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Research Article

Thermophysical and Mechanical Properties of Polystyrene: Influence of Free Quenching

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The effect of free quenching on the mechanical, thermal, and thermophysical properties of polystyrene has been investigated. Three different thermal treatments were investigated: a first quenching from the melt state to different temperatures, a second quenching from $T_g + 7^\circ$C, and finally an annealing. The results have shown that a slight improvement of the impact strength can be obtained after a second quenching at 40°C, and a correlation between the mechanical and thermal properties is observed. The improvement of this property was obtained at the expense of other properties such as the elastic modulus, density, hardness, and the heat distortion temperature (HDT). The little improvement of the impact strength after the second quenching is probably linked to the existence of a relaxation mode located around 40°C. However, no effects have been shown on the thermophysical properties.

1. Introduction

In a previous study [1], the effect of different heat treatments on the mechanical properties of polycarbonate (PC) was investigated. It was shown that the effect of quenching induces a larger ductility to the polymer. In the present work a similar study is carried out using polystyrene another amorphous highly brittle polymer. Polystyrene is a fragile transparent material which is commonly called "Crystal" PS to improve its mechanical properties, we resort to the generation of residual stresses (RSs) by a free quenching process. Residual stresses in inorganic and polymeric glasses have received a large attention in the past because of their technological importance [2–4]. In amorphous polymers, the RS are in fact totally attributed to volumetric fluctuations, associated with the chain conformation relaxation kinetics at the glass transition temperature (T_g). This leads to an incomplete viscoelastic relaxation during solidification. RSs are commonly classified as residual microstresses and residual macrostresses [5]. At a laboratory scale, two methods are available for introducing RS in polymers: nonuniform cooling (thermal quenching) and nonuniform plastic deformation (cold working). The RS term refers to those produced by transient thermal gradients. Many attempts have been made to determine the influence of residual stresses on properties of moulded polymers. During processing the residual stresses are introduced by nearly all techniques used for polymer manufacturing. For example the variations of the injection molding conditions may produce changes of molecular orientation in a preferred direction imposed to the macromolecular chains in the direction of flow in the mold. In order to avoid a contribution of flow induced orientation, free quenching experiments have been used by several investigators on semicrystalline and amorphous polymers [6–8]. In some cases, compressive residual stresses can improve the impact strength, fatigue behavior, and resistance to environmental stress cracking [9–11]. However, when the stresses are related to external loads, they are superimposed to tensile residual stresses so that in these conditions the plastic yielding will begin at a lower load. Polymers such as polystyrene (PS) and poly (methyl methacrylate) (PMMA) typically fracture after being stretched to a few percent strains. Such behavior obviously limits their use. To expand the usefulness of PS in a variety of applications, it is important to explore ways to increase its toughness. Generation of residual stresses has been known to be an effective method in toughening polymers. One of the first studies on the influence of injection molding process parameters on

the RS in PS was reported by Fett [12]. The surface RSs were found to decrease with increasing melt temperature as well as mold temperature. It was suggested that high mold temperature directly affects the relaxation of the surface residual stresses. Menges et al. [13] measured the RS in PS as affected by melt temperature, mold temperature, injection pressure, holding pressure, and time. The study concludes that RS are compressive at the surface layers and tensile in the inner core. Under extreme conditions, tensile stresses were developed at the surface and compressive ones in the center. Later, Siegmann and coworkers et al. [10] conducted thermal stress investigations on quenched sheets of polymethyl methacrylate and PS. The surface stresses in the PS sheets were qualitatively characterized by observing crazing behavior in n-heptane. Isayev and Crouthamel [14] have measured the RS for PS samples freely quenched from 130°C and 150°C to 23°C using the layer removal technique developed by Treating and Read for metals [15]. Surface compressive stresses of −9.8 and −8.2 MPa and centerline tensile stresses of 2.6 and 3.3 MPa have been reported for an initial temperature of 130 and 150°C, respectively. Hornberger and DeVries [16] using various techniques indicate that quenching of PS in ice water and allowing the samples to achieve thermal equilibrium at room temperature, results in surface residual stresses of approximately 15 MPa.

