

Improvement Of Mechanical Properties Of Polymers With A Supercritical CO₂ Based Process

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In this work the experimental results of crystallization kinetics of polycarbonate treated with supercritical carbon dioxide at pressure of 170 and 300 bar and at temperature of 60 and 80 °C in a batch type reactor are reported and discussed.

Mechanical properties polycarbonate samples treated with carbon dioxide under different experimental conditions have been measured and the influence of experimental conditions on hardness and elastic modulus are also reported and discussed.

INTRODUCTION

Supercritical fluids, especially supercritical CO₂, are used for extraction and impregnation processes [1, 2, 3]. For example, the impregnation of dyes into CO₂-plasticized PMMA or PET in order to produce advanced optical components [4, 5]. The use of scCO₂ allows lower operating temperatures and the use of thermally labile dyes.

Supercritical CO₂ has been also proposed to enhance the kinetics of crystallization of polymers [6]. The enhancement of the crystallization kinetics is due to the strong plasticizing and swelling effect of carbon dioxide adsorbed in the polymers. These effects are associated to a change of glass transition temperature (T_g), which decreases with increasing CO₂ solubility. The glass transition temperature of common glassy polymers can be decreased about 80 ÷ 100 °C by adsorption of supercritical CO₂ [7-12].

Bisphenol-A polycarbonate (PC) shows a very slow thermal crystallization kinetics [13]. Both solvents and vapors can be used to induce crystallization in PC, but this method cannot be used as an industrial process for the high residue of solvents left in the crystallized materials.

In this work, the kinetics of crystallization of PC induced by supercritical carbon dioxide is discussed and the mechanical properties of crystallized PC are evaluated.

I - MATERIALS AND METHODS

Bisphenol-A polycarbonate (Tecanat) was supplied by Ensinger Italia, carbon dioxide 99,9 was supplied by Rivoira.

PC glass transition temperature was measured with DSC and it was found to be 143°C.

The high-pressure equipment used for crystallization tests is a batch reactor, (Nova Swiss , 200 cm³, T max: 350°C, P max: 700bar), equipped for pressure and temperature measurement and control.

The crystallization behavior and morphology of polycarbonate were investigated by means of a polarized optical microscopy and XRD (X'Pert Philips PW 3710 MPD).

The mechanical properties, hardness and modulus of elasticity, were measured a microdurometer Leitz Miniload 2 and an Instron 5500R 1185, respectively. The modulus of elasticity was determined according to the test method ASTM F417-78.

The experimental tests were performed using PC samples of about 30 x 30 x 3 mm (length x width x thickness). After placing the PC samples in the batch reactor, pressure and temperature are set to the prefixed values. When the chosen contact time has expired, the batch reactor is depressurized and the PC samples are recovered. The depressurization rate is about 50 bar/min for all the experimental tests.

The experimental conditions must be chosen in such a way that the temperature is above the glass transition temperature to enhance the crystallization kinetics.

The glass transition temperature for polymers in equilibrium with supercritical CO₂ is well correlated by the Cha-Yoon equation [14]:

$$T_g = T_{g0} \cdot \exp\left\{-\left(M_p\right)^{-\frac{1}{3}} \cdot (\rho)^{-\frac{1}{4}} \cdot \alpha \cdot w\right\} \quad (1)$$

where T_{g0} is the glass transition temperature of polymer itself, T_g is the glass transition temperature of polymer in equilibrium with CO₂, M_p is monomer molecular weight, ρ is polymer density, w is the percentage by weight of absorbed CO₂, and α is a parameter of the model.

The parameters of the Cha-Yoon equation for the PC- CO₂ system have been obtained by correlation of literature equilibrium adsorption data at 5 and 10 bar [15, 16]. The Cha-Yoon equation for the PC-CO₂ system was found to be:

$$T_g = 140 \cdot \exp\left\{-\left(266\right)^{-\frac{1}{3}} \cdot (1.2)^{-\frac{1}{4}} \cdot 0.34 \cdot w\right\} \quad (2)$$

The Cha-Yoon equation, together with experimental data for the solubility of CO₂ in polycarbonate at 35°C and 50°C [16, 17], allows to correlate the glass transition temperature with pressure.

