Cellulose rich Composite materials from layer by layer coated fibers

Abstract

The exploitation of Layer-by-layer (LbL) assembly for the functionalization of cellulosic substrates, like fibers and particles, was investigated with for the production of polymeric composites as aim. Indeed, cellulose present great potentialities as component for composites manufacturing, which are compensated by some critical aspects like the poor compatibility with the matrix and its high flammability. LbL being a versatile and established method in coating technology can come in hands for introducing new functionalities on the surface of many substrates, being thus applicable also on cellulose. In this thesis, different LbL assemblies were developed for coating cellulose fibers and particles with a focus on flame-retardancy. Coated fibers were then used for the production of composites materials or as themselves to obtain self-standing lightweight materials. In a first attempt, short cellulose fibers were coated with a LbL assembly comprising halloysite nanotubes (Hal) suspended in chitosan (CH) and a phosphorous source, like ammonium polyphosphate (APP) or phytic acid (Phy). Both coatings investigated were successfully assembled on cellulose fibers and used to prepared composites with poly(butylensuccinate) (PBS). An increase in modulus, respect to neat PBS, was observed for all composites containing cellulose fibers, with coating that doesn't compromise the final mechanical properties. Flame-retardant properties of prepared composites were investigated via flammability test and cone calorimetry, with both systems presenting a beneficial effect. Indeed, materials containing LbL coated fibers presented self-extinguishing by melt dripping and a reduction in peak heat release rate (pkHRR). Following this, rigid polyurethane foams were selected as material for composites preparation in order to investigate the effect of LbL coated fibers in a lightweight composite material. Regarding this, LbL approach was exploited to coat both long cellulose fibers (700µm) and ballmilled cellulose with an assembly comprising CH and a phosphorous polyelectrolyte, such as APP or sodium hexametaphosphate (SHMP). The assemblies were successfully deposited on both cellulose substrates and their flammability were tested, pointing out that coated fibers can yield a non-ignitability behavior and thus becoming a good candidate for PUF preparation. Cellulose fibers were successfully incorporated in the PUF with a maximum concentration of 7.5 phr and 15 phr for long fibers and ballmilled fibers, respectively, without significant alterations in mechanical properties and slight better thermal conductivity. On overall, PUF containing cellulose presented higher pkHRR, and lower smoke production. Interestingly, PUF containing 15phr of ballmilled cellulose coated with SHMP-CH showed the best results with a significant reduction in pkHRR and smoke production respect to the use of untreated cellulose or to neat PU. The results obtained pointed out that coating on fibers seems to assert an increased effect in lightweight materials, this leads to the investigation of lightweight materials made from freeze-dried coated fibers. In order to do this, cellulose fibers were coated with an assembly, comprising SHMP and CH, tailored to improve the fiber-fiber adhesion.

The assembly was first studied on a model substrate, such as Si wafer, and then on fibers. Moreover, the composition of the coating was studied by polyelectrolyte titration, which gave the possibility to calculate the percentage compositions of coated fibers and coatings, resulting in a cellulose content that range from 80 to 90%. Upon freeze-drying, cellulose fibers form a self-sustaining, lightweight material, which is able to withstand moderate loads. Flame-retardancy of materials obtained pointed out outstanding properties, with non-ignitability reached after fe2 bi-layers and low pkHRR, associated to an extremely low smoke production. In an attempt to obtain similar materials, but with improved mechanical properties, cellulose nanofibrils (CNF) were incorporated into an assembly comprising of Phy and CH. Materials obtained presented indeed an increase in modulus, associated to CNF, but at the same time worse flame-retardant properties. Indicating the necessity to further study the role of CNF and other components for this kind of applications. In conclusion, LbL was investigated as tool for the coating of cellulose fibers, obtaining composite materials with improved properties, respect to the use of pure cellulose, in all applications investigated.