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PhD DISSERTATION

Biocomposites with Nanofibers Generated by Shear and Shear Induced Crystallization

ABSTRACT

Due to increasing awareness about the global environment a range of new polymeric materials is being developed, especially biodegradable materials and those produced from renewable resources. Contrary to conventional polymers, biodegradable polymers can be converted into biomass or carbon dioxide and water. Biopolymer blends market shares its continuous growth. It is widely known that the use of several polymers combined in a blend allows obtaining several advantages, in particular, a combination of the best of their properties. Nevertheless, the main drawbacks of polymer blends are the poor possibility of morphology control and low interphase adhesion that obstruct the realization of high- performance blends. Overcoming this problem can be achieved by conversion of polymer blends into all-polymer composites. The thesis introduces a novel concept of in-situ generation of all-polymer nanocomposites, where the nanofibers of one polymer are formed inside the second polymer during shear processing in a melt. The solidification of nanofibrous sheared inclusions is performed by shear-induced crystallization, all during processing. This concept allows the formation of “green all-polymer” nanocomposites in a single step for a range of biopolymers. The primary scientific goal of our studies was a development of the methodology constituting the precise control of phase morphology of the dispersed polymer inclusions and the polymer matrix during the processing of “green all polymer” composite via conversion of polymer blends into in-situ composites.

The concept of “in-situ generation of all-polymeric nanocomposites” has been proposed and developed to a range of biopolymers, namely polylactide (PLA), polyhydroxyalkanoate (PHA), poly(butylene adipate-co-succinate-co-glutarate-co-terephthalate) (PBASGT), poly(butylene adipate-co-terephthalate) (PBAT), bio-based polyamide (PA), poly(1,4-butylene succinate) (PBS), and poly(ϵ -caprolactone) (PCL). Sustainable green biopolymer–biopolymer nanocomposites were then fabricated. The critical role of applying a high shear rate to precisely control phase morphology of the dispersed polymer inclusions has been revealed. Employing high shear rates facilitated two simultaneous processes, namely, the transition from droplet to fibrillar morphology and the subsequent instantaneous stabilization of the formed fibrillar morphology via the shear-induced crystallization of the minor phase. Viscosity and elasticity ratios, as well as interfacial interaction, were found to be major parameters dominating the morphology of the dispersed polymer inclusions. To widely vary the viscoelasticity of the forming systems, Joncryl ADR4400 was used as a compatibilizer for polymer blends and as a chain-extender for polymer matrix before blending. Moreover, polymers with different viscosities were used. It was shown that there are upper and lower bounds for the ratios providing efficient in-situ fibrils formation. As these parameters decreased, thinner and longer polymer nanofibers formed, and ultimately a network of nanofibrils developed. Below the lower boundary, formed very thin nano-fibrils became unstable and their flow was accompanied by breaking-up into sub-nanodroplets. For instance, the critical values of viscosity and elasticity ratios regarding PLA/PA system found to be in the range of 0.3–2.8 and 2.0–15.0, respectively. Shear-induced crystallization allowed stabilization of minor polymer phase nanofibers immediately under applying a high shear rate without subsequent cooling. It has been shown that shearing increased the nonisothermal crystallization temperature of polymer inclusions. In particular, shearing at 300 s^{-1} led to the growth of nonisothermal crystallization temperature of PBAT, PBASGT, PBS, and PHA by

20, 25, 30, and 50 °C, respectively. In some cases (PASGT, PBAT), the formation of self-nucleation centers responsible for the melt memory was observed, which additionally contributed to the shear-induced crystallization of inclusions. The shear-induced crystallization of nanofibers found to be influenced by the viscosity of inclusions. It has been studied by the example of PA that the higher viscosity of PA, the more significant increase in the crystallization temperature and a narrower temperature range in which the crystallization process occurs. Applying a high shear rate decreased this crystallization temperature interval for molten PA by 30 °C. It was also discovered that shear stress affects preferably the nucleation rate rather than the growth of crystals. The shear-induced crystallization caused the formation of an orientation order in in-situ generated nanofibers which is important to get a true reinforcing component since its properties differ from those of the bulk material. Rapid crystallization induced at elevated temperatures also prevented the in-situ generated nanofibers to undergo instabilities of end-pinching, break-up fracture, and retraction. As a result, nanofibers with substantially high aspect ratios were achieved forming a 3D network at low concentrations of the minor phase.