At 80°C and 170 bar, the glass transition temperature of PC in equilibrium with CO₂ decreases to 80 °C from 140°C of the pure PC.

Experimental crystallization tests were performed at three different conditions: at 80 °C and 170 bar, i.e. at the glass transition temperature, at 80°C and 300 bar, i.e. above the glass transition temperature, and at 60°C and 170 bar, i.e. below the glass transition temperature.

The PC was allowed to remain in contact with sc-CO₂ for 2 h, 4 h, 8 h, 12 h and 24 h, in order to evaluate the crystallization kinetics.

II – RESULTS AND DISCUSSION

As the degree of crystallization increases polycarbonate loses its transparency as and it assumes a white color. The PC samples treated with CO₂ at 60°C and 170 bar for 24h loss their transparency near the surface, but are still transparent in the inner section. PC samples treated with CO₂ at 80°C and 300 bar for 24h are completely white. This qualitative observation confirm that the crystallization kinetics is enhanced as the glass transition temperature is approached or exceeded. Observation of the samples with optical microscope after etching shows different crystal morphology at the three different experimental conditions: at 60 °C and 170 bar, figure 1, and at 80 °C and 170 bar, figure 2, a crystal lamellae structure is observed, while at 80 °C and 300 bar the presence of spherulitic structure is found. Hu and Lesser [13] found a structure of fibrillar monocryallites associated with lamellar growth for PC treated for 8 hours at 95°C and 204 bar. This means that the experimental conditions have an influence on both crystallization kinetics and crystal morphologies.

In figure 4 and 5 are reported the results of wide-angle X-Ray diffraction (XRD) for PC samples treated at 80 °C/170 bar and at 80 °C/300 bar for 4, 12 and 24 h, respectively. On the same figures the X-ray pattern of untreated PC samples are reported for comparison. The untreated sample shows one broad reflection at 2θ of 17.6°, while the X-ray pattern for PC samples treated with supercritical CO₂ show a sharper peak at 17.6° and a peak at 25.8°, which becomes more evident with increasing time of treatment. This fact indicates an increase in crystallinity. Hu and Lesser [13] found that the X-ray pattern for samples of PC treated at 90 °C and 170 bar for 8 h appears the same as the untreated material, while a sharper peak at 17,6° is noticed when PC samples are treated at 95°C and 204 bar for 8 h. This observations confirm that at 170 bar and at 80 °C, the glass transition temperature of PC is about 80 °C.

The mechanical properties of PC treated with supercritical CO₂ depend on two main parameters: the degree of crystallization, and the degree of voids which is left in the treated PC samples after depressurization. The solubility of CO₂ increases with increasing pressure and increasing temperature: high pressure and temperature accelerates the crystallization kinetics, but higher degree of voids can be left in the samples after depressurization, which is detrimental for mechanical properties.

To quantify the dimensional changes of PC samples left after treatment with supercritical CO₂ the thickness of samples was measured before and after treatment. In figure 6 the percentage thickness change is reported against the time of treatment for different experimental conditions. The thickness increase is 22% for samples treated at 80°C/300 bar for 24 h and 15% samples treated at 80°C/170 bar for 24 h. These results demonstrate that the mechanical properties of the treated PC are strongly influenced by the residual dimensional changes, in addition to the degree of crystallization.

In figure 7 the hardness percent variation of PC samples treated with CO₂ with respect to the untreated sample is reported. In figure 8 the modulus of elasticity percent variation of PC samples treated with CO₂ with respect to the untreated sample is reported.

A maximum hardness increment of 66% is obtained for PC samples treated at 80 °C/170 bar for 12 h, while the maximum degree of crystallization is obtained for samples treated at 80°C/300 bar for 24 h, as shown by the XRD patterns reported in figure 5. At 80°C/300 bar the maximum hardness increment is obtained for contact time of 12 h, even if the hardness increment is only 46%.

The modulus of elasticity shows a maximum increment of 44% at 300 bar/80 °C and for contact time of 12 h, while it shows a decreasing for contact time of 2 h and 24 h.

