
Macromolecular and Morphological Characterization of Medical Grade PEEK Polymers

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Financial Disclosure

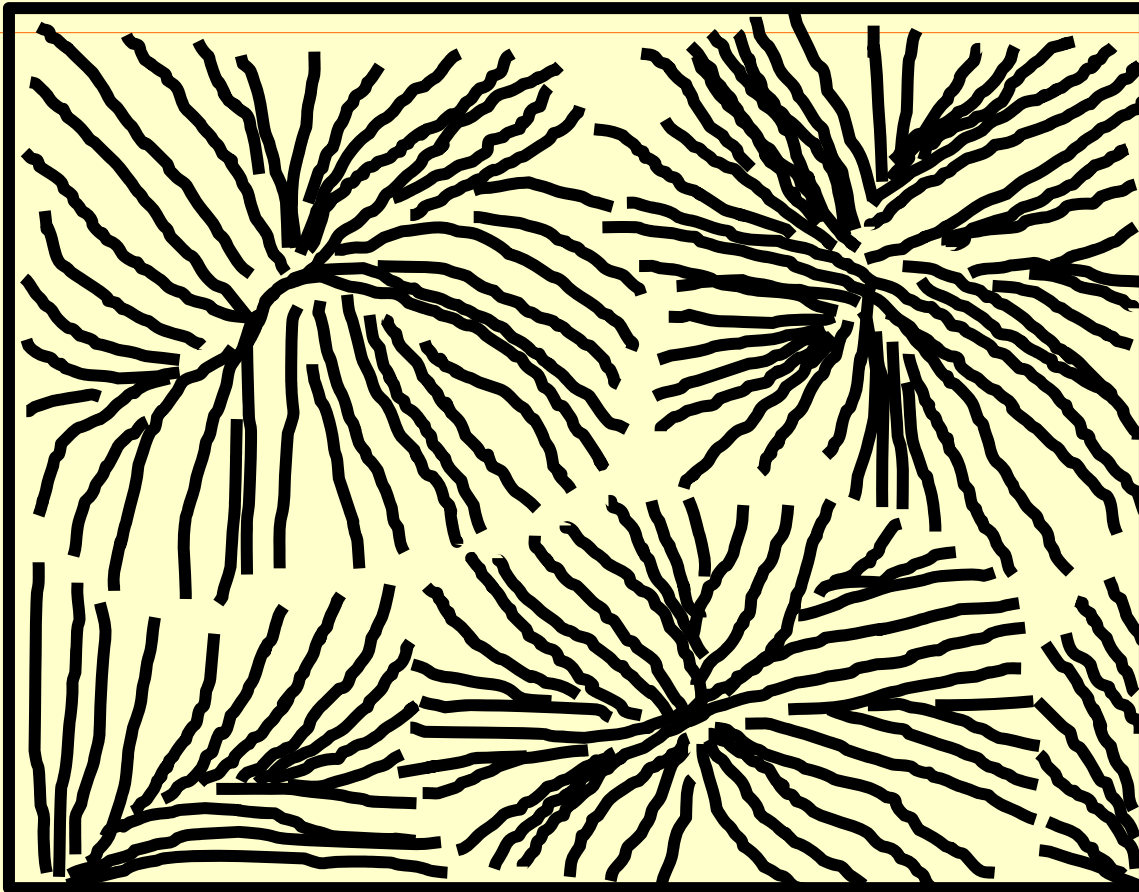
- Anuj Bellare - None
- K-P Le & S-S Yau – Stryker Orthopaedics
- S. Spiegelberg – Royalties from Zimmer, Corin, Renovis, Iconacy, Conformis, Mako

Poly (ether ether ketone) - PEEK

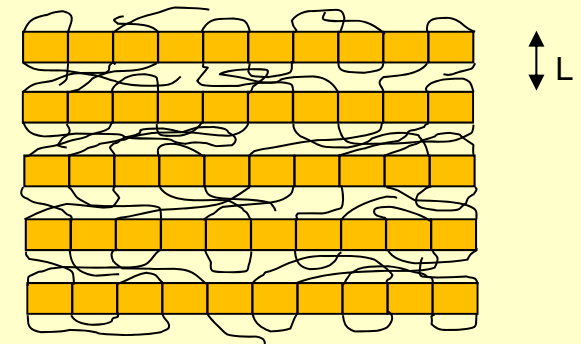
- Tg ~ 143°C
- Tm ~ 335-345°C
- Micrometer level structure - spherulitic
- Nanometer level structure - lamellae
- High ultimate tensile stress, high modulus
- Carbon-Fiber reinforced PEEK ~ modulus of cortical bone
- Application in trauma, orthopedic and spinal implants

