

NEW MATERIALS FROM FLAX TEXTILE FIBERS PRESERVING NATIVE CELLULOSE ALLOMORPH

*Elena Vismara *, Francesco Briatico, Andrea Pavan
Dipartimento di Chimica, Ingegneria Chimica e Materiali del Politecnico "G. Natta"
20131 Milano, Italy*

*Giangiacomo Torri, Maura Comoli, Sabrina Bertini, Rocco Di Modugno
Istituto di Ricerche Chimiche e Biochimiche "G. Ronzoni"
20133 Milano, Italy*

*Giorgio Rondi
Linificio e Canapificio Nazionale S.p.A
24018 Villa D'Almè (Bergamo), Italy*

Cellulose is a natural polysaccharide, the chief constituent of fibers of plants and it is widely used for the preparation of cellulose products such as, for example, textile fibers and fabrics, absorbent fluffs, artificial skin or ion-exchange resins. It is the basic material for the paper industry and it is also used in the food industry as stabilizer, thickener or as additive with no calories in dietetic preparations. Furthermore some derivatives of cellulose, such as nitrocellulose or cellulose acetates, are utilized for manufacturing explosives, lacquers, rubber and celluloid substitutes, water-proofing fabrics and so on.

From a chemical point of view, cellulose is a β -1,4-linked polymer of D-glucopyranose and it occurs in several distinct crystalline forms known as allomorphs, such as for instance cellulose I, II, III and IV [see A. Sarko in New developments of industrial polysaccharides, page 87, Ed. V. Crescenzi, I.C.M.]. Cellulose I and cellulose II are the commercially dominant allomorphs of cellulose. Cellulose I ("native cellulose") is the form naturally occurring in nearly all plants while cellulose II, also known as "hydrate" cellulose, is mainly produced by treatment of cellulose I with strong basic agents. Such a treatment, known as mercerization, is widely used for removing the non-cellulose components, such as lignin and hemicelluloses, from raw materials containing cellulose. It causes the irreversible

transition of cellulose I to the thermodynamically more stable cellulose II.

Cellulose I fibers are characterized, in the dry state, by a greater breaking load resistance and, most of all, by a typical brightness and luster that are particularly appreciated in the textile field. On the contrary, mercerized cellulose fibers and fabrics are deprived of the beauty and resistance of natural materials. Nevertheless natural cellulose I fibers show a significant drawback, that is they lose much of their strength when wet. In fact the hydrogen bonds between hydroxyls of neighboring fibers, which are very strong in a dry state, are considerably weakened by water. This inconvenient can limit the applicability of natural fibers, especially in those fields in which a high breaking resistance, even in a wet state, is required. Furthermore another aspect of the same problem is represented by the low wet and dry crease resistance of some textiles made of cellulose I. In this case cellulose I micro fibers do not spontaneously recover the initial arrangement after washing and drying and, unavoidably, an additional ironing step is required in order to return to the original shape. This inconvenient is particularly relevant for flax fabrics.

With the aim to improve wet strength and crease recovery of raw cellulose materials, and optionally, to confer new additional advantageous properties, chemical treatments are usually performed on natural fibers.

In this context, alkylation reactions to form stable ether bonds are suitable for the preparation of new products, as required, for instance, in the textile industry or in the field of ion-exchange resins. The known processes for preparing cellulose ethers are generally carried out in two steps, with the preparation of the "alkali cellulose" followed by etherification as shown by *Figure 1*. Alkali cellulose is initially prepared by mixing cellulose with water and alkali metal hydroxides in suitable industrial units. The etherification stage is usually carried out by reacting the alkali cellulose produced in the first stage together with an etherifying agent. However the strong initial treatment with aqueous alkali unavoidably compromises the crystalline structure of native cellulose that changes from allomorph I to allomorph II, in addition to a decrease of the crystallinity index (CrI) from 57 % (allomorph I, native form) to 45 %.

The final objective of the present work was to prepare etherified new flax materials. In particular the starting cellulose materials used are flax slivers and yarns. Linen fabrics mainly made by native cellulose I is characterized by high resistance, unique beauty and freshness. As all these properties have to be maintained, the first step was to prepare native cellulose ethers in heterogeneous reaction media without inducing mercerization of cellulose fibers that means maintenance of the allomorph I status and preservation of the crystallinity index. That was possible when the flax fibers were exposed to basic media solubilized in different organic solvents during the preparation of the "alkali cellulose" as shown in *Figure 2*.

