



## Polymer Communication

# Direct transformation of cellulose fibres into self-reinforced composites by partial oxypropylation

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**Abstract**

Bulk oxypropylation limited to the outer layer of cellulose fibres constitutes a straightforward approach to the preparation of a novel type of composite material made up of a thermoplastic sleeve (matrix) surrounding the unreacted core of the fibres (reinforcing elements).

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**1. Introduction**

The use of cellulose fibres as reinforcing elements in composite materials based on macromolecular matrices has attracted considerable attention in recent years and a special issue of a specialised journal provides an updated account of the state of the art [1]. Numerous advantages justify this growing interest in calling upon natural fibres instead of glass counterparts, including their (i) renewable character, (ii) ubiquitous availability as cheap resources (albeit with different morphologies), (iii) good mechanical properties, (iv) low density, (v) modest abrasivity and (vi) biodegradability. If the matrix is also biodegradable (e.g. starch, polyhydroxyalkanoates and poly-L-lactide), the ensuing cellulose composites are ecologically sound, since they can complete their life cycle by a natural breakdown into the environment.

Composites in which cellulose is the source of both matrix and fibres have already been reported. The combination of cellulose esters and fibres was explored by two distinct approaches, viz (i) the incorporation of lyocell fibres into a cellulose acetate matrix [2] and (ii) the partial esterification of wood pulp fibres with *n*-hexanoic anhydride in an organic medium [3] that produced thermally deformable materials in which the thermoplastic cellulose ester constituted the matrix

and the unmodified fibres the reinforcing elements. The latter approach was also applied to the partial benzylation of sisal fibres in an aqueous medium [4]. The isolation, drying and hot-pressing of these benzylated fibres gave materials whose morphology showed features assembling those of a composite material in which the modified cellulose played the role of the thermoplastic matrix. In another vein, a recent report [5] describes the preparation of an all-cellulose composite by dissolving pre-treated ramie fibres in DMAc/LiCl and introducing untreated fibres into the ensuing solution. The composites were then isolated by coagulation with methanol and drying.

We wish to report here a novel strategy for the direct preparation of all-cellulose based composites, which involves a straightforward transformation of the fibres' outer layer, giving rise to a thermoplastic matrix around its unreacted reinforcing inner structure. The originality of this method resides in the fact that the chemical modification is carried out through the bulk reaction of cellulose with propylene oxide (PO), thus giving the desired materials directly, without the need of any processing associated with their recovery, like precipitation, solvent removal, etc.

**2. Experimental**

The oxypropylation of polysaccharides (cellulose, starch, chitin, etc.) is a well-documented process in the context of their conversion into viscous liquid polyols [6] that are used as such, e.g. as rheology modifiers, or as macromonomers in the synthesis of polyurethanes [7] or polymer electrolytes [8]. These reactions lead, therefore, to the total destruction of the original semi-crystalline structure of the natural polymer

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through its abundant grafting with PO oligomers. Typically, a strong Brønsted base is used in bulk or in an aqueous medium to activate the hydroxy groups of the substrate and thus provide the anionic initiation sites for the ‘grafting-from’ PO polymerisation, which is always accompanied by some PO homopolymerisation arising from transfer reactions.

We adopted this procedure in bulk, but called upon much more modest amounts of PO, in order to limit the oxypropylation to the outer sleeve of the fibres. The cellulose substrates tested included a conventional bleached kraft pulp, medium porosity filter papers, a commercial microcrystalline powder (Avicell) and regenerated rayon filaments.

Ca. 2 g of the chosen substrate were impregnated with an ethanol/KOH solution for 12 h and then, after evaporating the ethanol, mixed under nitrogen with the chosen amount of PO in a stainless steel autoclave. The closed autoclave, equipped with a manometer and a controlled heating system, was brought to the desired temperature while monitoring the corresponding pressure increase. In some systems, the onset of the oxypropylation reaction was revealed by a sudden increase in temperature and pressure followed by a progressive return to 1 bar, indicating total PO consumption. In others, the reaction was too slow to generate a temperature increase above the chosen value and thus the reaction time became the relevant parameter in terms of PO consumption. In all instances, the autoclave was allowed to return to room temperature at the end of the reaction and the solid products were withdrawn and exposed to a stream of CO<sub>2</sub> to transform the KOH into KHCO<sub>3</sub>.

