CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci
Copyright © 2007, AIDIC Servizi S.r.l., ISBN 978-88-95608-00-6

Crystallization of PC and PEEK with Supercritical Carbon Dioxide

Bologna S.(1), Del Re G. .(1), Mascia L. (2), Spagnoli G. .(1)
(1) Università di L'Aquila, Dipartimento di Chimica, Ingegneria Chimica e Materiali,
Monteluco di Roio – 67040 L'Aquila (ITALY)
e-mail: delre@ing.univaq.it
(2) Institute of Polymer Technology and Materials Engineering,
Loughborough University

In this paper the effect of supercritical carbon dioxide treatment on two different polymers was investigated.

For its swelling properties supercritical carbon dioxide can be used instead of thermal treatment or solvent process (SINC) to induce crystallization in polymers.

Amorphous polycarbonate (PC) sheets and amorphous and semi crystalline poly (ether ether ketone) (PEEK) films were subjected to carbon dioxide treatments at different temperature, pressure and process time.

PC crystallization is difficult because of its chain rigidity and it can be obtained using a very low cooling rate.

Amorphous PEEK is crystallized by SINC process and semi crystalline PEEK by high temperature thermal processes.

By use of $scCO_2$ amorphous PC and amorphous/crystalline PEEK can be crystallized at milder conditions and in shorter time.

Our gaol is to point out differences between amorphous and semi crystalline polymers behaviour when subjected to supercritical carbon dioxide treatment.

Differential scanning calorimeter and X–ray diffraction measurements were used to evaluate the crystallinity index of polymers.

Experimental swelling data for sorption/desorption processes show that carbon dioxide is more soluble into amorphous films than in semi crystalline polymers for the absence of barriers presented by crystalline domains.

The experimental results show that $scCO_2$ treatment of polymers causes an improvement of crystallinity index, which increases with increasing pressure and increasing temperature.

1. Introduction

Supercritical treatments effects on polymers are: the reduction of glass transition temperature and increase of polymer chains mobility.

Supercritical fluid treatment of polymers causes a swelling effect with the consequent reduction of polymer glass transition temperature (Tg). In addition, when a polymer is exposed to a supercritical fluid, the polymer chains mobility increases, that is to say that the polymer free volume increases. For these reasons SCF are used as agents to produce polymer nanocomposites (Tomasko et al. 2003) or to introduce additive substances into the polymer matrix (Berens et al., 1989).

Another important property of SCF is the capability to induce crystallization in treated polymers: the increased polymer chains mobility favours the formation of crystalline domains.

Swelling effects on the polymers can be obtained also by using common liquid solvents, able to reduce the polymer Tg; the SINC (Solvent Induced Crystallization) process is based on this effect. Cornelis et al. (1996) have found that solvents like methylene chloride, tetrahydrofuran and acetone have a plasticizing effect on PEEK and can induce further crystallization. A drawback of SINC process is that it is necessary to start from a completely amorphous polymer. In addition, it is difficult to remove completely the solvent from the polymer.

In comparison with common liquid solvents, supercritical fluids are characterized by high diffusivity and low viscosity that allow to enhance the transport processes (Schnitzler and Eggers, 1999) and can be easily removed from polymer.

To obtain crystalline polycarbonate it is necessary to use very low cooling rates (Hu and Lesser, 2004). The treatment with $scCO_2$ dramatically decreases the crystallization process time. This is due to the lowering of the PC glass transition and increased chain mobility. The rate and extent of crystallization depends on the polymer morphology and process conditions such as pressure, temperature and process time (Kemmere and Meyer, 2005). No examples of polycarbonate crystallization at temperature below Tg are reported in the literature (Mascia et al., 2006).

In this paper the results of the treatment of PC and PEEK by supercritical carbon dioxide are reported and discussed, pointing out the different behaviour of amorphous and semi crystalline polymers.

2. Experimental

Materials

Polycarbonate (PC) amorphous sheets 5 mm thick were supplied by Parlam ltd, molecular weight 28,000 – 30,000 g/mol, Tg: 140°C.

Polyetereterketone amorphous and semi crystalline films (100 μm thick) were supplied by Victrex, molecular weight about 35,000 g/mol, Tg:143°C.

