

Mechanical and Thermal Properties of Polycarbonate, Part 1: Influence of Free Quenching

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ABSTRACT: The effect of different thermal treatments on the mechanical and thermal properties of polycarbonate was investigated. The first quenching procedure which involves the quench of the samples from the melt state to different temperatures allowed improving impact strength and elongation at break for a quenching temperature of 0°C. A second quenching procedure, corresponding to specimens heated again at 160°C ($T_g + 15^\circ\text{C}$) and quenched a second time, showed a better enhancement of

the impact strength and elongation at break to the detriment of other properties such as elastic modulus, density, yield stress, and heat distortion temperature, for a quenching temperature of 40°C. This effect was associated to the existence of a relaxation mode around 35°C. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1505–1514, 2008

Key words: free quenching; polycarbonate; mechanical properties; thermal properties

INTRODUCTION

Residual stresses (RSs) produced by transient thermal gradients in inorganic and polymeric glasses have received a large attention in the past because of their technological importance.^{1–3} RSs are commonly classified as residual microstresses and residual macrostresses.⁴ In laboratory, two methods are available for introducing RS in polymers: nonuniform cooling (thermal quenching) and nonuniform plastic deformation (cold working). During processing, the RSs are introduced by nearly all techniques used for polymer manufacturing. For example, the variations of the injection molding conditions may produce changes in molecular orientation. To avoid a contribution of flow-induced orientation, free-quenching experiments have been used by several investigators on semicrystalline and amorphous polymers.^{5–7} In some cases, compressive RSs can improve the impact strength, fatigue behavior, and resistance to environmental stress cracking.^{8–10} Polycarbonate (PC) is used in various applications for its outstanding properties and especially high toughness, high impact strength, and high optical transparency. One of the main applications is for building windows because of its low density relatively to glass. This article will describe how to produce favorable RSs in PC by optimizing the process of thermal quenching

and the subsequent effects on mechanical and thermal properties.

The high impact strength of PC is partly explained by a greater free volume in this material than in most polymers. Besides, this property is maintained between -125°C and 100°C which corresponds to the temperature range where mechanical relaxation modes exist.^{11,12} According to Cheng et al., for sub-annealing temperatures close to T_g , the toughness is decreased and this effect was attributed to the physical ageing which induces a severe brittleness.¹³

PC applications are also limited to thin molded articles because its impact strength is highly sensitive to the presence of notches.¹⁴ The presence of sharp notches or even small notches caused by a microscopic surface degradation decreases the impact strength.¹⁴ However, the addition of appropriate polymers or terpolymer and core shell impact modifiers can be one way of effective toughening methods for PC that can be used in thick sections.^{15,16} To expand the usefulness of PC in a variety of applications, it is important to explore ways to prevent or minimize loss of toughness during sub- T_g annealing and to reduce the sensitivity to the presence of notches and consequently the loss of the impact strength. RS generation by the quenching process is known to be one effective method in toughening PC. RS measured in polymers free quenched, without flow history, are parabolic in profile, with the maximum tensile stress in the center of the sample and the maximum compressive stress on the surface with a magnitude twice the one of tensile maximum as

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reported by Kwok et al.¹⁷ Several studies indicated that residual compressive stresses improve Izod impact strength by suppressing crazes.^{7,18} Moreover, the presence of compressive stresses reduces the sensitivity to fatigue crack initiation at surface, cracks, and flaws.¹⁹ The higher values of birefringence corresponding to higher stresses are obtained with the lower quenching temperature.^{6,20–22} Shyu et al.⁶ have studied the effects of the initial temperature, quenching temperature, and quenching media on the development of RS in PC. They found that the birefringence in freely quenching PC plates was positive at the center and negative at the surface at any initial temperature.⁶

Akay and Ozden showed that heat distortion temperature (HDT) and Izod impact strength were also sensitive to the RS.²³ RSs imposed by the process of free quenching determined by photoelastic measurements are stable with time and allow effective improvement of mechanical properties of PC.^{10,24}

To improve the impact strength of PC, the effect of a first quenching from the melt state and a second quenching from $T_g + 15^\circ\text{C}$ has been investigated. In addition to impact characteristics, tensile and thermal properties were measured and presented in this article for pure PC. The Part 2 of this article is dedicated to the study of TiO_2 pigmented PC.²⁵

EXPERIMENTAL

Materials

The polymer used in this study is a commercial PC, Makrolon[®] 2620, supplied by Bayer (Germany), with average molecular weight of about $M_w \sim 57,404$. The melt index at 300°C is 19.6 g/10 min, the polydispersity index is 2.16, and the glass transition temperature is about 144.5°C .

First quench procedure

Pellets were dried in an oven at 120°C and then put into the mold and pressed at 25 bars for 12 min at different molding temperatures ranging from 220 to 260°C . Then the samples were immediately quenched from molding temperature into water bath at 0, 20, 30, 40, 60°C or air quenched during 15 min. All samples were 3 mm thick and this step was named as “first quench.”

Second quench procedure

The second quench procedure was carried out only for samples initially molded at 230°C . These specimens were heated again in an oven at 160°C ($T_g + 15^\circ\text{C}$) for 3 h and were immediately quenched a second time in water baths at different temperatures (0,

20, 30, 40, 60°C) for 15 min. This procedure was named as “second quench.”

Annealed samples

Finally, to get a sample as reference, an annealing is performed. Annealed specimens were prepared using samples first quenched in air. These samples were heated again at 160°C for 2 h and finally slowly cooled in the oven until room temperature at a rate of about $0.5^\circ\text{C min}^{-1}$. These samples were named as “annealed samples.”

DMA samples

Some samples molded at 230°C and cooled in air were used for dynamical mechanical analysis measurements to study the effect of second quenching temperature. The following thermal cycle was applied: the samples were first heated at 160°C for 2 h and slowly cooled at room temperature. Then, they were heated again at 160°C for 2 h and immediately quenched into water baths at different temperatures (0, 20, 30, 40, 60, 80°C) for 15 min.

