Mechanical and Thermal Properties of Polycarbonate. II. Influence of Titanium Dioxide Content and Quenching on Pigmented Polycarbonate

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ABSTRACT: The effects of quenching temperature including different thermal histories on mechanical, physical, and thermal properties of pigmented polycarbonate (PC/TiO_2) were investigated. Tensile test, Izod impact strength and heat distortion temperature (HDT) were performed on specimens of 3 mm thickness. Pigment content and quenching temperature are two key factors that affect the properties of the materials. A higher content of pigments results in an increase of modulus of elasticity and a decrease of unotched and notched Izod impact strength, as well as elongation at break. A maximum of yield stress and HDT is obtained at 3% of TiO_2, which was considered as the optimum level of pigment. An additional second quenching at 40°C has allowed to improve Izod impact strength and elongation at break of specimens with 3% of TiO_2; whereas modulus of elasticity, density, yield stress, and HDT were minimum at this quenching temperature. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2710–2717, 2007

Key words: residual stresses; free quenching; pigmented polycarbonate; mechanical properties

INTRODUCTION

The main reason why inorganic materials (fillers) such as titanium dioxide (TiO_2) are compounded with thermoplastics is to enhance the mechanical properties, such as yield stress and modulus of elasticity. However, increasing the filler load can induce a dramatic loss of impact strength and elongation at break. In polycarbonate (PC), the incorporation of pigment has an effect on mechanical properties, even at low filler loading. The dramatic loss of impact strength is the major problem to the application of pigmented PC. In general, pigmentation of a thermoplastic allows polymer molecules to be absorbed on the surface and this can induce a densification of the material. Blackwood *et al.*[1] studied the effect of pigmentation of PC with TiO_2 and their effect on the fracture energy and failure mechanism. The results showed that the failure mechanism changes because of the formation of a large area of densified polymer around pigment particles. Generally, silane-coupling agents are used to improve the adhesion between polymer and filler. In this case, Izod impact strength is improved.[2] Nevertheless, tensile and Izod impact strengths do not exceed the value of pure material when the composite contains treated titanium dioxide.

To expand the usefulness of PC in many applications, it is important to explore processes to prevent or minimize the loss of impact strength during the incorporation of pigment. The generation of residual stresses (RS) is known to be effective for a toughening of PC, like for inorganic glasses.[3,4] RS are generated by quenching the polymer from a higher temperature than the glass transition temperature until a lower temperature. Then thermal stresses are parabolic in profile, compressive at the surface layer, and tensile inside.[3] The presence of compressive stresses at the surface improves significantly the impact strength of PC, poly(vinyl chloride) (PVC) and polysulfones for example.[5] Broutman and Krishnakumar[6] reported also that PC, normally failing in a brittle mode exhibit a ductile failure mode with a higher energy after a selected thermal treatment. Heat distortion temperature (HDT) is also particularly sensitive to RS.[7]

In amorphous polymers, the existence of compressive stresses is postulated to restrict the extent of craze growth at the notch tip, and the impact specimen can

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yield rather than fail in a brittle manner if the stress state is sufficient. In semi-crystalline materials, the mechanism of the formation of RS is greatly complicated by accompanying crystallisation during processing. Unlike amorphous polymers its RS arise because of the passage through the glass transition temperature T_g during cooling, RS in semicristalline polymer are present because of the occurrence of crystallisation. It well known that the increase of the degree of crystallinity decrease the impact strength of polymers.

The objective of this work is on the one hand to study the effect of pigment content on physical properties of PC/TiO_2 blends and, on the other hand, to try to improve these properties. These two steps will be presented in two separate parts. In the first part, the evolution of the physical properties of PC/TiO_2 blends as a function of TiO_2 percent is presented. The improvement of pigmented PC properties is first obtained by choosing the optimum level of TiO_2 content and secondly by using a peculiar thermal treatment. The choice of the thermal treatment is based on a precedent study, where we showed that a second quenching at 40°C improve the Izod impact strength and elongation at break of neat PC. This unusual behavior was linked to the existence of a molecular relaxation around 35°C. These results were presented in a separate article (Part I). The study of the optimization of the second quenching of the PC/TiO_2 blends is now presented in this article (Part II).