Carbon Dioxide (99,99% purity) was supplied by Rivoira.

Equipment

Apparatus used to carry out the experimental tests on polycarbonate and poly (ether ether ketone) was a Nova Swiss batch reactor, volume 200 cm^3, maximum temperature 350°C, maximum pressure 700 bar.

A standard experimental procedure consists in the following steps: loading samples (30x30 mm) into the reactor, heating the apparatus to prefixed temperature and pressurization at the prefixed pressure. When the prefixed process time is reached, the apparatus is depressurized and cooled to room temperature under running water. Treated samples are extracted from the reactor and analyzed.

The depressurization rate was of about 50 bar/min and the cooling rate was of about 5 °C/min.

Experimental tests

Experimental tests were performed at temperatures from 80 to 180 °C and at 150 and 300 bar, process time was in the range 8 – 24 hours.

The crystallinity degree was evaluated by both XRD and DSC.

X-ray measurements were performed with a Philips X' Pert PW 3710 MPD at room temperature. The percent crystallinity was calculated by evaluating the area under the peaks:

$$\%\ Cry = \frac{A_C}{A_C + A_A} 100 \qquad (1)$$

A_C and A_A are the area under the crystalline peaks and under the amorphous halo, respectively (Cornélis et al., 1996).

Differential scanning calorimetry runs were performed using a Perkin-Elmer DIAMOND. 10 to 20 mg samples were heated from room temperature to 380 °C at a rate of 10 °C/min under N_2 flow. The percent crystallinity of samples was estimated by integrating the area under the melting peak and dividing it by the theoretical value of 130 J/g for 100% crystalline PEEK heat of fusion (Cornélis et al., 1996) and 109.8 J/g for 100% crystalline PC heat of fusion (Hu and Lesser, 2004).

Dimensional change of processed samples were also evaluated.

3. Results and discussion

In table 1 are reported the experimental conditions and the percent crystallinity determined by both DSC and XRD for PC samples.

When amorphous PC sheets were treated with supercritical CO_2, samples became opaque and the opalescence took place from the outer to inner layers. The opalescence is caused by crystallization. With increasing temperature, pressure and process time, PC crystallinity increases.

In figure 1 are reported some DSC curves for PC samples treated at different experimental conditions: it is evident the presence of two broad endothermic peaks for samples treated at lower temperatures (80-130 °C) and a sharp endothermic peak with a shoulder for samples treated at higher temperatures (130-180 °C). The double peaks occurred at 175 and 215 °C for samples treated up to 100 °C, the sharper peak occurred at 225 and 243 °C for treatments at 150 and 180 °C, respectively.

In figure 2 are reported the XRD spectra of untreated PC and of PC samples treated at 300 bar for 24 hours at 80 and 180 °C. The spectra of treated samples show two peaks at $2\theta = 17.6°$ and $2\theta = 25.8°$, the observed peaks become sharper with increasing temperature.

At 80 °C and 300 bar for process of 8 hours, the PC crystallinity raised to 5.5 %, for longer time (24 h) the crystallinity increases up to 7.3%. When the process temperature is increased to 140 °C, under 300 bar of pressure and for process of 24 hours, PC degree of crystallinity is higher than 20%.

In table 2 are reported the experimental conditions and the percent crystallinity determined by XRD for amorphous and semi crystalline PEEK film. Experimental tests 1 and 3 were carried out at room pressure to evaluate the influence of temperature on the increase of degree of crystallinity. The results show that at 80°C there is no increase

Table 1. Polycarbonate sheet: experimental conditions and DSC/XRD results.