Narkis et al. [17] have measured the state of the residual stresses on heat distortion temperature (HDT) of various styrene copolymers. They have found that HDT is very strongly influenced by heat treatment. Also, Siegmann et al. [10] investigated the effects of the residual stresses on crazing and softening behaviours of PS and PMMA quenched from various temperatures into iced water. Both PS and PMMA showed a decrease in heat deflection temperatures as the magnitude of the residual stresses increased. It was concluded that the presence of residual stresses across the material accelerated the softening of the polymers.

This paper describes a method to produce favorable RS in polystyrene by optimizing the process of thermal quenching and the subsequent effects on mechanical, thermal, and thermophysical properties.

2. Experimental

2.1. Materials. The polymer used in this study is a commercial polystyrene (trade name: Lacqrene 1450N), produced by Atofina (France) with an average molecular weight of about (M_w ~190000). Its melt flow index at 200°C is 6.5 g/10 min. The polydispersity index is 2.7 and the glass transition temperature is around 103°C.

2.1.1. First Quenching Procedure. PS pellets were dried in an oven at 110°C and then put into the mould and pressed at a pressure of 25 bars during 12 minutes at a moulding temperature of 200°C. Then the samples were immediately quenched from the moulding temperature into water bath until 0°C, 20°C or in the air at room temperature during 15 minutes. This procedure was named "*first quenching*." All the samples were 3 mm thick.

2.1.2. Second Quenching Procedure. In a second time, another free quenching was carried out for samples which were first moulded at 200°C and quenched from the moulding temperature to 0°C and 20°C in a water bath or in the air during 15 minutes. These specimens were then heated in an oven at 110°C (T_g + 7°C) during 2 hours and were immediately quenched a second time into a water bath at different temperatures (0, 20, 30, 40, 60°C) during 15 min. This procedure was named "*second quenching*."

2.1.3. Annealing Procedure. Finally, in order to get a sample as a reference, annealing was performed for comparison purposes. Annealed specimens were prepared using samples which were first quenched in air. Then, these samples were heated at 110°C during 12 hours and finally slowly cooled in the oven until room temperature at a rate of about $10°C \cdot h^{-1}$. These samples were named "annealed samples."

2.2. Tensile Testing. The tensile properties were determined using dumbbell specimens 115 mm long, 13 mm wide, and a gauge length of 20 mm. The tests were carried out using a universal testing machine with a crosshead speed of $10\,mm \cdot Min^{-1}$. The test procedure followed ASTM D638-72 specifications. From the experimental stress-strain curves, the tensile modulus of the quenched PS were obtained at room temperature. Five specimens were tested and the average values were used for the data plot.

2.3. Notched Izod Impact Strength. Izod impact properties were determined at room temperature with a CEAST 6546/000 machine provided with a 15 J pendulum according to the ASTM D256-73 specifications, and using specimens of $3 \times 12.7 \times 63\,mm^3$ dimensions. Some specimens were moulded with a notch radius of 0.5 mm. For the other specimens a notch with a radius of 0.5 mm was machined. At least 5 specimens were tested and average values were used. The mean values are shown in Tables 1 and 2.

2.4. Density Measurement. According to the principle of Archimedes a specimen immersed in a liquid receives a pressure equal to the displaced liquid. This principle was applied for the determination of the density of the specimens of PS. Therefore, by knowing the density of the liquid, it is simple to calculate the volume of the specimen and its specific mass. The density, which is the inverse of specific volume, may be calculated after the determination of the specimen weight in the air and its occupied volume in a liquid of known density. We have used distilled water as the liquid at 25°C, and an HB Mettler analytical balance.

2.5. Hardness Testing. The shore D hardness was determined on PS sheets ($50 \times 50 \times 3\,mm^3$). The measurements were conducted following ISO/869 test procedure. A 5 Kg load was used on the test stand to apply the durometer indenter onto the flat specimen surface. The mean values are shown in Figure 4.

