Crystallization Of Amorphous Peek: A Comparison Among Thermal Treatment, Sinc Process And Supercritical Carbon Dioxide Treatment

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Polyetheretherketone (PEEK) is an high performance thermoplastic polymer used in applications where thermal stability and chemical resistance are required.
Amorphous PEEK can be swollen and crystallized by immersion in liquid organic solvents as THF, methylene chloride and acetone [1], or by exposure to supercritical fluids [2] or by thermal treatment at high temperature [3].
Aim of this paper is to compare sorption, swelling and enhancement of the crystallinity level caused by these three different processes.
Solvent-induced crystallization and $scCO_2$ treatment are complex phenomena involving many parameters such as internal stresses, samples thickness, temperature, carbon dioxide density.
For the SINC process acetone was chosen as solvent. Samples of amorphous PEEK film were soaked in acetone for 2 hours at 25°C and at 45°C; after removing the samples from solvent, the solvent uptake was recorded and X ray measurements were performed on samples in order to estimate the crystallinity index, which was found to be 7% for the experimental test at 45°C.
Samples of amorphous PEEK film were thermally crystallized at 140°C for 8 hours: the index of crystallinity was found to be 6 %.
The index of crystallinity for PEEK samples treated in autoclave with $scCO_2$ at 150 bar and at 140°C for 8 hours was found to be 14.5%.

INTRODUCTION

Poly(ether ether ketone) is an amorphous or semicrystalline thermoplastic used in applications when chemical resistance and thermal stability are required. PEEK crystallinity ranges from 30 to 50%, depending on crystallization method.
Solvents as methlylene chloride, THF or acetone can plasticize and induce crystallinity in PEEK [1]. Solvent-induced crystallization (SINC) process involves three steps: solvent diffusion into the matrix polymer, swelling and crystallization. The extent of crystallization depends on process temperature, on polymer sample thickness, molecular weight and solvent chemistry.
Amorphous or semicrystalline PEEK films can be plasticized and crystallized also by supercritical fluid treatments. In this case, the extent of crystallization depends on process temperature, pressure and time.
Supercritical carbon dioxide has the properties of swelling polymers and enhances the kinetics of crystallization for the strong plasticizing effect of carbon dioxide adsorbed in the polymer [2 ÷ 4].
Below polymer glass transition temperature, T_g, polymer is glassy and chains mobility or rotation is hindered. When polymer is exposed to organic solvent or to supercritical fluids,

polymer glass transition temperature is lowered; the material becomes soft and rubbery and polymer chains mobility in the amorphous domains increases. At temperatures higher than T_g the kinetic of crystallization process is increased.
Segmental mobility of polymer chains is also increased by thermal treatment. When system temperature is increased, thermal energy and molecular mobility increase [5].
In literature, PEEK amorphous film is crystallized by thermal treatment at high temperature: when PEEK is crystallized below 300°C typical spherulitic morphologies can be observed, while during isothermal crystallization above 300°C single crystal aggregate structure are observed [6].
Tan et al. [7] performed PEEK crystallization at 220°C for 24 h. The peek samples were then post-annealed at temperatures from 100°C to 400°C for 30 min. After isothermal crystallization, two endothermic peaks has been found by DSC: a main melting peak and a minor peak just above the post-annealing temperature.
Ko e Woo [6] crystallized PEEK for 30 min at 230°C, 250°C, 270°C, 290°C and 310°C: DSC thermograms showed a minor endothermic peak in addition to the main melting peak.
Below 300°C; the temperature of the main melting endotherm peak is not influenced by crystallization temperature, on the contrary the minor peak is influenced by the crystallization temperature and at higher temperatures it becomes sharper.
In this work a comparison among SINC, isothermal crystallization and supercritical treatment of PEEK film samples are presented. The increase of crystallinity induced by SINC with acetone as solvent are compared with the thermal treatment and the $scCO_2$ treatment.

MATERIALS AND METHODS

Amorphous PEEK was supplied by Victrex in form of extruded sheet (0.5 cm) and film (100 μm); carbon dioxide (99,99%) was supplied by Rivoira and acetone was supplied by Fluka.
PEEK glass transition temperature was measured with DSC (TA Instrument, model 2920) and it was found 146°C.
The apparatus used for the experimental tests was a batch reactor (Nova Swiss, 200 cm^3, max temperature: 350°C and max pressure 70 MPa).
The degree of crystallinity of PEEK treated samples was measured by XRD (X'Pert Philips PW 3710 MPD). The crystallinity index was calculated using the following equation:

$$\%Cry = \frac{A_C}{A_A + A_C}$$

where A_C is the area under the crystalline peaks and A_A is the area under the amorphous halo [1].
The experimental tests for SINC process were performed at 25 and 45 °C using acetone. Samples were treated for 2 h, which allows to reach the saturation of polymer with solvent.
Supercritical and thermal treatments were both performed in the high pressure reactor: samples were loaded into the vessel, temperature and pressure were set to the prefixed values, when the process time has elapsed, the reactor was cooled to room temperature and depressurized.
Supercritical treatment were carried out with CO_2 at 15 and 30 MPa, while thermal treatments were carried out in nitrogen atmosphere.