Tensile test

The tensile properties were determined using dumb-bell specimens of 115 mm length, 13 mm width, and a gauge length of 20 mm. The test was carried out using a universal testing machine with a crosshead speed of 10 mm/min. The test procedure followed ASTM D 638-72. From the experimental stress–strain curves, tensile properties (modulus of elasticity, yield stress, and elongation at break) of the quenched PC were calculated at room temperature. Five specimens were tested and the average values were used for the data plot.

Notched Izod impact strength

Izod impact strength properties were determined at room temperature with a CEAST 6546/000 machine provided with a 15 J pendulum according to the ASTM D 256-73, and using specimens of $3 \times 12.7 \times 63 \text{ mm}^3$ dimension. Some specimens were molded with a notch radius of 0.5 mm. For others specimens, a notch of radius 0.5 mm were machined. The radius was chosen such that the tip of the notch was located in the residual compressive zone. These stress zones were determined by photoelastic examination of the sample between cross Polaroid's under white light. The depth of compressive stresses was estimated at $\sim 15\%$ of the sheet depth below the surface by Polaroid light. The color of neuter line is black (zero order). The radius of 0.5 mm was localized in the zone of compressive stresses, it was well

observed by Polaroid light. At least five specimens were tested and the average value was used for the data plot.

Thermomechanical tests

Dynamic mechanical analysis

Dynamic mechanical properties were determined using an AR2000 from TA Instruments (see the "DMA samples" section). Samples were studied at a frequency of 1 Hz in the linear viscoelastic range. Samples of $50 \times 10 \times 3 \text{ mm}^3$ were tested using a normal force of $2 \pm 1.75 \text{ N}$ and a strain controlled sinusoidal torsion loading of maximum amplitude 0.05%.

Experiments were performed between -130°C and 170°C with a heating rate of 3°C min^{-1} . The relaxation spectra were obtained by recording the storage modulus (G'), loss modulus (G''), and loss factor ($\tan \delta$) in the whole temperature range.

Heat distortion temperature

The HDT was obtained in accordance with ASTM D 648, which describes HDT as the temperature where a specimen ($3 \times 13 \times 127 \text{ mm}^3$) deflects by 0.25 mm under 1.8 MPa while heated in an oil bath at a rate of 2°C/min . At least two specimens were tested and the average value was used for the data plot.

RESULTS AND DISCUSSIONS

Effect of first quenching

Impact strength and elongation at break

Figure 1 shows the molded and machined notched Izod impact strength (a_k) as a function of molding temperature for different first quenching temperatures. In all cases, the values of Izod impact strength reach a maximum for the molding temperature of 230°C . On the other hand, we notice that the Izod impact strength (a_k) values decrease with the increase of the first quenching temperature. For example a_k decreases from 147 to 125 kJ/m^2 for quenching temperatures ranging between 0 and 80°C , for molding temperature of 230°C . These variations are more prominent for the annealed sample.

Broutman and Krishnakumar explained that the increase in impact strength of PC is due to the craze suppression thanks to surface compressive stresses.⁸ This is in agreement with the work of Hornberger and Devries, who explained that the notched Izod impact strength transition phenomenon in PC was dependent on the triaxial stress field at the tip of the notch.¹⁰ This phenomenon is associated with a transition from a low-energy-absorbing mechanism

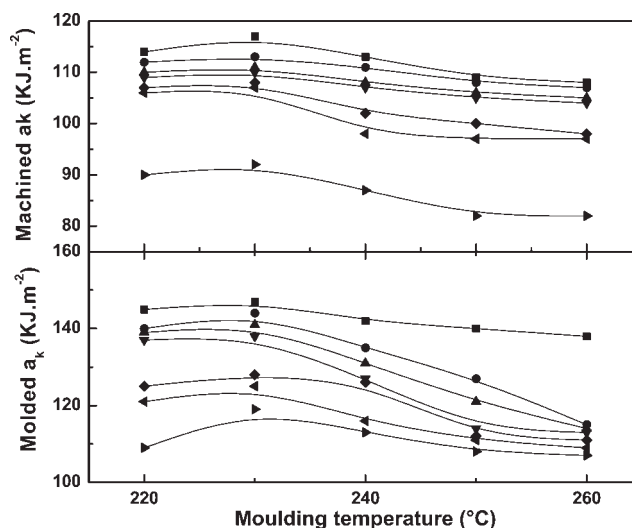


Figure 1 Molded and machined notched Izod impact strength of PC as a function of molding temperature of PC first quenched at (■) 0°C , (●) 20°C , (▲) 30°C , (▼) 40°C , (◆) 60°C , (◄) 80°C , (►) air (molded annealed sample, $a_k = 45 \text{ kJ m}^{-2}$, machined annealed sample, $a_k = 25 \text{ kJ m}^{-2}$).

to a higher-energy-absorbing mechanism at the notch tip.

The reduction of Izod impact strength at 220°C can be explained by an incomplete melting of pellets that favors the propagation of cracks; this was observed by using a polarizing microscope. The reduction of the Izod impact strength as molding temperature increases is explained by the reduction of compressive stresses. The reduction of compressive stresses comes from thermal inertia of the core of the sample; this phenomenon is called "self annealing."²⁶

Our results are in agreement with Fett's work dedicated to the effect of melt temperature on the RSs in injection molding of polystyrene material.²⁶ He also attributed this behavior to "self annealing." The self annealing phenomenon is equivalent to a slower cooling for some material zones (core). It is favored when the molding temperature is increased. Thus the increasing of molding temperature tends to reduce free volume as visible on density measurements (cf. Fig. 3).