Table 1: The influence of thermal history on unnotched Izod impact strength.

2nd quenching T (°C)	1st quenching T (°C) Unnotched Izod impact strength (kJ · m^{-2})		
	Free air	Water at 20°C	Water at 0°C
0	6,613 ± 0,300	7,033 ± 1.008	6,298 ± 0.52
20	6,256 ± 2.262	6,281 ± 1.906	6,141 ± 0.70
30	6,540 ± 1.196	6,981 ± 0.468	5,879 ± 0.42
40	7,161 ± 0.95	7,978 ± 2.586	7,664 ± 0.574
60	6,716 ± 0.282	5,879 ± 0.508	6,824 ± 1.658
Annealed sample		5.070 ± 0.50	

Table 2: The influence of thermal history on notched Izod impact strength.

2nd quenching T (°C)	1st quenching T (°C) Notched Izod impact strength (kJ · m^{-2})		
	Free air	Water at 20°C	Water at 0°C
0	3,114 ± 0,620	2,895 ± 0.694	2,294 ± 0.632
20	2,995 ± 0,298	3,223 ± 1.034	2,240 ± 0.456
30	2,053 ± 1.048	2,694 ± 0.418	2,185 ± 1.092
40	2,950 ± 0.456	3,229 ± 0.458	2,564 ± 0.732
60	3,1212 ± 0.542	1,256 ± 0.448	2,240 ± 0.456
Annealed sample		3,332 ± 1,132	

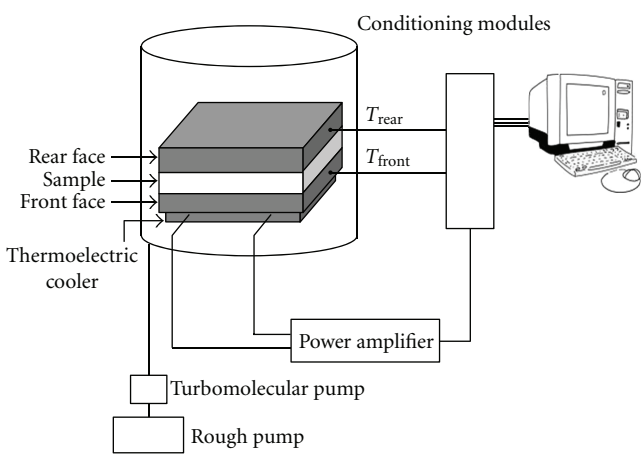

Figure 1: Thermophysical measurements setup.

2.6. Thermal Tests

2.6.1. Heat Distortion Temperature (HDT). The HDT was measured in accordance with ASTM D648 specifications, which describe HDT as the temperature where a specimen ($3 \times 13 \times 127\,\text{mm}^3$) deflects by 0.25 mm under a load of 1.8 MPa while heated in an oil bath at a rate of $2°\text{C} \cdot \text{min}^{-1}$. At least 2 specimens were tested and the average value was used for the data plot.

2.6.2. Thermophysical Properties Measurements. Generally, conductivity and thermal diffusivity of PS are determined from the analysis of the temperature response of a material to thermal excitation. Conductivity and thermal diffusivity of PS were measured using a method of periodic measurements described in detail in reference [18]. The periodic method allows simultaneous measurements of conductivity and diffusivity at room temperature and generally provides accurate data. The ratio of the Fourier transforms of the temperatures of the two plates is used to identify these parameters. Indeed, the sample ($40\,\text{mm} \times 40\,\text{mm} \times 2\,\text{mm}$) is inserted between two metal plates (see Figure 1) and presented on one side at a heat flux modulated at different frequencies. Temperature measurements on both sides of the sample allow calculation of the experimental heat transfer function. The function of heat transfer theory, written from a 1D model using the method of quadrupoles, has two unknown parameters (k and a). These properties are identified by minimizing the squared difference between the two functions of heat transfer using the method of Levenberg-Marquardt [19]. The statistical uncertainties are obtained from the calculation of the variance-covariance matrix.

