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Melt state behaviour of PEEK and processing window interpretation for fast compression moulding process

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Abstract. Fast mould heating is nowadays possible by using induction technology for example with the Cage System® developed by RocTool. It allows heating and cooling kinetics of about 100°C per minute and new perspectives are thus possible to optimize the compression moulding process of long fibre reinforced thermoplastic composites. Indeed, a high forming temperature may favour polymer creep and so on composite consolidation. Nevertheless, the processing time of PEEK composite above melt temperature must be reduced to a few minutes due to the fast thermal degradation of the matrix. On the other hand, high cooling rates may have negative effect on matrix crystallinity. The proposed procedure consists in performing a few minutes isotherm around 300°C during the fast cooling. It would favour a high degree of crystallinity of PEEK without extending the cycle time.

Keywords: thermoplastic, thermo-compression, PEEK.
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INTRODUCTION

PEEK/Carbon composites are usually processed in a hot press or by autoclave at a temperature set between 380 and 400°C [1,2]. The autoclave process is usually preferred (APC2) but the processing time and the use of vacuum bag still limit the development of these thermoplastic composites. Compression moulding is more convenient but the air environment induces fast degradation of the polymer matrix [5,6]. Nowadays, induction technology (Cage System® from Roctool) allows mould heating and cooling kinetics of about 100°C/min. Fast compression moulding is thus possible, but processing conditions (applied stress, compression temperature, …) still need to be optimized.

This study focuses on the PEEK matrix behaviour in the fast compression moulding process. The melt rheology has been characterized as well as its evolution with time. Then, the influence of the cooling conditions on the degree of crystallinity is analysed by calorimetry, in order to propose ways of optimization.

MATERIAL AND EXPERIMENTAL

The investigated PEEK has been provided by Victrex as powder, granules and injected plates. This is a neat polymer that is commercialized with the reference 151G. Its melt temperature is 343°C as measured by DSC.

All the rheological properties of the samples were measured in the melt state with a Haake Mars apparatus equipped with a plane-plane geometry. Dynamic mechanical behaviour have been measured between 0.01 and 100Hz with applying a shear strain of 1% for different temperatures between 380 and 420°C. This strain level has been chosen in the linear viscoelastic domain where the viscosity is described by a linear relation of the elastic and viscous moduli.

The Differential Scanning Calorimetry investigation has been performed with a TA-Instrument Q20 previously calibrated with indium and zinc. The DSC sealed caps have been prepared from 5 to 8mg of PEEK powder and in order to impose the cooling conditions from a nuclei-free melt, the samples have been systematically heated from room temperature to 390°C and held 10 minutes in the molten state. The degree of crystallinity has been determined from the melting peak obtained with a heating rate of 10°C/min in considering an melt enthalpy of 130J/g [3]. The cooling conditions have been carried out with the DSC up to 20°C/min but higher cooling rates have also been achieved by quenching samples in nitrogen or cold water.

WAXS has been used to identify the crystalline structure of the samples. All X-Ray diffraction tests have been performed with a Phillips X-Ray diffractometer and the specimens have been prepared from PEEK powder or plates heated to the melting point and then cooled at different cooling rate. Quenched specimens have also been analysed by WAXS.

EVOLUTION OF PEEK VISCOSITY WITH TIME IN AIR ENVIRONMENT

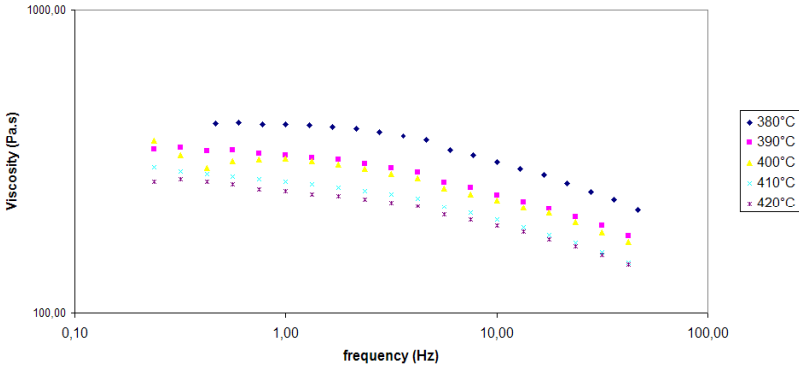


FIGURE 1. Melt rheology of PEEK

Figure 1 shows the viscous behaviour of PEEK in the molten state between 380 and 420°C. PEEK exhibits a conventional plastic behaviour for high strain rates which can be fitted with a power law with an Arrhenius parameter of 35000 J/mol [4].

The low viscosity of PEEK at high temperature is a way to optimize the compression moulding process of PEEK composites. It may facilitate fibre impregnation and so on composite consolidation. Nevertheless, the air environment as a large influence on the stability of PEEK in the melt state and in order to characterize the influence of thermal degradation in air, the evolution of the PEEK viscosity with time has thus been measured for different temperatures (figure 2). The results show that PEEK viscosity remains mostly constant during a few minutes but quickly increase for longer time of exposure due to crosslinking [5,6]. At a temperature of 400°C, this thermal degradation occurs after 15 minutes and the viscosity, initially of about 350 Pa.s, reaches 800 Pa.s after 35 minutes. Therefore, thermal degradation limits the processing conditions in conventional compression moulding process and the use of processing temperature over 400°C is impossible. With induction technology, the high heating and cooling kinetics allow to control the time of exposure of PEEK to high temperature. Processing temperatures of about 420°C may thus be used but the processing time must be limited to a few minutes.