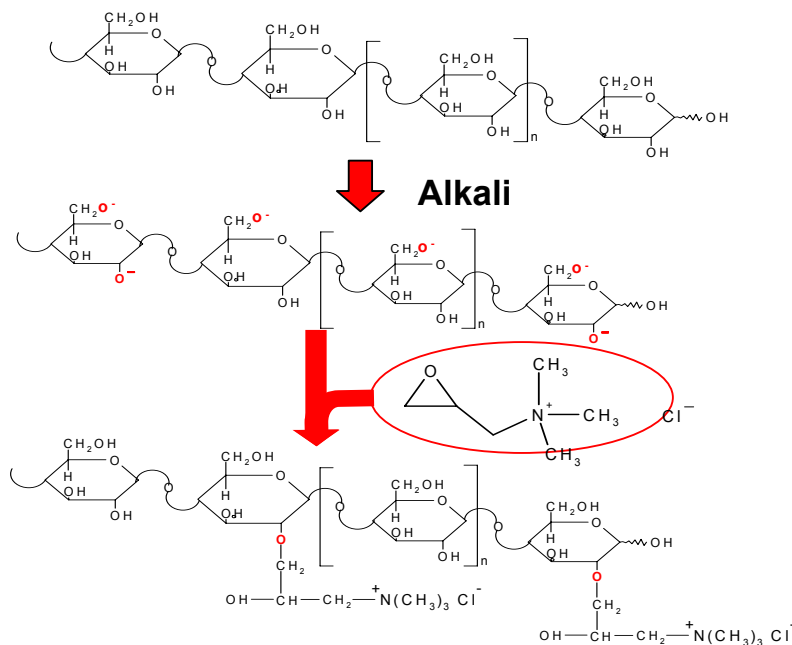


Figure 1 - Reaction scheme. Activation in basic media to obtain an alkoxy cellulose intermediate. The activated alkoxy cellulose was derivatized by alkyl substituents. The scheme shows the reaction with glycidyl trimethyl ammonium chloride.

The activation step influenced the material property; both a mild/midway basic treatment and/or a solvent effect induced a solubilization of hemicelluloses, and produced an increase of the homogeneity of the sample as confirmed by T_{1H} NMR relaxation values. The only activation led to more or less rigid structure compared with the untreated cellulose fibers as demonstrated by solid-state NMR relaxation measurements. Breaking-load resistances decreased in comparison to the starting material while CrI remained unchanged (56-57 %).

Etherification reaction of the activated alkoxy cellulose with *glycidyltrimethylammonium chloride* provided *cationic flax*, shown in *Figure 1*; it induces further mobility at the cellulose I backbone as shown by NMR spectra and related data, causes a breaking-load resistance similar to the alkali cellulose and maintains CrI (56-57 %).

Cross-linking reactions represents a particular example of etherification process. Such reactions, by linking together hydroxyl groups of different cellulose chains with strong covalent bonds instead of weak hydrogen bonds, can improve several

properties of the final products, such as wet strength or crease resistance. According to the presented activation method, reactions with *epichlorohydrin* or with *polypropylenglycol (diglycidylether)* provided **cross-linked flax** without altering the initial crystalline state, the loss of solubility in cuproethylendiamine (Cued - cellulose system solvent) and a significant solubility reduction in DMAc/LiCl respect to the untreated cellulose fibers. The loss of the solubility in Cued, as well as the reduction of solubility in DMAc/LiCl, that represents the stronger specific cellulose solvent, indicates the presence of cross-linking between the cellulose chains, which are stable to the strong basic conditions of Cued.

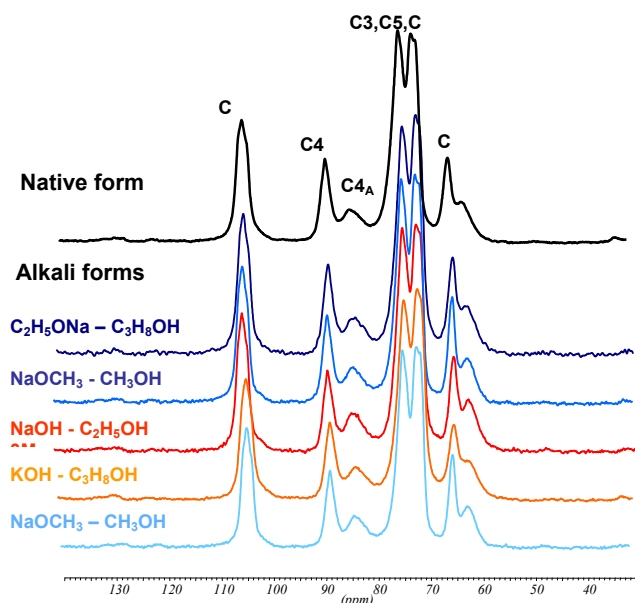


Figure 2: ^{13}C NMR CP-MAS spectra of flax cellulose after alkaline treatment in different conditions and following washing.

The presented **new modified flax materials** maintain resistance values (g/tex) similar to the starting materials and show a higher stiffness, evaluated from tensile Young Modulus (N/tex), which should improve the spontaneous recovery to the initial arrangement of the cellulose fibers. This should affect the capability of recover creases: measurements of crease recovery after folding linen slivers and yarns in a controlled way were performed, and the effect of reaction was found to be an increase in the total crease recovery, up to 35% respect to the parent flax fibers, due mainly to an immediate (elastic) recovery, and partly to a recovery occurring over time.