EXPERIMENTAL PROCEDURE

Materials

The polymer used in this study is a commercial PC, Makrolon 2620, supplied by Bayer (Germany) with average molecular weight about (M_w = 57,404). The melt index at 300°C is 19.6 g/10min, the polydispersity index is 2.16 and the glass transition temperature is about 144.5°C. The pigment used is a fine rutile crystal grade TiO_2. Titanium dioxide is a known pigment that is often useful in making white or opaque products. Furthermore, titanium dioxide is used as sub-pigment because of its UV shielding property. The average size of TiO_2 particles is 0.2 μm. The maximal size of particles is 0.3 μm. Six compound formulations were prepared and TiO_2 weight content was set to 0, 0.5, 1, 2, 3, 4, and 6 % respectively. PC is a transparent polymer, and TiO_2 a white powder. All the specimens of PC/TiO_2 are white and opaque.

First, the compounds were mixed into a laboratory two-roll mill (Schbentran 150), with a friction ratio 1 : 1.2 at 230°C for 15 min, to obtain sheets of composite. Then the sheets were ground, dried, put in a mould and compressed during 12 min at 230°C. Finally the mould was immediately cooled into air or an ice-water mixture at 0°C during 15 min. All specimens have 3 mm of thickness and this step is named ''*first quench.*'' According to Mills,[5] heating PC to 160°C and rapidly cooling it produces residual compressive stresses in the surface of the material that significantly improves its impact strength as long as the material is not thicker than 5 mm. Above this thickness, the RS produced by this process have little effects on impact strength.

In a second time, free quenching was carried out only for specimens of 3% weight content named ''*optimal content.*'' All specimens were heated in an oven at 160°C during 3 h and then quenched into water baths at different temperatures (20, 30, 40, and 60°C) or into an ice-water mixture at 0°C during 15 min; this procedure was named ''*second quench.*'' Finally, in order to get a sample reference, an annealing is performed. Annealed specimens were prepared using samples first quenched in air. Then, these samples were heated at 160°C during 2 h and finally slowly cooled in the oven until room temperature at a rate of about 0.5°C min^{-1}. These samples were named ''annealed samples.''

Heat distortion temperature

The HDT was obtained in accordance with ASTM D648, which describes HDT as the temperature at which the specimen (3 × 13 × 127 mm^3) deflects by 0.25 mm under 1.8 MPa while heated in an oil bath at a rate of 2°C min^{-1}. At least 2 specimens were tested and the average value was used for the data plot.

Tensile test

The tensile properties were determined using dumbbell specimens of 115 mm length, 13 mm wide, and gauge length of 20 mm. The test was carried out using a universal testing machine with a crosshead speed of 10 mm min^{-1}. The test procedure followed ASTM D638-72. 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 D256-73. Specimens of (3 × 12.7 × 63 mm^3) were compression moulded. Parts of them were milled with a notch radius of 0.5 mm. 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 exami-

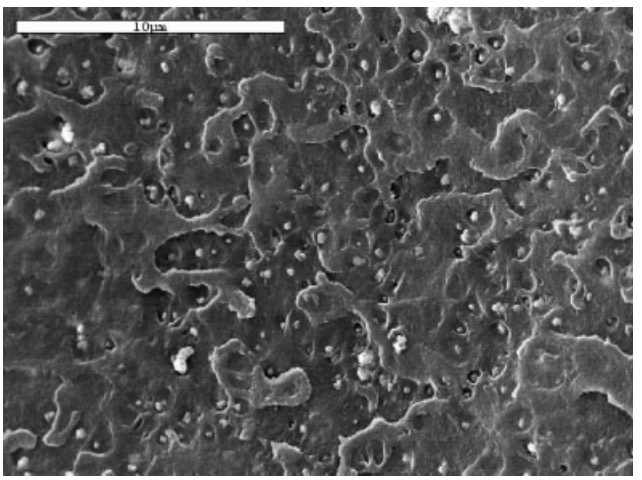


Figure 1 Scanning Electron Micrograph of transversal section of PC/TiO_2 (6% weight content).

nation of the specimen between cross Polaroid's under white light. At least 5 specimens were tested and the average value was used for the data plot.

Density measurements and calculations

According to the principle of Archimede 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 PC. 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 liquid at 25°C, and an HB Mettler analytical balance.