The same behavior is observed for the machined notched samples. However, the values of molded notched Izod impact strength are greater than the machined notched Izod impact strength ones. The notching reduces the effect of the surface compressive RS and reduced the impact strength. On the other hand, in molded Izod samples, the notch is still completely under RSs, and hence their Izod impact results are higher.

The elongation at break as a function of molding temperature is presented in Figure 2. The highest

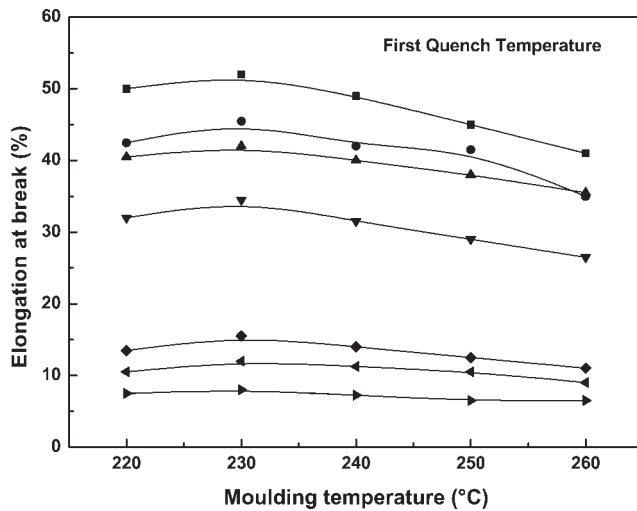


Figure 2 Elongation at break as a function of melt temperature of PC first quenched at (■) 0°C, (●) 20°C, (▲) 30°C, (▼) 40°C, (◆) 60°C, (◄) 80°C, (►) air (annealed sample, $\varepsilon_r = 6\%$).

elongation at break is obtained at the molding temperature of 230°C, which is again related to a good melting of polymer pellets. The results show a dramatic decrease of the elongation at break value as first quenching temperature increases. For a given molding temperature, the increase of the gradient temperature (molding temperature – quenching temperature) induces an increase of the free volume as macromolecules have less time to reorganize. So, we see here a correlation between elongation at break and free volume.

The free volume increase was verified by performing standard density measurements. These results will be presented in the following part. As the impact strength can be correlated with the ability of polymer chains to execute segmental motion and hence dissipate the energy associated with crack propagation, an increase in free volume may also be responsible of the increase of impact strength.

Density and modulus of elasticity

The variations of density and modulus of elasticity as a function of first quenching temperature are shown in Figures 3 and 4, respectively. Density changes have even been reported as a result of various thermal treatments in polystyrene and PC.^{27,28} The density increases clearly as the first quenching temperature increases. In the faster cooling case, which corresponds to a 0°C first quenching temperature, the macromolecular chains have less time to reorganize. This induces an increase of the free volume and therefore a lower density. If one assumes a value of 16% as the effective free volume at T_g in PC,²⁹ then a 2.25% decrease in density as observed

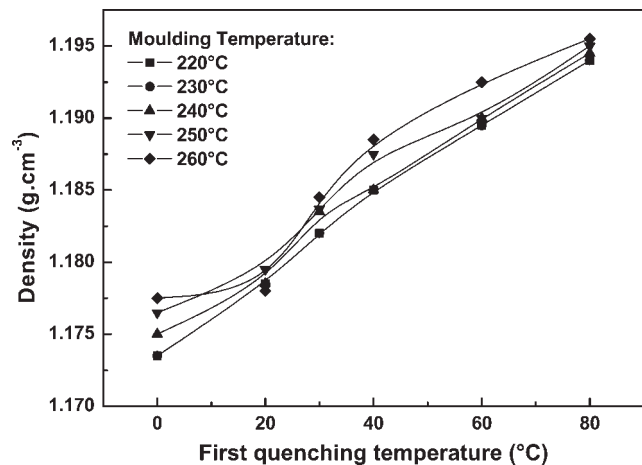


Figure 3 Density as a function of first quenching temperature (annealed sample, $d = 1.20$).

here between the annealed sample ($\rho = 1.2 \text{ g cm}^{-3}$) and the sample quenched at 0°C corresponds to a 36% increase in free volume. It has been also reported that the free volume (and hence density) is governed by two effects, the rate of temperature change and the thermal stresses.³⁰ According to Van Krevelen, the density (ρ) is correlated to the Young's modulus (E): $E \propto \rho^7$, i.e., the samples having a lower density also have a lower Young's modulus.³¹

Yield stress and HDT

Usually, yield stresses decrease while tensile stresses increase. The yield stress is also sensitive to free volume, which favors the physical sliding of molecular segments. The variation of yield stress as a function of first quenching temperature for different melting temperatures is shown in Figure 5. It was found that a low first quenching temperature decreases the

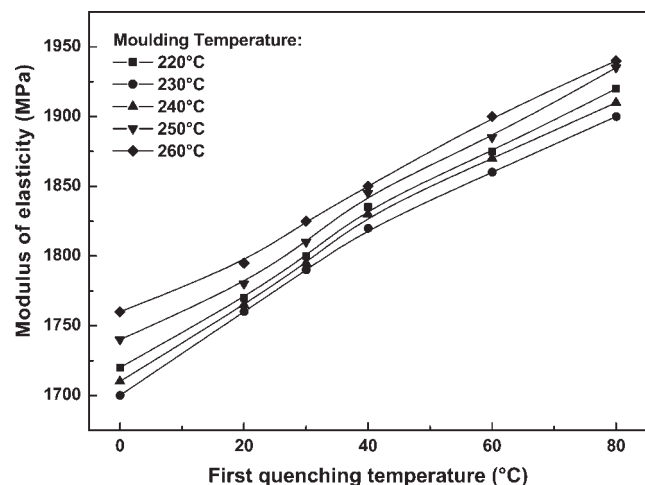


Figure 4 Modulus of elasticity as a function of first quenching temperature (annealed sample, $E = 2250 \text{ MPa}$).

