



Nanocomposites Based on Poly(alkylene Furanoate)s In Situ Reinforced by Various Nanofillers: Crystallization and Dynamics



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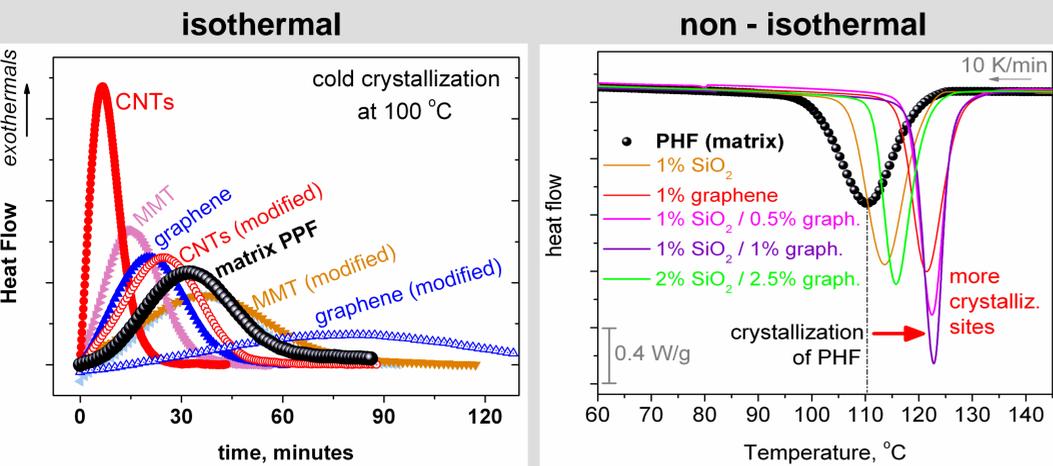
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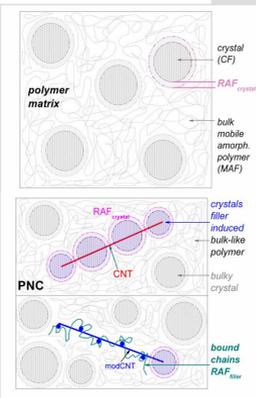
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Bio-based and renewable poly(*n*-alkylene furanoate)s (PAFs) [1,2] with *n*= 3, 4 and 6 were synthesized, in the form of bulk polymers (PPF, PBF, PHF) and nanocomposites, reinforced by the *in situ* introduction of a variety of inorganic nanofillers: graphene nanoplatelets [3], montmorillonite, MMT, nanoclays [4], halloysite nanotubes [5], carbon nanotubes (CNTs) [5,6], graphene oxide [6] and silica [7]. The nanofillers were used both in the initial (natural) state and upon surface modifications, as well as in the forms of mixtures and hybrid particles. Differential scanning calorimetry (DSC) and broadband dielectric spectroscopy (BDS) were employed as characterization techniques, supplemented by Fourier transform infrared spectroscopy (FTIR), polarized optical microscopy (POM) and X-ray diffraction (XRD). All initial fillers were found to enhance crystallization acting as additional nuclei, with the strength of this facilitation increasing systematically with the aspect ratio or the specific surface area of the fillers [5]. Subsequently, this enhancement has led to mechanical reinforcement [3-5]. Contrariwise, upon surface modification and development of strong polymer-particle interactions (FTIR) the nucleation action is hindered, which is demonstrated in PAFs for the first time [6]. As expected, crystallization, semicrystalline morphology and interfacial interactions impose strong impacts on molecular dynamics. BDS allowed the detection of a variety of molecular dynamics processes, namely, local, segmental, global chain and filler related (interfacial polymer), in some cases, for the first time in the literature.