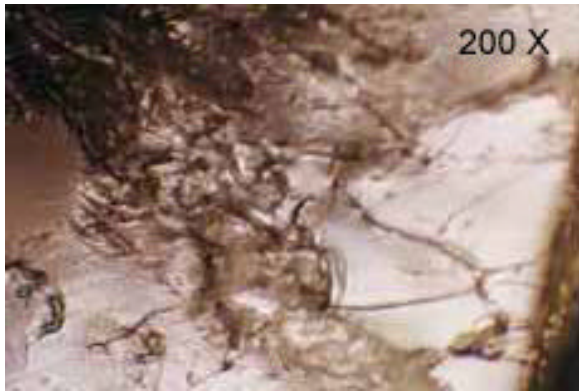


Figure 1 – Crystal lamellae structure of PC treated with CO₂ at 170bar/60 °C/24 h.

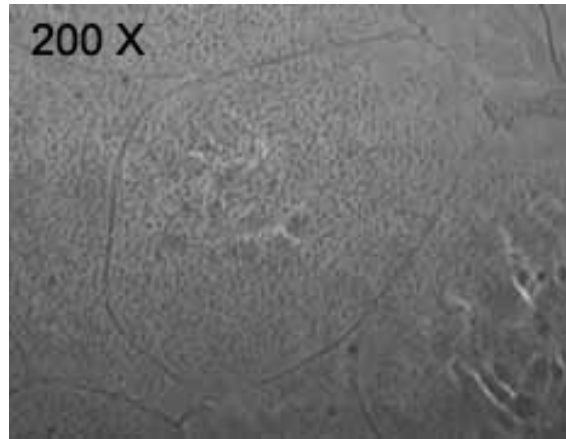


Figure 2 – Crystal lamellae structure of PC treated with CO₂ at 170bar/80°C/24 h.

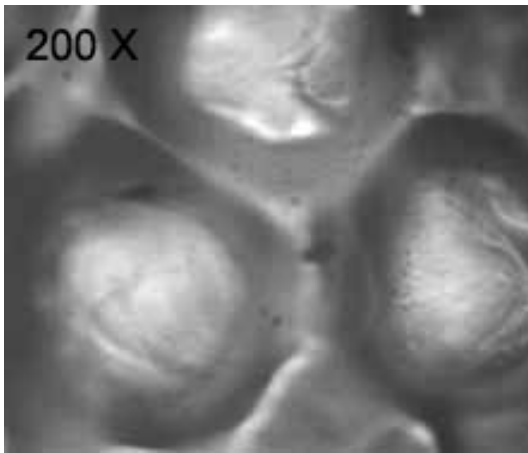


Figure 3 – Spherulitic structure of PC treated with CO₂ at 300bar/80°C/24 h.

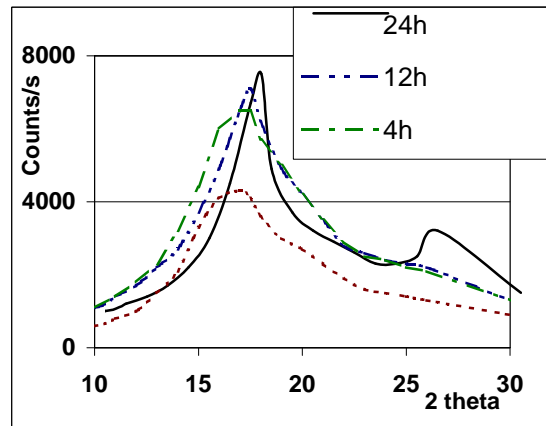


Figure 4 – XRD results of untreated PC and treated with CO₂ at 170 bar/80°C/24 h.