RESULTS

The experimental tests condition are reported in table 1. XRD spectra of treated samples are reported in figures 1 ÷ 3.

In figure 1 are reported XRD spectra of PEEK film treated with SINC process using acetone for 2 hours at 25 °C and at 45°C (A-7, A-8). At 25 °C the treated sample is still amorphous, while at 45°C an increase of crystallinity was found.

Ko e Woo [6] reported that the diffraction peaks for PEEK are at 2□ = 18.7°, 20.7°, 22.6° and 28.7°.

XRD spectrum of samples treated at 45°C show three peaks at 2□ =18.8°, 20.8° and 29.1°: three out of four characteristic peaks of PEEK; the index of crystallinity was 7%.

The results are in agreement with the data of Cornelis et al. [1] for acetone-exposed amorphous PEEK.

Sample ID	Crystallization Method	Experimental Conditions			% Cry
		T (°C)	P (MPa)	t(h)	
A-1	Thermal treatment	80	-	8	0
A-2	Thermal treatment	140	-	8	5
A-3	Supercritical treatment	80	15	8	0
A-4	Supercritical treatment	140	15	8	14.5
A-5	Supercritical treatment	80	30	8	0
A-6	Supercritical treatment	140	30	8	21.3
A-7	SINC with acetone	25	-	2	0
A-8	SINC with acetone	45	-	2	7

Table 1. Experimental tests carried out on PEEK samples.

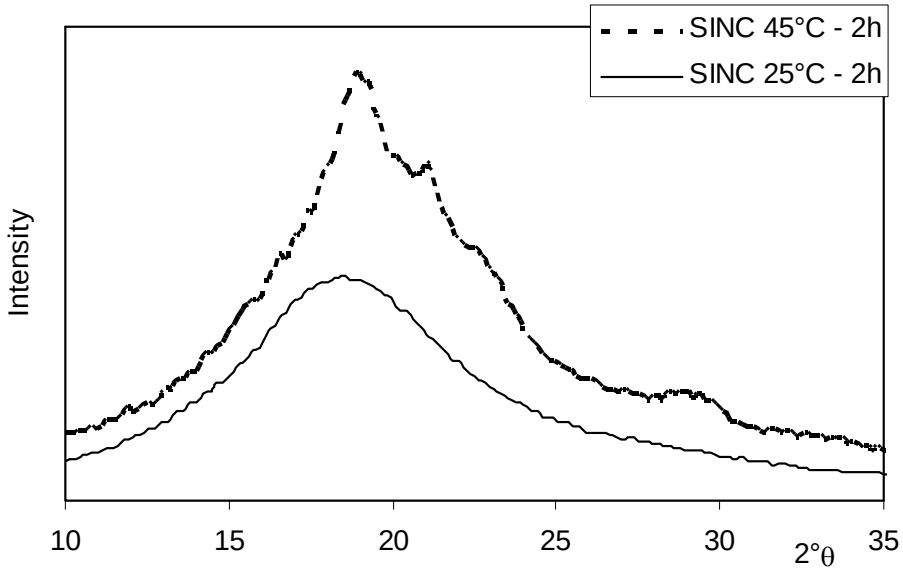

Figure 1. XRD Spectra of PEEK film treated with SINC process with acetone.

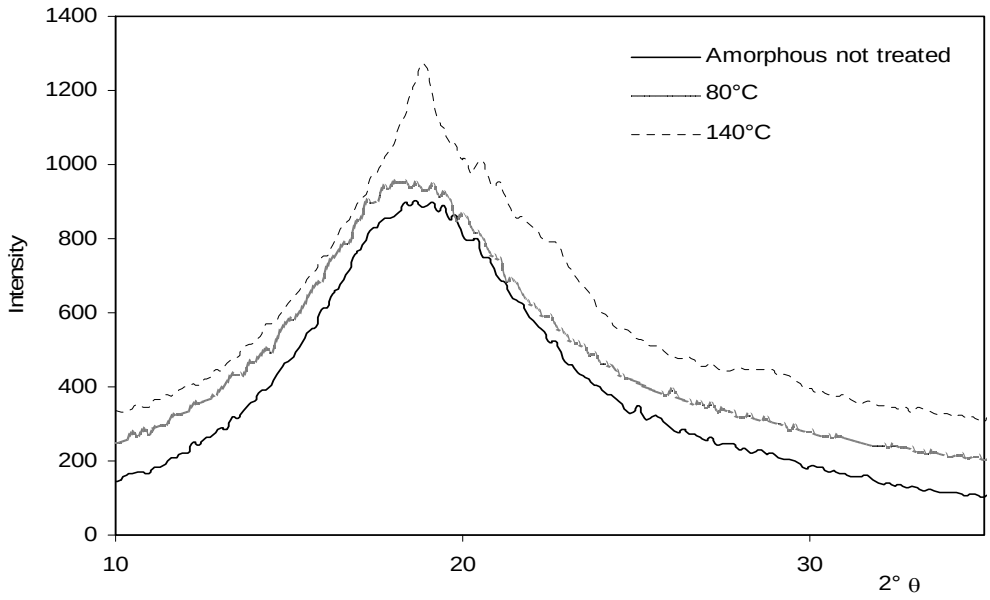

Figure 2. XRD spectra of PEEK films thermal treated in autoclave at 80°C and at 140°C in comparison with untreated amorphous PEEK.

