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Review Article

Surface Treatment Effects of the Knitted Cotton Textile Pre-Forms in All-Cellulose Composites

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Abstract

The aim of this paper is to report the surface treatment effects of the knitted cotton textile preforms on the behavior of all-cellulose cotton composites. Surface modified knitted cotton pre-forms were used for preparation of so called all-cellulose bio-composites by using a fiber surface dissolution method in lithium chloride dissolved in N,N-dimethylacetamide (LiCl/DMAc). The main advantages of the obtained all-cellulose composites are the facts that being fully bio-based and biodegradable, they meet the needs of green transformation and are at the same time fully bio based, easily recyclable and biodegradable.

Cotton fiber surface was modified with two different methods: (i) alkaline scouring with bleaching and (ii) enzymatic scouring with acid and alkaline pectinases followed with bleaching. The mechanical properties of the obtained all-cellulose cotton based bio-composites were characterized through tensile test measurements. The composite morphology was observed by using scanning electron microscopy. Better effects and higher mechanical strength was measured for the all-cellulose composites based on enzymatic scoured and subsequently bleached knitted cotton fabrics.

Keywords: All-cellulose composites; Kknits; Cotton pre-forms

Introduction

Last decades, due to the enlarged efforts for sustainable development, the interest for eco-composites reinforced with natural fibers remarkably was increased [1-4]. Compared to the conventional technical fibers usually used as an reinforcements of the composite materials, Natural Fibers (NF) have demonstrate several advantages such as very good price/performance ratio, low density, non-toxicity, recyclability, renewability and biodegradability. It was shown that natural fiber reinforcements can be divided into three main groups: vegetables (based on cellulose), animals (based on proteins such as wool and silk) and mineral fibers (mainly based on silica sand) [4]. Furthermore, vegetable fibers were classified by the part from they were formed such as bast fibers (jute, flax, hemp), leaf fibers (sisal, manila hemp) and seed and fruit fibers (seed-hairs and flosses cotton). Application of natural fibers in polymer eco-composites is growing continuously every day [5]. One of the biggest sector is their application in the automobile industry where natural fiber reinforced eco-composites are incorporated in door panels, trunk trims and many other interior parts [6,7]. Usually NF was combined with both polymer matrices, thermoplastic and thermosets. One of the types of the developed eco-composites are so called All-Cellulose Composites (ACCs). Primary, the concept of “All-Cellulose Composites” was promoted by Nishino and his co-workers [8]. They applied the natural fibers in the concept of “All-Polymer Composites” and designed new eco-composite based on mono-cellulose component with both functions, as the incorporated fiber reinforcement and the matrix [8,9]. In fact, all-cellulose composites were designed using the original concept of self-reinforced composites, developed for thermoplastic high density polyethylene and polypropylene “all-fiber composites” [9]. Ligno-cellulosic fibers were selected to be a single-constructive element of the all-cellulose composites since they belong to the group of renewable and biodegradable biopolymer resources with concurrent mechanical properties [4,5,8]. Among them, cotton fibers were representative material which contains all cellulose components (cellulose, hemicellulose, lignin, pectin) as well and non-cellulose components, waxes. It is known that cellulose is a polydisperse linear homopolymer, consisting of β-1,4-glycosidic linked D-glucopyranose units (so-called anhydro-glucose units). The cellulose polymer chain contains free hydroxyl groups (OH) at the C-2, C-3, and C-6 atoms. Based on the OH groups and the oxygen atoms of both the pyranose and the glycoside bond, ordered hydrogen bond networks form various types of supramolecular semi-crystalline structures. So, from the composite structural point of view, the reinforcing component was played by the spirally oriented cellulose fibrils, while the matrix was a soft hemi-cellulose and non-cellulosic components. In order to create the matrix phase,

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it was necessary to dissolve the cellulose and again to regenerate it because the cellulose does not exhibit a melting point. Physical structure of the natural cellulose fibers consists of several layers where the surface layer of the fibers can be partially dissolved and transformed into the composite matrix phase. On this way, composite structural phases, the fiber and matrix one, are of the same, chemically identical composition.

