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A new synthesis of bis(acyl)phosphane oxide (BAPO) photoinitiators was developed which can be used to functionalize cellulose nanocrystals surfaces for polymer grafting. Hybrid materials with excellent graft yields can be rapidly obtained under mild and acid-free conditions.

Bis(acyl)phosphane oxides (R¹PO(COR²)₂; BAPOs) are widely used as photoinitiators (PIs) to initiate radical polymerizations and found industrial applications in the preparation of pigmented and clear coatings, adhesives, photo-resists, printing plates, and dental restoring materials.1 Cellulose nanocrystals (CNC) have recently attracted much attention because of their excellent mechanical properties, biodegradability, and renewability.2 However, the inherent hydrophilicity and self-aggregation upon drying often limit their applications.3 Such obstacles can be overcome by surface graft polymerization.4 Free radical polymerization (radicals are generated by various methods from an initiator in the presence of cellulose and monomer)5-7, controlled radical polymerization [atom transfer radical polymerization (ATRP)8 or reversible addition–fragmentation chain transfer polymerization (RAFT)9] and ring opening polymerization (cellulose surface hydroxyl groups act as initiating sites) were used for this purpose. Free radical polymerization is able to polymerize a wide range of monomers in a short time and is tolerant to water or other impurities, but rather harsh conditions are required to generate radicals in most cases.

To the best of our knowledge, few photoinitiators have been used to modify cellulose surfaces.11 Here, we present a new and straightforward synthesis of highly photoactive BAPO derivatives and the use of this reaction for a simple and highly reliable modification of CNC surfaces under mild conditions.12
In order to functionalize CNC (derived from wood pulp by sulfuric acid treatment, provided by the University of Maine), methacryloyl groups were attached to their surfaces as shown in Scheme 2. To these, HP(Comes)₂ was added to give CNC-BAPO and subsequent oxidation with aqueous H₂O₂ generated quantitatively CNC-BAPO. Elemental analysis of the final yellow powder indicates a phosphorus content of 1.0% which corresponds to 0.33 mmol bis(acyl)phosphane oxide (BAPO) per gram of CNC.

The successful immobilization was confirmed by Fourier transform infrared spectroscopy (FT-IR), see Fig. 1. The peaks at 1716 cm⁻¹ and 1635 cm⁻¹ in the CNC-MMA sample are attributed to the stretching vibration of the carboxyl (ν(C=O)) and alkene groups (ν(C=C)), respectively. After the addition of BAPO, a new absorption at 1608 cm⁻¹ is observed which is assigned to the stretching vibration of the C=C bonds in the mesityl (Mes) ring while ν(C=O) is shifted to a higher wavenumber at 1732 cm⁻¹.

The presence of BAPO was further proved by ¹³C and ³¹P CP-MAS NMR spectroscopy (Fig. 2). A single signal at 23.7 ppm in ³¹P CP-MAS NMR spectrum of CNC-BAPO is similar to the chemical shift of 3a and 3b. Typical ¹³C signals of cellulose nanocrystals at δ = 105.0 (C₁), 88.6 (C₄ crystalline), 83.8 (C₄ amorphous), 74.7/72.4 (C₂,₃,₅), 65.0 (C₆ crystalline), and 62.9 ppm (C₆ amorphous) are observed in all spectra. In the CNC-BAPO sample, the characteristic signals of the BAPO unit at δ = 216.4 (C₁OMes), 141.4 (C₄ Mes), 136.1 (C₂,₆ Mes), 129.4 (C₃,₅ Mes), and 20.0 (o,p-CH₃ Mes) are clearly observed, which are absent in the spectrum of CNC-MMA. The ¹³C signal of the C=O group from methacrylate unit is shifted from 168.1 to 174.7 ppm, due to the addition of the BAPO group.

The TEM images in Fig. 3 show that the morphology of the CNC was maintained during the modification procedure with BAPO units. The unmodified nanocrystals exhibit an average diameter of 5-10 nm and lengths of 100-150 nm. The BAPO functionalized nanocrystals are less individualized. This aggregation may be due to a decrease of sulfate groups or activation of the surface BAPO groups under the conditions of the TEM experiment (Table S1, ESI†). The X-ray diffraction patterns of unmodified CNC, methacrylate, and BAPO modified CNC show that all three samples have similar crystallinity and
CNC-BAPO was used to polymerize acrylic monomers under UV light irradiation (the dimension of CNC was preserved after UV irradiation, Fig. S3) at room temperature for 1 hour. The monomers used include methyl methacrylate (MMA), butyl acrylate (BuA), N-isopropylacrylamide (NIPAAm) and 2-hydroxyethyl acrylate (HEA). Graft yield (G), graft efficiency (G_e) and elemental analysis of the polymer graft CNC are recorded in Table S1, ESI†.