It is to be noted that the results are presented as the mean value of two specimens for the HDT, density, the flexural modulus, and hardness.

3. Results and Discussion

3.1. Effect of the Second Quenching

3.1.1. Impact Strength. In Tables 1 and 2, the evolution of unnotched and notched Izod impact strength is presented as a function of second quenching temperature. In the case of unnotched samples, a slight maximum for a second quenching temperature of 40°C is observed.

Indeed, heating of the samples, allows conformational reorganization of the macromolecular chains resulting in

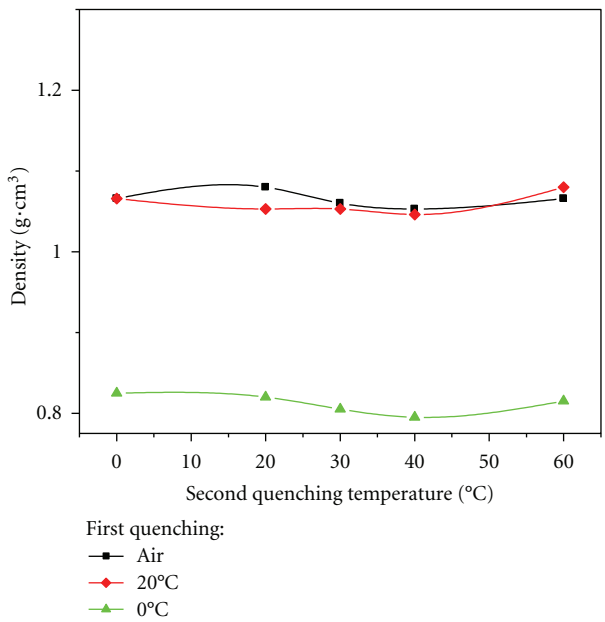

Figure 2: Density as a function of the second quenching temperature of PS first quenched at (▲) 0°C, (♦) 20°C, and (■) air (annealed sample, $d = 1.05\,\mathrm{g \cdot cm^{-3}}$).

a relaxation of the orientation of these chains generated by RS induced by the step cooling of the first quenching during compression molding.

The second thermal treatment including a heat treatment of 2 hours at 110°C (i.e., at $T_g + 7$°C) has not totally erased the first thermal treatment. In fact, the same evolution is observed with the samples which were first quenched in water at 0°C, 20°C, and in air at room temperature.

From the values of the Izod Impact strength, the magnitude of the compressive stresses appears to be smaller and not sufficient to give higher values of Izod impact strength. The presence of compressive stresses at the surface of the unnotched specimens enhances the Izod impact strength by promoting the plane stress failure. The compressive residual stresses help in preventing crack formation and/or propagation at the surface of the specimens. Indeed, the compressive stresses field that develops under these conditions is somewhat lower because even with a notch of 0.5 mm, the value of Izod impact strength shows no improvement. It remains almost constant and does not exceed the value found with the annealed samples. However, the presence of the notch alters somewhat the fields of compressive stresses which are already low. This may explain the almost constant values of Izod impact strength as a function of the second quenching temperature.

The Izod impact strength should logically decrease as the quenching temperature increases. Nevertheless, a maximum of rupture properties is observed for a second quench at 40°C. This behaviour could be linked to the existence of a molecular relaxation (β) located around 40°C [20]. The β relaxation that involves a crankshaft type motion produces probably less free volume, and, secondly, the low thermal conductivity of PS (~0.15 $\mathrm{Wm^{-1}\,K^{-1}}$). This reduces the cooling rate and generates less residual stresses. The β-relaxation process is associated with motion of the phenyl side groups. Several authors have shown that molecular relaxations of polymers contribute strongly to many important engineering properties, such as impact strength or ductility of glassy amorphous polymers [21–23]. Boyer [21] 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, Vincent [23] has shown for PTFE that three well-defined mechanical loss peaks were observed. In a previous work with PC, a maximum ductility is also reached for a second quenching from 160°C until 35°C. This unusual behavior was also linked to the existence of a molecular relaxation β_1 around 35°C and coincides with similar peaks in Izod notched impact strength of PC [1].