Literature review has shown that up to today, several methods were developed, but mainly, two methods (2-steps and 1step methods) were applied for ACCs processing [9,10,11]. In two-steps method, first step covered the part of cellulose dissolved in a solvent which is then, in the second step, regenerated in the presence of undissolved cellulose. In the one-step method, partial dissolution of the surface of cellulosic fibres proceeds and then regenerated in situ to form a matrix around the undissolved portion. Several types of solvent systems were used for dissolution, usually solvent mixtures: Lithium Chloride/N,N-dimethylacetamide (LiCl/DMAc), Dimethyl Sulfoxide (DMSO)/Tetrabutyl-ammonium fluoride, NH_3/NH_4SCN, NaOH/urea, ionic liquids, PEG/NaOH, *etc* [8,9,10,11].

Nishino *et al*. prepared the all-cellulose composites from pure cellulose and ramie fibers in LiCl/DMAc system [8]. The obtained ACCs, created by their method exhibited high mechanical properties due to the fact that this method overpassed the overheating of the fibers during the thermal processing. Gindl and Keckes worked on a special type of optically transparent all-cellulose composite from Microcrystalline Cellulose (MCC) using the method of partial dissolution of cellulose surface with the same solvent system of LiCl/DMAc [12]. These researchers designed also all-cellulose composite based on cellulose and Rice Husk by using ionic liquid, 1-N-butyl-3-methylimidazolithium chloride ([C4mim]/Cl-)) as processing medium [13]. The obtained results clearly confirmed that silica was evenly distributed, and silica content in ACCs increased with the Rice Husk loading. In addition, higher crystallinity and better mechanical properties were registered for this type of ACCs. Duchemin *et al*. analyzed the effect of processing parameters such as dissolution time and cellulose concentration on the crystallography of precipitated cellulose, in Microcrystalline Cellulose (MCC) based composites [14]. The obtained results of their work contributed to further understanding of the phase transformations that occurred during the formation of all-cellulose composites by partial dissolution. Shibata *et a*l. have compared ACCs based on cotton fabric with hinoki lumber – all wood composites [15]. They have used 1-butyl-3-methylimidazolium chloride (BMIM-Cl) for impregnation of cotton fabric and hinoki lumber.

Cotton fibers usually contain various natural non-cellulose impurities on its cuticle and primary wall that can provoke bad interface in ACCs. Because of that, in order to improve the surface absorbency, all of these natural impurities such as waxes, pectin's, proteins and other, should be removed. Generally, the common industrial method used for removing the non-cellulosic impurities was performed by the alkaline treatment of the cotton yarn. Cotton fibers were treated by sodium hydroxide solution in the presence of chelating agents and surfactants at a boiling temperature for one/or two hours. These working conditions contribute the waxes and fats to be saponify or emulsify, and to turn pectin into soluble sodium pectat, proteins into soluble sodium salts of different amino acids, solubilize the ash and dissolve hemicelluloses with low DP. The scoured cotton exhibited improved wettability, and almost completely removed cuticle and non-cellulosic components. On this way, applying various fiber surface pretreatments (alkaline or enzymatic), the fiber surface sorption capacity of the cotton fabrics was tailored to result in better mechanical and structural properties of the all-cellulose composites. For this purpose, an attempt was made to replace the conventional alkaline with enzymatic scouring. Also, several enzyme classes (cellulases, pectinases, lipases, proteases, and their mixtures) were tested. Research investigations confirmed that the best results were obtained with pectinases [16-18]. Mechanism of enzyme treatment was based on pectinases penetration on the cuticle through cracks or micro-pores digesting the pectin. In the same time the enzyme facilitated the partial removal of the cuticle components [19].

