The Role of Thermal History on the Semicrystalline Morphology and Impact Strength of PEEK

Anuj Bellare[1], Adam Kozak[2] and Stephen Spiegelberg[2]

[1]Department of Orthopedic Surgery, Brigham & Women's Hospital, Harvard Medical School, Boston, MA
[2]Cambridge Polymer Group, Boston, MA

INTRODUCTION

• Poly(ether ether ketone) (PEEK) is a high performance, chemically resistant, high strength thermoplastic with a variety of orthopedic and trauma applications.

• The glass transition temperature T_g = 143°C and melting temperature T_m = 345°C

• Crystalline morphology of semicrystalline polymers such as PEEK affect macroscopic mechanical properties

• We hypothesized that the impact strength of the PEEK resin investigated here will be affected by crystallization conditions

MATERIALS

• Starting material - Ketaspire-820 (Solvay Specialty Polymers) PEEK pellets.

METHODS

• Compression molded into plaques of 12.5 mm thickness by heating to a temperature of 400°C and crystallization using the following 5 different protocols:

- Slow cooling at 3°C/min (SC)
- Quenching at 15°C/min (Q)
- Quenching and annealing at 250°C for 16 hours (QA)
- Quenching, remelting at 380°C and quenching again to maximize nucleation (QQ)
- Isothermal crystallization at 330°C for 16 hours (IC)

• Differential Scanning Calorimetry (DSC) (TA Q2000 DSC) to measure crystallinity using a heat of fusion, ΔH_f = 130 J/g for PEEK (n = 3)

• Small Angle X-Ray Scattering (SAXS) (Rigaku S-Max3000) to determine inter-lamellar spacing measured between scattering angles q_{min} = 0.05 [nm^{-1}] and q_{max} = 1.0 [nm^{-1}] where:

- $q = (4\pi/\lambda)\sin\theta$
- λ = 0.154 nm (wavelength of CuKa x-rays)
- θ = One-half the scattering angle

• A combination of DSC crystallinity and SAXS provided the lamellar thickness, D [nm].

• Izod impact strength was conducted according to ASTM D256 using an Instron

RESULTS

• PEEK-IC had a higher crystallinity and lamellar thickness ($p<0.05$, ANOVA) compared to PEEK crystallized via other crystallization conditions (see Table 1)

• PEEK-SC had a significantly higher lamellar thickness compared to PEEK-Q and PEEK-QA ($p<0.05$) but all of the PEEKs had lamellar thicknesses less than 10 nm.

Table 1. Crystallinity (X) and Lamellar thickness (D) for various PEEK groups

Sample ID	X [%]	D [nm]
PEEK-SC	49.0 ± 3.3	6.2 ± 0.4
PEEK-Q	46.5 ± 1.9	5.7 ± 0.2
PEEK-QA	47.3 ± 1.5	5.7 ± 0.2
PEEK-QQ	47.7 ± 0.9	5.9 ± 0.1
PEEK-IC	53.9 ± 2.2	7.2 ± 0.3

• Two dimensional SAXS patterns of PEEK showed that there was no lamellar orientation induced by the compression molding, evident from the ring-like scattering around the main beam (see Fig 1).

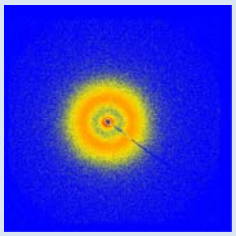

Figure 1. A representative two-dimensional SAXS scattering pattern of PEEK

• Radial averaged Lorentz corrected scattering functions of PEEKs crystallized via different crystallization mechanisms showed discernible differences in the location of the maximum scattering intensity with respect to the scattering angle, q, as shown in Figure 2.

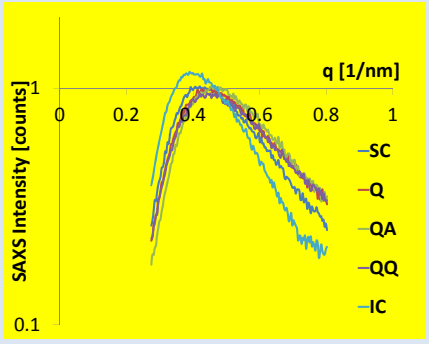

Figure 2. Lorentz corrected SAXS intensity [counts] versus scattering angle q [nm^{-1}] for PEEK groups.

• The impact strength of PEEK-QA and PEEK-QQ was lower than the impact strength of PEEK-Q, PEEK-SC and PEEK-IC ($p<0.05$) except for the comparison of PEEK-QQ and PEEK-SC which were not significantly different ($p=0.136$) (see Figure 3).

• The impact strength of PEEK-SC, PEEK-IC and PEEK-Q were not significantly different ($p>0.05$).

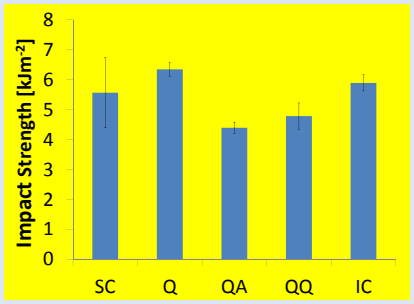

Figure 3. A histogram of the Impact strength [kJm^{-2}] for various PEEK groups.

DISCUSSION

• This study showed that the impact strength of Ketaspire-820 PEEK was not significantly affected regardless of the different crystallization routes employed during compression molding from the melt state.

• A likely reason for this result is the low thermal conductivity of PEEK combined with a high rate of crystallization, which dominates the formation of the lamellar nanostructure.

• The indirect evidence of low thermal conductivity is that there was no statistically significant difference in the degree of crystallinity whether the PEEK plaque was quenched or slow cooled, which would otherwise show significant differences in thin films where issues of low thermal conductivity are not negated by the high rate of crystallization.

• In summary, this study showed that Ketaspire-820 PEEK is a robust polymer whose impact strength is not strongly dependent on thermal history, and, for components having larger dimensions, there is no advantage gained in applying complicated thermal histories during the cooling cycle following molding.

• Impact strength represents only high rate of crack propagation. Other more clinically relevant mechanical tests, such as resistance of fatigue crack propagation are required to