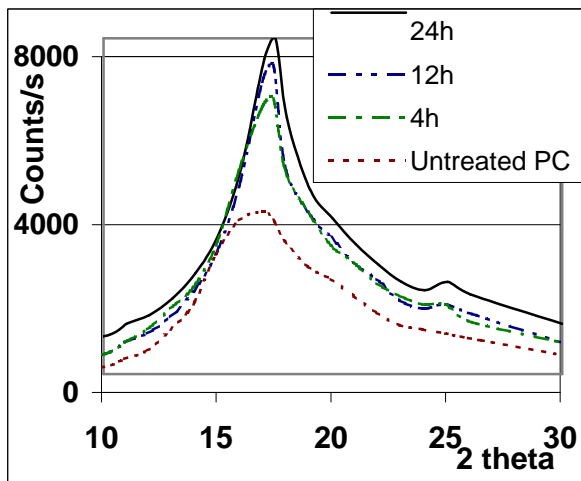


Figure 5 – XRD results of untreated PC and treated with CO₂ at 300bar/80°C/24 h.

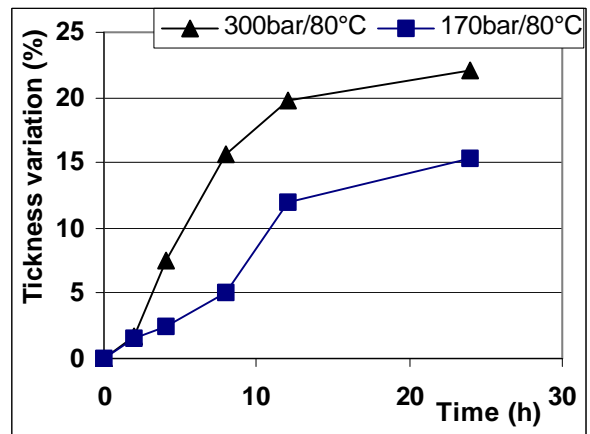


Figure 6 – Thickness variation of polycarbonate treated for a period of 24 h.

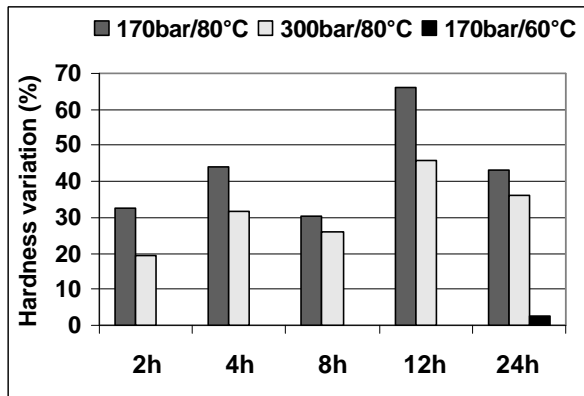


Figure 7 – Hardness variation of polycarbonate treated with sc CO₂.

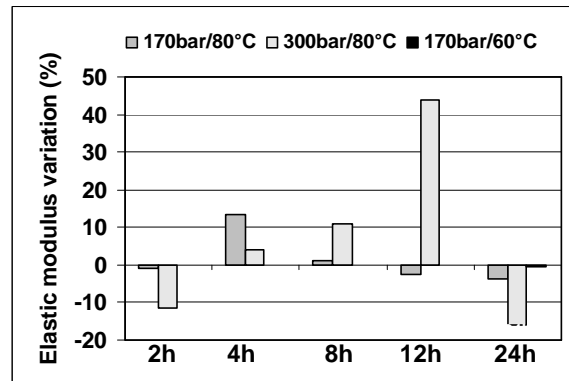


Figure 8- Elastic modulus variation of PC treated with CO₂.

At 170 bar/80 °C the behavior of modulus of elasticity is similar, with a maximum increment of 13% for contact time of 4 h. These results confirm that both degree of crystallization and damage caused by the CO₂ have an influence on mechanical properties of treated PC samples.

The different behavior of hardness and elastic modulus is due to the fact that hardness is a measure of the properties near the surface of the sample, while elastic modulus is a measure of the whole section of the sample.

CONCLUSION

The degree of crystallization of PC samples induced by supercritical carbon dioxide at different temperature and pressure conditions has been investigated.

Mechanical properties of PC samples treated with supercritical carbon dioxide have been measured, showing that they are strongly influenced by both degree of crystallization and experimental temperature and pressure conditions: the best results are not obtained when the maximum degree of crystallization is obtained.

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