Useful results obtained for the all-cellulose composites based on cotton woven textile fabrics have encourage us to design and tested all-cellulose composites based on cotton knitted fabrics, also [20]. So, this paper reports the results of the analysis of the all-cellulose composites produced from 2D – cotton knitted textile preforms using the method of partial fiber surface dissolution in the solvent mixture of N.N-dimethylacetamide and Lithium chloride (LiCl/DMAc). In the same time, the effects of the various fiber-surface treatments, enzyme and alkaline scouring, on the composite structural performances were followed.

Experimental

Knitted textile preforms based on cotton fibers were used for preparation of all-cellulose composites using the method of a fiber surface dissolution in solvent system of Lithium Chloride and *N,N*-dimethylacetamide (LiCl/DMAc). Knitted cotton textile preforms of two-layers were mounted on the metal frame and bonded on the angles to avoid fabric deformation. Then the knitted preform was activated in acetone (2h) and then (with 3 wt/v cellulose concentrations) were immersed in 8 % wt/v LiCl/DMAc for the immersion time of 24 h in order to provide good impregnation of cotton textile pre-forms. After 24 h, the knitted cotton fabrics were washed with distilled water and hot-pressed between two Teflon sheets at 130°C for 20 min and allowed to cool down at room temperature alone.

Characteristic parameters of the cotton knitted fabrics used in this research are presented in Table 1.

Table 1: Characteristic parameters of the cotton knitted fabrics.

Knitted cotton preform	M $[g/m^2]$	d [mm]	Dh $[cm^{-1}]$	Dv $[cm^{-1}]$	D $[cm^{-2}]$
D-L 1:1	143.19	0.57	12.83	22.00	282.33

M–Mass per unit area $[g/m^2]$, d-thickness [mm], D-density $[cm^{-2}]$, Dh- course density $[cm^{-1}]$, Dv-wale density $[cm^{-}]$

Table 2: Maximum load and deformations for the all-cellulose composites based on cotton knitted pre-forms.

SAMPLE	Maximum load [N]	SD [N]	Deformation [%]	SD [%]
1. Control sample	49,8	6,2	111,5	8,2
2. Alkali treated	51,9	6,0	90,8	2,4
3. Alkali treated + bleaching	36,9	2,5	121,7	5,7
4. Enzyme treated (alkaline pectinase)	49,9	5,2	94,4	2,3
5. Enzyme treated (alkaline pectinase) + bleaching	54,5	2,9	100,0	6,3
6. Enzyme treated (acid pectinase)	58,4	7,4	97,8	5,6
7. Enzyme treated (acid pectinase) + bleaching	58,9	9,5	104,9	9,5

Table 3: Crystalline index of the studied all-cellulose composites based on cotton knitted pre-forms.

Sample	Treatment	CrI (A_{1430}/A_{898})
1	Control sample – untreated	3,7
2	Alkali treated	4,8
3	Alkali treated + bleaching	3,3
4	Enzyme treated (alkaline pectinase)	3,4
5	Enzyme treated (alkaline pectinase) + bleaching	2,6
6	Enzyme treated (acid pectinase)	2,9
7	Enzyme treated (acid pectinase) + bleaching	3,2

Conventional alkaline scouring was done in a bath with liquor ratio 50:1 with 3.2g/dm^3 NaOH, 1 g/dm^3 nonionic surfactant Kemonecer NI (Kemo-Croatia) as a wetting agent, and 2 g/dm^3 Cotoblanc HTD-N (CHT-Germany) at 100°C for 60 min. After scouring, the yarns were rinsed twice at 90°C for 10 min and several times with cold water to complete neutralization.

Alkaline pectinase scouring was done with 0.666 g BioPrep 3000L per kg material, 0.15g/dm^3 Na_3PO_4 (pH 9), 1 g/dm^3 nonionic surfactant Kemonecer NI (Kemo-Croatia) as wetting agent at 55°C for 30 min at Liquor Ratio (LR) 50:1. After that 0.4 g/dm^3 EDTA was added to the scouring bath and the temperature was raised to 90^{o}C for 15 min to stop the enzyme activity. Yarns were rinsed at 90°C 10 min, at 70°C 10 min and once with cold water [21].

