Measurement of Percent Crystallinity of Polyaryletherketone Composites using Fourier Transform Infrared Spectroscopy

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Abstract. The drive for lightweight, high-performance, and cost-effective aircraft in the aerospace industry has brought thermoplastic polymer composites to the forefront. These materials offer significant advantages over traditional thermosetting composites, including rapid consolidation, reformability, and excellent fracture toughness. As their material properties are intimately linked to crystallinity, understanding and controlling the crystalline structure of these polymers is crucial for advanced manufacturing processes. The National Aeronautics and Space Administration (NASA) Hi-Rate Composite Aircraft Manufacturing (HiCAM) project is actively developing new technologies for the rapid production of composite aircraft, with a strong focus on these advanced thermoplastic systems. The material properties of semi-crystalline polymers are influenced by the crystallinity of polymer molecules. The processing conditions, including tool temperature, placement speed, and material heating/cooling rate, can change the polymer crystallinity and homogeneity of the composite matrix. A homogeneous distribution of crystallinity is desired in consolidated composites. Fourier transform infrared spectroscopy (FTIR) has been used to characterize the crystalline phase of polyaryletherketone (PAEK). This technique enables identification of crystalline regions on the surface. Differential scanning calorimetry (DSC) is widely used for characterizing polymer crystallinity. In this work, the results from DSC were compared to those from FTIR. The crystalline phase quantities of PAEK materials including polyetheretherketone (PEEK), polyetherketoneketone (PEKK), and low-melt PAEK were investigated from the FTIR spectra using the peak ratio of the peaks at 1305 cm-1 and 1280 cm-1. The DSC and FTIR results were correlated to results generated from X-ray diffraction (XRD) data.

Keywords: Orthotropic, Thermal Analysis, Composites, Thermoplastic, Crystallinity, Carbon Fiber.

1 Introduction

The aerospace industry constantly seeks advanced materials and manufacturing methods to meet the growing demand for lightweight, high-performance, and cost-effective aircraft. Thermoplastic polymer composites are a highly promising class of materials, offering significant advantages over traditional thermosetting composites. These benefits include faster consolidation, easier reformability, weldability, repairability, excellent fracture toughness, virtually unlimited material out-time, and low gas permeability. These characteristics are especially attractive for high-rate manufacturing. Recognizing this potential, the National Aeronautics and Space Administration (NASA) Hi-Rate Composite Aircraft Manufacturing (HiCAM) initiative aims to develop cutting-edge technologies to accelerate the production of composite aircraft, addressing the increasing global need for commercial single-aisle aircraft [1-3].

A key focus in advanced manufacturing is the use of high-performance polymers like semi-crystalline polyaryletherketone (PAEK) resins, such as polyetheretherketone (PEEK) and polyetherketoneketone (PEKK). These polymers offer an exceptional balance of mechanical properties, thermal stability, and chemical resistance, making them ideal for demanding aerospace applications. Their rapid processability, especially via automated fiber placement (AFP), is crucial for achieving high production rates. AFP benefits immensely from the ability of thermoplastics to be melted and consolidated in-situ, which reduces cycle times and enables complex geometries. However, understanding the complex relationship between processing conditions (tool temperature, placement speed, heating/cooling rates) and the final material properties of these PAEK composites is essential. These processing parameters profoundly affect the microstructure and performance, directly impacting the quality and reliability of the final part in high-rate AFP manufacturing.

Traditional and advanced characterization techniques are used to quantify and assess the crystalline phase of PAEK materials [4-6]. Differential scanning calorimetry (DSC) is a widely used technique that quantifies overall bulk crystallinity by measuring thermal transitions associated with melting and crystallization. Fourier transform infrared spectroscopy (FTIR) offers a valuable method for characterizing crystalline regions, especially on the surface, by identifying specific absorption peaks linked to crystalline molecular conformations. X-ray diffraction (XRD) is a powerful analytical technique that provides information about the crystallographic structure and crystalline content of materials through the diffraction pattern of X-rays. This work compares the results from DSC with those from FTIR to provide a comprehensive understanding of crystallinity. Specifically, the crystalline phase quantities of various PAEK materials, including PEEK, PEKK, and low-melt PAEK, were investigated from their FTIR spectra using the peak ratio of characteristic peaks at 1305 cm^{-1} and 1280 cm^{-1}. The resulting polymer crystallinity percentages from FTIR and DSC were correlated to XRD measurements.