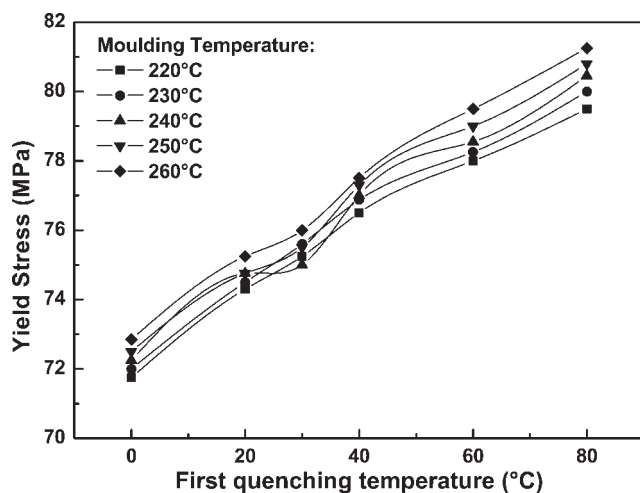


Figure 5 Yield stress as a function of first quenching temperature (annealed sample, $\sigma_y = 89.5$ MPa).

yield stress. This is due to larger tensile stresses and higher free volume for this quenching temperature.

As observed for the modulus of elasticity, yield stress, and density, the HDT decreases when the first quenching temperature decreases (Fig. 6). HDT decreases when tensile stresses exist in the sample because they increase the total tensile stress applied to the sample. So, HDT evolves like the yield stress. Nevertheless, the molding temperature does not affect HDT. (So, we present in Figure 6 the data for only a molding temperature of 230°C.) This may be linked to the fact that during HDT measurements the sample is heated and the compressive stresses lying close to the sample surface are allowed to relax during the heating, whereas tensile stresses in the internal layers are not.⁹ In other respects, Siegmann et al. without calculating the change in free volume

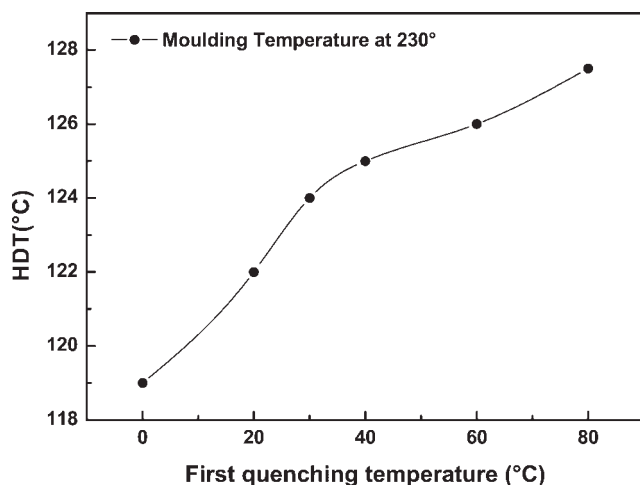


Figure 6 Heat distortion temperatures as a function of melt temperature (annealed sample, HDT = 137°C).

speculated that the increase in HDT was related to the decrease of free volume as a result of relaxation of thermal stresses and molecular orientation.⁹ As HDT and density vary in the same way, the evolution of HDT may also be partially due to the evolution of free volume with the different thermal treatments.

Summary of first quenching procedure influence

To summarize, PC properties depend strongly on first quenching conditions. A faster cooling, corresponding to the lower quenching temperature, generates probably more RSs and free volume; this increases the Izod impact strength and decreases the modulus of elasticity, density, yield strength and HDT. It could be thought that the same evolution should appear after a second quench. The following results will show that this is surprisingly not the case.

Effect of second quenching

Samples were prepared following the procedure described in the section "Second quench procedure."

Impact strength and elongation at break

In Figure 7, the evolution of molded and machined notched Izod impact strength is presented as a function of second quenching temperature. In both cases,

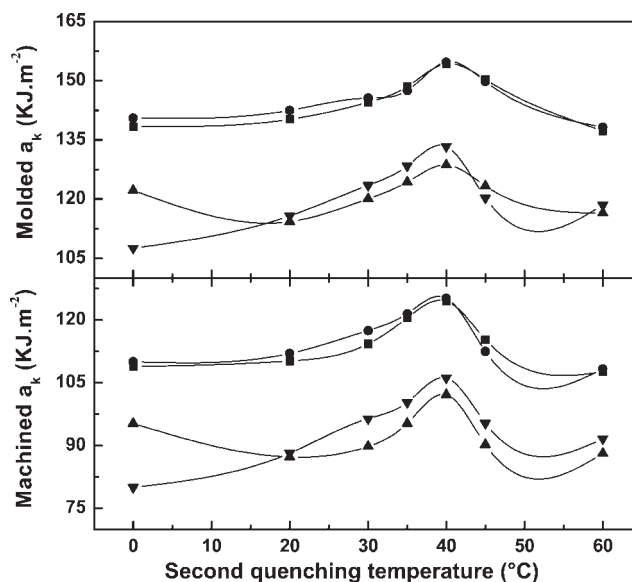


Figure 7 Molded and machined notched Izod impact strength of PC as a function of second quenching temperature of PC first quenched at (■) 0°C, (●) 20°C, (▼) 80°C, (▲) air (molded annealed sample, $a_k = 45$ KJ m⁻²; machined annealed sample, $a_k = 25$ KJ m⁻²).