The PC/TiO_2 densities were calculated using the mixtures law:

$$d = d_{PC}\ \phi_{PC} + d_{TiO2}\ \phi_{TiO2}$$

where d: density of PC/TiO_2 composite

d_{PC} is the measured density of PC for a first cooling in air (=1.196) or a first quench in water (=1.173).

d_{TiO2} is the density of TiO_2, (d = 4.20)[2]

$\phi_{TiO2:}$ Volumic fraction of TiO_2,

$\phi_{PC:}$ Volumic fraction of PC, $\phi_{PC} = 1 - \phi_{TiO2}$

with:

$$\phi_{TiO_2} = \frac{\frac{w_{TiO_2}}{\rho_{TiO_2}}}{\frac{w_{TiO_2}}{\rho_{TiO_2}} + \frac{(1-w_{TiO_2})}{\rho_{PC}}} \quad (1)$$

where, $w_{TiO_2}$is the weight fraction of TiO_2.

As density changes over the cross section, it should be noticed that the present measurements correspond to the whole thickness.

Morphological characteristics

Light Microscopy (LEITZ MP 12) and Scanning Electron Microscopy (JEOL 6301 F) fitted with a device for semi quantitative analysis by X-Ray Energy Dispersive Spectrometry (Oxford, Link isis) were used to characterize: (i) morphological feature of PC/TiO_2 fractures; (ii) morphological and granulometric size of TiO_2 powder; (iii) dispersion of TiO_2 powder inside pigmented PC specimens.

RESULTS AND DISCUSSIONS

Effect of content of TiO_2 and first quench

Figure 1 shows that TiO_2 is well dispersed inside the matrix even at 6%. Several microscopic observations showed that the fillers are not agglomerated inside the composite whatever the TiO_2 weight content. The variations of density and modulus of elasticity as a function of TiO_2% content are shown in Figures 2 and 3 respectively. It is clearly seen that the values of these two properties increase as the TiO_2 content increases. This was previously observed by other authors for the modulus of elasticity and Izod impact strength.[2] These results are foreseeable because TiO_2 modulus and density values are higher than PC ones. The density increase is also due to the reduction of free volume corresponding to the densification of the polymer around the fillers.[1] This is confirmed by the theoretical calculation using the mixture law presented in Figure 2. The difference of density observed between the specimens quenched at 0°C in water and the one cooled at room temperature comes from the fact that the specimens quenched in water were cooled more rapidly. This variation can be associated to the difference of thermal effusivity of air and water and to the higher temperature gradient when quenching in water at 0°C.

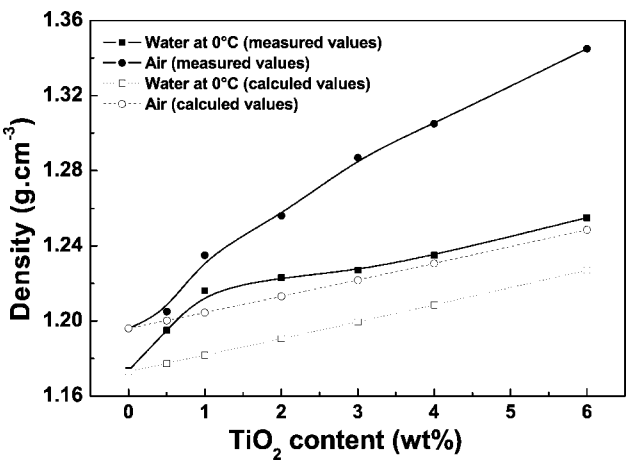


Figure 2 Density as a function of titanium dioxide content and quenching conditions.

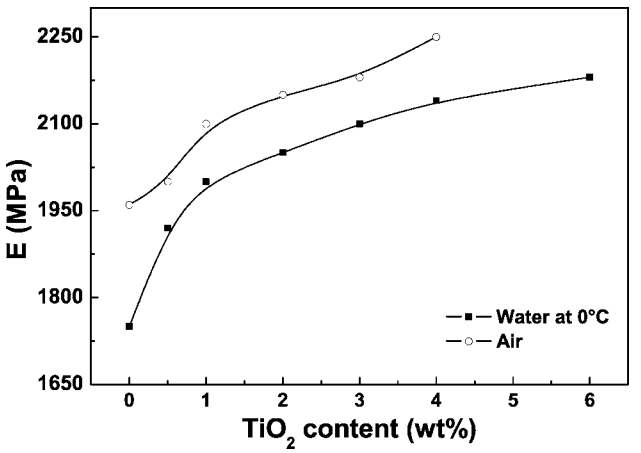


Figure 3 Modulus of elasticity as a function of titanium dioxide content and quenching conditions.