1.1 Crystallinity of Semi-Crystalline PAEKs

The macroscopic properties of semi-crystalline polymers like PAEKs are inherently tied to their crystalline structure. Crystallinity (defined as the proportion of ordered,

crystalline regions within the largely amorphous polymer matrix) dictates critical attributes such as stiffness, strength, toughness, thermal expansion, and solvent resistance. A homogeneous distribution of crystallinity throughout the composite matrix is vital for achieving good quality, consistent mechanical performance, and structural integrity. Heterogeneous crystallinity distribution can lead to residual stresses, warpage, and reduced performance. Therefore, precise control and characterization of polymer crystallinity are fundamental to successfully using PAEKs in advanced manufacturing processes.

The formation of crystalline regions in semi-crystalline polymers like PAEKs is a complex process involving two primary mechanisms: primary and secondary crystallization [7-14]. Primary crystallization involves the initial formation of stable nuclei within the supercooled polymer melt, followed by the growth of lamellar crystals from these nuclei. This growth occurs as polymer chains align into ordered, folded chain structures, forming larger spherulitic superstructures. The kinetics of primary crystallization are highly sensitive to temperature and cooling rate; rapid cooling can suppress this process, leading to lower overall crystallinity, while slower cooling allows more time for crystal growth. Secondary crystallization, on the other hand, refers to the ongoing perfection and reorganization of crystalline regions after the initial primary crystallization phase. This includes processes like the thickening of existing lamellae, the infilling of interlamellar amorphous regions, and the slow crystallization of polymer chains initially unable to crystallize during the primary phase due to kinetic limitations. Secondary crystallization contributes to a further increase in crystallinity, albeit at a slower rate, and can significantly influence the ultimate mechanical properties and long-term stability of the composite. Both mechanisms are profoundly affected by the material's thermal history during manufacturing, making their understanding critical for controlling the final properties of AFP-processed PAEK composites.

1.2 Kilian and Jenckel Method for XRD Analysis

In this work, the Kilian and Jenckel method was employed to analyze XRD data for determining polymer crystallinity [15,16]. Originally developed in a study using 4,6-polyurethane, this method provides a robust approach for quantifying the integral degree of crystallization. As illustrated in Fig. 1, which shows the XRD baseline-corrected pattern of a PEEK sample after a cooling cycle, the method leverages the distinct contributions of crystalline and amorphous phases to the overall diffraction signal. The integral degree of crystallization is calculated using Eq. 1. This equation defines the integral degree of crystallization as the ratio of the total crystalline intensity to the total intensity (crystalline plus amorphous contributions) observed in the XRD pattern.

Beyond the integral crystallinity, the original work by Kilian and Jenckel also detailed equations for calculating partial degrees of crystallization related to specific intermolecular interactions, such as van der Waals forces and hydrogen bonds, as further outlined in their related study [15]. The versatility and reliability of this method are underscored by its subsequent application by Kilian and Jenckel to determine the degree of crystallization in various other polymers [17-19]. This widespread applicability

makes it a valuable tool for understanding the crystalline structure of materials like the PAEKs investigated in this study.

