

Effect of protein derivatives on the hydrolytic stability of polylactic acid fibres during simulated dyeing

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Abstract: Greige PLA knitted fabric was scoured with sodium carbonate in the presence of non-ionic detergent followed by bleaching with hydrogen peroxide. The scoured and bleached fabrics were processed in a laboratory IR dyeing machine over a range of temperatures, pH and time intervals. The levels for temperature, time and pH were so selected as to simulate the industrial scale disperse and reactive dyeing systems. The processed fabric was tested for weight loss and tensile strength to assess the degradation of PLA during simulated dyeing processes. Various commercially available protein derivatives were also added to the simulated dyeing bath to investigate their effect in retarding the degradation of fibres. SEM was employed to investigate the surface morphology of fibres.

Keywords: PLA, biodegradable polymers, hydrolysis, protein hydrolysates, mechanical properties.

Wpływ pochodnych białkowych na stabilność hydrolytyczną włókien polilaktydu poddanych symulowanemu barwieniu

Streszczenie: Badano podatność włókien polilaktydowych na rozkład hydrolytyczny podczas symulowanego procesu barwienia. Działanie polilaktydową oczyszczano za pomocą węgla sodu w obecności niejonowego detergentu, a następnie wybielano przy użyciu nadtlenu wodoru. Oczyszczoną i wybieloną działanie poddawano obróbce w laboratoryjnym urządzeniu do barwienia, w przedziałach temperatury, pH i czasu, symulujących warunki rzeczywistego procesu barwienia przemysłowego. Na podstawie wyników badań wytrzymałości na rozciąganie oraz ubytku masy barwionej działanie oceniano stopień degradacji włókien PLA. Do kąpeli barwiącej dodawano różne, handlowo dostępne pochodne białkowe i, na podstawie analizy zdjęć wykonanych skaningowym mikroskopem elektronowym, określano ich wpływ na opóźnianie degradacji włókien PLA podczas procesu barwienia.

Słowa kluczowe: polilaktyd, polimery biodegradowalne, hydrolyza, hydrolyzaty białek, właściwości mechaniczne.

PLA [poly(lactic acid)] is a biodegradable synthetic thermoplastic material derived from annually renewable resources [1]. It is an alkyl polyester manufactured from the ring opening polymerization of cyclic dimers of lactic acid, the latter being obtained by the enzymatic action on corn [2]. Nature Works LLC of USA is the largest manufacturer of melt-spun PLA fibers marketed under the trade name of Ingeo[®] [3]. Since PLA is manufactured from sustainable materials, it does not depend on petrochemical resources as the PET [poly(ethylene terephthalate)] does. Some of the characteristics of PLA such as moisture regain, tensile strength, and crease resistance behaviour are comparable to PET [4]. The drawbacks of PLA are its poor thermal and hydrolytic stability [5]. The glass transition temperature (T_g) and melting temperature (T_m) of PLA lie in the range of 55–65 °C and 130–

175 °C, respectively [6]. Therefore, PLA should not be treated at the harsh and severe process conditions as are employed for industry standard polyester *i.e.* PET and blends of PET-natural fibres [7]. The wet processing of PLA, therefore, requires a new process design that ensures retention of good overall mechanical, aesthetic and performance properties by the end of dyeing and finishing [8, 9].

The hydrolytic stability of textile materials depend on various physical factors such as the morphology, crystallinity and molecular weight of the constituting polymers and chemical factors such as functional groups of the polymer backbone, pendant groups and to some extent on the steric factors and pH of the medium [10]. PLA in aqueous medium was studied by various workers, *e.g.* Joziassé *et al.* studied the hydrolysis of PLA and reported that hydrolysis was autocatalytic due to the formation of carboxylic acid groups at the polymer chain ends [11]. Grizzi *et al.* and Nakamura *et al.* studied the hydrolysis of PLA at pH 7.4 and 37 °C and reported that bulk hydrolysis was faster than surface due to the accumulation of oli-