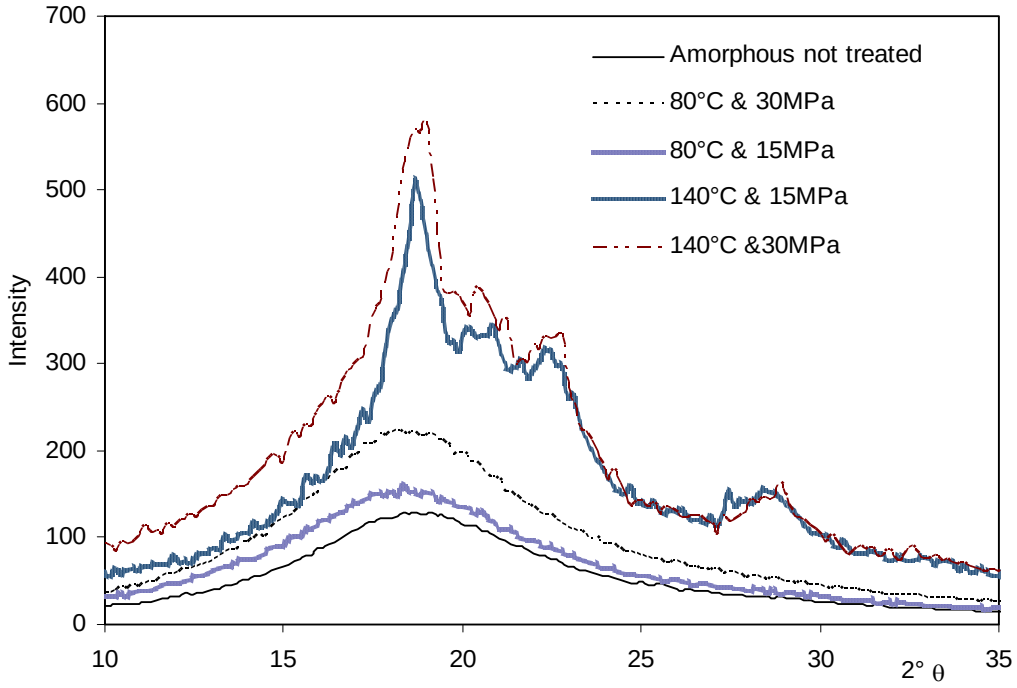

Figure 3. XRD spectra of PEEK sample treated with $scCO_2$ at 15 or 30 MPa and two level temperature: 80°C and 140°C.

In figure 2 XRD spectra of samples subjected to thermal treatments are reported (A-1, A-2). Sample treated for 8 h at 80°C does not show an increase of crystallinity: its spectrum is close to the spectrum of untreated PEEK.
At 140°C, thermal treatment induced crystallization in PEEK films: three out of the four PEEK characteristic peaks can be identified in the XRD spectrum. The index of crystallinity for PEEK treated at 140°C is around 5%, similar to the index of crystallinity obtained with SINC process at 45 °C.
Supercritical carbon dioxide was chosen as solvent for supercritical treatment. Experiments were carried out at temperatures of 80°C and 140°C under pressure of 15MPa or 30 MPa for 8 h. XRD spectra of samples A-3÷A-6 are shown in figure 3.
No crystallization is noticed for PEEK samples treated with CO_2 at 80°C and at 15 MPa or 30 MPa.
Samples treated at higher temperature, 140°C, show an increase of degree of crystallinity. The degree of crystallinity increases with increasing pressure. XRD spectra of samples treated with $scCO_2$ at 140°C and at 15 MPa or 30 MPa show all the four characteristic peaks of semicristalline PEEK.
Amorphous PEEK treated at 15 MPa reaches 14.5% of crystallinity content, while at 30 MPa it rises up to 21.3 %. These results show the effectiveness of supercritical treatment: at the same temperature the increase of crystallinity content for thermal treatment is only 5%.

CONCLUSION

Three different crystallizations method are compared in this paper: thermal treatment at high temperature, SINC process with acetone and supercritical treatment with CO_2 at high pressure and temperature.
Thermal treatment for 8 h at 80°C has no effect on crystallinity, while at 140°C the index of crystallinity increases up to 5%, similar to the index of crystallinity obtained with SINC process at 45 °C.
No increase of crystallinity have been noticed for treatment at 80°C both for thermal treatment and treatment with supercritical carbon dioxide at 15 or 30 MPa.
At 140°C, close to PEEK T_g, after thermal treatment the samples show an index of crystallinity of 5%, while after treatment with supercritical carbon dioxide the samples show an index of crystallinity of 14.5 % and 21.3 % for pressure of 15 MPa and 30 MPa, respectively.
Amorphous PEEK samples exposed to acetone at 45°C show an increase of crystallinity around 7%, after two hours of exposing.

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