Innovative eco-dyed composites obtained by inclusion procedure

D. Coman[1], N. Vrînceanu[1], S. Oancea[2]

[1] Department of Industrial Machinery and Equipment, "Lucian Blaga" University of Sibiu, Romania
[2]Department of Agricultural Sciences and Food Engineering, "Lucian Blaga" University of Sibiu, Romania
E-mail: diana.coman@ulbsibiu.ro

Key words

Inclusion method, black cherry extract, adsorption attributes, fastness evaluation, abrasion resistance.

1. Introduction

Micro-encapsulation/inclusion is an upcoming technology that textile manufacturers are looking to keep ahead of the competition and challenged to find innovative materials that provide benefits The encapsulation and enclosing techniques are used in wide range of features, including medical and cosmeto-textiles, phase change materials, thermochromic and photochromic dyes, antimicrobial and deodorizing finishes, flame retardant finishes, chemical protection, etc [1, 5, 6].

The rationale of our research was the idea that textile coloration should be performed according to environmental standards, as well as finding of some sustainable solutions in terms of dyeing stability when using natural extracts.

There are a lot methods to improve dyeing properties of cellulosic supports:

- the given cationic or positively charged ions;
- the addition of quaternary ammonium groups. Fibers modified in this manner provide significantly stronger attraction for anionic dyestuffs;
- corona plasma technology.

As an ecological safe option/alternative to metallic salts, which very much modify the colour, the fibre cross linking with polycarboxylic acids can be used to improve certain properties of textile products, including wet tensile and compressive strength. The mordanting with citric acid as a assist bio-mordant is recommended [9].

Cyclodextrins are natural molecules derived from starch that have a remarkable capacity to form inclusion complexes (microencapsulation) in solution or in solid state with organic molecules, especially aromatics, through host/guest interaction. There are a lot of studies, demonstrating their role of textile finishing agents, being grafted onto flax fabrics. Previous researches assumed that the sorption mechanism combines the inclusion complex formation resulting from the presence of MCT-ß-CD but also from physicochemical interactions [3, 6].

Consequently, our present work combines/uses the efficiency of the two promoters of a stable and sustainable natural dyeing with black cherry extract, meaning: CA and MCT-ß-CD. It was assumed that citric acid (CA) could crosslink the cellulosic fibres by inducing the self-catalysed esterification of cellulosic hydroxyl groups. Besides it consolidates the bond between natural dye and fiber.

On the other hand, using cyclodextrins as an alternative to standard dyeing, since they possess a hydrophobic cavity in which a number of chemicals can form inclusion complexes.

Due to this aspect, the novelty of our study consists in the durability of natural textile dyeing given the enclosing technique by an inclusion complex.

In terms of methodology, the textile material was dyed using two different paths: dyeing by encapsulation/inclusion of dye into the CD molecule used as grafting agent for flax fibre and classic dyeing using as mordant citric acid. The same authors have previously investigated the use of black cherry extract, resulting positive values of abrasion strength, the selected extract being rich in anthocyanins which are plant pigments known for their dyeing properties [2].

2. Experimental details

2.1. Pretreatment of fabrics (flax fabric grafting), dye extraction and dyeing procedures

The experimental protocol of grafting (impregnation-squeezing-drying-curing) consisted in the following stages: curing in an exicator for 24 hours; preparation of impregnation bath having a 100 g/l concentration of MCT-ß-CD of and 50 g/l for Na_2CO_3; containing 30 g/l of MCT-β-cyclodextrin; drying at room temperature for 12 hours; curing at 90÷170°C for different periods of time (1÷15 minutes), for grafting

Table 1. The variants of flax fabric samples for experimental investigation.

Samples name	Description
Flax textile supports	
F	Reference flax fibers support (without MCT-ß-cyclodextrin)
F –MCT-ß-cyclodextrin	Flax fibers support functionalized with MCT- ß-cyclodextrin
1	Non-functionalized flax fibers support dyed with 1% solution of black cherry natural extract
2	Functionalized flax fibers support with MCT-ß-cyclodextrin dyed with 1% solution of black cherry natural extract
3	Flax fibers support dyed with 1% solution of black cherry natural extract without mordant
4	Flax fibers support dyed with 1% solution of black cherry natural extract and mordant

performing; washing with tap hot and cold distilled water, up to pH=6.5-7; air drying.