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gomers inside PLA material [12, 13]. Vert *et al.* also discussed the autocatalytic and leaching effects as identified previously [14]. Mauduit *et al.* reported that the rate of degradation was directly related to the number average molecular weight (\overline{M}_n), the lower the \overline{M}_n the higher the hydrolysis rate [15]. Hyon *et al.* reported that PLA with lower \overline{M}_n and with high levels of oligomers degraded faster [16]. Iwata and Doi studied the changes in morphology and crystallinity of PLA and reported that the amorphous regions degraded faster than crystalline [17]. Tsuji and Nakahara tested PLA film at various pH values (2, 7.4 and 12) and concluded that the relative hydrolysis rate was in the following order: alkaline > acidic > neutral [18]. Tsuji *et al.* studied the hydrolysis of PLA film in buffers at 97 °C and showed that hydrolysis took place preferentially in the amorphous regions [19]. Avinc [20] and Suesat studied the effect of various textile processes on the mechanical properties of PLA fabric and concluded that bleaching with hydrogen peroxide severely degraded PLA fibres [21–23]. Under high temperature and humidity conditions PLA fibres disintegrated quickly, the primary mechanism being hydrolysis followed by microbial attack [24]. Li *et al.* studied the hydrolysis of PLA and concluded that water absorption increased with extent of hydrolysis presumably due to the formation of more hydroxyl and carboxylic acid groups [25]. Others supported the argument and suggested that there were two layers of water, one bound to the surface and the other mobile one [26]. Li *et al.* showed that the presence of 60 % coral in PLA-coral blend reduced the degradation of PLA by neutralising the effect of autocatalysis [27]. While degradation cannot be eliminated totally it is possible to decrease the rate of deterioration of the product. PLA fibres were reported to hydrolyse faster when subjected to high temperature and at extreme pH regions [28–32].

The work describes the mechanical stability of PLA fabric subjected to various simulated dyeing processes *i.e.* dyeing carried out in the presence of auxiliaries and chemicals but without dyes. The simulated processes include dyeing of cotton, polyester and polyester-cotton blends. To preserve strength, the fabric is processed in the presence of chemicals that potentially may hydrolyze at the expense of PLA in order to minimize the degradative effect on the polymeric fibre. The commercially available protein hydrolysates of various ionic natures are evaluated with the aim of avoiding loss in yarn and fabric strength.

EXPERIMENTAL PART

Materials

The greige Ingeo® PLA knitted fabric having pique' construction was obtained from Valuable Enterprises Co., Ltd., Taiwan. Staple yarn of count Ne 30^s had been used in the knitting of the fabric.

All the used chemicals were of laboratory grade while auxiliaries were of commercial grade.

Protein hydrolysates: Hydrotriticum QS, Hydrotriticum QM, Croquat L and Byco C were obtained from Croda (UK).

PLA fabric processing

The scouring and bleaching of the PLA fabric were carried out in pilot scale garment washing machine (Roaches, UK). High Temperature Infra-red dyeing machine Labomat BFA-12 (Mathis, UK) was used to process PLA fabric at various simulated dyeing conditions. The chemicals and fabric were weighed on weighing balance L310 (Sartorius, UK). The pH of the solution was measured using PH-201 (Henna, UK).

– The scouring was carried out with sodium carbonate 2 g/dm³ at 60 °C for 15 minutes at a liquor to material ratio (LMR) of 10:1.

– The scoured PLA fabric was bleached in a pilot scale garment dyeing machine. Hydrogen peroxide (35 % w/w) 5 cm³/dm³, NaOH 2 g/dm³ and sodium silicate 5 g/dm³ were added into the machine. The bleaching was carried out at 90 °C for 45 minutes, the LMR being 10:1. After bleaching PLA fabric was neutralized with 1 cm³/dm³ acetic acid solution, rinsed and subsequently dried at ambient conditions.

