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Electrokinetic properties of chemically modified jute fabrics

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Abstract: In this work, the electrokinetic properties of alkali and oxidatively modified jute fabrics were studied. In contrast to the control fabric, chemically modified jute fabrics had a small positive zeta potential in the basic pH range, which could be attributed to the presence of sodium cations (originating from the undertaken chemical modifications) on their surfaces. At lower pH values, the samples modified under milder alkali and oxidative conditions had about 2.2–3.5 times lower zeta potential since the protonation process led to the formation of a higher positive charge in the electrochemical double layer, causing higher adsorption of Cl⁻ (originating from the electrolyte). On the other hand, more intensive chemical modifications increased the zeta potential at lower pH values due to the increased amount of carboxyl groups and the ability of the fibres for water retention and hence swelling. The isoelectric point of the fabrics, having lower zeta potentials than that of the control fabric, was shifted towards higher pH values, indicating a lower contribution of surface acidic groups of the fabrics. In the case of extensive oxidation conditions (60 and 90 min), the isoelectric point was shifted toward lower pH values because of lignin removal and the mentioned higher availability of newly formed carboxyl groups.

Keywords: zeta potential; isoelectric point; hemicelluloses; lignin.

INTRODUCTION

In the past, jute fibres were considered as a source of raw material for the packaging industry but nowadays, they have emerged as a versatile raw material for diverse applications, such as household textiles, floor coverings, biobased composites, *etc.* To meet the worldwide demand for jute fibres, their production, processing and quality should be improved.

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Jute fibres are recognized by their complex structure and very heterogeneous chemical composition comprising of cellulose, hemicelluloses, lignin and other minor components. The main steps for the purification of jute fibres (*i.e.*, removal of non-cellulosic components) include the simplest, most direct, economical and efficient alkali and oxidative modifications. During these modifications, the selective removal of hemicelluloses and lignin in parallel with cellulose lateral swelling contributed to the liberation of elementary fibres, resulting in increased availability of surface functional groups.¹ The dissociation ability of these groups affects the distribution of the surface charge, as well as the thickness and distribution of the electrochemical double layer, altogether resulting in changed zeta potential and isoelectric point.² Accordingly, it could be stated that the alkali and oxidative modifications of raw jute fabric change its electrokinetic properties and alter its interaction with the components of the liquid phase. An extensive understanding of the electrokinetic properties of jute fabrics is still required to optimize the chemical modification processes, which might increase the utilization of such modified fabrics.

EXPERIMENTAL

Material

A raw jute fabric (in further text: control fabric or sample C) purchased from a commercial supplier was chemically modified with sodium hydroxide or sodium chlorite, as given in Fig. 1.

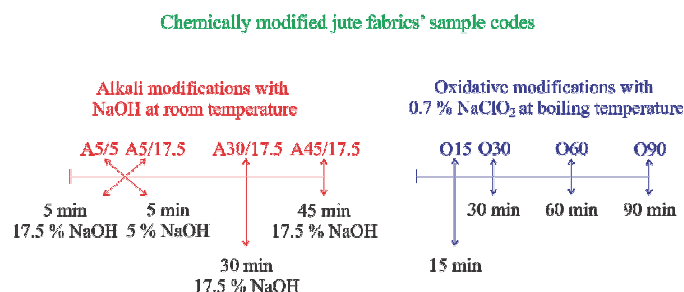


Fig. 1. Conditions for the chemical modifications of jute fabrics and the designation of the samples.

Characterization of the materials

Chemical composition of the jute fabrics. The chemical composition of the jute fabrics was determined according to a modified procedure described in the literature.³

Determination of the electrokinetic properties of the jute fabrics. The jute fabrics' electrokinetic properties, *i.e.*, the zeta potential (ζ) as a function of pH, were determined by a streaming potential method using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria), according to the procedure described by Lazić *et al.*⁴ Before the measurements, the samples were pre-swelled in distilled water to avoid the influence of fibre swelling on the zeta potential. Since the isoelectric point (IEP, the pH value where the value of ζ is 0) of jute fab-

rics is in the low pH region (*i.e.*, $\text{pH} < 3$), it was extrapolated from the experimental curve. Two measurements were performed for each sample, whereby the standard deviation was below 5 %.

RESULTS AND DISCUSSION

Chemical modification of jute fabric

The modification conditions shown in Fig. 1 were selected to obtain jute fabrics with different chemical compositions and to study their influence on the electrokinetic properties of the resulting fabrics.

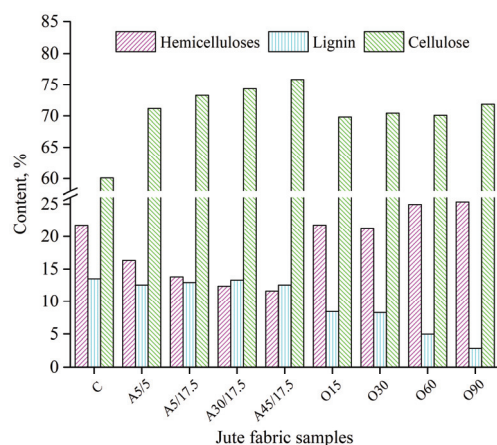


Fig. 2. Chemical composition of the jute fabrics.