Acid pectinase scouring was performed with 0.625g NS 29048 per kg material, in acetate buffer containing 0.5g/dm^3 CH_3COOH and 0.5 g/dm^3 CH_3COONa (pH 4), 1 g/dm^3 Kemonecer NI at 45°C for 30 min at LR 50:1. After that, 0.8 g/dm^3 EDTA was added and the temperature was raised to 90^{o}C for 15 min to stop the enzyme activity. Yarns were rinsed at 90°C for 10 min, at 70°C for 10 min and once with cold water [21].

Bleaching treatment was performed using the mixture of 8 ml/dm^3 H_2O_2 (30%), 3 g/dm^3 Na_2SiO_3, 1 ml/dm^3 NaOH (40%) at 80°C, 45 min, at LR 25:1. After the treatment, yarns were rinsed at 80°C for 10 min twice and several times with cold water to completely neutralization.

Characterization protocol included several techniques: SEM, FTIR-ATR and mechanical measurements. Composite morphology was followed by using the Scanning electron microscopy-SEM FEI QUANTA 200 FEG system. Mechanical measurements were assessed with a universal tensile tester INSTRON 5584 machine, at room temperature (sample size 10x600mm). The results were reported as the average value of at least six measurements. FTIR-ATR spectroscopy was used to characterize the structure of the cotton-based composites. FTIR-ATR spectra were recorded with a Perkin Elmer Paragon 500 analyzer, using 64 scans and a resolution of 2cm^{-1}.

Results and Discussion

Morphology of ACCs based on Cotton Knitted Fabrics

Structural changes and fiber surface morphology in the studied Cotton based knitted fabrics induced by different treatments, were observed by SEM. The obtained SEM microphotographs are shown in Figure 1. Figure 1a presents the control sample of untreated, raw cotton fiber surface with wave surface roughness due to the non-cellulose and wax components. With alkaline treatment these non-cellulose components were removed and fibrillated surface was obtained, shown in Figure 1b. Bleaching in combination with alkaline treatment caused severe surface fibrillations of the cellular structure and the ap