Anthocyanins were extracted conventionally using 0.1 % HCl acidified ethanol 80 % solution, at 4 °C overnight. The ratio of total anthocyanins content/amount of fruit used was 95.93 mg 100^{-1} g fresh mass.

The flax fabrics were dyed with black cherry anthocyanin extract, by exhaustion method meaning an immersing of the fabric in dye bath for about 30 minutes at 60°C. After dyeing, the dyed textile material was washed with cold water and dried at room temperature. Dyes are applied in alkaline pH 11-12 at higher temperature like 80-90°C having ML ratio 1:20 for 60 to 90 minutes. After dyeing, the dyed samples are washed and soaping is carried out at 60°C for 15 minutes.

The research was focused onto a comparison, in terms of both the efficiency of the natural extract inclusion and stability of the performed treatments. For this reason/purpose, dyeing conditions for both the MCT-β-CD grafted samples and for those dyed with the assistance of a biomordant (Cytric Acid 3% w.p.), were identical.

3. Characterization methods

The phase and the microstructure of the samples were characterized by using scanning electron microscopy-EDX. Scanning Electron Microscope (SEM) images of the samples were obtained from a Quanta 200 3D Dual Beam type microscope, from FEI Holland, coupled at a EDS analysis system manufactured by EDAX - AMETEK Holland equipped with a SDD type detector (silicon drift detector). Taking into account the sample type, the analyses have been performed, using Low Vacuum working mode, allowing the probes testing in their initial state, without a previous metallization (as in High Vacuum working type). Both for the acquisition of secondary electrons images (SE – secondary electrons) and EDS type elemental chemical analyses, LFD (Large Field Detector) type detector has been used, running at a pressure of 60 Pa in working room, and a voltage of 30 kV.

Sorption measurement/humidity sorption/desorption were performed by N_2 adsorption-desorption isotherms. Porosity and surface area studies were performed on a NOVA 2200e system, using nitrogen as an absorbate at liquid nitrogen temperature (-196 °C). All the samples were out gassed under vacuum, for 6 hours at 25 °C before adsorption measurements. The surface area was calculated using the BET method in the relative pressure range of 0.05-0.35. Pore volume was calculated at the relative pressure of 0.95. Pore size distributions were calculated from the desorption branches of the N_2 adsorption isotherms, using the Barett-Joyner-Halenda (BJH) model.

FT-IR spectroscopy was used to examine changes in the molecular structures of the samples. Analysis has been recorded on a FTIR JASCO 660+ spectrometer. The analysis of studied samples was performed at 2 cm^{-1} resolution in transmission mode. Typically, 64 scans were signal averaged to reduce spectral noise.

The abrasion strength was performed on a NU-Martindale Abrasion Tester according to SR EN ISO 12947-1:2002 Textiles - Determination of the abrasion resistance of fabrics by the Martindale method - Part 1: Martindale abrasion testing apparatus. Colour fastness properties were evalueted with the grey scale. The dry and wet rubbing was made according to SR EN ISO 105- X12:2003, using a 760 Crockmaster equipment.

4. Results and discussion

The SEM images below (Fig. 1) belong to flax support, non-functionalized (non-grafted), under different magnifications.

The differences between the reference sample and the samples dyed with the assistance of the two promoters CA, as mordant, and MCT-β-CD as cavity for inclusion complex are notable.