	Experimental Test Conditions	% Crystallinity (DSC)	% Crystallinity (XRD)
1	80°C – 300 bar – 8 h	5.5	-
2	80°C – 300 bar – 24 h	7.3	-
3	100°C – 300 bar – 12 h	8.0	-
4	130°C – 300 bar – 12 h	15.2	-
5	140°C – 300 bar – 24 h	20.1	-
6	180°C – 300 bar – 24 h	24.3	29.3

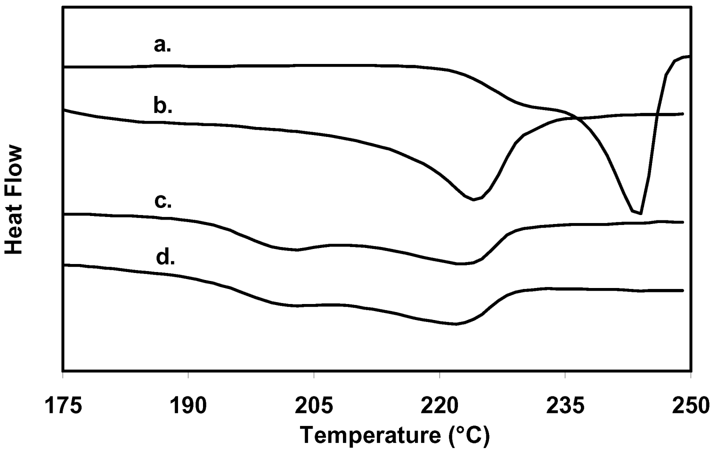

Figure 1. DSC Polycarbonate Sheet: a. treated at 180°C, for 24 h under 300 bar; b. treated at 150°C, for 24 h under 300 bar; c. 130°C, for 12 h under 300 bar; d. 100°C for 12 h under 300 bar.

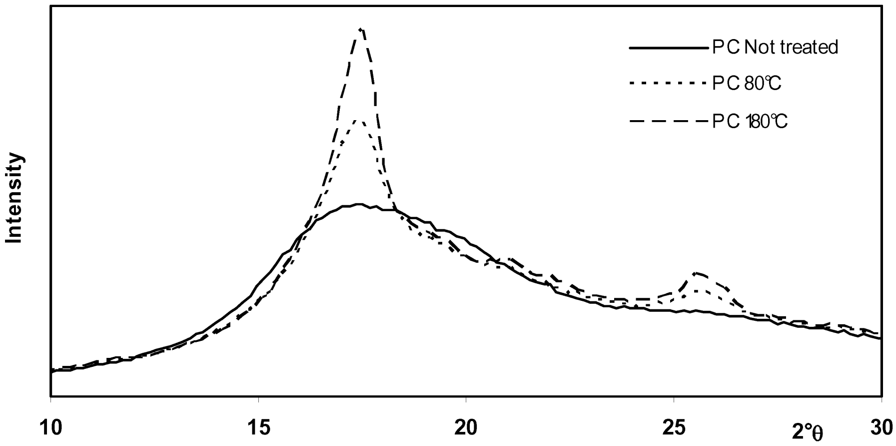

Figure 2. XRD Polycarbonate Sheet.