By increasing the modification intensity (duration and/or concentration of the chemical agent), jute fabrics with gradually decreasing hemicellulose or lignin contents as well as increased cellulose content were obtained, Fig. 2. Namely, the alkali modifications decreased the hemicellulose content by 25–47 %, compared to the control jute fabric. Moreover, depending on the duration of the oxidative modification (15–90 min), jute fabrics with 38–79 % lower lignin content were obtained. A detailed discussion regarding the influence of the chemical modification conditions on the chemical composition and structure of jute fabrics is given in the literature.^{3,5}

Electrokinetic properties of chemically modified jute fabrics

The chemical modifications of the fabrics not only lead to changes in their chemical composition, structure, sorption, mechanical and electro-physical properties,^{3,5} but also change their electrokinetic properties, *i.e.*, surface charge of the fabrics. In this investigation, the measurement of the zeta potential was chosen to give valuable insight into the surface charge of the fabrics. In order to monitor the changes occurring on the surface of the fabrics (*i.e.*, the presence, availability and nature of surface groups) caused by chemical modifications, the zeta potential is measured over a wide pH range, Fig. 3. Furthermore, the pH

value where the smallest zeta potential was detected ($\text{pH}_{\zeta_{\min}}$), the minimum value of zeta potential (ζ_{\min}) and the isoelectric point (IEP) determined by extrapolation are given in Table I.

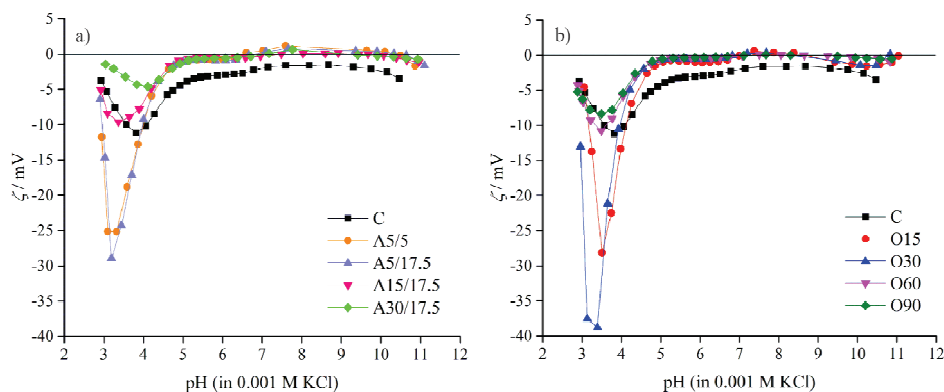


Fig. 3. Zeta potential (ζ) as a function of pH for control (C), alkali (a) and oxidatively modified jute fabrics (b).

TABLE I. pH Value where the smallest zeta potential was detected ($\text{pH}_{\zeta_{\min}}$), zeta potential minimum value (ζ_{\min}) and isoelectric point (IEP)

Sample code	$\text{pH}_{\zeta_{\min}}$	ζ_{\min} / mV	IEP
C	3.82	-11.17	2.52
A5/5	3.32	-25.16	2.84
A5/17.5	3.19	-28.93	2.83
A15/17.5	3.37	-9.60	2.44
A30/17.5	4.11	-4.61	2.67
O15	3.51	-28.11	2.98
O30	3.39	-38.79	2.74
O60	3.49	-10.76	2.46
O90	3.49	-8.34	2.24

The control jute fabric as other cellulosic materials has a negative zeta potential in the basic pH range ($\text{pH} > 7$, ζ_{plateau}) due to the presence of anionic functional groups (*i.e.*, hydroxyl and carboxyl) on its surface,⁶ Fig. 3. According to Hubbe *et al.*,⁷ these groups are prone to dissociation in the high pH range. In contrast, the chemically modified jute fabrics have a small positive zeta potential value in the mentioned region (ζ_{plateau}), which is probably caused by the presence of “strongly” adsorbed sodium cations (originating from the chemical modifications with NaOH or NaClO₂) on their surfaces.⁸

The applied chemical modifications increase the active surfaces of fabrics and the availability of their surface groups, which is characterized by a sudden change in the zeta potential of the fabrics at lower pH values (Fig. 3) and the $\text{pH}_{\zeta_{\min}}$ values are shifted towards lower pH values (excluding sample A30/17.5,

Table I), which may be a consequence of the protonation of acetyl or ether linkages in cellulose or lignin residues.⁹ Most remarkable decreases in the ζ_{\min} values (by 2.2–3.5 times) at lower pH values and in shifts in the $\text{pH}_{\zeta_{\min}}$ values toward lower pH values were noticed for the samples from which up to 36.6 % of the hemicelluloses (samples A5/5 and A5/17.5) and up to 38.8 % of the lignin (samples O15 and O30) had been removed, Figs. 2 and 3 and Table I. For these samples, protonation contributed to the formation of a higher positive charge in the electrochemical double layer, causing higher adsorption of Cl^- (originating from electrolyte), and therefore, resulting in a significant decrease in ζ_{\min} values at lower pH values.⁹ Change of the experimental curve shape in parallel with the decrease in ζ_{\min} value and simultaneously increased ζ_{plateau} were also reported for alkali modified jute⁸ and sisal⁹ fibres, as well as oxidized cotton² and flax⁴ fibres.

