Thermodynamics and Isochronal Crystallization Kinetics of Poly(ether-ether-ketone)-Boron Nitride Nanoplatelets Structural Deposits via Cold Spray Additive Manufacturing

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Abstract

Cold spray additive manufacturing (CSAM) imposes an extreme solid-state thermomechanical environment that is fundamentally distinct from melt-based polymer processing. During supersonic particle impact, polymers experience ultrahigh strain rates, localized adiabatic heating, rapid cooling, and severe plastic deformation without bulk melting. These conditions introduce a non-equilibrium molecular state characterized by pre-oriented chain segments, strained conformations, and crystalline precursors, collectively referred to here as cold-spray-induced molecular memory. While our prior work demonstrated that crystallization occurs in cold-sprayed PEEK deposits, the thermodynamic and kinetic mechanisms governing this behavior remain unresolved. In this study, pristine PEEK and PEEK-Boron nitride nanoplatelets (BNNP) powders and their corresponding cold-sprayed deposits were subjected to isochronal differential scanning calorimetry without melt reset to preserve the induced molecular memory. A strain-augmented classical nucleation theory is developed herein to analytically incorporate deformation-induced mechanical energy into the volumetric crystallization driving force. Crystallization kinetics were analyzed using a multi-model Kissinger-Jeziorny-Ozawa-Mo (KJOM) models with three-stage Avrami segmentation, while X-ray diffraction was employed to evaluate structural coherence. Stage-resolved Avrami analysis reveals a transition from homogeneous nucleation and limited two-dimensional lamellar growth in powder systems to multidimensional three-dimensional spherulitic crystallization in the composite deposit. XRD confirms progressive peak sharpening and without lattice distortion, indicating enhanced crystalline coherence. The results demonstrate that cold spray stores recoverable molecular memory that synergizes with nanoplatelet-induced heterogeneous nucleation to produce the most thermodynamically favorable and kinetically accelerated crystallization pathway observed. This work establishes a unified thermodynamic-kinetic-structural framework for understanding crystallization in solid-state additively manufactured high-performance thermoplastics.