High graft yields (after removing the homopolymers by Soxhlet extraction) were obtained for all tested monomers. The highest mass gain of up to 477% was achieved with MMA. BuA and NIPAAm both formed grafted polymers with masses three times greater than that of the starting CNC. HEA was less prone to graft, but the mass still increased by 200%. Elemental analysis was performed to quantify the composition of the grafted materials. The mass gain calculated according to phosphorus content correlates well with the gravimetric value. Homopolymers, generated by cleaved acyl radicals, were formed in smaller amounts which confirms that phosphinoyl radicals are more reactive than acyl radicals.16

The obtained samples were characterized by FT-IR (Fig. S4, ESI†). Intense absorption bands attributed to the νC=O of the carboxyl groups of the grafted polymers were observed in all spectra. The bending vibration of the N-H bond was detected at 1531 cm⁻¹ in the CNC-g-PNIPAAm sample. Moreover, the intensities of the O-H stretching bands of cellulose backbones at 3300 cm⁻¹ decreased significantly in PMMA and PBuA grafted samples. This is likely caused by the grafting of the polymers from the CNC surfaces.10 In contrast, the intensities increased in the PNIPAAm and PHEA grafted samples, due to the overlapping of N-H and O-H groups present in the grafted polymer chains.

13C CP-MAS NMR spectroscopy was used to characterize the polymer grafted CNC. In addition, to the signals of cellulose, the resonances of the 13C nuclei in the polymers were clearly observed, confirming the success of grafting (Fig. S5, ESI†).

The grafted polymer chains were cleaved from the CNC and independently investigated. 1H NMR indicated that the structures were maintained except for PHEA (Fig. S6, ESI†). The molecular weight of the polymers varies with the monomer (see Table S1, ESI†). MMA generated the longest chains, and the weight average molecular weight (M_w) is 250 kg/mol. BuA and NIPAAm gave shorter chains with M_w of about 17 kg/mol and 70 kg/mol, respectively. Polymeric films of CNC-g-PMMA can be obtained by solvent casting. A film of about 0.1 mm thickness is shown to the right of Fig. 4 and is less transparent than a neat PMMA film (Fig. 4 middle).

DSC and TGA thermograms were recorded (Fig. S7 and S8, respectively, and Table S2, ESI†). Glass transition temperatures (T_g) of the grafted products are slightly higher than the reported values of the homopolymers. The increase can be explained by the restriction of the mobility of grafted polymer chains to the CNC surfaces.17 In TGA thermograms, a significant increase of the onset temperature was observed for CNC grafted with PBuA, PNIPAAm and PHEA. The char yield of CNC-BAPO sample at 800 °C (18.3%) is much higher than the others because on cellulose substrates, organo phosphorus compounds favor char formation and suppress the concentration of combustible volatile species during thermal decomposition.18

The reinforcing properties of CNC-g-PMMA in a PMMA matrix were evaluated by tensile tests. The elastic modulus (E), tensile strength (σ), and elongation at break of the specimens are given in Fig. S9, ESI†. The incorporation of unmodified CNC (20 wt%) in a PMMA matrix decreases both the elastic modulus and the tensile strength by 25% and 56%, respectively. This finding can be explained by the poor compatibility between the hydrophilic CNC and the hydrophobic PMMA. The addition of CNC-g-PMMA (20 wt%) into PMMA proved to enhance the elastic modulus by 8% without loss of the tensile strength. Elongation at break decreases significantly but the values still remain better than the composites filled with unmodified CNC.

In conclusion, a new and straightforward approach to prepare phosphorus-functionalized bis(acyl)phosphane oxides was developed, which can be used to functionalize cellulose nanocrystals for polymer grafting. Under mild and acid-free conditions, excellent graft yields were achieved.
PMMA grafted cellulose nanocrystals show an improved mechanical performance when dispersed in a PMMA matrix. We believe that the results reported here may be developed into a reliable strategy to functionalize not only cellulose surfaces but also allow coating of other materials with polymers.

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Notes and references


