A COMPARATIVE ANALYSIS OF ELECTROKINETIC AND DYEING PROPERTIES OF ACRYLIC ACID GRAFTED BAMBOO RAYON

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The grafting of acrylic acid (AA) onto bamboo rayon (BR) results in the introduction of carboxylic acid groups onto the fibre, which enhances its cationic dyeability. In the current study, the dye–fibre interaction of grafted bamboo rayon (AA-g-BR) with cationic dyes was studied based on electrokinetic phenomena. The effect of graft add-on (%) on the zeta potential and hence on the hydrophilicity of the fibre was explored. In order to predict the adsorption of the dye and its effect on zeta potential, zeta potential measurements were also carried out in the presence of cationic dye in the streaming solution. The grafted fibres were dyed and then evaluated for colour values and fastness properties. The results obtained clearly demonstrate a good correlation between the zeta potential changes and the dyeability imparted to the fibres, along with their fastness properties. A correlation was also found between the zeta potential of the fibre at various pH values and its dyeability.

Keywords:bamboo rayon, zeta potential, grafting, cationic dyeing

INTRODUCTION

Wet processing of textiles involves the application of a number of chemical solutions to textile fibres. The electrokinetic properties of textile substrates are of major importance as they are considered to be one of the controlling factors in the uptake of colorants, sizing agents, finishing chemicals *etc*., and hence it is necessary to investigate the influence of electrokinetic properties on the dye–fibre interactions. Zeta potential describes the electrokinetic properties at the solid/liquid interface, which is accessible for interactions. The electrokinetic properties of cellulose polymers are especially important, since these parameters very often reflect technologically relevant information regarding the interaction of textile substrates with the component elements of the liquid phase,includingions, enzymes, surfactants and dyes. The theory of zeta potential has been explained previously.[1,2] The factors affecting the zeta potential,such as pH and conductivity,have been also discussed.[3]

The surface of various fibres intended for textile and technical application may be characterized by their zeta potential. Zeta potential is an important factor that provides an insight into the nature and dissociation of functional groups, as well as hydrophilicity or hydrophobicity of the fibre surface, and it can be claimed as an important tool to describe the surface modifications obtained by various treatments on textile materials. The electrokinetic properties of textile fibres are widely studied by the researchers. Ripoll *et al*. investigated the electrokinetic properties of polymethyl methacrylate polymer nanoparticles-functionalized textile fabrics *via* streaming potential measurements as a function of various parameters, such as pH, salinity, nanoparticles adsorption and washing steps.[4] Measurements of zeta potential in the presence of dye in the streaming solution have been also reported.[5-6]

Giménez-Martín *et al*. studied the electrokinetic effect and surface free energy behavior in the adsorption process of a reactive dye (Remazol Brilliant Blue R, RBBR) onto leacril fabric pretreated with polyethyleneimine ion (PEI).[7] Espinosa-Jimenez *et al*. performed the electrokinetic and thermodynamic analyses of the dyeing process of polyamide fabric with Mordant

Black 17.[8] Janhom*et al*. reported adsorption studies of lac dye on cotton fibres pretreated with polyethyleneimine (PEI) and bovine serum albumin (BSA).[9]

Grafting is a process that modifies a polymer backbone by introducing side chains.Desired properties can be imparted by selecting the monomer for grafting and hence the side chain to be formed. Grafting of vinyl monomers onto natural polymers is a fascinating research area for the development of new polymers suitable for various industrial applications.[10-11]

Grafting of cellulose to impart dyeability and functional properties has been extensively studied by the researchers. However, very few attempts have been made to explain the modification of these carbohydrate based fibres in relation to their electrokinetic properties. Some reports regarding the electrokinetic properties of grafted synthetic fibres, such as polyester, are available in the literature. For example, Lokhande *et al*. studied the electrokinetic properties of acrylic acid- and methacrylic acid-grafted polypropylene.[12] The same research group reported on the electrokinetic properties of methacrylic acid- and acrylonitrile-grafted polypropylene fibres, as well as of acrylic acid and acrylonitrile-grafted polyester fibres, in the presence of cationic dyes.[13,14]