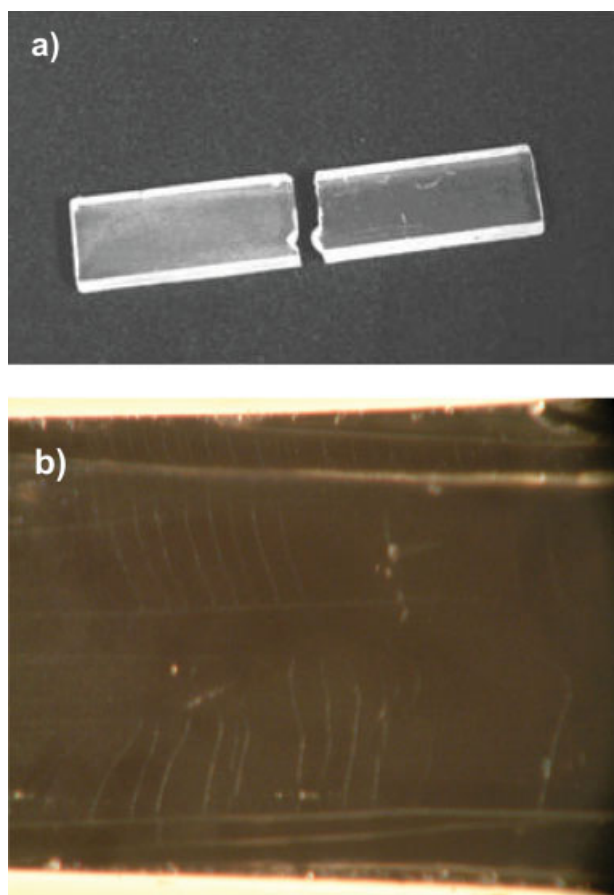


Figure 8 (a) Brittle failure, Izod impact test bar. (b) Fracture surface of notched Izod impact strength samples at 20°C and second quenched from 160 to 0°C.

there is a maximum for a second quenching temperature of 40°C.

The second thermal treatment including a heat treatment of 3 h at 160°C (i.e., at $T_g + 15^\circ\text{C}$) has not totally erased the first thermal treatment. Indeed, the same evolution is observed between the samples first quenched in water at 0, 20, 80°C and in air at room temperature. The influence of the first quenching will appear on all the following properties. The properties obtained after a first quench at 0 and 20°C are close; they correspond to a rapid first quench. Again, properties corresponding to a first quenching temperature of 80°C and to a cooling in air are close, indicating a slower first quench.

As it can be seen, the curves' shapes of Izod impact strength are similar, but with somewhat smaller values in the machined notched specimens case as previously observed. The samples of notched Izod impact measurements exhibited two types of failure mechanisms:

The samples exhibiting low impact strength (corresponding to a sample quenched at 0°C) have a tendency to fail by brittle fracture [Fig. 8(a)];

the smooth rupture face of the sample is presented in Figure 8(b).

The specimen presented in Figure 9(a) exhibits a high Izod impact strength. It corresponds to a sample quenched at 40°C. The sample has failed by ductile process, indicating a plastic deformation in the region of the notch. Chains movements due to the presence of free volume usually cause plastic deformation. The two edges of notched Izod impact strength after fracture remained attached and the fracture surface is typically rough [Fig. 9(b)].

The elongation at break as a function of second quenching temperature is presented in Figure 10. Again, for Izod impact tests, the elongation at break is higher for a faster first quenching (0°C, for example) and reaches a maximum for a second quenching temperature of 40°C.

The elongation at break and Izod impact strength should logically decrease as the quenching temperature increases. This decrease has been observed after the first quenching (Fig. 3). Nevertheless, a maximum of rupture properties is observed for a second quench at 40°C. This behavior could be linked to the existence of a molecular relaxation around 35°C.³² A

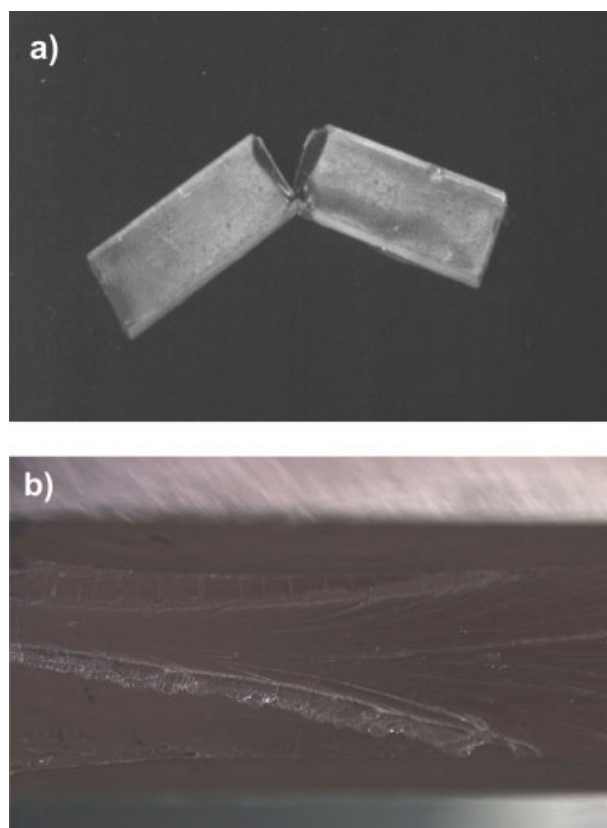


Figure 9 (a) Ductile failure, Izod impact test bar. (b) Fracture surface of notched Izod impact strength samples at 20°C and second quenched from 160 to 40°C.

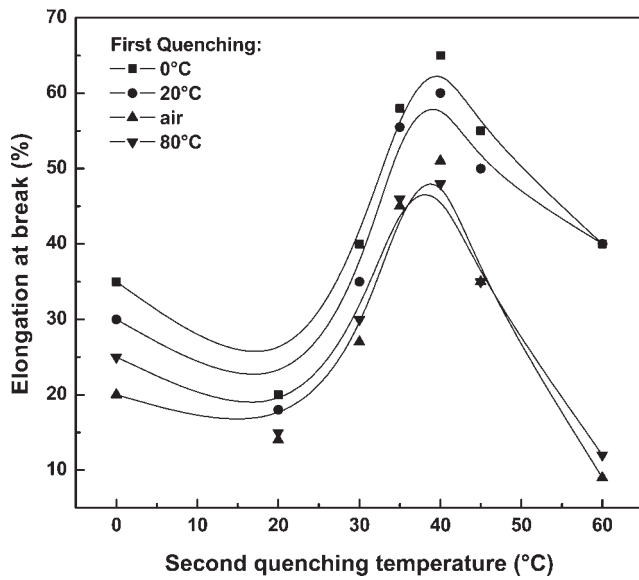


Figure 10 Elongation at break as a function of second quenching temperature (annealed sample, $\epsilon_r = 6\%$).