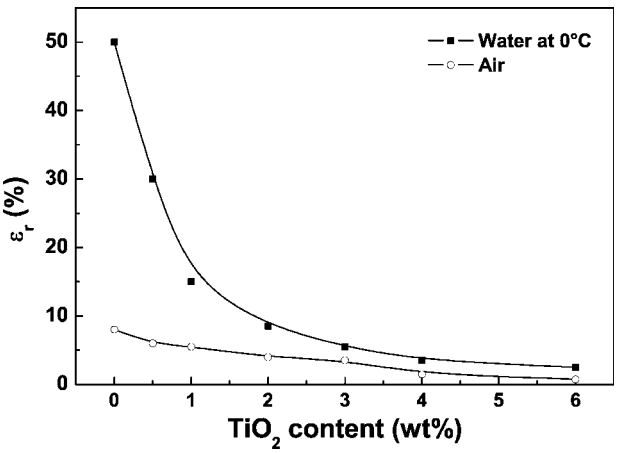


Figure 5 Elongation at break as a function of titanium dioxide content and quenching conditions.

In the faster cooling case, the macromolecular chains have less time to reorganize which induces an increase of the free volume and therefore the observation of a lower density. This last interpretation is supported by the observation of a higher modulus of elasticity for slowly cooled specimen for a given TiO_2 content.

According to Van Krevelen,[8] the density (ρ) is correlated to the modulus of elasticity (E): $E \propto \rho^7$. This means that the specimens having lower modulus of elasticity have also a lower density.

Figure 4 shows the unotched and notched Izod impact strength as a function of TiO_2 content. For unotched Izod impact strength, the specimens reach higher values of fracture energy than for the notched one. This is related to the energy dissipated in the region of crack growth, which is evidenced by the fact that the dramatic drop of Izod impact strength is observed for TiO_2 pigment contents higher than 3%. In the case of notched specimens, the increase of TiO_2 content induces an almost linear decrease of the Izod impact strength because the crazes easily propagate between the fillers. Otherwise, the pigmentation of PC can cause the absorption of polymer molecules on the particles and can induce a densification, which reduces the free volume, the segments motions and thus the associated Izod impact strength and elongation at break.

The elongation at break as a function of TiO_2 content is presented in Figure 5. The results show a dramatic decrease of the elongation at break with increasing of TiO_2 content particularly for specimens first quenched in water at 0°C. Indeed, the stresses induced by the quench prevent the specimen from the rupture as long as the filler content remains low.

The variations of yield stress and HDT (Figures 6 and 7) as a function of TiO_2 content exhibit a maximum corresponding to a filler content of 3%. This

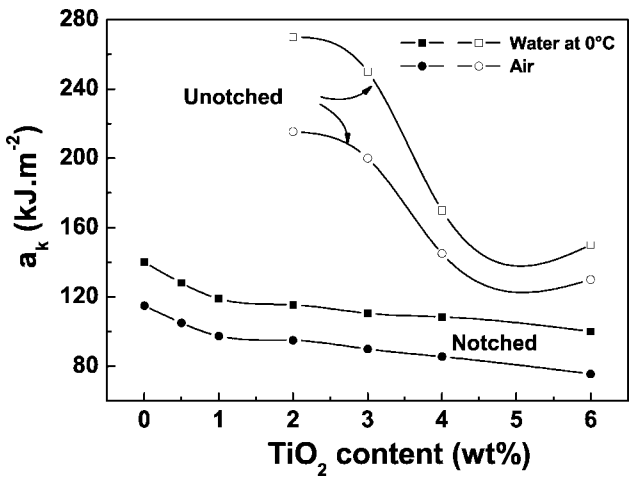


Figure 4 Notched and unotched Izod impact strength as a function of titanium dioxide content and quenching conditions.