3.1.2. Density, Modulus of Elasticity, Flexural Modulus, Hardness, and HDT. The evolutions of density, modulus of elasticity, flexural modulus, hardness, and HDT upon second quenching temperature are, respectively, presented from Figures 2 to 6. These properties reach a minimum at a second quenching temperature of 40°C.

A minimum in density values is observed for a second quenching temperature of 40°C and is associated with an increase of the free volume (Figure 2). The increase of free volume leads to a higher chain mobility which explains the increase of the Izod impact strength previously observed. Besides, the Izod impact strength is higher after a second quench at 40°C than after a first quench at 0°C. This may be directly linked to the greater increase of free volume induced by the second quench.

Figure 3 which presents the variation of the modulus of elasticity shows a similar trend as that of the density.

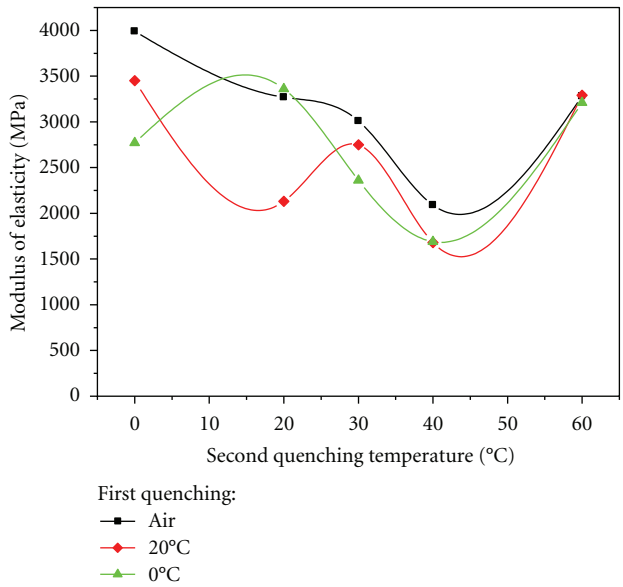

Figure 3: Modulus of elasticity as a function of the second quenching temperature of PS first quenched at (▲) 0°C, (♦) 20°C, and (■) air (annealed sample, $E = 3450$ MPa).

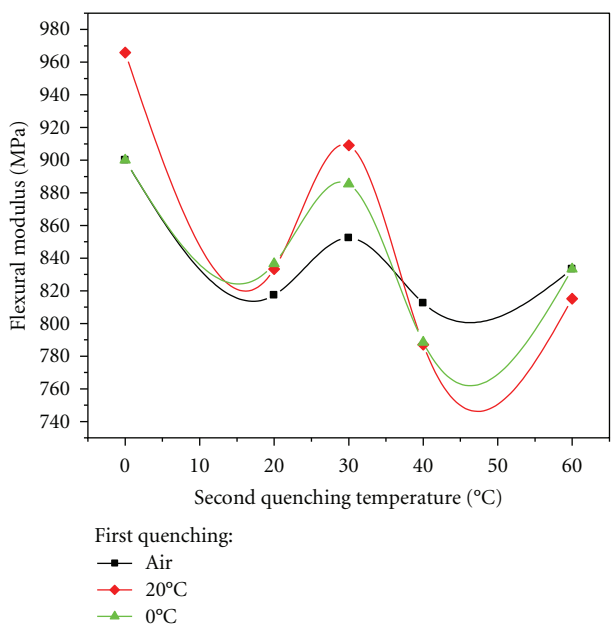

Figure 4: Flexural modulus as a function of the second quenching temperature of PS first quenched at (▲) 0°C, (♦) 20°C, and (■) air (annealed sample, $E = 885.41$ MPa).