DMA study of pure PC samples submitted to the same thermal treatments has revealed the existence of such a molecular relaxation. These results will be presented in the following part.

Several authors have shown that molecular relaxations of polymers contribute strongly to many important engineering properties, like impact strength or ductility of glassy amorphous polymers.^{29,33,34} Boyer²⁹ has found that variations of ultimate strength and impact strength as a function of temperature were correlated to the transitions and relaxations occurring in PC. Moreover, Vincent³⁴ has shown for PTFE that three well-defined mechanical loss peaks coincide with similar peaks in Izod notched impact strength.

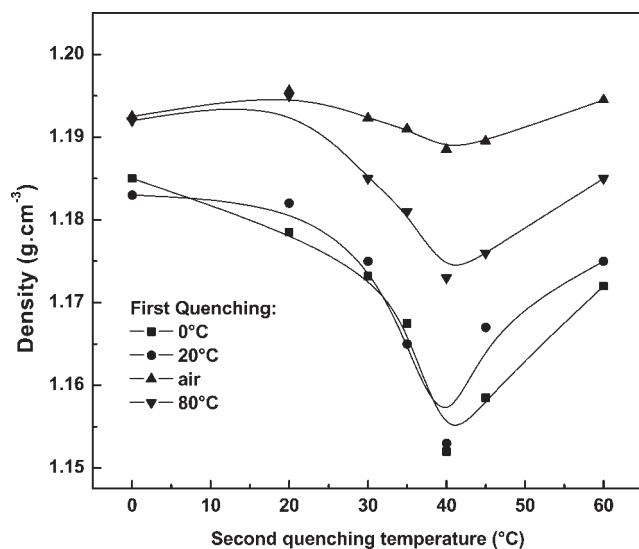


Figure 11 Density as a function of second quenching temperature (annealed sample, $d = 1.20 \text{ g cm}^{-3}$).

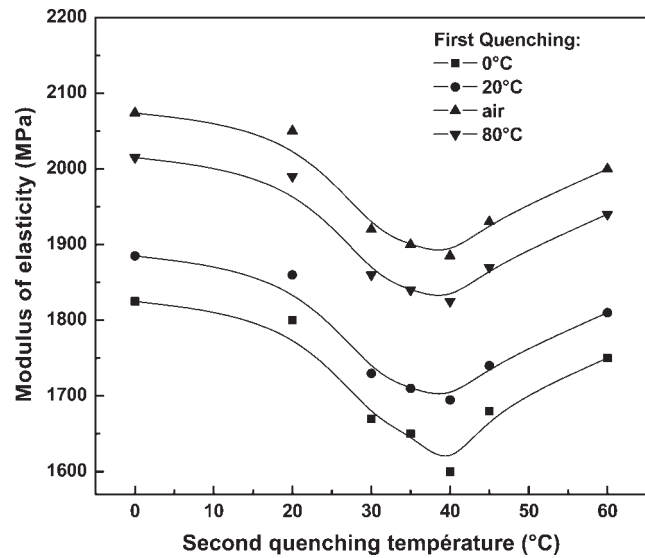


Figure 12 Modulus of elasticity as a function of second quenching temperature (annealed sample, $E = 2250 \text{ MPa}$).

Density, modulus of elasticity, yield stress, and HDT

The evolution of density, modulus of elasticity, yield stress, and HDT upon second quenching temperature are presented in Figures 11–14, respectively. These properties reach a minimum for a second quenching temperature of 40°C. As seen in the section “Effect of first quenching,” an opposite behavior is observed between Izod impact strength and elongation at break, on one hand, and density, modulus of elasticity, yield stress, and HDT, on the other hand.

The minimum of density observed for a second quenching temperature of 40°C is associated to an

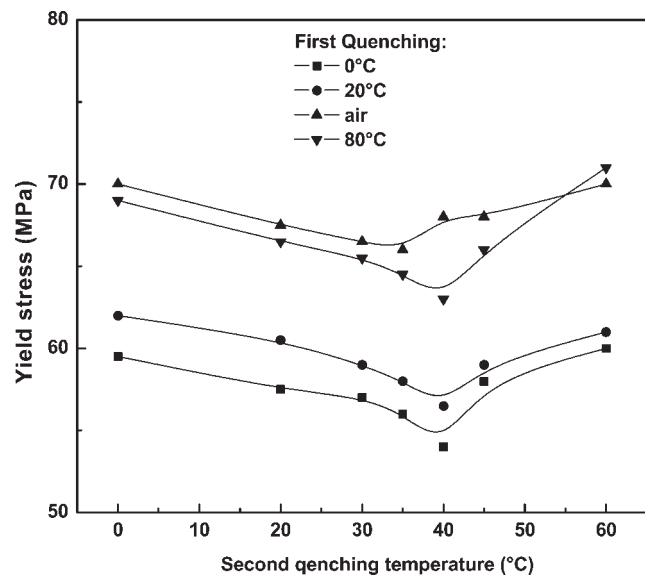


Figure 13 Yield stress as a function of second quenching temperature (annealed sample, $\sigma_y = 89.5 \text{ MPa}$).