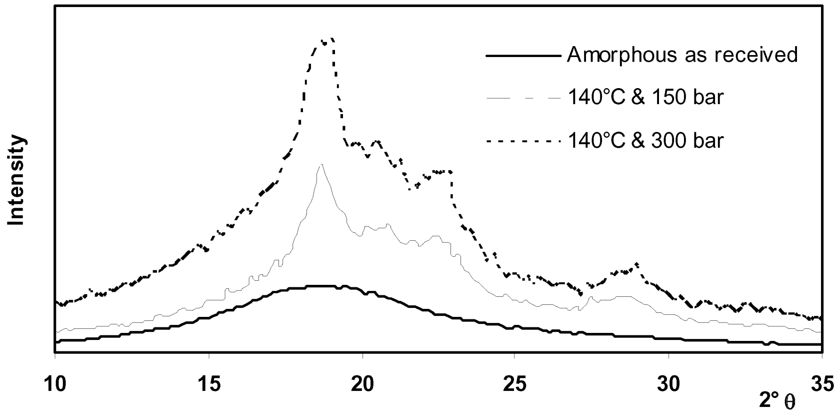

Figure 3. XRD of Amorphous Peek Films

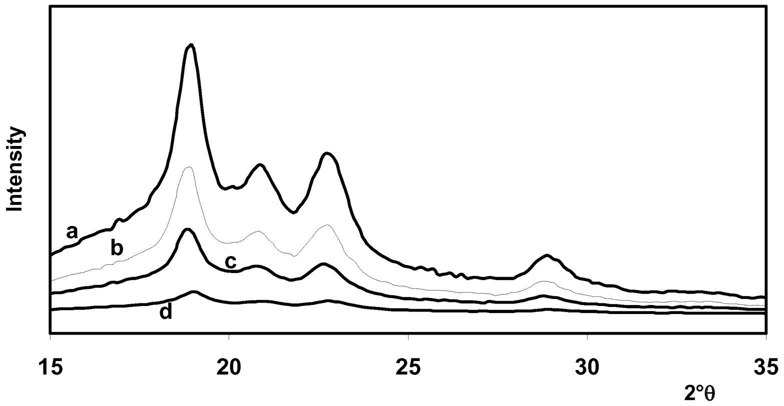

Figure 4. XRD of semi crystalline Peek Films: a. treated at 140°C and 300 bar for 8 h; b. treated at 140°C and 150 bar for 8 h; c. treated at 140°C bar for 8 h; d. as received.

of crystallinity, while at 140 °C there is an increase of 5.2% for amorphous and of 1.5% for semi crystalline PEEK film.

Experimental tests performed at 80°C using CO_2 at 150 bar showed no increase of degree of crystallinity: at this temperature the solubility of CO_2 is too low to induce crystallization. Experimental tests performed at 140°C show that an increase of degree of crystallinity is obtained for amorphous PEEK. Such increase is significantly higher than that one obtained in test N. 3, which accounts for the effect of temperature alone. By comparing the results of tests 4 and 5 it is evident the effect of pressure: the degree of crystallinity increases to 14,6% at 150 bar and to 21.4% at 300 bar.

As shown by the results of tests 4 and 5 for semi crystalline PEEK, at 150 bar there is no significant effect of CO_2 on degree of crystallinity in addition to the temperature

Table 2. PEEK film: experimental conditions and XRD results.

Test N.	Experimental Test Conditions	Amorphous Film	Semicrystalline Film
		% Crystallinity (XRD)	% Crystallinity (XRD)
	Peek as received	0	21.4
1	80°C – 8 h	0	22.8
2	80°C – 150 bar – 8 h	0	22.8
3	140°C – 8 h	5.2	22.9
4	140°C – 150 bar – 8 h	14.6	23.5
5	140°C – 300 bar – 8 h	21.4	30.7

effect (test No. 3). On the contrary, when the CO_2 pressure is increased to 300 bar, it is evident the CO_2 effect: the degree of crystallinity raises up to 30.7%.

The different behaviour of amorphous and semi crystalline PEEK can be ascribed to the higher diffusion rate of $scCO_2$ in amorphous polymer: diffusion is not hindered by crystalline domains which are present in semi crystalline PEEK.

In figure 3 and 4 are reported XRD curves for samples of amorphous and semi crystalline PEEK, respectively.

4. Conclusion

The experimental results show that it is possible to increase the degree of crystallinity of amorphous and semi crystalline polymers using supercritical carbon dioxide at rather mild temperature conditions. Crystalline PC can be obtained using $scCO_2$ and avoiding the long treatment time needed to obtain crystallization by thermal treatment. The crystallinity of PC can be increased up to 24.3% at 180 °C and 300 bar.

The crystallinity of amorphous PEEK can be increased up to 21.4% at 140°C and 300 bar. At the same conditions, crystallinity of semi crystalline PEEK can be increased from 21.4 % up to 30.7 %.

References

Berens, A.R., Huvard, G.S., Korsmeyer, R.W., 1989, US Patent. 4820752

Cornèlis, H., Kander, R.G. and Martin, J.P., 1996, Polymer 37, 4573.

Hu, X. and Lesser A. J., 2004, Polymer 45, 2333.

Kemmere, M.F. and T. Meyer, WILEY-VCH Eds., 2005.

Ko, T. Y. and Woo, E. M., 1996, Polymer 37, 1167.

Mascia, L., Del Re, G., Ponti, P.P., Bologna, S., Di Giacomo, G., Haworth, B, 2006, Advances in Polymer Technology 25, 225.

Schnitzler, J.V. and Eggers, R., 1999, The Journal of Supercritical Fluids 16, 81.

Tomasko, D.L., Han, X., Liu, D., Gao, W., 2003, Current Opinion in Solid State & Material Science 7, 407.