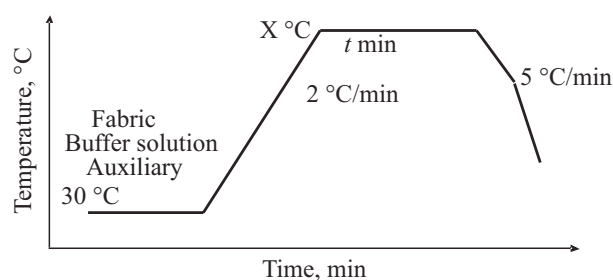


Fig. 1. Schematic process profile for PLA fabric

– The scoured and bleached PLA fabric was subjected to simulated dyeing conditions in IR dyeing machine at various temperature, time and pH. Figure 1 shows the schematic dyeing profile. Throughout the experiments the heating and cooling rates were constant (2 and 1 °C/min, respectively) and LMR was kept at 10:1.

Methods of testing

Weight loss

PLA fabric was conditioned overnight at 25 °C and 65 % R. H. before testing. Following formula was used to calculate the weight loss of samples after processing, where W_1 and W_2 were the weights of the samples before and after dyeing, dried at ambient conditions. The negative sign shows a decrease in weight.

$$\text{Weight loss} = - [W_1 - W_2] \cdot 100 / W_1$$

Tensile strength

Yarns taken out from control and the treated knitted fabric were conditioned at 25 °C and 65 % R. H. before testing. Tests were performed according to BS EN ISO 2062:1995, using Instron Model 1122 tensile tester with a gauge length of 100 mm and at a strain rate of 1 min⁻¹. Ten tests were performed on each of the samples and the results acquired through desktop computer interfaced to the testing machine. The data were received and analyzed through computer software QT.

SEM analysis

Surface morphology of the PLA fibres was investigated using scanning electron microscope. Samples were sputter-coated with gold in a coating unit (model E5100, Polaron) followed by loading sample holder in the SEM (model EVO[®] 50, ZIESS). Gun-to-sample distance was 8–9 mm and voltage of 5 kV was applied to accelerate electron toward the samples under high vacuum. Electron beam focusing, image magnification and brightness/contrast were adjusted to take the photographs.

RESULTS AND DISCUSSION

Effect of temperature, time and pH on weight loss of PLA fabric

Figure 2 shows the effect of processing temperature, time and pH on weight loss of scoured PLA fabric. At low temperature, low pH and short processing time the weight loss was low. At 60 °C, the dyebath pH-changes and weight loss were the lowest. It is known from the literature that T_g of PLA lies in the range of 55–65 °C [32]. The hydrolysis, therefore, was restricted mainly to the surface of fibres. Even at pH 11 there was negligible weight loss at the end of the processing. In the temperature range of 80 °C to 100 °C, PLA lose weight more readily at pH 11 than at pH 7 or 5. The high alkaline conditions caused hydrolysis of the PLA polymer (Scheme A). The bath pH-changes were high at the beginning and then

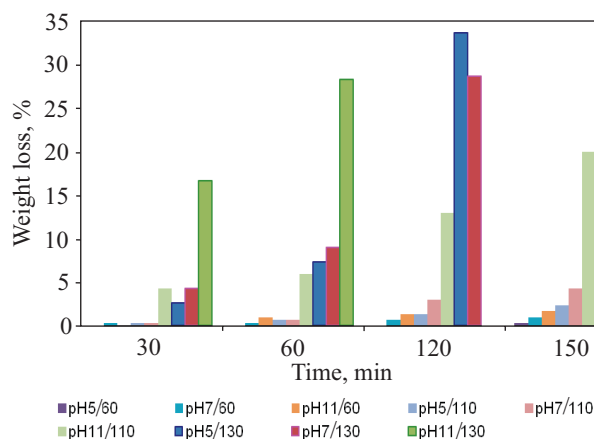
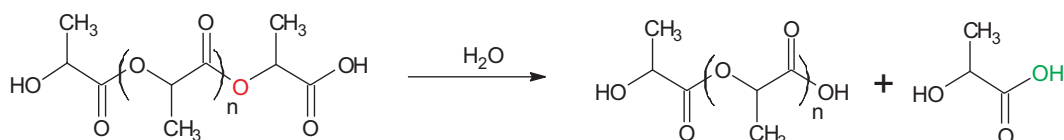