Micro- and Nano-structure

IMPINGED SPHERULITES



Stack of Lamellae



Objective

- To measure molecular weight distribution and characterize semi-crystalline morphology of various grades of PEEK

Materials and Methods

- Four medical grade PEEK polymers
 - PEEK-1, PEEK-2, PEEK-3, PEEK-4
- Gel Permeation Chromatography – Mn, Mw, Mz
- Density Measurements (ASTM D792)
- Differential Scanning Calorimeter (ASTM F2026)
- Fourier Transform Infrared Spectroscopy (ASTM D2778-09)
- Small Angle X-ray Scattering – L, D

Molecular Characterization

ID	Mn [g/mol]	Mw [g/mol]	Mz g/mol]	PI
PEEK-1	35,726±181	114,026±121	209,294±808	3.19
PEEK-2	34,314±194	108,352±470	227,540±958	3.16
PEEK-3	42,074±1448	115,913±86	210,317±1654	2.75
PEEK-4	30,278±683	74,426±432	124,297±1617	2.46

$$M_n = \sum N_i M_i / \sum N_i$$

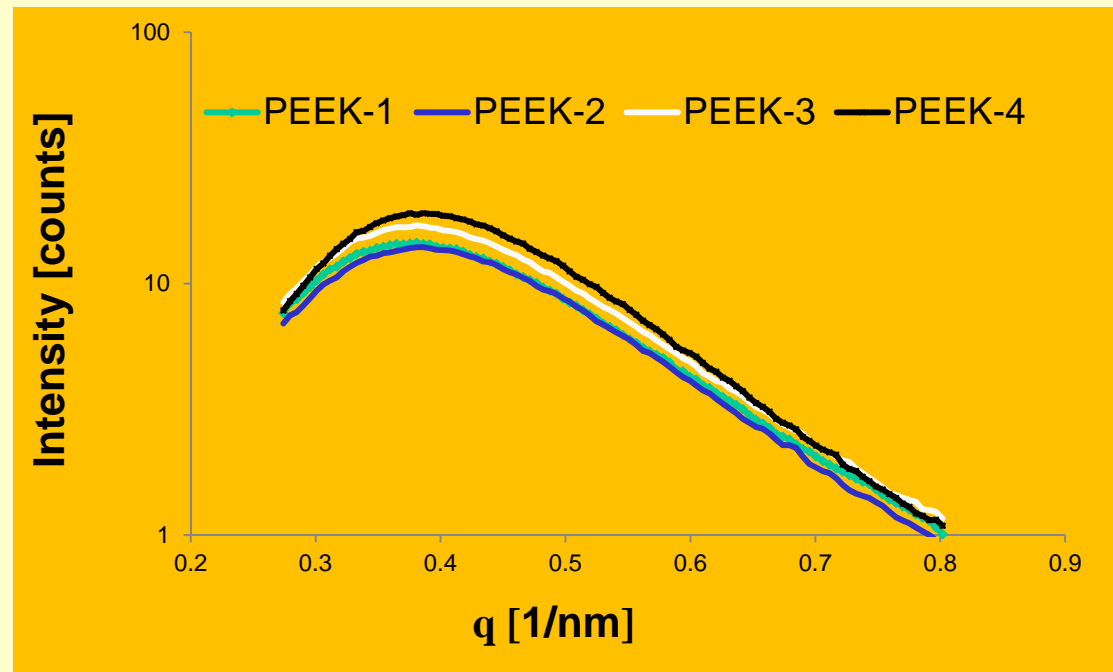
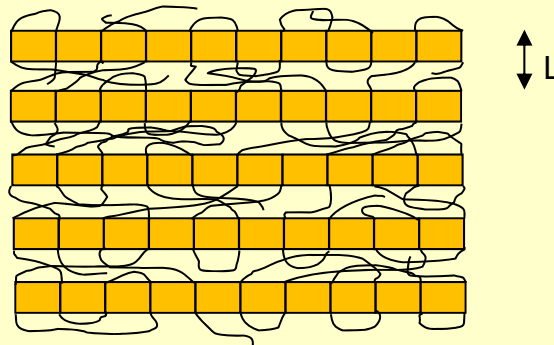
$$M_w = \sum N_i M_i^2 / \sum N_i M_i$$