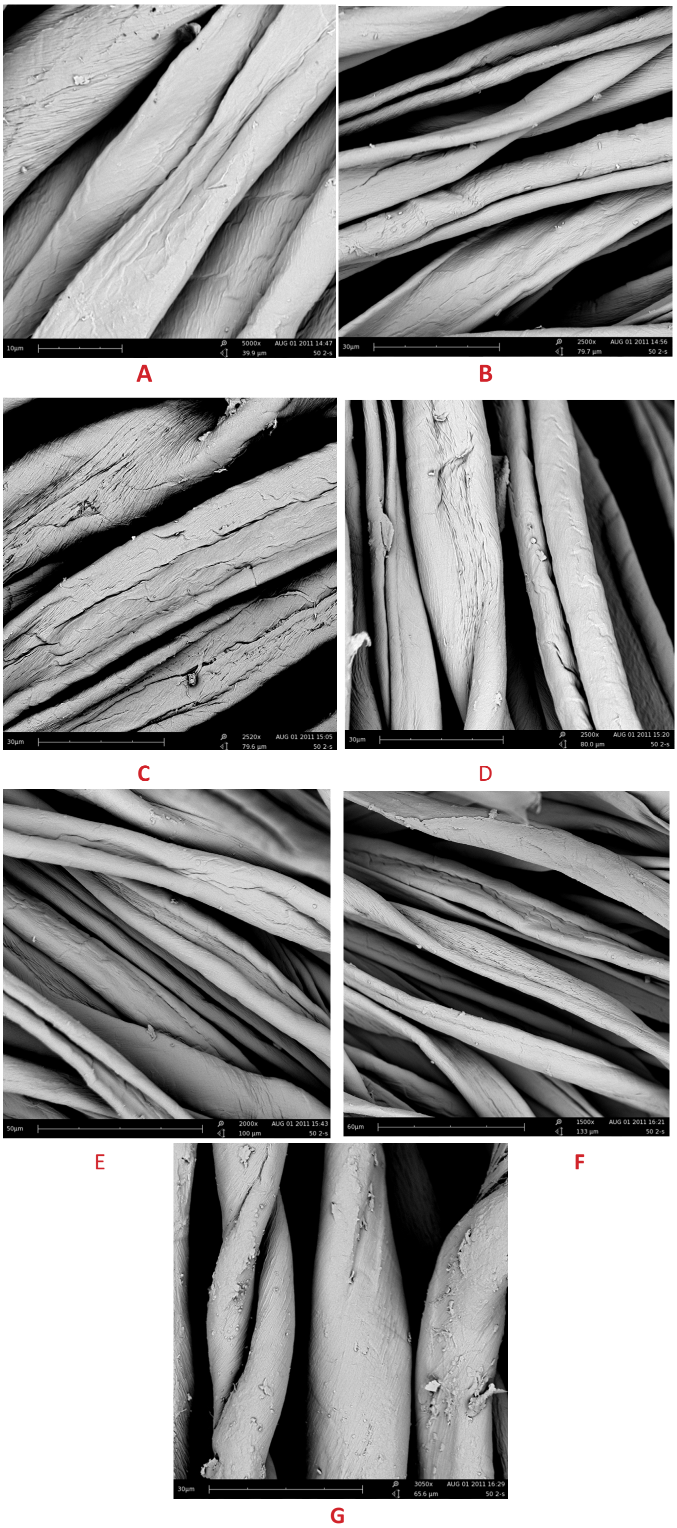

Figure 1: SEM microphotographs of various treated cotton based knitted fabrics.

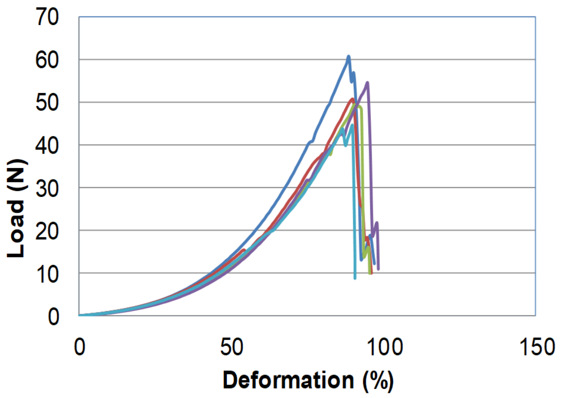

Figure 2a:

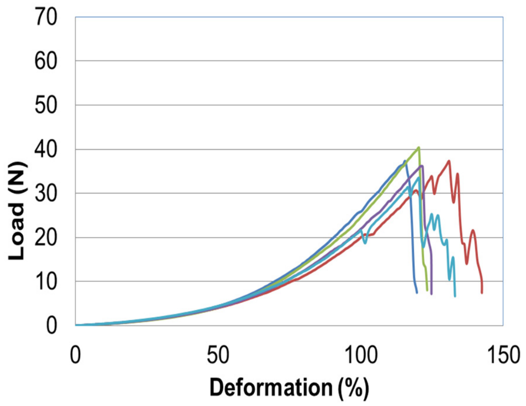

Figure 2b:

Figure 2: Stress-strain curves for alkaline treated cotton knitted preforms (2a- alkaline scoured, 2b- alkaline scoured and bleached).

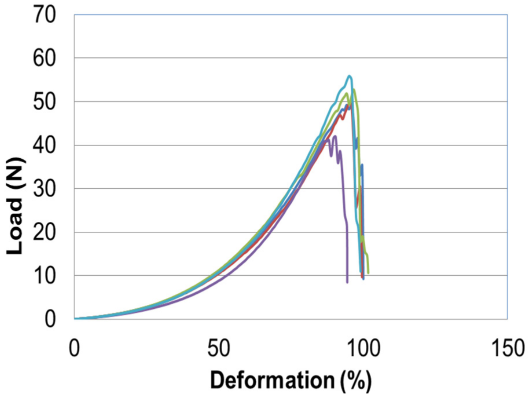

Figure 3a:

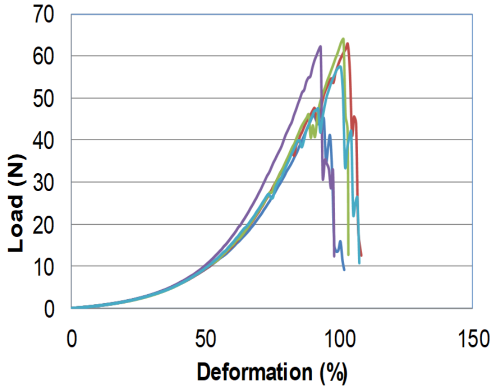

Figure 3b:

Figure 3: Stress-strain curves for enzyme treated cotton knitted preforms (3a- enzymatic scoured, 3b-enzyme scoured and bleached knitted fabrics).

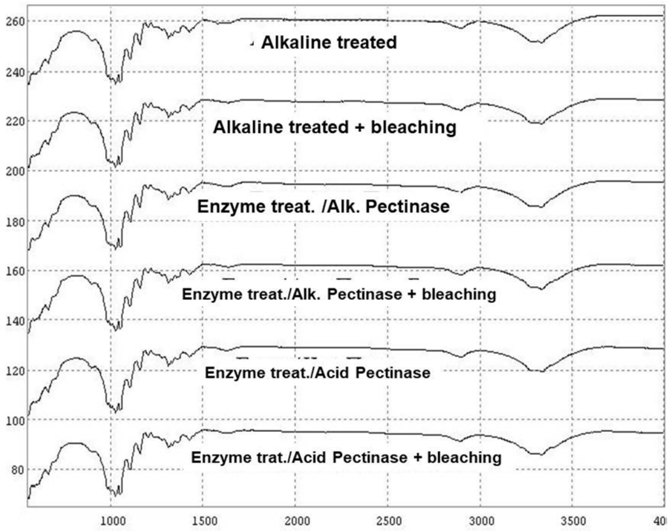

Figure 4: FTIR spectra of the ACCs based knitted - cotton fabrics.

pearance of thinning pores and cracks that can be seen in Figure 1c. As a result of the enzyme treatment (with alkaline and acid pectinase), cotton fiber surface became more smooth due to the substantial presence of the non-cellulosic components of the cuticle – Figure 1d and Figure 1e. Bleaching after enzyme treatment results in inter-fibrillar disintegration in the longitudinal direction of the cotton fibers – Figure 1f and Figure 1g. Besides the surface treatment with alkaline and enzyme media, SEM images of all treated fabrics have shown that the shape of the treated fibers was considerably kept.

The inter-fibrillation of the cellulosic cotton fibers contributed to the formation of the self-cellulosic composite and to the mechanical interlocking effect of the cotton fibers among two adjacent cellulosic layers. This effect, together with the effect on the surface swelling and impregnation of the cellulosic fibers, resulted in better mechanical performances of the all-cellulosic composite, up to 15%.

Mechanical Behavior of Knitted based All-Cellulose Cotton Composites

Characteristic stress-strain curves obtained for the prepared cotton based 2D-knitted all-cellulose composites, based on various pretreated cotton fabrics, are shown in Figure 2 (for alkaline scoured, Figure 2a and alkaline scoured and bleached knitted fabrics, Figure 2b) and Figure 3 (for enzymatic scoured, Figure 3a and for anzyme scoured and bleached knitted fabrics, Figure 3b). For each composite, 6 samples were tested and the obtained results were reported as the average value. The obtained data for the maximum load as well as for the deformations are given in Table 2.