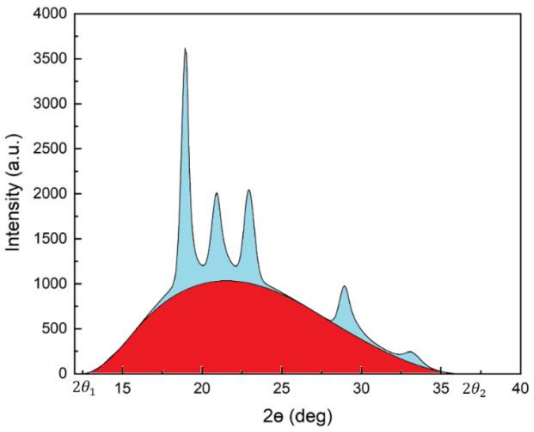

Fig. 1. The baseline-corrected XRD pattern of a PEEK sample after a cooling cycle.

$$\chi(\%) = \frac{\int_{2\theta_1}^{2\theta_2} I_c d\theta}{\int_{2\theta_1}^{2\theta_2} I_t d\theta} \times 100 \quad (1)$$

2 Experimental

2.1 Materials

The PAEK materials[1] used in this work are summarized in Table 1. The code names are used throughout this work for clarity. All materials were used as received from the vendors.

Table 1. Polyaryletherketone material characteristics used in this work.

Material resin	Vendor label	Additional information
PEEK	Toray® TC1200 resin by Victrex™	Powder, 1.30 g/cm³ density
PEEK	Solvay® (Syensqo®) KetaSpire® PEEK KT-800P	Unreinforced resin, coarse powder, 1.30 g/cm³ density
PEKK	Kepstan® 7002 by Arkema	Milled pellets, unfilled resin, 1.29 g/cm³ density, ratio of terephthalic (T) to isophthalic (I) monomers 70/30
LM-PAEK	Victrex AE™ 250 LMPAEK polymer	Powder, 1.30 g/cm³ density

[1] Specific vendor and manufacturer names are explicitly mentioned only to accurately describe the experimental work. The use of vendor and manufacturer names does not imply an endorsement by the U.S. Government, nor does it imply that the specified materials or equipment are the best available.

2.2 Thermal Analysis via DSC

The thermal measurements were conducted using a differential scanning calorimeter (DSC25, TA Instruments®). The amount of tested material ranged from 5 to 7 mg for the PAEK resins. The materials were placed in aluminum pans and then hermetically sealed for thermal analysis. Two non-isothermal tests were conducted, and the samples were heated at 10 °C/min to 400 °C, held for 5 min, then cooled at 10 or 60 °C/min to room temperature.

2.3 Fourier Transform Infrared Spectroscopy

The FTIR measurements were conducted with a Nicolet® iS5 (Thermo Scientific®) spectrometer with an iD7 attenuated total reflectance (ATR) accessory. The analysis was conducted following the ASTM F2778 [20]. For PEEK polymers, the crystallinity index (CI) was determined as the ratio of the height of two specific infrared absorption peaks: 1305 cm^{-1} (HA) and 1280 cm^{-1} (HB) (Fig. 2). The HA peak corresponds to carbonyl linkages and increases in height with higher crystallinity. In contrast, the HB peak, primarily influenced by the diphenyl ether groups of the PEEK molecular chain, remains invariant to the level of crystallinity, serving as a stable reference for the CI calculation. The analysis has been expanded to the other two PAEK resins: PEKK and LM-PAEK.

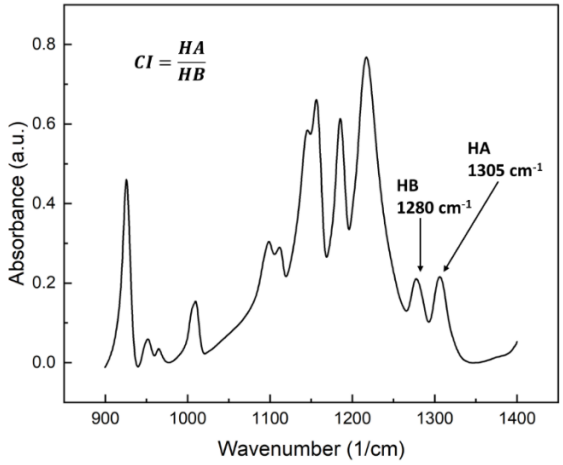

Fig. 2. Representative FTIR spectrum and the crystallinity index (CI) calculation.