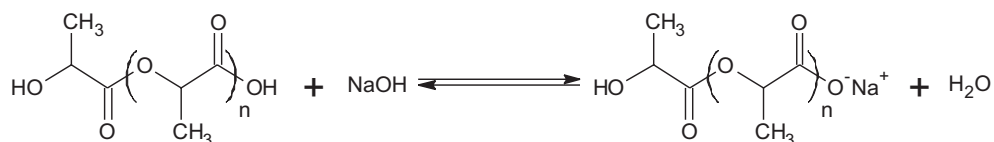
Fig. 2. Weight loss of scoured knitted PLA fabric during simulated processing

settled suggesting that lactic acid moieties might have formed a buffer with alkali in the bath (Scheme B). The weight loss of fabric at various pH was in the following order: alkaline > neutral > acidic. At 130 °C ($t = 120–150$ min), weight loss was higher at pH 5 than at 7 and this might be due to the acidity of bath decreased to such a low level that it triggered auto-catalytic hydrolysis of PLA [11].

PLA belongs to the ester class of polymers. It is known from organic chemistry that ester groups are prone to hydrolysis under acidic as well as alkaline conditions [33]. Ester hydrolysis is a reversible reaction between esters and water molecules. The reaction is affected by concentration of reactants, temperature, pressure, catalyst (acid or base) and polymer morphology. The hydrolysis of PLA resulted in the formation of oligomers of random molecular weights [34]. These oligomers possessed carboxylic acid groups at the chain ends and were neutralized by free alkali thereby lowering the bath pH. At high temperature the rate of hydrolysis was high and this led to excessive polymer degradation. If the pH were buffered to around 5, the weight loss would be decreased. The treatment time was another factor that affected weight loss of PLA. As the time passed, PLA continued to hydrolyse thus generating acidic products. The acidity was



Scheme A



Scheme B

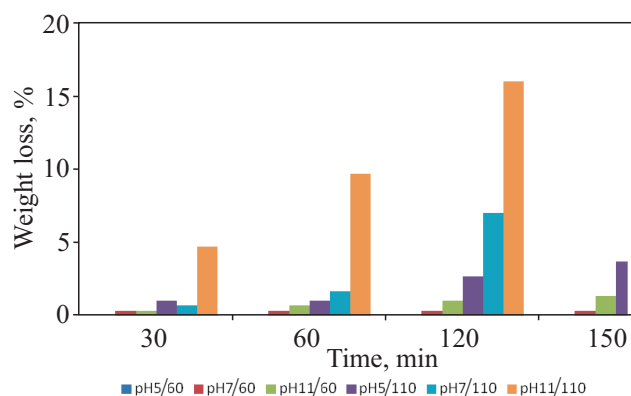


Fig. 3. Weight loss of bleached knitted PLA fabric during simulated processing

compensated for by the buffering system until the solution exceeded its buffering capacity. Once this limit was crossed, buffering action ceased to exist thus resulting in autocatalytic hydrolysis of PLA polymer.

Figure 3 shows the weight loss of bleached PLA fabric subjected to various process conditions. The pH measurements of the bath showed that initial bath pH of 5 and 7 did not change while pH 11 dropped to 10. The results showed that PLA was sensitive to degradation in the alkaline pH medium. At 110 °C weight loss was the highest at pH 11 followed by pH 7 and 5. The weight loss behaviour of bleached PLA at 130 °C was not different from the scoured fabric. The weight loss increased with the pH of the bath in the following order: alkaline > neutral > acidic. At 130 °C PLA fabric was completely disintegrated in the bath so no measurements of weight were made.