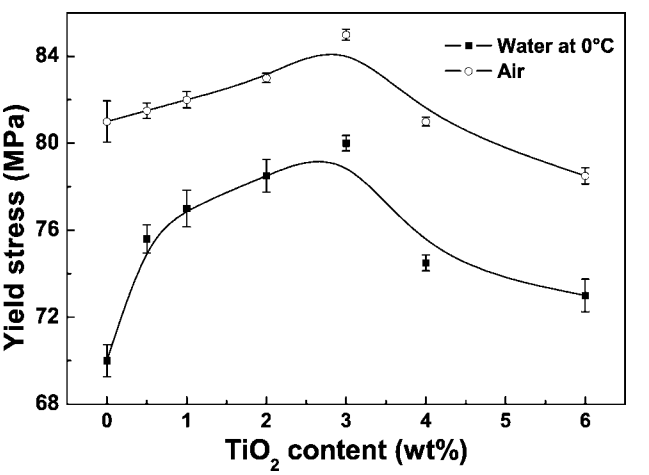


Figure 6 Yield stress as a function of titanium dioxide content and quenching conditions.

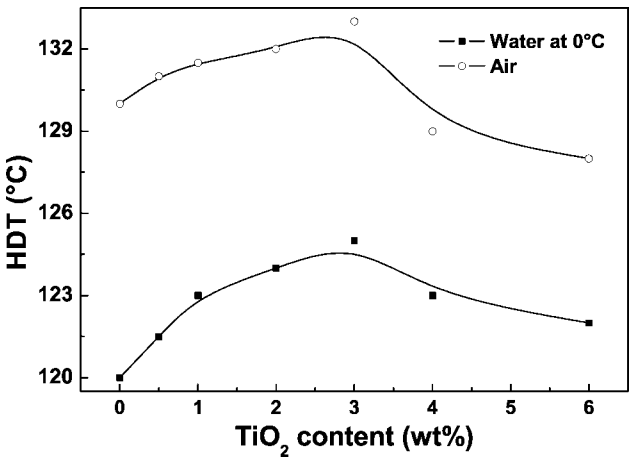


Figure 7 HDT as a function of titanium dioxide content and quenching conditions.

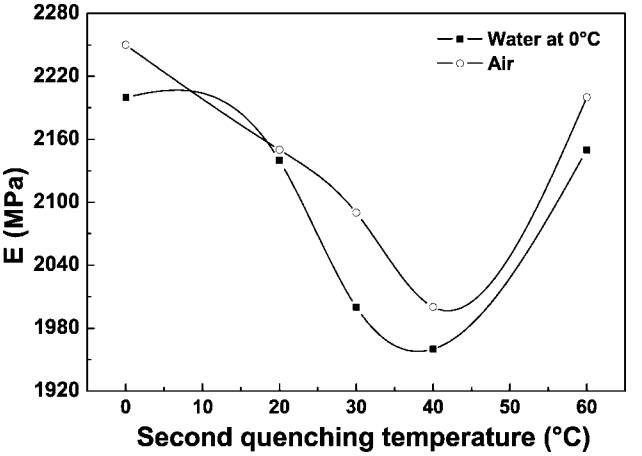


Figure 9 Modulus of elasticity as a function of second quenching temperature.

maximum is not observed in the modulus of elasticity and Izod impact strength cases where E increased and a_k decreased. The maximum of HDT and yield stress exists for the two thermal histories and is probably due to the best interactions occurring between the components.

As for Modulus of elasticity and density, the values of the yield stress and of the HDT are lower after a quench in water at 0°C than after a slow cooling in air at room temperature. For the properties associated with a break (Izod impact strength and elongation at break), the best results are obtained for specimens first quenched in water at 0°C. This is due to the presence of more RS in these specimens. So and Broutman[9] have invoked the same explanation in the PC and PMMA case as in the quenched inorganic glass case. They have suggested that RS prevent crack formation and growth. In fact, compressive stresses generated in free quenched material surface delay the fracture of the sheet by preventing flaw generation.

Nevertheless, all other properties like modulus of elasticity, yield stress and HDT are lowered by a rapid quench. This may be linked to the presence of larger tensile stresses inside the specimens.

Effect of second quenching temperature

This section is dedicated to the effect of second quenching temperature on the mechanical and thermal properties of PC/TiO_2 composites. The choice of this thermal treatment is based on the study of PC presented in Part I where it has been shown that the second quenching was more efficient than the first one to improve impact strength. On the basis of the results presented in the precedent section, we decided to perform all experiments for a single TiO_2 content (3%), keeping in mind that some properties such as HDT and yield stress were optimum for this loading.