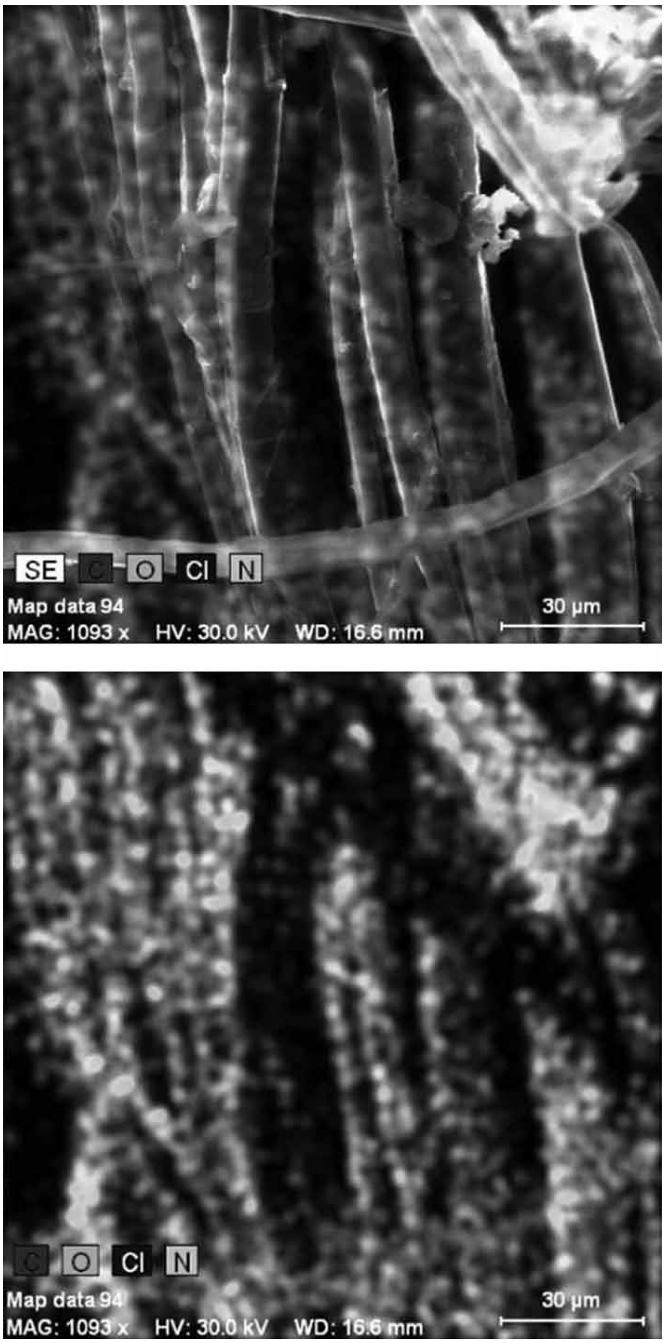

Figure 1. SEM/EDX images at X 1090 magnification for: F- reference flax support; F-MCT-β-CD grafted (functionalized) flax support.

The morphology of surface in case of the grafted sample dyed with natural extract is more consistent than that belonging to sample dyed in the presence of CA (Fig. 2). In addition, according to the SEM images, the uniformity of the MCT-β-CD grafted sample and dyed with natural extract, is better than that of sample dyed with the assistance of citric acid.

Here the SEM results showed that the convolution of the flax fiber surface was smooth and there was no distinguishable physical modification of the surface.