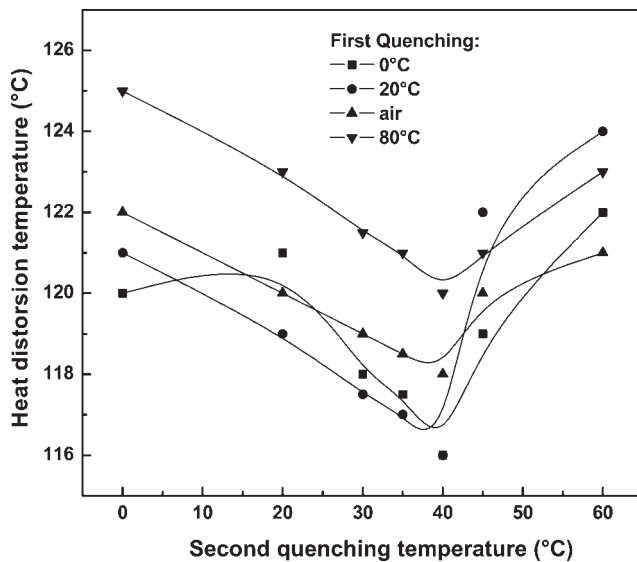


Figure 14 Heat distortion temperature as a function of second quenching temperature (annealed sample, HDT = 137°C).

increase of the free volume. A 4% density decrease is obtained between the annealed sample and the sample quenched at 40°C. This decrease is twice than that in the first quench case and corresponds to an increase of 64% of the free volume. As noted earlier, the increase of free volume leads to a higher molecular mobility; thus, this explains the increase of the Izod impact strength and elongation at break previously observed. Besides, the fact that the Izod impact strength is higher after a second quench at 40°C than after a first quench at 0°C may be directly linked to the greater increase of free volume induced by the second quench.

Also, the modulus of elasticity variation is similar to the one of density (cf. section "Density and modulus of elasticity"). As presented earlier (see section "Yield stress and HDT"), yield stress and HDT decrease when tensile stresses and free volume increase. So the minimum of Yield stress and HDT for a second quenching temperature of 40°C is again attributed to the presence of more tensile stresses and free volume.

So, here again, properties are governed by the presence of both RSs and enhanced free volume. However, the relative influence of each phenomenon on mechanical properties appears here to be more complex.

Thermomechanical properties: Dynamic mechanical analysis

The variation of storage modulus G' and damping factor $\tan \delta$ versus temperature are plotted in Figures 15 and 16, respectively, for some investigated

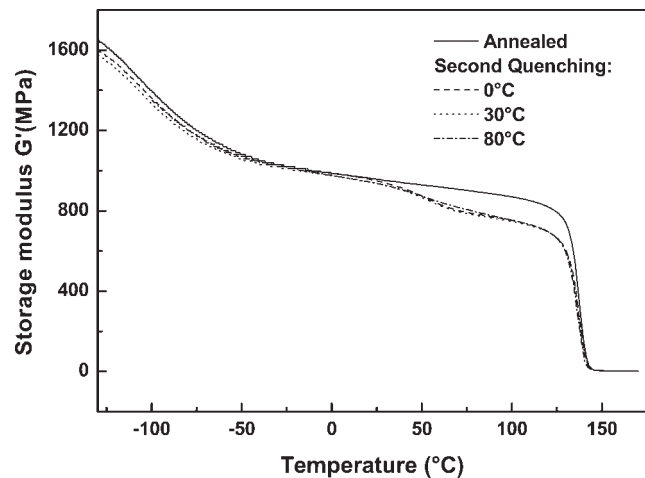


Figure 15 Storage modulus E' as a function of temperature for PC specimens annealed and second quenched temperature at 0, 30, and 80°C.

samples (annealed sample and samples obtained after a second quench at 0, 30, and 80°C). Three molecular relaxation modes are observed. They were named α , β , and γ from high to low temperature. As usually observed each relaxation mode visible on $\tan \delta$ curves corresponds to a drop of the storage modulus. The drop associated with the γ relaxation (at -97°C) is observed between -130°C and -50°C . The γ relaxation amplitude and position are not dependent on the samples thermal history. The dominant α relaxation mode at 144.5°C on $\tan \delta$ curves corresponds to the glass transition and is associated with a dramatic decrease of the storage modulus G' . This peak is slightly affected by the thermal treatment. Complementary studies (not presented in Figs. 15 and 16) allowed to plot the evolution of the α peak maximum as a function of the second quench-

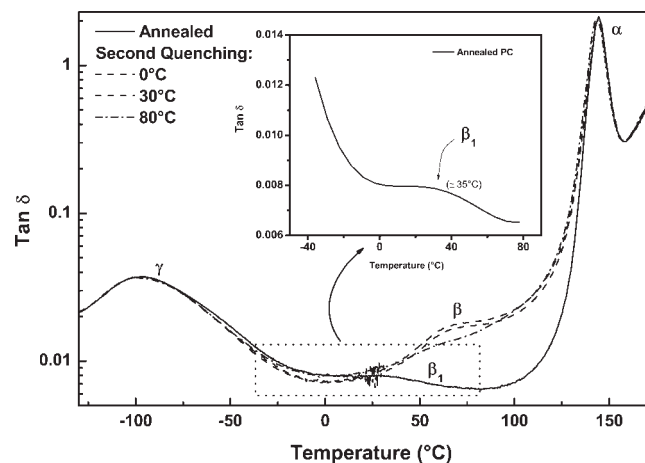


Figure 16 $\tan \delta$ as a function of temperature for PC specimens annealed and second quenched temperature at 0, 30, and 80°C.