As observed in the first part, an opposite effect is noted for modulus of elasticity, density, yield stress, and HDT (Figures 8–11). These properties reach a

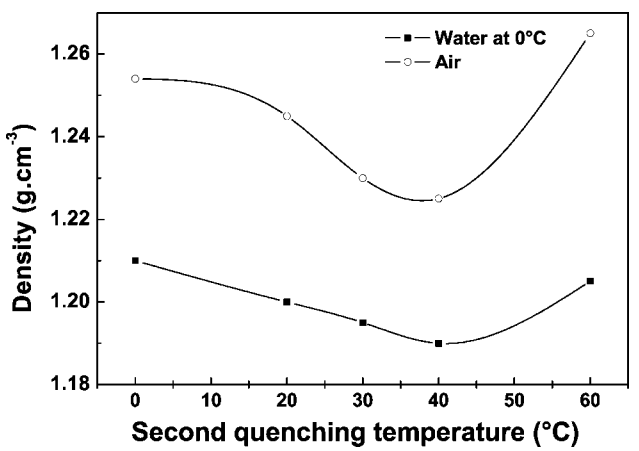


Figure 8 Density as a function of second quenching temperature.

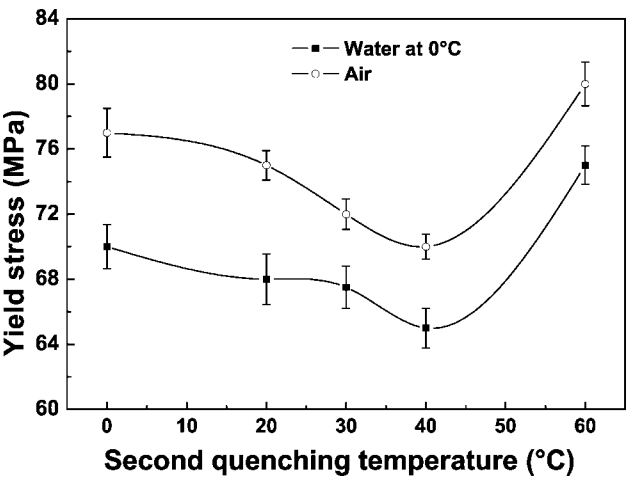


Figure 10 Yield stress as a function of second quenching temperature.

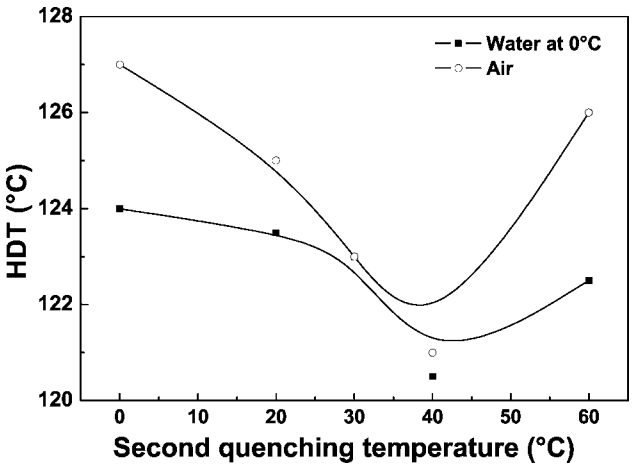


Figure 11 HDT as a function of second quenching temperature.

minimum for a second quenching temperature of 40°C.

The minimum of density observed for a second quenching temperature of 40°C is associated to an increase of the free volume. The increase of free volume leads to a higher molecular mobility. This explains the increase of the Izod impact strength and elongation at break previously observed. It decreases also the elasticity modulus.

As the yield stress involves physical sliding between molecular segments, the increase of free volume makes sliding easier and decrease the yield stress. Siegmann *et al.*,[10] without calculating the change in free volume, speculated that the decrease of HDT may also be related to the increase of free volume. The same phenomena have been observed for neat PC.

