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One-Component Nanocomposites Materials Based on Polymer-Decorated Cellulose Nanocrystals

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Cellulose nanocrystals (CNCs) have been widely used as reinforcing fillers in polymer nanocomposites due to their intrinsic properties, notably the crystallinity, the high specific area and the outstanding mechanical properties. CNCs are bio-sourced, with common sources being cotton, bacteria, or tunicates, and through hydrolysis of cellulose, highly crystalline domains can be extracted providing CNCs with unique properties and available hydroxyl groups for chemical modification. In polymer nanocomposites made with CNCs, a major downside is the aggregation of CNCs within a polymer matrix at high loading content, which compromises the mechanical reinforcement of the material. One-component nanocomposites (OCNs) based on polymer-grafted CNCs represents an attractive solution to this problem because these materials do not suffer, by design, from phase separation and display homogenous nanoparticle dispersion at larger content ranges. At the same time, chain entanglements between the polymer grafted from the surface of CNCs provide stress-transfer among the particles. In this thesis, two distinct materials based on the grafting of homopolymers and block copolymers from the surface of CNCs are investigated to demonstrate this.

The first approach expands on the development and investigation of OCNs based on CNCs that are grafted with homopolymers exhibiting glass transition temperatures (T_g) above and below room temperature. For this purpose, poly(methyl methacrylate) and poly(hexyl methacrylate) were chosen and grafted from the surface of CNCs via surface-photoinitiated free radical polymerization. This approach affords easy-to-process nanocomposites through melt-processing into homogenous films with CNCs content of 10 or 20 wt%. These nanocomposites display higher stiffness yet remain ductile in comparison to conventional two-component nanocomposites of unmodified CNCs and the respective polymers, especially for OCNs containing low-T_g grafts.

In addition to homopolymers, block copolymers of different order and individual block length grown from the CNC surface are investigated. By changing the grafted polymer on the surface of CNCs, OCNs with several morphologies can be envisioned that give rise to properties that are a blend of the block copolymer phases and the CNCs. For instant, grafting block copolymers having a soft inner block (first grown from the CNCs) and a hard outer block (grown from the initial polymer block) are thought to afford tough, yet stiff OCNs. The synthesis of such materials was performed by grafting poly(hexyl methacrylate)-block-poly(methyl methacrylate) from the surface of CNCs via surface-initiated atom transfer radical polymerization. A preliminary study on this material showed that the mechanical properties can be tailored at will, and the length of grafted polymer is a significant feature in the melt processability of these polymer-grafted CNCs into homogenous OCNs films.

In order to determine the grafts chain lengths, a simple in-situ method to estimate the molecular weight of the polymers grafted from the CNC surfaces was developed.

Exploiting a well-known solution-based characterization technique, such as ^{1}H NMR spectroscopy, the analysis of the supernatant from the grafting polymerization was performed to determine the monomer conversion and thus estimate the molecular weight of the grafts by knowing the initial concentration of the initiators on the surface of CNCs. The method allows an in-situ estimation of the molecular weight of grafts, without any further treatment, as well as following the evolution of the chemical-modification of CNCs, which appears to be reproducible and could be applicable to other nanoparticles systems.
To summarize, the investigations presented in the framework of this thesis demonstrated the potential of such OCNs in the preparation of materials with improved mechanical properties compared to their two-component counterparts. These improvements are a result of the presence of CNCs in the material and the prevention of nanoparticles aggregates. Variations of the polymers grafted from the surface of CNCs afford OCNs with different bulk properties and micro-morphologies. In addition, a simple method is proposed to estimate the molecular weight of the polymers grafted from CNC surfaces without any additional chemical modification of the product.

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