Such a nanofibril network-matrix morphology led to an exceptional combination of strength, modulus, and ductility. Moreover, this physically entangled network of nanofibers established the possibility of hybridization via the formation of an interpenetrating fiber network, as well as the creation of multi-shape memory polymers (SMPs) with non-covalent bonds between switching and permanent domains. This network structure demonstrated a significant increase of extensional viscosity above linear viscoelastic region during uniaxial extensional deformation, known as strain hardening. As an example of remarkable improved mechanical properties, the in-situ generated PLA/PBAT (94/6) composite, compared to the blend, exhibited a 1.4-fold increased Young's modulus, 1.1-fold increased yield stress, 1.7-fold increased tensile impact strength, 1.3-fold increased stress at break, and 10-fold increased

strain at break.

The microstructural evolution, as well as the mechanisms of plastic deformation and fragmentation of crystalline lamellae, were studied for blends and nanocomposites. The change in morphology from droplets/matrix to fibrils/matrix one, as well as an increase in the concentration of the minor polymer phase, led to a gradual transition from crazing to intense crazing, followed by cooperative development of crazes and shear bands, and finally to the development of only shear bands. Owing to the formation of so-called dormant shear bands, the nucleation rate of crazes was intensified. The presence of nanofibrils stopped the propagation of the crazes, stabilizes them, and hindered the fracture through bridging the craze gap. Therefore, crazes could thicken up to few tens of μm in the zone of neck formation. In addition, it has been revealed that extensive fragmentation of the crystalline lamellae takes place for nanoblends, while limited fragmentation occurs for nanocomposite over a wide range of deformations. This limited fragmentation facilitated the plastic flow of nanocomposites and was associated with the nanofibrillar network of minor phase which effectively transfers local stress to the matrix polymer's lamellae, enforcing their local deformation.

Additional improvement in the performance of nanocomposites has been achieved through introduction of a new hybrid configuration, i.e. interpenetrating fiber networks. As an example, a hybrid network was produced by combining tough, in situ generated PBS nanofibers with rigid, ready-made electrospun polyoxymethylene (POM) nanofibers. PLA was chosen as matrix and the concentration of PBS and POM components was 10 wt.% to establish a continuous fiber network. POM fibers acted as effective nucleation sites for the in-situ generated PBS fibers, which led to an additional increase in their crystallization temperature and degree of crystallinity. This also contributed to the retarded relaxation of PBS fibers during shear-induced crystallization and preservation of the achieved degree of

elongation of PBS fibers.

The mechanical properties with positive hybrid effect, higher characteristics than the mixing rule, were obtained. Compared to the hybrid blend, the hybrid composite was characterized by a 1.4-fold increased Young's modulus, 1.2-fold increased yield stress, 1.3-fold increased tensile impact strength, and 4-fold increased strain at break.

Finally, a triple shape memory hybrid nanocomposite was realized using the PLA/PBAT/cellulose nanofibers (CNFs) blend. The in-situ fibrillation of the dispersed PBAT component promoted the formation of more effective physical entanglements at the interfaces due to their higher specific interfacial area compared to droplet dispersed fillers, playing the role of physical cross-links (net-points). The introduction of CNFs boosted the conversion of PBAT droplets to nanofibers. Consequently, thinner and longer PBAT nanofibers were formed effectuating stronger interaction at the PLA-PBAT and PBAT-CNF interfaces. The in-situ generated shape memory composite showed drastically higher values of strain recovery ratios, strain fixity ratios, faster recovery rate, and better mechanical properties compared to the blend.