The flexural modulus is also sensitive to tensile stresses. It decreases when the tensile stresses are increased. It is also sensitive to free volume. The variation of flexural modulus as a function of the second quenching temperature for different first quenching temperatures is shown in Figure 4. It was found that there are two minima for a second quenching temperature of 20°C and 40°C, respectively.

The minimum of flexural modulus is very pronounced at the second quenching temperature of 40°C. This is due to larger tensile stresses and higher free volume for this quenching temperature. Again, the flexural modulus decreases when tensile stresses exist in the sample because they increase the total tensile stress applied to the sample. So, the flexural modulus evolves similarly as the density and the modulus of elasticity.

The measured values of shore D hardness are summarized in Figure 6. It is interesting to note that a minimum in hardness occurs at the same quenching temperature and correlates with a similar decrease in HDT. At this temperature the chains spread apart resulting in a loose structure

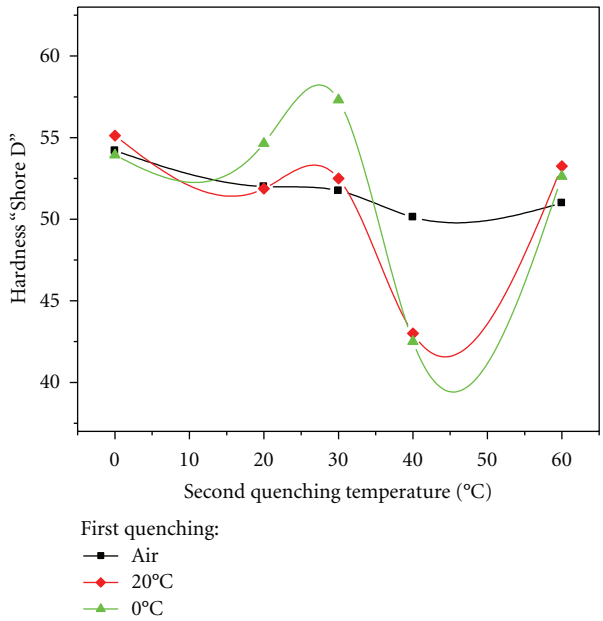

Figure 5: hardness shore D as a function of the second quenching temperature of PS first quenched at (▲) 0°C, (♦) 20°C, and (■) air (annealed sample, hardness = 54.5).

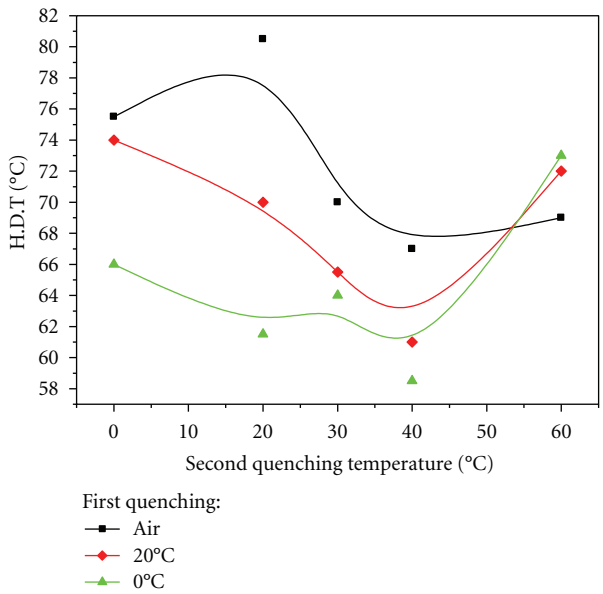

Figure 6: Heat distortion temperature as a function of the second quenching temperature of PS first quenched at (▲) 0°C, (♦) 20°C, and (■) air (annealed sample, HDT = 85.5°C).

and offering a relatively low resistance to indentation during hardness measurement. This explains the minimum on the hardness values in Figure 5.