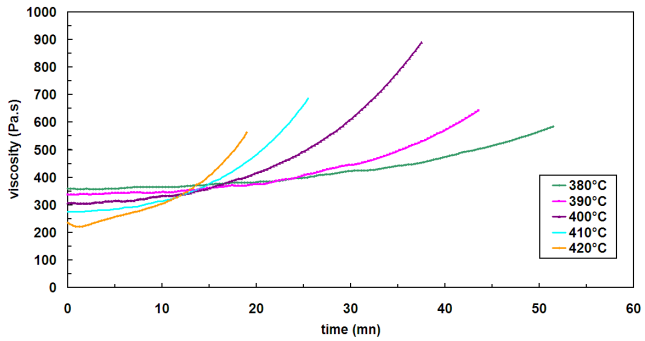


FIGURE 2. Viscosity as a function of time for different temperatures (f=1Hz, ε_0=1%)

INFLUENCE OF COOLING CONDITIONS ON PEEK CRYSTALLINITY

Influence of cooling conditions on the degree of crystallinity

High cooling kinetics may reduce considerably the processing time of PEEK composites. Nevertheless, it induces low crystallinity and so it may have an influence on the composite properties. The influence of cooling conditions on the degree of crystallinity of PEEK have thus been investigated and the cooling conditions conciliating fast cooling and high crystallinity have been prospected.

The influence of constant cooling rates on crystallinity has been firstly studied by DSC (cooling rates up to 20°C/min). Quenched specimen have also been prepared but the degree of crystallinity could not be determined by DSC due to cold crystallisation for high cooling rates. The volume mass fraction of these samples have then been estimated from WAXS scans. Figure 3 shows the evolution of the crystallization and melting heat flux of PEEK for different low cooling rates. The measured degree of

crystallinity is reported in table 1. With increasing the cooling rate, PEEK crystallinity decreases drastically. For a cooling rate of 20°C/min, the degree of crystallinity is only 31%.

TABLE 1. degree of crystallinity of PEEK for different cooling conditions (X_m % +/- 0.5)

Cooling rate (°C/min)	**Anisothermal crystallisation**	**Isothermal crystallisation**			
		300°C	310°C	313°C	317°C
1	46.5				
10	41.3				
20	31,5	35,6	35,9	34,5	31,9
Quenched in nitrogen	<20				

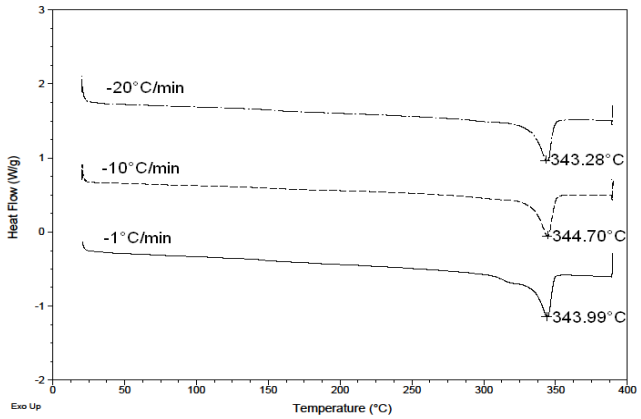


FIGURE 3. DSC thermogrammes of PEEK for different cooling rates

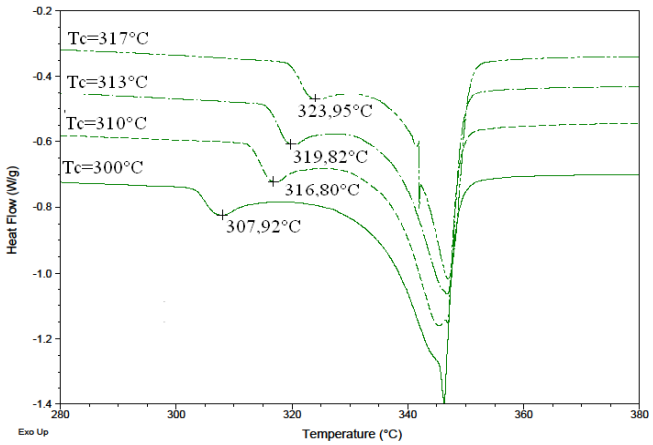


FIGURE 4. DSC thermogrammes of PEEK for different isothermal crystallisation

In order to improve the degree of crystallinity without increasing the cycle time, an isothermal cristallization can be performed. While cooling the PEEK samples from the melt state to room temperature with a constant rate of 20°C/min, the cooling has been stopped during 5 minutes at different temperatures from 300°C to 317°C and the degree of crystallinity has been measured. As presented in table 1, isothermal crystallisation performed between 300°C and 313°C favours PEEK crystallinity. For

higher isotherm temperatures, the crystallisation is not initiated and only occurs during the cooling stage.