Since all the analyzed knitted based ACCs - samples kept the integrity and compact forms, it was concluded that a dissolution time of 24 h lead to bio-based materials with good overall mechanical performances. Dissolution time of 24h is enough to provide dissolution of a sufficient amount of fiber surface (cuticle and part of primary wall) that will ensure good interfacial bonding among the cotton fibers. In the same time, a considerable amount of remaining fiber cores will be kept to provide a strong reinforcing effects to the composite. Actually, the structural base for the reinforcing role of the cotton fibers in this all-cellulose composites was based on the fact that the outer primary cellulosic wall mainly consists of unordered or poorly oriented crystalline cellulosic fibrils compared to the inner secondary and tertiary layers. Only less oriented thin outer layers of the fibers (that does not contribute much to the original fiber strength) were dissolved which profit of this selective surface dissolution process. Due to the transformation of less oriented fiber skin into an isotropic matrix phase, it was ensured that the highly crystalline fiber core will remain mainly unaffected and will result in a highly efficient reinforcing effect into the composites.

In order to select better fiber surface treatment, the obtained stress-strain curves were compared. Comparison of the stress-strain curves of ACCs based on alkaline scoured and bleached (max load ~ 40 N) cotton pre-forms and enzymatic scoured and bleached (max load ~ 60 N) cotton knitted fabrics clearly confirmed that the fiber surface treatments could effectively improve the mechanical strength of the composites. Enzymatic scouring was quite selective way for removing non-cellulosic components from the cuticle and it was resulted in the higher values for the mechanical strength of the all-cellulose composites based on enzymatic scoured cotton knitted textile pre-forms. Non-cellulosic components remained on the surface of enzymatic scoured cotton fibers to reduce the penetration of LiCl/DMAc solution into the secondary layer and to prevent cellulose dissolution and degradation on supramolecular structure. Due to this mechanism, 2D cotton based all-cellulose composites prepared with enzymatic scoured knitted cotton fabircs exhibited better mechanical properties than all-cellulose composite made from alkaline scoured cotton pre-form.

FTIR Analysis Results

FTIR spectra for the studied all-cellulose composites based on knitted cotton fabrics are shown in Figure 4. Evidently, there is no any remarkable difference. The obtained FTIR spectra were used for the calculation of the “Lateral crystalline index” which was obtained as a ratio of the FTIR bands at 1430cm^{-1} (CH$_2$ symmetric band) and 898 cm^{-1} (group C1frequency: -CH2=C-R), and it is presented in Table 3. The obtained data for the FTIR-crystalline index have shown that there were not registered remarkable changes in the crystalline structure of the produced cotton based composites. Very small changes of the crystalline structure of cellulose I was explained by the dissolution of only minimal amounts of cellulose. Comparison of the obtained values for the lateral crystalline index of the composites based on enzymatic and alkali scoured and bleached knitted cotton pre-forms has shown that higher lateral crystalline index was found in the composites based on alkali scoured knitted pre-forms. The same trend was registered also, for the lateral crystalline index calculated for the ACCs based on the woven cotton fabrics [15,20].

Conclusions

New type of all-cellulose composites based on cotton knitted textile fabrics were prepared using the method of a surface selective or partial dissolution of the cotton fibers. Fiber surface was treated with two different media: i) alkaline scouring with bleaching and ii) enzymatic scouring with acid and alkali pectinases combined with bleaching. It was found out that using the preparation method described in this work, the amount of outer layer of the fibers which was dissolved was enough to connect the remaining core fibers keeping them efficiently together. Due to this fact, a good interfacial bond and stress transfer in the obtained all-cellulose composites was obtained. Comparison of the two different media used for the surface treatment has shown that for alkali treated pre-forms progressive build-up of covering thermoplastic films around the fibers were found, while for the enzyme treated performs bonding bridges were registered between two fibers.

All-cellulose composites based on enzymatic scoured and bleached knitted cotton pre-form have better mechanical properties and unchanged crystallinity obtained by FTIR, The main advantages of the obtained all-cellulose composites are the facts that they are at the same time fully bio based, easily recyclable and biodegradable, still reasonable strong materials. The same trends were obtained and for the all-cellulose composites based on cotton – woven textile preforms.

Author Statements

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