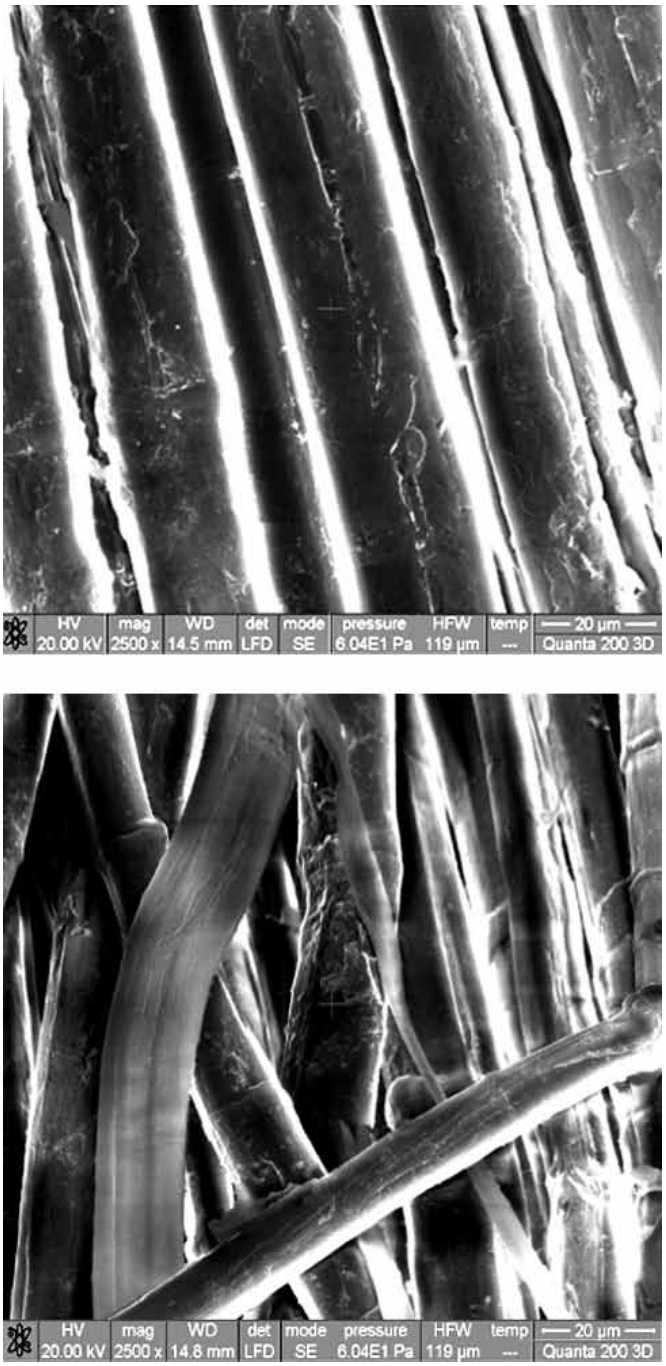

Figure 2. SEM images at X 2500 magnification for: 3- flax fabric dyed with 1% black cherry extract by exhaustion, without mordant; 4- flax fabric dyed with 1% black cherry extract by exhaustion, with mordant.

The fact that a certain inclusion compound was obtained was confirmed by comparing the FTIR spectra recorded for flax support with those grafted with MCT-β-CD and for the sample naturally dyed with mordant.

As shown in the FTIR spectra (Fig. 3), there are some specific absorption bands: for MCT-β-CD (monochlorotriazinyl - β - cyclodextrin), the absorption bands between 1000 and 1200 cm^{-1} are ascribed to the – C –O– stretching on polysaccharide skeleton. The peaks at 1420 and 1610 cm^{-1} correspond to the symmetrical and asymmetrical stretching vibrations of the carboxylate groups [7].

The peak at 2920 cm^{-1} was ascribed to C–H stretching associated with the ring methane hydrogen atoms. Due to the wide distribution of hydrogen-bonded hydroxyl groups, a broad band centered at 3450 cm^{-1} was noticed.

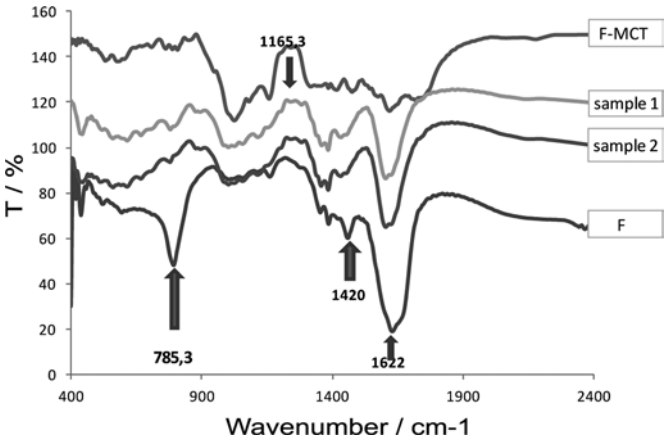

Figure 3. FT-IR spectra for flax fibers supports (functionalized and non-functionalized) dyed with black cherry extract dye.

In Figure 4, the spectrum ascribed to sample dyed with the assistance of citric acid solution has a stretching band at 1625 cm^{-1} attributed to the C=O in the dissociated carboxylic acid, while it is 1730 cm^{-1} when not dissociated [8].

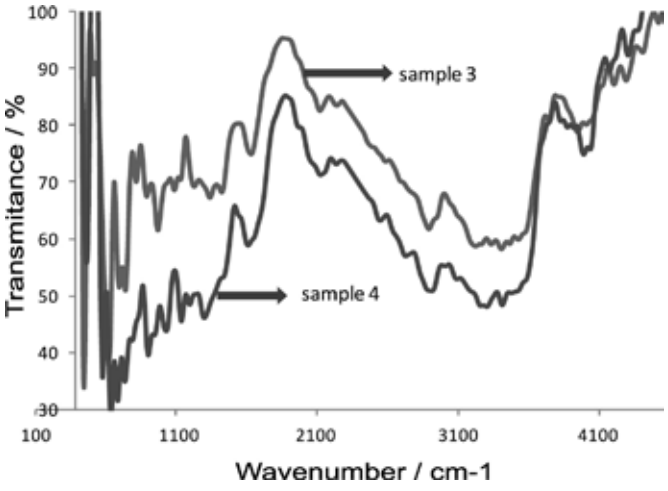

Figure 4. FT-IR spectra for flax fibers supports dyed with black cherry extract, without the assistance of mordant / in the presence of the mordant.