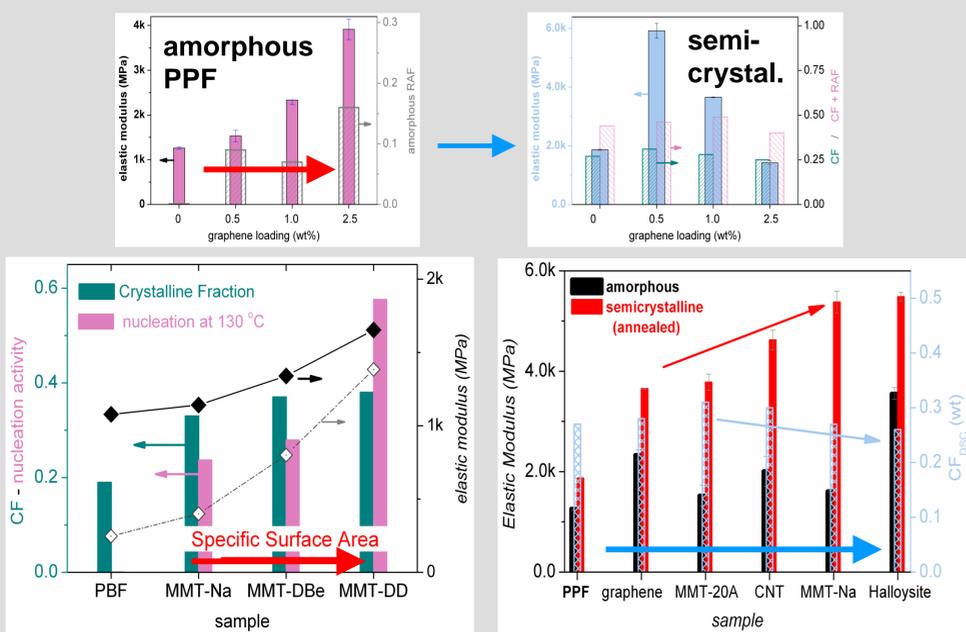
Crystallization



- Fillers offer crystallization sites (accelerated crystallization)
- Correlations with filler geometry and aspect ratio
- Variety of alternations in the semicrystalline morphology
- Filler modifications result in decelerated crystallization – loss of nuclei at the profit of interfacial adhesion



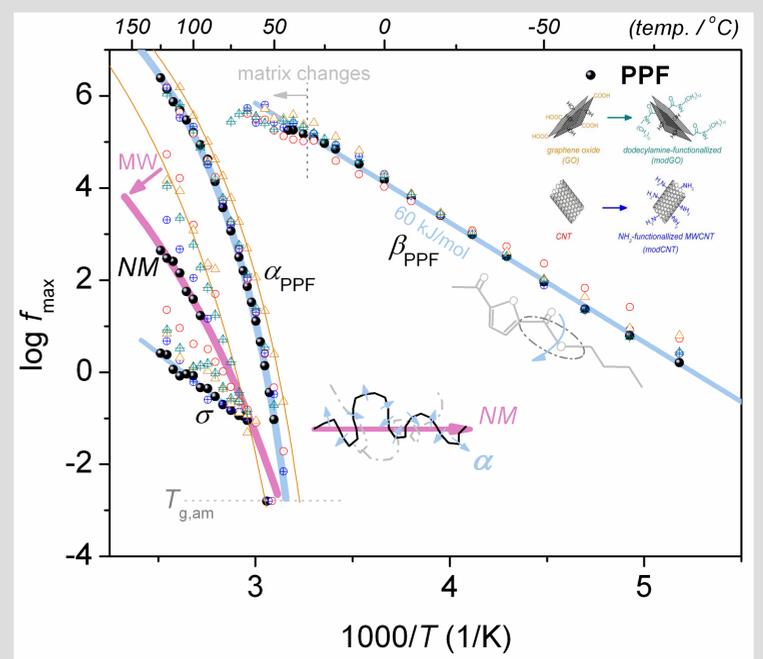
Direct and indirect improvements on the mechanical performance by altered crystallizability



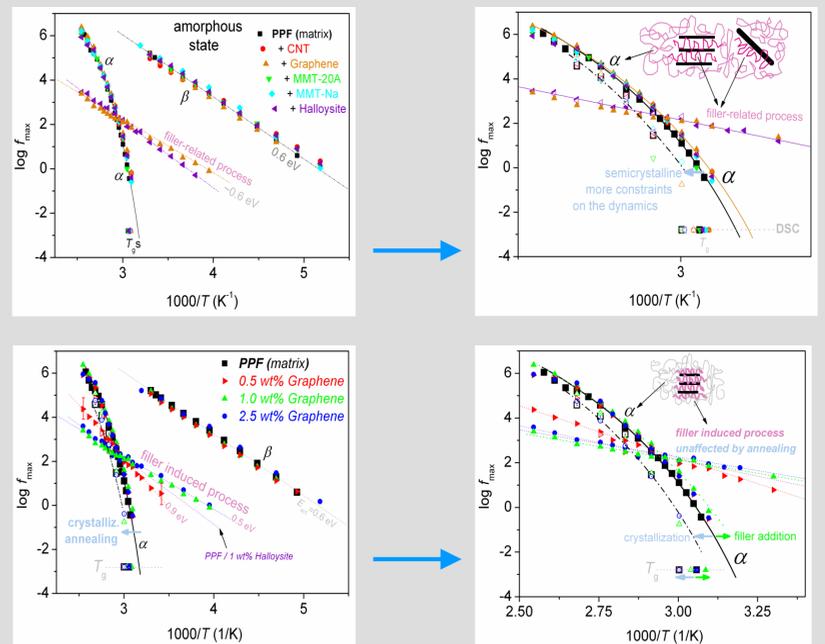
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Molecular Dynamics (BDS)



- Segmental dynamics 'α relaxation' - effects of MW and CF
- Global chain dynamics 'NM relaxation' - when MW is too low
- Local dynamics 'β relaxation' – sensitive to global changes
- Filler related relaxations – interfacial polymer dynamics



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