The prediction of the behavior of fibres during wet processing can be done when electrokinetic properties are well understood. The dye–fibre interaction can also be explored using such a study. The zeta potential values measured through the electrokinetic study can serve as an important tool for correlation the dyeing behaviour of fibre and the modification of the fibre through grafting. Grafting of acrylic acid onto bamboo rayon and its effect on cationic dyeability was reported earlier by our research group,[15] revealing a good correlation between graft add-on and dyeability. A study on the zeta potential of grafted bamboo rayon can explore the dye–fibre interactions that result in enhanced dyeability and fastness properties. Apart from this, the pH of dyeing can be a critical factor in dyeing such grafted fibre and it can be optimized to obtain the best pH conditions.

In the current study, grafted fibre samples were investigated with regard to their zeta potential at various pH values. In order to observe the changes in zeta potential after the dye adsorption onto the grafted substrates, the measurements were also carried out in the presence of the dye in a streaming solution. The fastness properties were also evaluated in order to assess the attachment of dye molecules to the modified bamboo rayon. In other words, the dyeability and dye–fibre interactions were explored through the electrokinetic analysis of the grafted bamboo rayon. This study can be extrapolated to the interaction of modified cellulosic materials (acrylic acid grafts) with cationic chemicals.

EXPERIMENTAL

Materials

AA-g-BR fibres with five different graft add-on levels were taken from our previous study.[15] All the chemicals used (acrylic acid, potassium persulphate, KCl, NaOH, HCl) were supplied by SD Fine Chemicals and were of laboratory grade. Cationic dye (Bismark Brown G) was supplied by Amritlal Chemicals.

Methods

Determination of zeta potential

Electrokinetic measurements were carried out using an Electrokinetic Analyzer (EKA) system (Anton Paar, Austria), based on the streaming potential, Fairbrother and Mastin method. The instrument was equipped with Ag electrodes coated with AgCl. Before mounting the samples in the cell, the samples were kept in an aqueous solution of 1mM KCl for 15 min. The samples were adjusted to give a pressure of 400 mbar at 35% flow rate, prior to the measurement. Pressure from 0 to 400 mbar was applied, for 2 min during the measurement. Measurements of ζ *versus* pH were performed in the pH range from 3 to 9 in a solution of 1mM KCl. The pH was adjusted to about 9 with a few drops of 0.1M NaOH at the beginning of the measurement and was then decreased stepwise by adding 0.1M HCl. The ζ in the presence of dye was also measured using different concentrations of dye in the streaming solutions.

Swelling of the fibres

In order to correlate fibre swelling during the measurement of zeta potential, the swelling capacity of the grafted bamboo rayon was evaluated in 1mM KCl solution. The swelling percentage values were evaluated using the procedure available in the literature,[10-11,16] with a slight modification. The dry fibre sample was weighed (0.2 g) and immersed in 1mM KCl solution for 24 h to reach absorption equilibrium. The fully swollen fibres were separated from the unabsorbed water with a 65-mesh screen. Then, the fibre mass was weighed. The relative water absorbency was determined using Equation 1:

$$Swelling\ (\%) = \frac{M_2 - M_1}{M_1} \times 100 \qquad (1)$$

where M_1 and M_2 are the mass of dry and fully swollen fibre, respectively.

Dyeing with cationic dyes

The ungrafted and grafted bamboo rayon fabrics were dyed with cationic dye Bismark Brown G. The dyebath was prepared with the required dye solution (0.5% shade), maintaining a material to liquor ratio of 1:30 and the required pH. It was heated up to 90 °C with a heating rate of 2.5 °C/min. Dyeing was continued at 90 °C for 30 min. The fabric samples were then washed with cold water, followed by a soaping treatment using Auxipon NP (non-ionic soap) at 60 °C for 20 min. Finally, they were given a cold wash. The pH of the dye bath was maintained using a citrate buffer.