The modified fibres were then submitted to a soxhlet extraction with *n*-hexane to determine the amount of PO homopolymer [9]. This operation was carried out to assess the behaviour of the different systems tested and the structure of the modified fibres, but was not necessary in the context of the actual use of the composites, since we found that modest amounts of oligo PO could be left as part of the matrix. The characterisation of the grafted materials, as obtained and after hot-pressing, included mass gain, percentage of PO homopolymer, FTIR spectroscopy, DSC, contact angle measurements and SEM imaging after liquid nitrogen fracture.

The reaction variables investigated were the [PO]/[cellulose OH] molar ratio (1–5), the [KOH]/[cellulose OH] molar ratio (0.05–0.5) and the reaction temperature (130–160 °C) and time (2–6 h). The oxypropylation rate was also affected by the actual cellulose substrate used, particularly in terms of its accessibility to the pressurised PO. Thus, with a given set of operating conditions, the Avicell powder, which had the highest specific area, gave the highest grafting rate, whereas the regenerated rayon filaments were the least reactive, because of their filled morphology, in contrast with the hollow character of all the other tested fibres.

### 3. Results and discussion

In the search for the most appropriate conditions for each substrate, the reactions leading to very modest grafting, i.e. limited to the fibre surface, or to excessive in-depth transformations giving pasty products with little fibrous

residues, were discarded. The most relevant results, associated with an adequate thickness of the thermoplastic sleeve surrounding the unmodified fibre cores, gave mass gains comprised between 40 and 90%, after the extraction of the 5–10% of PO oligomers. These materials were flexible and could be readily converted into films by pressing them at 135 °C and 11 ton. A visual and optical microscopy inspection of the semi-transparent films revealed the presence of opaque regions constituted by residual cellulose fibres. The oxypropylation front progressing through the fibre wall obviously attacked preferentially the amorphous cellulose domains.

Fig. 1 shows an example of the changes in the FTIR spectrum induced by increasing extents of (partial) oxypropylation of Avicell, after the removal of the PO homopolymer. The relevant features here were (i) the increase in absorption of the aliphatic C–H stretching region (2800–2990 cm<sup>-1</sup>), with the appearance of a new peak at 2970 cm<sup>-1</sup> associated with the methyl groups of the grafted oxypropylene units; (ii) the increase and shift in the absorption of the C–O stretching region (1000–1100 cm<sup>-1</sup>) associated with the ether moieties borne by those units and (iii) the new peak at 1375 cm<sup>-1</sup> confirming the presence of methyl groups. The other substrates gave entirely similar spectral changes as a function of the extent of grafting. As expected, all the products extracted with *n*-hexane displayed the typical FTIR and <sup>1</sup>H NMR features of PO macrodiols.

The DSC tracings of the products after extraction showed systematically a glass transition at ca. –50 °C (albeit with different ΔC<sub>p</sub>, depending on the extent of oxypropylation), absent in the corresponding pristine substrates, which was assigned to the modified portion of the fibres, in tune with the T<sub>g</sub> of commercial hydroxypropylcelluloses, which ranges from –60 to –70 °C. As discussed previously, [8,10] polysaccharides grafted with oligoether chains only display the glass transition of the grafts, which explains the constant value of T<sub>g</sub> in the present context.