On the other hand, the removal of more than 36.6 % of the hemicelluloses (samples A15/17.5 and A30/17.5) and more than 38.8 % of the lignin (samples O60 and O90) increase the ζ_{\min} value by 4–59 % compared to that of the control sample. The alkali and oxidative chemical modifications increase the amount of carboxyl groups and the fibre ability for water retention and hence swelling,⁵ which together increase the ζ_{\min} value of the fabrics. The results are in accordance with the data reported for mercerized cotton in which the ζ_{\min} value increased due to the considerable increase in the available surface of the fibres caused by the intensive interfibrillar and intrafibrillar swelling of the fibres. It should be mentioned that in the case of sample A30/17.5 (the most intensive alkali modification conditions), the $\text{pH}_{\zeta_{\min}}$ was shifted toward higher values ($\text{pH}_{\zeta_{\min}}$ 4.11) compared to that of control fabric ($\text{pH}_{\zeta_{\min}}$ 3.82), indicating that the protonation process became more difficult.

The IEP, as an indicator for the nature of functional groups and surface charge of fabrics, was determined by extrapolation, Table I. The IEP shifted towards higher pH values for fabrics with a lower ζ_{\min} value than that of the control fabric (samples A5/5, A5/17.5, O15 and O30) as well as for sample A30/17.5, indicating to a lower contribution of the surface acidic groups of the fabrics. In the case of intensive oxidation conditions, the IEP was shifted towards lower pH values (from pH 2.52 for the control fabric to 2.46 and 2.24 for fabrics O60 and O90, respectively), which could be ascribed to selective lignin removal, *i.e.*, the formation of dicarboxylic groups and conversion of aldehyde to carboxyl groups during oxidations followed by the simultaneous increase in their availability.⁵ The IEP at pH 2.46 and 2.44 extrapolated for the samples O60 and A15/17.5, respectively, indicate that these samples had very similar surface chemistry, while the lower $\zeta_{\min}/\zeta_{\text{plateau}}$ value of fabric A15/17.5 reflects its higher swelling ability.

CONCLUSIONS

In this investigation, the effects of alkali and oxidative chemical modifications on the electrokinetic properties of jute fabrics were studied. The control fabric had a negative zeta potential in the basic pH range due to the presence of anionic functional groups on its surface, while the chemically modified fabrics has a small positive zeta potential in that region caused by the presence of sodium cations on their surfaces. The samples modified under milder conditions (5 % NaOH for 5 min, 17.5 % NaOH for 5 min and 0.7 % NaClO₂ for 15 and 30 min) had 2.2–3.5 times lower zeta potential at lower pH values; their isoelectric points were shifted toward higher pH values indicating a lower contribution of the surface acidic groups of the fabrics. In contrast, intensive oxidation conditions (0.7 % NaClO₂ for 60 and 90 min) increased the availability of newly formed carboxyl groups, which contributed to increased zeta potential at lower pH values and shifted the isoelectric point towards lower pH values.

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ИЗВОД

ЕЛЕКТРОКИНЕТИЧКА СВОЈСТВА ХЕМИЈСКИ МОДИФИКОВАНЕ ТКАНИНЕ ОД ЈУТЕ

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У овом раду испитивана су електрокинетичка својства алкално модификоване и оксидисане тканине од јуте. Супротно сировој тканини, хемијски модификоване тканине имају малу позитивну вредност зета потенцијала у базном подручју рН вредности, што може бити проузроковано присуством натријумових јона (који потичу из поменуте хемијске модификације) на површини тканине. При нижим рН вредностима, тканине модификоване при блажим алкалним и оксидативним условима имају око 2,2–3,5 пута мањи зета потенцијал што се може објаснити чињеницом да процес протонизације доводи до формирања већег позитивног наелектрисања у електрохемијском двојном слоју, што може да изазове повећану адсорпцију Cl⁻ (који потичу из електролита). С друге стране, интензивнији услови хемијског модификовања доводе до повећања зета потенцијала при нижим рН вредностима као резултат повећаног садржаја карбоксилних група и повећане способности влакана за задржавање воде, а самим тим и бубрење. Померање изоелектричне тачке ка вишим рН вредностима је запажено код тканина код којих је запажен мањи зета потенцијал у поређењу са сировом тканином, што указује на то да је допринос киселих група на површини тканина нижи. Код интензивнијих услова оксидације (у току 60 и 90 min), уочено је померање изоелектричне тачке ка нижој рН вредности због селективног уклањања лигнина, али и формирања нових карбоксилних група уз истовремено повећање њихове доступности.

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