

## NEW FLAX YARN CROSS-LINKED WITH CITRIC ACID BY THERMAL TREATMENT OR BY MICROWAVE IRRADIATION

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Industrial flax yarn can be successfully cross-linked with citric acid by thermal treatment or by microwave irradiation. Both the methods were applied to an industrial yarn, exactly as it is produced and commercialized. Treatments were run on 100-200 g of yarn spun on polypropylene cones, i.e. common industrial textile supports. The proposed cross-linking of flax cellulose with citric acid affords a new cross-linked flax yarn, ready to produce new materials of industrial applications, in relationship to the introduced cross-linkage. The new yarn maintains the morphology of the fiber and the textile potentiality of the flax itself and moreover it can be further modified, due to the presence of the citric acid functional group.

The bond between cellulose and citric acid is an ester bond, of general interest for polysaccharides. Nevertheless, this bond is critical for the textiles, as it can be broken by high temperature and hydrolyzed in basic media, typical of washing operations. In this context, esterification with polycarboxylic acids like citric acid was found to afford cross-linked cellulose more resistant to heating and basic media. Figure 1 shows how a molecule of citric acid cross-links two cellulose chains preserving a free carboxylic acid group that can partially neutralize a basic medium or undergo transesterification to repair a broken ester bond.

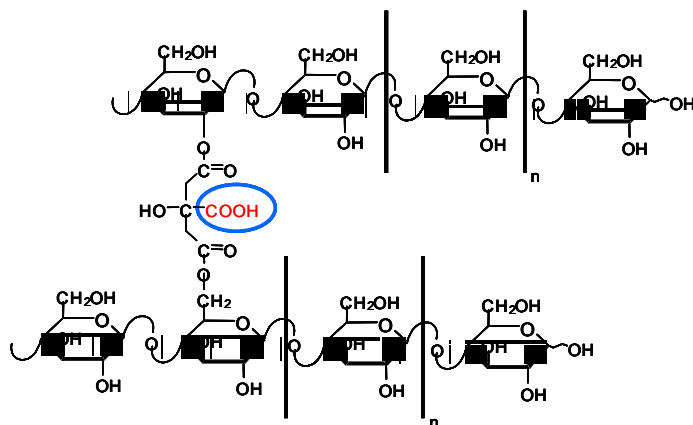
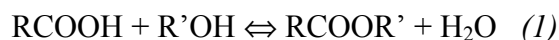


Figure 1. Cellulose chains cross-linked with citric acid.

From a chemical point of view, the formation of an ester bond between an acid and an alcohol is an equilibrium reaction (*Eq. 1*). Both thermal treatment and microwave irradiation of yarn previously impregnated in a water solution of citric acid monosodium salt diverted the equilibrium towards the ester form via water molecule elimination.



For the investigated methods different reaction conditions on a laboratory scale were checked, like citric acid concentration, time of treatment and, above all, the temperature, on one hand, and the microwave power, on the other. Yarns of apparent DS of 0,1-0,2 were thus prepared. Two preparations on the scale of kilograms were setted on the basis of these results. Thermal treatment A afforded yarn named A and microwave irradiation B respectively afforded yarn named B, see Schemes 1 and 2. As concerns thermal treatment, a semi-industrial finish bath at forced circulation (maximum number of 1 Kg cones = 100) has been successfully employed to obtain an equal distribution of the cross-linking agent and as a consequence a homogeneous derivatization. Single cones, impregnated in a simple vat with the same finish solution, have been treated in a commercial multimode oven working at a 2,45 GHz. Beside electromagnetic irradiation, heating with a fluxed warm air has been associated, to remove the steam produced by the microwave irradiation and to make the thermal profile homogeneous.

Gravimetric analysis of A and B verified that the esterification occurred. Samples of the new materials A and B have been characterized by NMR spectroscopy (solid state  $^{13}\text{C}$  CP MAS) and by FTIR spectroscopy. Noteworthy, NMR spectra showed that the derivatization does not alter the morphology of flax. FTIR spectra exhibited a peak at  $1730\text{-}1750\text{ cm}^{-1}$ , due to the new ester bond, see Figure 2. The area of the ester band was normalized with respect to the characteristic cellulose band ranging from  $780\text{ to }465\text{ cm}^{-1}$  ( $A_n = \text{area}_{\text{N(ester)}} = \text{area}_{\text{ester}}/\text{area}_{\text{cellulose}}$ ), the resulting  $A_n$  value being prop