2.4 X-ray Diffraction

The XRD system used was the SmartLab® high-resolution vertical theta-theta diffractometer (Rigaku), with a Cu kα X-ray tube operating at 40kV and 40mA. Measurements were performed using cross beam optics in Bragg-Brentano configuration, 10 mm beam width, beta stage sample holder, K-beta filter, incident slit at 2/3, and both receiving

slits set at 20 mm, D/Tex ultra-high speed silicon strip linear (1D) detector. The scans were performed from 10-80 degrees (2θ), step size 0.01 deg, speed 2 deg/min. The samples measured were placed on low background glass slide holders. The scan time was ~37 minutes.

3 Results and Discussion

A comparison of PAEK resins characterized using DSC, XRD, and FTIR is presented in Fig. 3. Test 1 and Test 2 correspond to the cooling rates 10 and 60 °C/min, respectively. Figs. 3(a) and 3(b) display the characterization results for two distinct PEEK polymers. While the DSC and FTIR analyses yielded comparable results, a notable divergence was observed in the XRD data for the TC1200 PEEK resin, which exhibited a lower overall signal. This lower XRD signal in the Toray® TC1200 PEEK resin may suggest that the specific region inspected had a higher amorphous concentration.

The DSC and XRD results for Syensqo® PEEK, PEKK, and LM-PAEK resins, shown in Figs. 3(b-d) respectively, demonstrated more consistent trends. This alignment suggests that both techniques effectively assessed the crystalline content for these specific polymers, which is expected when evaluating solid-state order, reflecting the degree of crystalline arrangement within the material. However, some discrepancies between DSC and XRD may arise from differences in probed volume, sensitivity to various crystalline phases, or the influence of amorphous components.

Interestingly, the CI from FTIR remained largely similar for all samples, despite preparation at two different cooling rates. This indicates that the inherent crystallization tendency of these polymers, as reflected by the CI, was not substantially altered by the tested cooling rate variations.

The degrees of crystallinity for the PEEK polymers were consistently higher than those of the other polymers (PEKK and LM-PAEK). This is consistent with the well-established semi-crystalline nature of PEEK and the strong tendency for PEEK to crystallize. This inherent difference in crystallinity can be attributed to the molecular structure of PEEK, which facilitates efficient chain packing and crystal formation. Compared to PEKK and LM-PAEK, PEEK's aromatic rings and symmetrical molecular structure promote more regular chain arrangements and stronger intermolecular forces, leading to higher degrees of crystallinity under typical processing conditions. Conversely, subtle variations in the ether and ketone linkages within the polymer backbones of PEKK and LM-PAEK can introduce structural irregularities and/or reduce chain mobility, thereby inhibiting their ability to form highly ordered crystalline domains to the same extent as PEEK.

The XRD results generally correlated well with those obtained from DSC, providing reinforcing evidence for the determined levels of crystallinity. However, the observation that the CIs remained similar despite potential differences in actual crystallization degrees among these polymers highlights a critical limitation: the CI, typically a ratio derived from specific peak intensities in FTIR patterns, primarily reflects the relative abundance of certain crystalline planes or overall order within a given material system. While useful for comparing different processing conditions or modifications within the

same polymer, it may not be directly transferable for quantitative comparisons between fundamentally different polymer chemistries. This is because the absolute intensity and shape of FTIR peaks are influenced by factors such as scattering factors, crystal structure, and preferred orientation, all of which vary significantly among different polymers. To obtain a truly quantitative insight into the degree of crystallinity and enable meaningful comparisons across diverse materials, FTIR results would necessitate an analytical correlation with another robust technique, such as DSC, for each specific material. This is because FTIR provides information about vibrational modes sensitive to local molecular order, and an empirical correlation with a technique that quantifies bulk crystallinity (e.g., DSC, which measures enthalpy changes associated with melting) is essential to establish a reliable quantitative relationship for each unique polymer system.