$$M_z = \sum N_i M_i^3 / \sum N_i M_i^2$$

$$PI = M_w / M_n$$

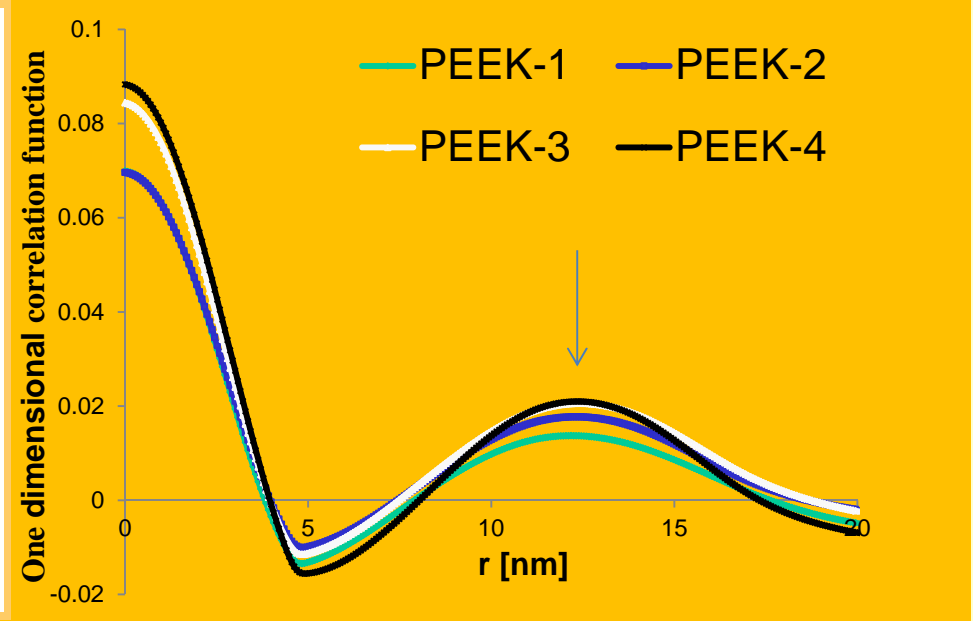
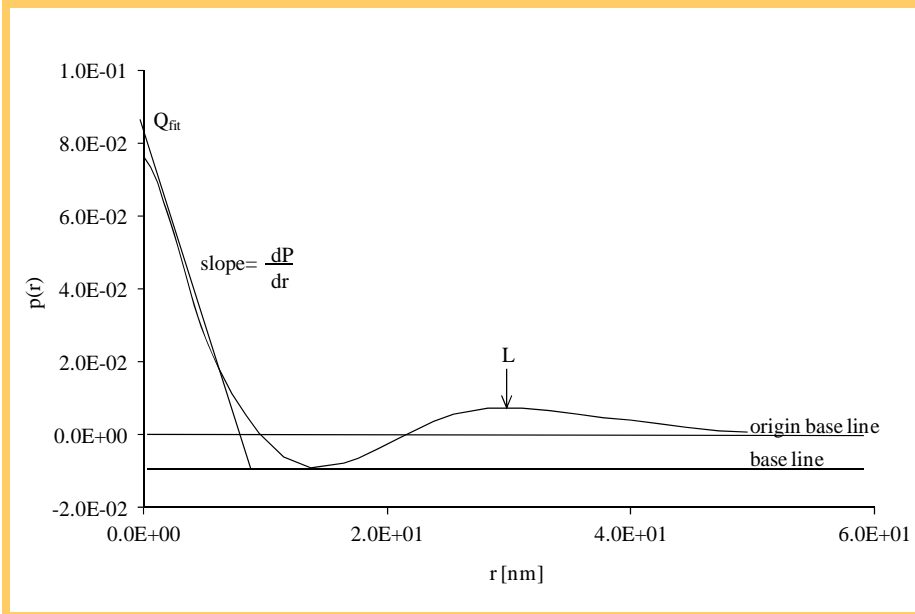
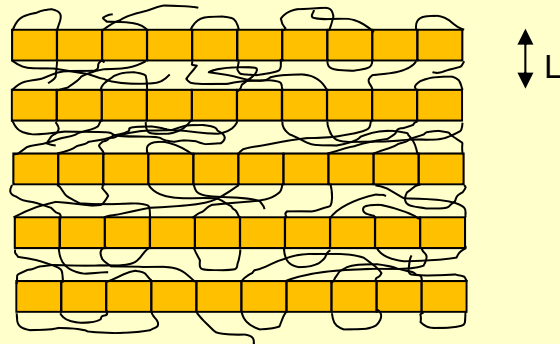
- PEEK-3 had highest Mn
- PEEK-4 had lowest Mn and lowest PI

Small Angle X-Ray Scattering



- Long Period $L = 2\pi/d \sim$ Inter-lamellar spacing almost same for all PEEKs ₈