Analysis of dyed fabrics

The dyed samples were evaluated for the depth of colour by the reflectance method using a 10degree observer. The absorbance of the dyed samples was measured on a Spectraflash SF 300 (Datacolor International, U.S.A.) equipped with reflectance accessories. The K/S values were determined using the following expression:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (2)$$

where R is the reflectance at complete opacity; Kis the absorption coefficient and Sis the scattering coefficient.

Colour fastness of the fabrics was assessed to washing according to ISO II methods,[17]and to light according to ISO 105/B02 test methods.[18] The valuation of colour fastness to rubbing (dry and wet) was carried out using a "crock-meter" with 10 strokes of rubbing.

RESULTS AND DISCUSSION

Effect of graft add-on (%) on zeta potential of AA-g-BR at various pH values

The electrokinetic properties of fibres can be influenced by factors such as chemical composition of fibres, surface polarity, microstructure, fibre porosity and swelling behavior. In the case of grafted cellulosic fibres like bamboo rayon, the electrokinetic properties were found to be governed by two factors,*viz.*the introduction of functional groups as a result of grafting and the increased swelling of fibre mass during measurement.

The effect of graft add-on (%) on the zeta potential of the AA grafted bamboo rayon at various pH is presented in Table 1. The results clearly indicate a decrease in the negative value of zeta potential with an increased graft add-on (%) and, in general, the negative zeta potential values were lower compared to those of ungrafted bamboo rayon, which indicates the enhanced hydrophilicity of the grafted bamboo rayon (AA-g-BR). The results obviously indicate a decrease in the negative zeta potential with the increase in the hydrophilic character. The carboxylic groups induce the hydrophilic character to bamboo rayon. The hydrophilicity was also confirmed by the moisture regain values of AA grafted bamboo rayon.

Two factors seem to affect the zeta potential in the case of grafted bamboo rayon,*viz.* surface polarity with the introduction of carboxylic groups after grafting and the increased swelling with the increase in graft add-on. The two factors affect the zeta potential in exactly opposite ways.The introduction of carboxylic groups results in negative surfaces of the fibre, causing an increase in the negative zeta potential, as indicated by a number of researchers in the case of other fibres. On the other hand, increased swelling of fibrous mass causes a shift of the shear plane of the electrochemical double layer into the electrolytic solution. During fibre swelling, potential determining electrolytes ions are further replaced due to competitive adsorption of water molecules. Researchers found the relative change in zeta potential to be proportional to the water uptake capability of the fibre.[19] The current system of grafted bamboo fibres swells immediately when in contact with water, hence neutralizing the effect of negative surfaces offering increased negative zeta potential and resulting in a decreased negative zeta potential due to swelling.

In order to confirm the swelling, in an independent test, the swelling of grafted fibres in 1mM KCl solution was measured and results are summarized in Table 2. The fibre swelling increased with increased graft add-on (%) and resulted in lower values of negative zeta potential. The higher swelling is due to the hydrophilic carboxylate groups; hence, the grafted samples with higher graft add-on showed higher hydrophilicity and swelling percentage.The results are well in accordance with the literature as far as effect of swelling on the zeta potential is concerned, *i.e.* the higher the fibre swelling, the lower the value of negative zeta potential.[3,20-21]

Table 1
Variation in zeta potential of AA grafted bamboo rayon with pH

Graft add-on	Zeta potential (mV) at different pH						
(%)	3	4	5	6	7	8	9
0	-7.982	-12.19	-13.289	-13.314	-12.939	-12.798	-13.243
2.13	-8	-12.012	-10.201	-8.901	-8.752	-9.504	-10.301
7.93	-8.7	-8.312	-7.248	-4.902	-4.493	-4.798	-6.302
11.1	-9.002	-8.103	-6.749	-4.005	-3.054	-4.202	-5.954
11.64	-9.45	-7.952	-5.003	-2.89	-1.749	-3.705	-4.754
14.85	-10.803	-7.752	-2.032	-1.249	-0.648	-2.55	-3.248

Table 2
Effect of AA graft add-on on swelling and zeta potential

Samples	Graft add-on (%)	Moisture regain(%)	Swelling (%)	Zeta potential at pH 7 (mV)
Ungrafted	0	11.11	138.03	-12.939
	2.13	11.30	190.95	-8.752
	7.93	12.64	290.98	-4.493
AA-g-BR	11.20	12.95	367.32	-3.054
	11.64	13.12	380.34	-1.749
	14.85	13.51	420.53	-0.648

