at a considerably lower temperature, 243 K, i.e., at the beginning of the effective range of this relaxation.

Internal arrangement and the relaxation theory seem to support each other rather well. In earlier impact studies[13] our group found that the peak, even if a small one, remained at all treatment temperatures. Obviously, even small internal conformation changes are adequate to cause this molecular motion.

Referring to the relaxation theory,[18] it can be noted that medium strain rate tensile tests give such fracture energy results to PC that are proportional to the loss factor of the material. The effect of T_g relaxation is manifested in the rise in energy curves at 433 K, and at low temperatures the peak for energy curves can be expected at $T < T_g$ relaxation temperatures.[17,18]

CONCLUSIONS

Due to the method of calculation and the surface of the specimens, there was a high degree of scatter in the results of the rapid tensile tests ($\dot{\epsilon} = 2\ s^{-1}$), which affected the analysis of the results. However, the following conclusions could be drawn:

1. The annealing of 48 h at 403 K caused a degree of embrittlement in the polycarbonate, which was displayed as a drop of elongation at break and fracture energy at all test temperatures. Yield strength, by contrast, showed a slight increase.
2. With untreated PC the curves of the elongation at break and fracture energy showed a wide peak between 220 and 390 K. This maximum was not visible in annealed PC. The obtained curves are analogous with impact strength and tan δ curves.
3. The present study shed no new light on phenomenon of embrittlement, but the results support the findings published earlier.
4. The fracture surfaces revealed that in untreated specimens the fracture nucleated at one point while in treated specimens there were several nucleation points. From the temperature of 363 K upward untreated PC

had fractured by the shear yielding mechanism. With annealed PC partly ductile fractures started at a considerably lower temperature of 283 K.

5. Although the results concerning annealing embrittlement were analogous with earlier impact test results, fracture morphology was completely different.

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