Water contact angles on the films were 70–80° (indefinitely constant with time), depending on the substrate and the extent

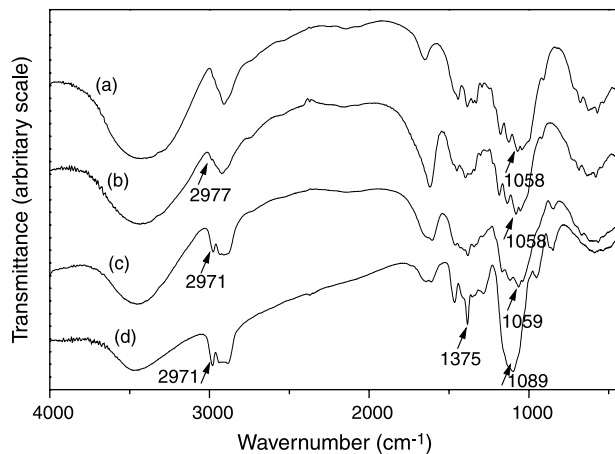


Fig. 1. FTIR spectra (KBr pellets) of Avicell powder before (a) and after oxypropylation using [PO]/[cellulose OH] molar ratios of 1 (b), 3 (c) and 5 (d), and after extraction of the PO homopolymer with *n*-hexane.

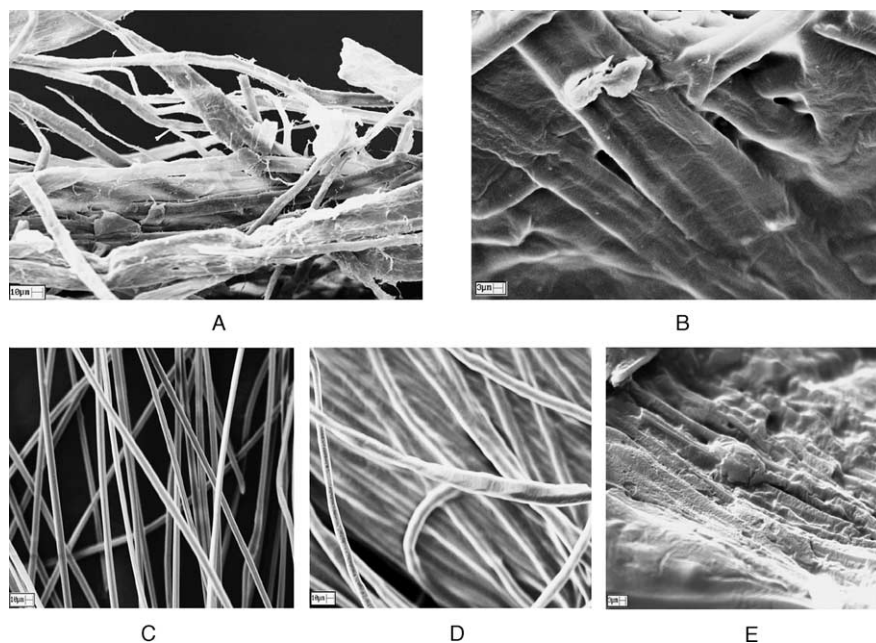


Fig. 2. SEM micrographs of filter paper fibres before (A) and after (B) partial oxypropylation; rayon filaments before (C) and after (D) partial oxypropylation and after hot-pressing into a film (E).

of grafting, compared with initial values of 25 (filter paper) to 40° (Avicell pellet) for the untreated substrates, for which the water droplets were then rapidly absorbed, except in the case of the regenerated rayon filaments.

The SEM micrographs of these materials, a small selection of which is shown in Fig. 2, validated the working hypothesis on which this investigation was based. Indeed, a thermoplastic sleeve was clearly visible around the modified fibres and, after hot pressing, the typical morphology of a composite material appeared.

Furthermore, it is important to emphasise that, given the structural continuity associated with these treatments, the compatibility between fibres and matrix was particularly good, giving rise to a highly adhesive interface.

In conclusion, this preliminary study gave clear evidence that it is possible to prepare all-cellulose based composites via a simple one-pot procedure with green connotations. Work is in progress to assess the mechanical properties and the biodegradability of these novel materials.

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