In Figure 12, the evolution of notched and unotched Izod impact strength is presented as a function of second quenching temperature. The same

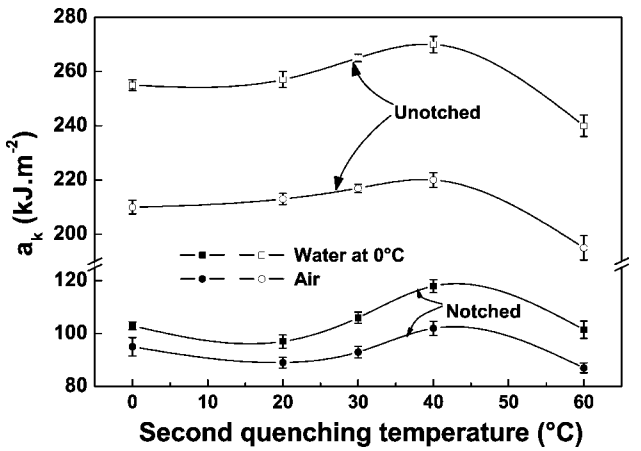
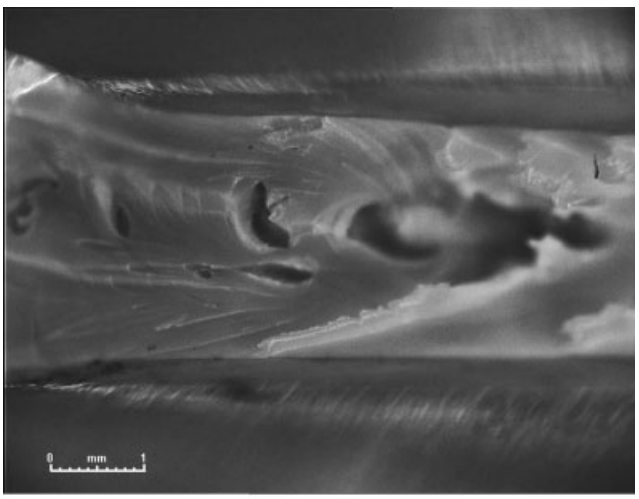


Figure 12 Unotched and Notched Izod impact strength as a function of second quenching temperature.

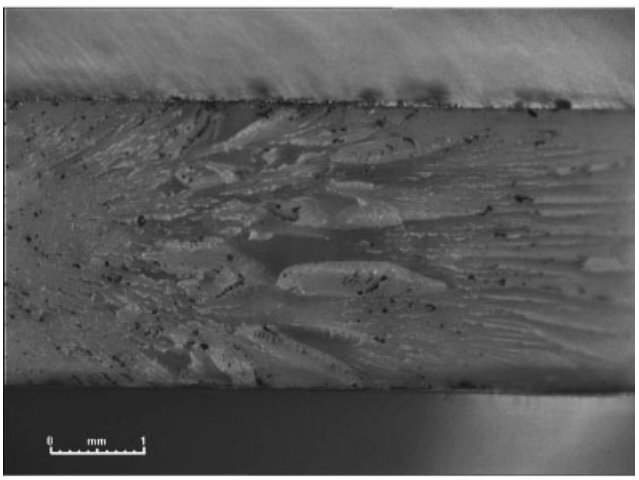
differences as observed before appear between the specimens first quenched in water at 0°C and the specimens quenched in air at room temperature. This means that the second thermal treatment including an annealing of 3 h at 160°C has not totally erased the first thermal treatment. As it can be seen, the shapes of curves of Izod impact strength are similar, but with somewhat smaller values in the notched specimens case as even observed. In both cases, there is a maximum for a second quenching temperature of 40°C.

The second quench has produced surface compressive RS, which leads to an increase of energy absorption during the failure of the material.

Like for neat PC, the specimens of notched Izod impact measurements exhibited two types of failure mechanisms. The specimen presented in Figure 13(a),



(a)



(b)

Figure 13 (a) Optical micrography of broken specimen quenched at 40°C. (b) Optical micrography of broken specimen annealed.