The HDT as a function of second quenching temperature is presented in Figure 6. The maximum decrease in HDT takes place at the same quenching temperature of 40°C. It is important to note that the cooling rate affects the residual surface stresses. These compressive stresses at the surface layers probably relax but the internal layers are not able to relax [24]. Therefore, the HDT is controlled by the internal tensile stresses of the material to some extent and the external stresses of the load. However, because external stresses are constant during the test of bending, it is therefore the internal stresses that cause the variation of HDT. These tensile stresses are a function of the quenching temperature. The superposition of the external stresses and the internal stresses facilitates the distortion of the material, and consequently leads to the reduction of HDT. Finally, the lowering of HDT at 40°C may also be linked to the increase of free volume. As HDT and density vary in the same way, the evolution of HDT

Table 3: The values of the thermal conductivity and the thermal diffusivity of PS annealed and the second quenching at different temperatures and their standard deviations.

Thermal history of PS	Thermal conductivity (k_c) ($Wm^{-1} K^{-1}$)	Standard deviation $\pm 2\sigma_d$	Thermal diffusivity a_c ($m^2 s^{-1}$)	Standard deviation $\pm 2\sigma_d$
Annealed sample	0.15	0.01	1.22×10^{-7}	0.06×10^{-7}
Second quenching at 0°C	0.14	0.01	1.40×10^{-7}	0.18×10^{-7}
Second quenching at 20°C	0.15	0.01	1.42×10^{-7}	0.18×10^{-7}
Second quenching at 30°C	0.14	0.01	1.23×10^{-7}	0.10×10^{-7}
Second quenching at 40°C	0.15	0.01	1.37×10^{-7}	0.10×10^{-7}
Second quenching at 60°C	0.14	0.01	1.23×10^{-7}	0.18×10^{-7}

may also be partially due to the evolution of free volume with the different thermal treatments.

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

3.1.3. Thermophysical Properties. The obtained values of the thermal conductivity and the thermal diffusivity and their associated standard deviations of the PS annealed and the second quenched are given in Table 3. It is observed that the standard deviations of the thermal conductivity of PS are almost constant and are in the order of $0.01(Wm^{-1} K^{-1})$. However, the standard deviations of the thermal diffusivity vary between 0.06×10^{-7} and 0.18×10^{-7} ($m^2 s^{-1}$). These are satisfactory and do not have too much dispersion.

Table 3 shows the evolution of the thermal conductivity and the thermal diffusivity of PS as a function of the second quenching temperature. In this case, it is observed that the values of the thermal conductivity remain almost constant as a function of the second quenching temperature. However, the values of the thermal diffusivity reach two little maxima at the second quenching temperature of 20°C and 40°C, respectively.

In previous studies, the comparison between a quenched and annealed neat PS has been studied in considerable details by Goldbach and Rehage [25]. One notes a double-peak in the quenched specimen around 20 and 50°C, consistent with DSC observations reported by Wunderlich [26]. In the case of the neat PS, our study supports only the occurrence of one maximum of all properties at a second quenching temperature of 40°C, except for the thermal diffusivity.

4. Conclusion

To summarize, PS properties depend slightly on the second quenching conditions. A faster cooling, corresponding to the moderate quenching temperature, generates probably more residual stresses and free volume. This increases slightly the Izod impact strength and decreases the density, modulus of elasticity, flexural modulus, hardness, and HDT.

The effect of the quenching process on the mechanical and thermal properties of PS was investigated via impact, tensile, and thermal measurements. A slight maximum ductility is reached for a second quenching from 110°C until 40°C as evidenced from the slight increase observed in the values of the unnotched impact strength. This unusual behaviour is more probably linked to the existence of a molecular β relaxation around 40°C. The minimum of density reached after a second quench between 110°C and 40°C is associated with the presence of more free volume, which leads to a higher molecular mobility. This also explains the slight increase of Izod impact strength, and the decrease of density, modulus of elasticity, hardness, and HDT. However, no effects have been shown on the thermal conductivity and the thermal diffusivity as a function of second quenching temperature. The free quenching remains only efficient for ductile polymers like PC where great changes have been observed.

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