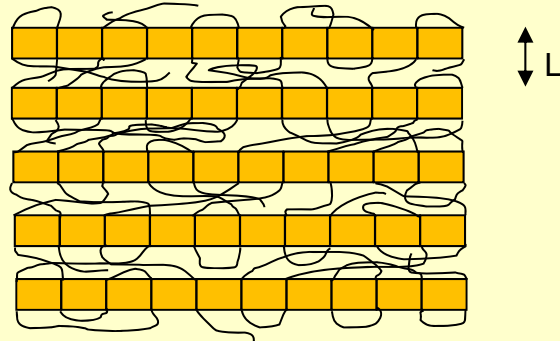
One Dimensional Correlation Function



$$p(r) = (1 / 2 \pi^2 A) \int_0^\infty q^2 I(q) \cos(qr) dq$$

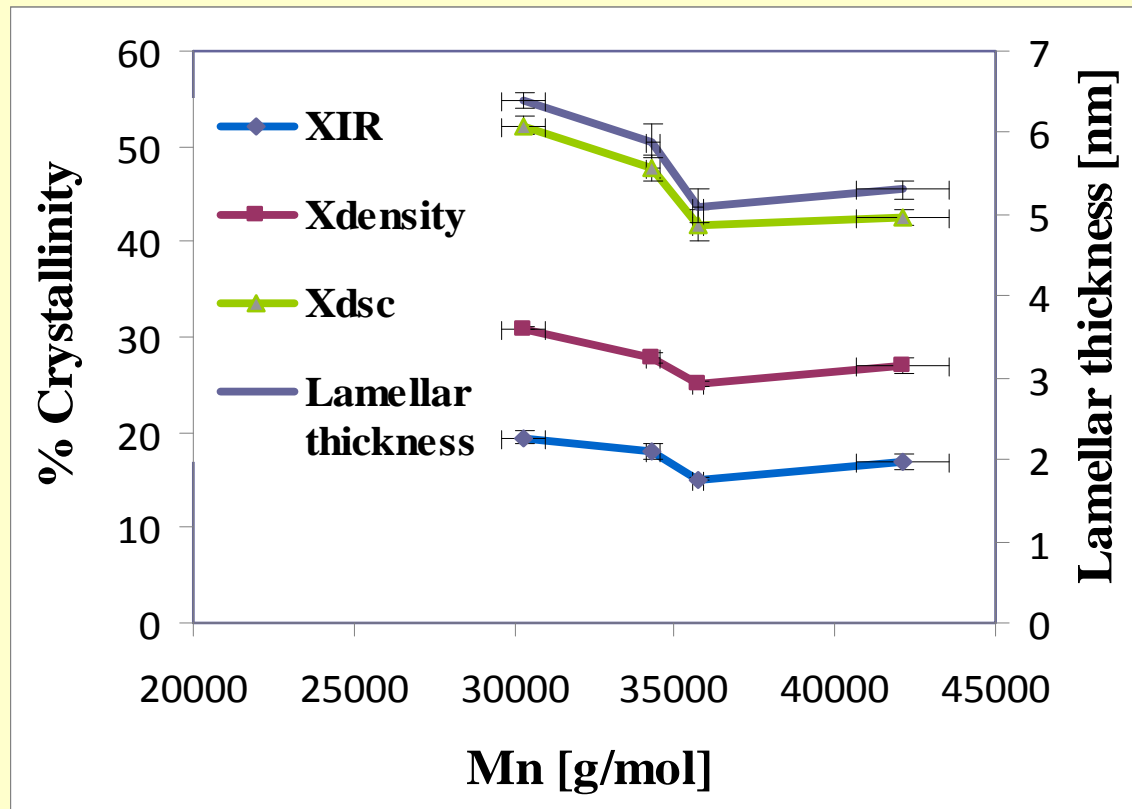
O. Glatter, 1977

Crystalline Morphology



ID	L [nm]	X _{DSC} [%]	D [nm]
PEEK-1	12.2	41.8±1.7	5.1±0.2
PEEK-2	12.3	47.8±1.3	5.9±0.2
PEEK-3	12.4	42.5±0.8	5.3±0.1
PEEK-4	12.3	52.2±0.9	6.4±0.1

Crystallinity and Lamellar Thickness



Summary

- All medical grade PEEK resins showed relatively small differences in molecular weights and morphology
- PEEK-4 had the lowest Mn and highest crystallinity
- Differences in crystallinity associated with differences in lamellar thickness
- Consistent trend in crystallinity obtained from DSC, FTIR and density

Future Work

- Micrometer scale morphology – Low voltage SEM
- Alter crystallization conditions (nucleation/crystal growth)
- Correlate crystalline morphology on the nano- and micro-scale with macroscopic mechanical properties

THANK YOU FOR YOUR ATTENTION