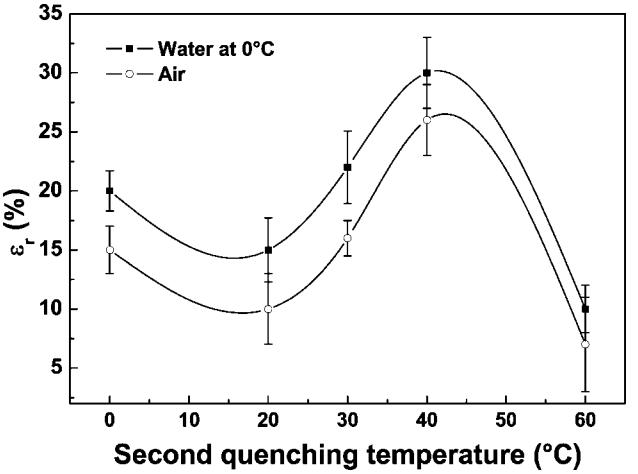


Figure 14 Elongation at break as a function of second quenching temperature.

which corresponds to a specimen quenched at 40°C during the second quench, possesses a high Izod impact strength. The specimen has failed by ductile process and presents a disturbed surface with large holes indicating a plastic deformation in the region of the notch. The two edges of the specimen after fracture remained attached.

This has ever been observed in the study of PC. A rough surface was obtained for specimen second quenched at 40°C.

The specimen presented in Figure 13(b), which corresponds to the annealed, exhibits a low impact strength and has tended to fail by brittle fracture. Like in the study of neat PC, the fracture evolution from brittle to plastic and present a relatively smooth surface may be linked to the presence of more free volume in the specimen second quenched at 40°C than in the specimen second quenched at 0°C.

The elongation at break as a function of second quenching temperature is presented in Figure 14. The results exhibit a maximum position, which corresponds again to a second quenching temperature of 40°C. It is obvious that the specimens containing the highest RS produced the highest elongation at break and ductility. So, the elongations at break values are greater for the specimens first quenched at 0°C.

The elongation at break and Izod impact strength should logically decrease as the quenching temperature increases. In most of the studies concerning neat PC this decrease has been observed after a first quench. Nevertheless, we have also observed the same increase of rupture properties for a second quench at 40°C of neat PC. Thus, these results reported in Part I are in agreement with the behavior observed now for pigmented PC. As for the case of neat PC, this behavior could be linked to the existence of a molecular relaxation located around 35°C.[11] We will recall here that DMA experiments presented in part I have demonstrated the existence of this relaxation in neat PC specimens submitted to annealing treatments.

Besides, many authors have shown that molecular relaxations of polymers contribute strongly for several important engineering properties (impact strength or ductility of glassy amorphous polymers).[12–14] Moreover, it has been shown that three well defined loss peaks coincide with similar peaks in Izod notched impact strength for PTFE.[14]

CONCLUSION

The effects of free quenching temperature including different thermal histories on mechanical, physical, and thermal properties of pigmented polycarbonate (PC/TiO_2) were investigated. The incorporation of TiO_2 into PC leads to an increase of the modulus of elasticity and a decrease of Izod impact strength and elongation at break. The fillers act as a default in the material, initiating the breaking of the material during mechanical tests. The fact that both HDT and yield stress exhibit a maximum at 3% of TiO_2 has induced a deeper study of this peculiar blend. So, for such a titanium dioxide concentration, the effect of free quenching was studied to improve the pig-

TABLE I
Variation Examples of Milled Notched Izod Impact Strength, Elongation at Break and Modulus of Elasticity as a Function of Quenching and Pigment-Addition

Material	Thermal treatment	Milled notched Izod impact strength a_k (kJ m^{-2})	a_k evolution (%)	ε_r (%)	ε_r evolution (%)	E (MPa)	E evolution (%)
PC	First cooling in air	117		8		1950	
PC	First quenching in water at 0°C	140	+20	50	+525	1750	−10
PC + 3% TiO_2	First quenching in water at 0°C	110	−21.5	7	−86	2090	+20
PC + 3% TiO_2	First quenching in water at 0°C + Second quenching in water at 40°C	117	+7	30	+329	1960	−7

mented PC properties. Normally, Izod impact strength and elongation at break should decrease when the quenching temperature increases because less thermal stresses are generated. The fact that a maximum is reached for a second quenching temperature of 40°C was linked to the existence of a molecular relaxation which increases the free volume. The increase of free volume is visible on density curves. It corresponds also to the lowering of modulus of elasticity, yield stress, and HDT and the improvement of both Izod impact strength and elongation at break. A higher molecular mobility, because of the increase of free volume, explains the increase of the Izod impact strength and elongation at break.

Some results have been reported in Table I to summarize the evolution of the properties with the pigment addition and quenching. For example, the decrease of Izod impact strength with the addition of 3% of TiO_2 is compensated by an adapted thermal treatment: a second quench at 40°C.

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