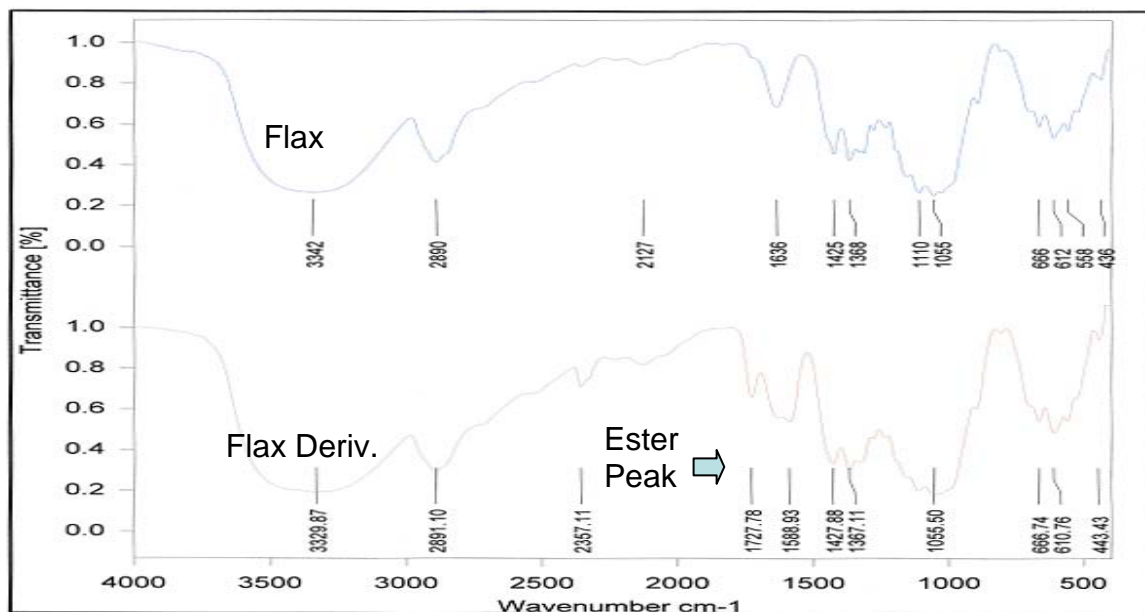


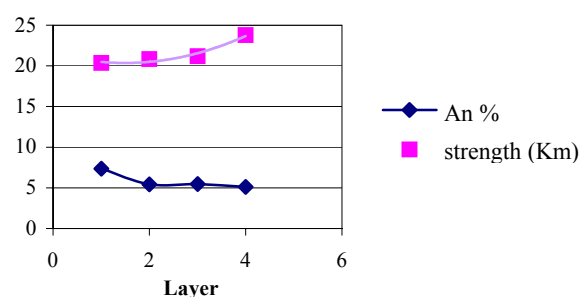
Figure 2. FTIR spectra of flax yarn.

Determinations of the conductivity of free COOH, providing  $DS_{apt}$ , and determinations of  $A_n$  were run on a set of different cross-linked flax samples produced on a laboratory scale. These measures allowed to build up a calibration line of  $DS_{apt}$  versus  $A_n$ ,  $DS = 0,0211 \times A_n \% + 0,0186$  ( $R^2 = 0,9642$ ) that makes absolute the FTIR analysis. Single cones of yarn A and B were divided into layers that were separately analyzed by FTIR, as shown in in Graphics 1 and 2. The derivatisation appears quite homogeneous and similar with the two methods, an average  $DS_{apt}$  of 0,14 being evaluated for A and of 0,15 respectively for B. Noteworthy, microwaves needed shorter times than heating to reach the same DS.

### Thermal treatment A

- Impregnation in H<sub>2</sub>O sol. of 10% w/v citric acid, weight increase 200% , maximum  $DS_{apt} = 0,3$ .
- Activation in stove at 90 °C, 1h.
- Cross-linking at 130 °C, 1h in forced circulation stove.

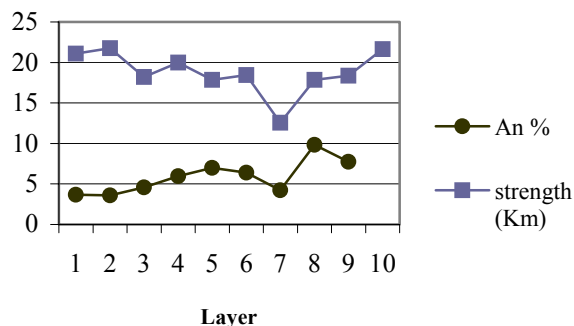
Graphic 1. Characterization of A



### Thermal treatment B

- Impregnation in H<sub>2</sub>O sol. of 20% w/v citric acid
- Manual Centrifugation, weight increase 100% , maximum  $DS_{apt} = 0,3$ .
- Treatment in comm. multimode oven 2,45 GHz, P 650 W , fluxed warm air 125°C, 10 minutes.

Graphic 2. Characterization of B



appears quite homogeneous and similar with the two methods, an average  $DS_{apt}$  of 0,14 being evaluated for A and of 0,15 respectively for B. Noteworthy, microwaves needed shorter times than heating to reach the same DS.

Layer strengths were also measured. The thermal treatment maintains the strength better the microwave irradiation. A reasonable lower limit is 20Km to weave, being the strength of the starting yarn is around 26Km. Layer 7B is clearly an accident due to a visible local combustion. The presented results suggest that both the proposed methods can be transferred on an industrial scale, through a scale-up setted on the basis of their intrinsic potentiality and on the basis of their specific results obtained for this application.