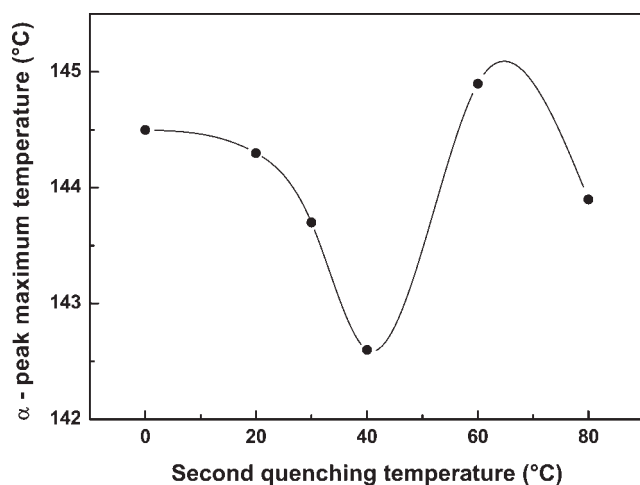


Figure 17 Glass transition temperature as a function of second quenching temperature (annealed sample, $T_g = 144.5^\circ\text{C}$).

ing temperature. These results are presented in Figure 17. We assume here that the variations of the α peak maximum temperature are typical of glass transition temperature variations.

An interesting result is observed: indeed a slight decrease of T_g of about 2°C is noted for a second quenching temperature around 40°C . A decrease of 1°C of the T_g of polystyrene quenched in ice water ($T_g = 100^\circ\text{C}$) or liquid nitrogen ($T_g = 99^\circ\text{C}$) have been previously observed by Devries and Hornberger.¹⁹ These authors have concluded that "the glass transition temperature was an indicator of the thermal equilibrium and of the available free volume"¹⁹: the lower T_g the higher is free volume. Consequently, we can again conclude using DMA results that there is more free volume on the samples quenched at 40°C .

The β relaxation mode, between α and γ modes, is also sensitive to thermal treatments. It was attributed in literature to the relaxation of orientational residual surface stresses due to quenching or manufacture and is often considered to be a nonequilibrium relaxation or a precursor to α .^{35,36} According to Varadarajan and Boyer,³⁷ it is due to cooperative motions of two or three repeat units.

The β relaxation mode intensity remains approximately the same for quenching at 0, 20, 30, 40°C ; this tends to indicate that RSs are quite similar for these samples. In this case, the relaxation mode intensity decreases for quenching at 60 and 80°C , indicating that the RSs decrease.

The case of annealed sample is interesting because a small peak named β_1 appears at about 35°C . As the sample was cooled very slowly, no RSs are present inside this sample. Most of the time, this peak is not evidenced by DMA studies on PC. Moreover, Sacher¹² showed that the rigidity of PC chains leads

to secondary losses of low magnitude, requiring sensitive equipment for their observation.

Lee-Sullivan et al. as well as other authors have observed this peak and they have concluded that it was insensitive to thermal history, elusive and unaffected by thermal ageing.^{32,38,39} The origin of this relaxation mode remains unclear; it is simply described to be due to segmental motions of intermediate length, i.e., between long chain motions occurring at the α glass transition and short chain motions responsible for the γ relaxation.³²

Matsuoka⁴⁰ described the α relaxation as being composed of coordinated cooperative motions between about seven to 10 closely packed conformers (i.e., two or three repeating units, although the units are not necessary part of the same chain). He described also the unit responsible for the γ relaxation at -100°C as approximately the same size as the PC repeating unit, which consists of three distinct flexible segments or conformers, each capable of independent rotation. According to Varadarajan and Boyer, the γ peak consists of three overlapping peaks, γ_1 , γ_2 , and γ_3 , in descending temperature with γ_1 involving phenylene motion, γ_2 being combined carbonate and phenylene motion, and γ_3 resulting from motion of the carbonate group.³⁷

Sacher concluded his study of relaxations as follows: the large number of degrees of freedom available in all three relaxation modes may be responsible for high impact strength of PC.¹² In our case, the β_1 relaxation mode evidenced at about 35°C for the annealed sample is hidden by the β mode around 65°C for the second quenched samples. The existence of the β_1 mode for the quenched samples should be evidenced in the future by complementary studies at lower frequencies, for example, or by a dielectric study. Lee-Sullivan has already observed β_1 and β modes at the same time during a DMA study of PC; this tends to prove that the β_1 mode exists independently of the thermal treatment.³² The existence of this relaxation mode at about 35°C should be at the origin of the behavior of PC samples after a second quenching; the difference between the first and the second quenching is probably linked to the relaxation time of the molecular segments which are moving at 40°C .

The difference between the first and the second quench might also be linked to the beginning temperature of the quenching: 230°C or 160°C . In the first case, the temperature gradient is higher and during the cooling the relaxation mode action is hindered. Indeed, the signature of the relaxation is slightly visible on some results of the first quenching.

The storage modulus G' results shown in Figure 15 reveal that G' values between 20 and 140°C are significantly greater for the annealed sample in

comparison to second quenched specimens. For example, G' values at $\sim 30^\circ\text{C}$ is about 937 MPa for the second quenched specimen at 0°C , whereas a value of 951 MPa is reached for the annealed specimen. This difference is relative to the relaxation of RSs and the presence of free volume. Of course, the stress relaxation takes place between ambient temperature and glass transition temperature.

CONCLUSIONS

The effect of quenching process on mechanical and thermal properties of PC was investigated via impact, tensile, and thermomechanical measurements.

It was shown that a larger ductility can be obtained by quenching the samples from the melt state to the lowest temperature (0°C). This quenching generates probably more RSs and free volume which increase the Izod impact strength and elongation at break. It was also shown in this case that the modulus of elasticity, density, yield strength, and HDT decrease. An opposite behavior was observed when increasing the molding temperature due to the presence of self-annealing effect.

A higher ductility was also reached for a second quenching from 160 to 40°C . This unusual behavior was linked to the existence of a molecular relaxation β_1 around 35°C . Indeed, DMA investigations showed that a more intense peak (β), resulting from the relaxation of RSs, hides the (β_1) relaxation in quenched samples and in the same time explains why β_1 relaxation mode is not often reported in literature.

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