The effect of graft add-on the isoelectric point (IEP) of the grafted fibres can be remarked from the zeta potential values at various pH (Table 1). At pH 3, the higher the graft add-on (%), the higher were the values of negative zeta potential. This clearly indicates the shifting of IEP towards lower pH values with an increase in graft add-on (%). The carboxylic groups show no dissociation below their pKa and hence behave like the acidic fibre at a pH lower than the pKa of polyacrylic acid, *i.e.* the more the carboxylic acid groups, the lower is the IEP.

The variation in zeta potential in three pH ranges can give a clear idea about the effect of graft add-on (%) on the electrokinetic properties. In the acidic region, from pH 3 to 5, the decrease in negative zeta potential was observed because of more dominant swelling of fibres over the negative surfaces due to dissociation of carboxylic groups (dissociation constant of AA is pKa = 4.25). The higher the graft add-on, the higher is the extent of swelling, hence the higher the extent of reduction of the negative zeta potential values. Another important pH region is the neutral one, *i.e.* pH 7, which gives a clear idea about the hydrophilicity of the grafted samples with the graft add-on (%). The higher the graft add-on, the lower would be the values of negative zeta potential and the higher would be the hydrophilicity. In the alkaline region, *i.e.* from pH 7 to 9, carboxylic groups are increasingly neutralized by the alkali and result in the formation of sodium carboxylate groups. The sodium carboxylate groups are more freely dissociable than the corresponding carboxylic acid and hence lead to increasing negative zeta potential values. The extent of the increase in the negative zeta potential in the pH range of 7-9 was higher with higher graft add-on (%). In the alkaline pH range, two competing mechanisms work on the fibres, *i.e.* increased hydrophilicity lowering negative ζ and increased dissociation of –COOH increasing negative ζ. Eventually, the latter is more pronounced as compared to the former one in the alkaline pH range, resulting in increased negative ζ. Meanwhile, in the acidic pH range, however, it is the former that is more pronounced due to suppression of the dissociation of –COOH groups.

Zeta potential in presence of dye in streaming solution

In order to study the dyeing behavior of grafted fibre in cationic dyeing bath, the zeta potential measurements were carried out in the presence of cationic dye and the results are presented in Table 3. In the case of ungrafted fibre, the increase in dye concentration resulted in a decrease in the negative value of zeta potential. This trend was also observed in the case of grafted fibres, indicating the adsorption of dye cations on the surface of fibres. Adsorption of dye cations resulted in a decrease in the negative charges on the surface and hence resulted in lowering of the negative zeta potential. The higher the graft add-on (%), the greater the adsorption of dye cations and the more pronounced is the decrease in negative zeta potential. This trend was quite obvious as the cationic dye requires carboxylic groups for the attachment, so that dyeing is carried out. The higher the graft add-on, the higher is the swelling of fibre, offering better accessibility to the carboxylic groups of the fibre and hence the more pronounced is the adsorption of dye cations.

Cationic dyeability of AA-g-BR

The effect of graft add-on (%) on the dyeability of grafted bamboo rayon at different graft add-on (%) was studied using Bismark Brown dye and the results are summarized in Table 4. In the case of ungrafted bamboo rayon, the dyeability was at the minimal level, showing just a tint of the dye without proper attachment, which was further confirmed by inferior fastness ratings. In the case of grafted bamboo rayon, the colour values were found to be increasing with increasing graft add-on levels. Since carboxylic acid groups are required for the attachment of dye onto the fibres and hence the removal of less dye during the after-washing process of the dyed fabric, the ionic bonds formed between the carboxylate groups in grafted bamboo rayon and the cationic dye molecules resulted in both enhanced dyeability and improved dye–fibre interaction. The colour values improved initially with the extent of grafting with increasing graft add-on (%). Later, from the graft add-on (%) of 11.10 to 14.85, the improvement in colour values was relatively lower, indicating the attainment of equilibrium. Similar trends were observed in the case of other cationic dyes used for dyeing grafted fibres.[13]

The results in Table 4 also indicate the improvement in all the types of fastness in the case of grafted bamboo rayon, as compared to ungrafted bamboo rayon. The improvement in fastness properties confirms the better dye–fibre interaction resulting in better attachment of the dye to the fibre.