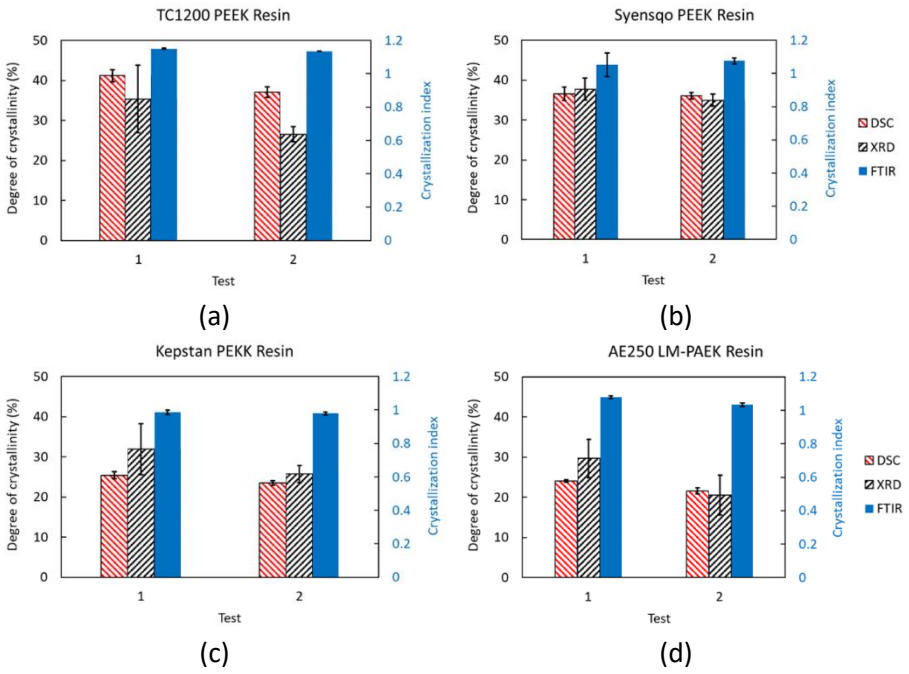

Fig. 3. Comparison of PAEK resins characterized using DSC, XRD, and FTIR; a) TC1200 PEEK, b) Syensqo PEEK, c) Kepstan PEKK, and d) AE250 LM-PAEK. The degree crystallinity was obtained from DSC and XRD, and the crystallinity index from FTIR.

4 Conclusions

This study compared the characterization of PAEK resins using DSC, XRD, and FTIR spectroscopy, revealing both consistencies and specific insights into their crystalline structures. For the Syensqo® PEEK, PEKK, and LM-PAEK resins, DSC and XRD generally demonstrated good agreement between analytical techniques in assessing

crystalline content, indicating their effective application for evaluating solid-state order within these polymer types. Similarly, DSC and FTIR analyses showed comparable results for the distinct Toray and Syensqo PEEK polymers examined.

However, each technique offers unique perspectives and exhibits specific limitations. The lower XRD signal observed in the TC1200 PEEK resin, for instance, suggests localized variations in amorphous concentration, highlighting the sensitivity of XRD to the specific region probed. While the crystallization index from FTIR remained largely consistent across the two different tests probing cooling rate for a specified polymer, its utility for direct quantitative comparisons between fundamentally different PAEK chemistries is limited. This is because the absolute intensity and shape of FTIR peaks are influenced by material-specific features like scattering factors, crystal structure, and preferred orientation which makes comparison between different chemistries difficult. Therefore, FTIR, while providing valuable information on local molecular order, also requires empirical correlation with a bulk quantitative technique like DSC to achieve reliable crystallinity measurements across diverse materials.

Considering these findings, DSC emerges as the most robust and direct technique for quantitative assessment of bulk crystallinity and crystallization kinetics in these PAEK polymers. Its measurement of enthalpy changes associated with melting provides a fundamental and quantifiable metric of crystallinity. While XRD is invaluable for elucidating crystalline structure and long-range order, and FTIR offers insights into local molecular environments, their quantitative application for inter-material comparisons necessitates careful calibration, often against DSC. Therefore, for comprehensive crystallization analysis, a complementary approach integrating DSC with structural techniques like XRD and FTIR is recommended to provide a holistic understanding of polymer crystallinity and its influencing factors.

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