To elucidate this behavior we refer to the isotherms presented in Figure 5. The isotherm alure of the inclusion compound reveals a small contributions of micropores for N_2 adsorption, demonstrating the fact that dye molecules are located inside of the inclusion complex micropores. Knowing that the attraction between the hydrophobic parts of MCT-ß-CD and dye molecules is due to the sorption mechanism combining the presence of MCT-ß-CD but also from physicochemical interactions in the micropores.

Figure 5 revealed an IUPAC IV type isotherm characteristic of the porous adsorbers, showing the so-called capillary condensation phenomenon [4].

The inset presents the pore distribution calculus indicating some mesopores, whose radius is 6.22 nm for MCT-β-cyclodextrin and 5.88 nm radius for dye pore, respectively. In

the domain of partial pressure values higher than p/p0 >0.5, the isotherm unveils the appearance of an H3 type hysteresis, indicating the existence of pores with a relatively even distribution.

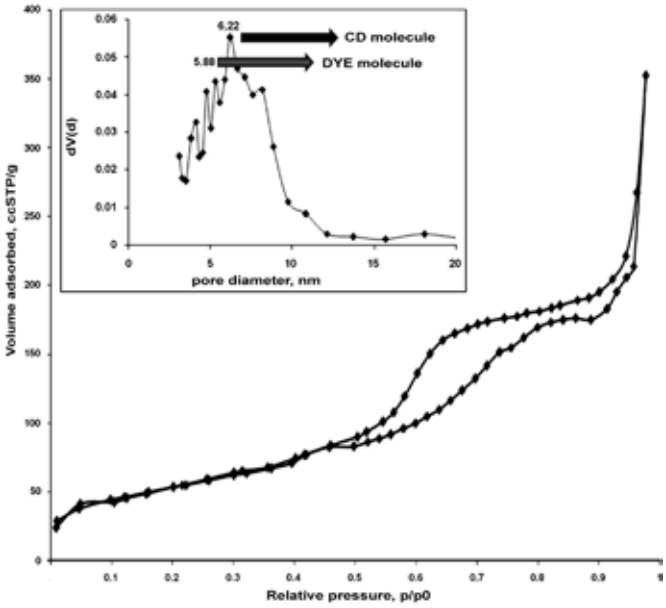

Figure 5. The N_2 adsorption/desorption isotherms of the complex compound obtained by inclusion black cherry extract in MCT-β-cyclodextrin-as host molecule.

The use of citric acid in the dyeing of flax fabric with black cherry extract gave good and moderate fastness values as given in Table 2.

Table 2. The fastness values of flax composites dyed with black cherry extract.

Textile sample	Dry and wet rubbing fastness		Washing fastness	Abrasion resistance	
				control	abraded
F	2	1-2	2	5	3
F/MCT-ß-cyclodexrin	3-4	3	2-3	5	3-4
1	4	3	3	5	3-4
2	4-5	4	3-4	5	4-5
3	4	3	3	5	3-4
4	4	3-4	3	5	3-4

To obtain stable shades with acceptable colorfastness behavior the inclusion method is compulsory. Abrasion resistance testing was performed for determining the color resistance of samples before and after dyeing treatment.

5. Conclusions

Earlier studies demonstrated the benefits provided by the assistance of polycarboxylic acids in dyeing, due to their capacity to improve certain properties of textile products, including wet tensile and compressive strength, but the most important is their ability to consolidate the bond between natural dye and fiber.

The experimental results of the study revealed that the modified dyed flax fibers by inclusion technique can enhance the usual procedure for obtaining sustainable composites with better performances and durability, in terms of resistances to washing treatment, friction and abrasion.

The applied standard tests of wash, rubbing and abrasion fastness (shade change and staining) showed that black cherry extract dye was entrapped within the MCT-β-CD molecule. In light of this, and due to the results obtained by the previous studies, the dyeing method using enclosure of a natural dye in the MCT-ß-CD, could be a more promising way, because it can obtain textile products with enhanced fastness to washing treatment, friction and abrasion performance of composite scores and attributes, over the traditional mordant dyeing technique.

FTIR and BET isotherms of the flax fabrics–MCT-β-cyclodextrin-black cherry extract dye composite showed changes compared with the samples dyed with the assistance of CA, as well as a greater stability of host-guest complex consisting in anthocyanins embedded in MCT-β-cyclodextrin, with high efficiency in natural textile dyeing procedure, which make the method feasible from an industrial perspective.

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