To study the optimum pH for cationic dyeing of grafted bamboo rayon, the dyeing was carried out at various pH ranging from 3 to 7 and the resulting colour values of the dyed fabrics are summarized in Table 5.

Table 3
Variation in zeta potential of AA grafted bamboo rayon using cationic dye in streaming solution

Graft add-on	Zeta potential (mV) at different dye concentration in streaming solution (M)				
(%)	0	$1*10^{-6}$	$2*10^{-6}$	$5*10^{-6}$	$10*10^{-6}$
0	-11.905	-11.76	-11.376	-11.22	-11.02
2.13	-10.4	-10.05	-9.683	-9.333	-9.032
7.93	-7.441	-6.891	-6.368	-5.781	-5.391
11.1	-7.41	-6.8	-6.194	-5.623	-5.201
11.64	-7.21	-6.6	-5.97	-5.37	-4.95
14.85	-6.961	-6.312	-5.702	-5.058	-4.7

Table 4
Variation in colour values and fastness properties of dyed AA grafted fabrics at different graft add-on
(dye used BismarkBrown, λ_{max}470nm)

Graft add-on (%)	K/S	% Increase in K/S over control	L*	a*	b*	Washing fastness		Rubbing fastness		Light fastness
						C*	S*	D*	W*	
0.0	1.0777	0	71.37	14.83	21.60	3	3-4	2	1-2	2
2.13	2.0505	90.266	65.81	23.08	27.28	3-4	3-4	3	2-3	3
7.93	2.2870	112.211	61.83	20.14	23.70	4	4	3	3	4
11.10	3.4235	217.667	60.95	24.08	32.14	4	4	3-4	3	4
11.64	3.5578	230.129	58.43	24.07	28.74	4	4	3-4	3	4
14.85	3.6087	234.852	59.86	26.82	32.10	4	4-5	3-4	3-4	5

C* –change in shade, S* – staining, D* – dry rubbing fastness, W* – wet rubbing fastness

Table 5
Effect of pH on colour values of dyed bamboo rayon (AA-g-BR)

pH	K/S	L*	a*	b*	Zeta potential (mV)
3	3.527	63.1	26.49	36.03	-10.803
4	5.155	58.68	31.15	38.01	-7.752
5	5.4655	56.7	28.12	36.22	-2.032
6	7.6737	55.36	33.9	41.71	-1.249
7	6.0997	58.21	33.18	40.7	-0.648

The colour values were found to be increasing pH from 3 to 6 and later decreased at pH 7. There are two types of factors which are of major importance in dyeing grafted fibre with cationic dyes, *viz.* fabric-related factors, such as the presence of carboxylic acid groups for the attachment of the dye, the state of dissociation of the groups, the accessibility of the carboxylic groups resulting because of fibre swelling; and dye-related factors, such as solubility of the dye, exhaustion of the dye and fixation of the dye to ensure lower removal through washing.

At pH 6, the colour values were found to be maximum, since the carboxylic groups are in the dissociated form above the pKa of the polyacrylic acid, resulting in better swelling of the fibres. Slightly acidic pH also ensures better solubility of the dye.

CONCLUSION

The electrokinetic properties of grafted bamboo rayon fabrics were investigated, along with their dyeing behavior towards cationic dye. The optimum pH for dyeing of AA-g-BR was found to be 6 for cationic dyeing, based on electrokinetic measurements and dyeing. The zeta potential measurements in the presence of cationic dye showed the changes occurring due to adsorption of the dye. The fabrics were dyed with various graft add-on and the colour values were successfully correlated with the corresponding zeta potential values. The results showed promising correlation between the electrokinetic properties and the dyeing behaviour of the grafted bamboo rayon fabrics.

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