Origin of double melting peak

However, the heat curve exhibits two melting peaks which have been taken into account when measuring the degree of crystallinity (figure 4). Indeed, the major melting peak at 343°C is accompanied with a second peak which appears for a temperature of 7°C over the isotherm temperature. It must be noticed that a second peak was already distinguishable for slow cooling rates (1°C/min, figure 3).

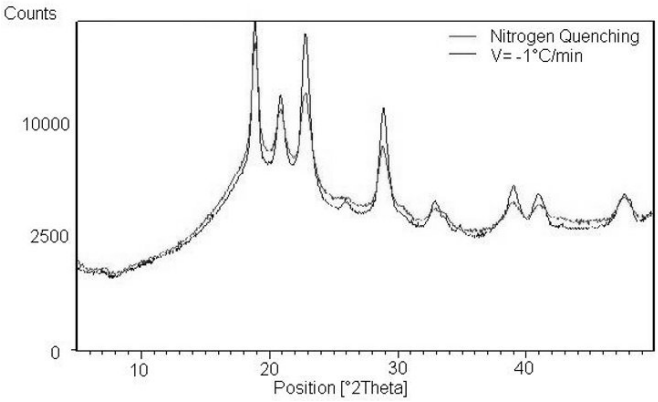


FIGURE 5. X-ray diffraction scans of PEEK cooled with extreme rates

In order to analyse the origin of this second melting peak, X-ray diffraction has been performed on a sample cooled at 1°C/min and on a sample quenched in nitrogen from the melt state. The first sample exhibits a second melting peak around 310°C (low cooling rate) while it is supposed that high rates inhibit the apparition of this second peak (quenched specimen).

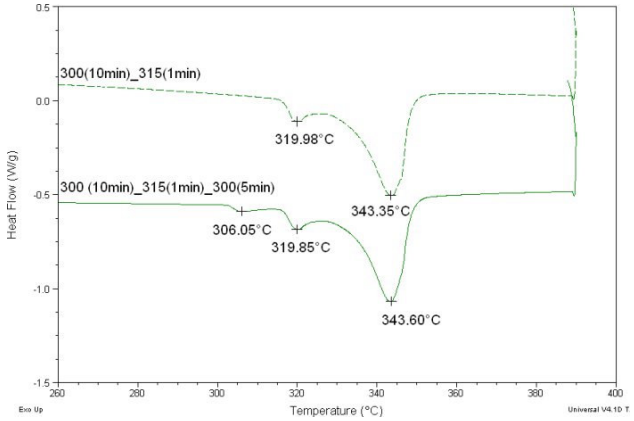


FIGURE 6. Influence of heat temperature on DSC thermogrammes of PEEK

The figure 5 shows the diffraction scans obtained for the two specimens. One can see that both scans exhibit the same diffraction peaks which positions correspond to the orthorhombic structure of PEEK crystal. The ratio of amorphous and crystalline

structure is the only difference between the specimens and this ratio is in agreement with the influence of cooling rate on the crystallinity. The two meting peaks may thus be characteristic of the same crystalline structure.

The apparition of a second melting peak has also been analysed by DSC. A sample previously cooled at 20°C/min with an isotherm at 300°C during 5 minutes has been heated up to 315°C during 1 minute and then cooled again at 20°C/min. By heating the sample up to 315°C, the crystalline structure of the lower peak is supposed to be melt. On a second sample, the same procedure has been applied but during the second cooling stage, a 5 minutes isotherm at 300°C has been performed.

The figure 6 shows the heating thermogrammes of both samples. The first specimen still exhibits two melting peaks : the major peak temperature is still 343°C but the second one appears at T=320°C i.e. 5°C over the isotherm temperature. On the other hand, the second thermogramme presents three distinct peaks : the same two peaks at T=343°C and T=320°C as observed for the first sample and a new one at a temperature of 306°C. Actually, this last peak can be considered as the consequence of the isotherm at 300°C during the cooling stage while the heating temperature of 315°C induces a new endothermic peak to a higher temperature.

Thus, theses results suggest that the presence of a double melting peak is the consequence of a physical ageing, due to a reorganisation of the polymer chains. This phenomenon is in agreement with the conclusions of Wei et al. and contradict the hypothesis of a second crystalline phase [7].

CONCLUSIONS

High heating and cooling kinetics are new ways of optimisation of fast compression moulding process of PEEK composites. On one hand, higher moulding temperatures may be favourable but the processing time must be carefully controlled due to the fast thermal degradation of PEEK above its melt temperature. On the other hand, fast cooling induces poor matrix crystallinity and it may have negative influence on the composite properties. Moreover, the analysis of the origin of the second melting peak suggests that physical ageing occurs in PEEK and that this peak could be considered as a crystalline phase when measuring the matrix crystallinity. An isotherm crystallisation at 300°C is thus a way to keep a high degree of crystallinity. In future work, the influence of carbon on the melt behaviour should be investigated because it would induce a different nucleation process and thus a different crystallisation [8,9].

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