When comparing the results of scoured and bleached PLA fabric, it became evident that weight loss was more apparent in the case of bleached fabric than scoured one. During scouring a light alkaline treatment was given to the fabric that did not lead to excessive fiber damage. The scouring treatment was done at relatively low temperature and for short length of time. In the case of bleaching, the process conditions were severe with high alkalinity and temperature up to 90 °C leading to excessive damage to the fibres [7–9, 35]. Since PLA had a low T_g , this resulted in high weight loss of the material. From the above discussion it was concluded that weight loss of PLA could be minimized if bleached PLA possessed sufficient strength to bear the high temperature processing. Moreover, PLA should not be subjected to industrial disperse-dyeing conditions of PET.

Effect of temperature, time and pH on the tensile strength of PLA yarn

Table 1 presents the tensile strength loss of scoured PLA yarn, taken from fabric, subjected to various process conditions. The dyeing of PLA with disperse dyes at pH 5 and 110 °C for 30 min are the recommended dyeing conditions by DyStar [36]. The simulated dyeing of PLA with disperse dyes under these conditions did not cause appreciable decrease in tensile strength. Since during industrial practice of dyeing the right-first-time approach does not work all the time, some dye-additions have to be made to correct for faulty shades. These dye-additions implied processing PLA for long intervals at 110 °C and it was evident that extended processing up to 150 minutes

Table 1. Effect of simulated dyeing on the tensile strength of scoured PLA yarn

Temperature °C	Time minutes	pH 5		pH 7		pH 11	
		pH*	tenacity, %	pH*	tenacity, %	pH*	tenacity, %
60	---	---	---	---	---	10.9	-3.0
	---	---	---	---	---	10.85	-3.1
	---	---	---	---	---	10.75	-5.2
	---	---	---	---	---	10.70	-7.0
80	30	5.00	-2.2	6.90	-1.5	10.68	-6.5
	60	4.94	-2.8	6.81	-2.0	10.38	-7.1
	120	4.92	-3.0	6.76	-2.5	10.20	-9.8
	150	4.91	-7.0	6.62	-5.1	10.17	-11.0
110	30	4.98	-18.5	6.75	-21.4	8.65	-47.9
	60	4.97	-25.7	6.63	-40.0	7.36	-69.2
	120	4.94	-49.2	6.27	-68.5	6.08	-84.2
	150	4.97	-63.5	5.95	tendered	5.92	tendered
130	30	4.90	-61.4	5.82	-73.5	5.54	tendered
	60	4.84	tendered	4.20	tendered	4.23	tendered
	120	4.43	tendered	3.36	tendered	3.75	disintegrated
	150	4.23	disintegrated	3.05	disintegrated	3.44	disintegrated

(Greige: 14.7 cN/tex, Scoured: 12.9 cN/tex); *pH measured at the end of process.

Table 2. Effect of simulated dyeing on the tensile strength of bleached PLA yarn

Temperature °C	Time minutes	pH 5		pH 7		pH 11	
		pH*	tenacity, %	pH*	tenacity, %	pH*	tenacity, %
60	30	---	---	---	---	11.00	-7.0
	60	---	---	---	---	10.98	-7.1
	120	---	---	---	---	10.96	-7.2
	150	---	---	---	---	10.95	-7.2
80	30	5.00	-2.5	6.99	-1.4	10.95	-7.0
	60	4.99	-2.8	6.97	-7.1	10.73	-7.1
	120	4.95	-5.0	6.95	-11.4	10.48	-10.0
	150	4.89	-5.7	6.93	-20.0	10.45	-11.4
110	30	4.92	-19.2	6.99	-20.0	8.26	-49.2
	60	4.90	-21.4	6.94	-42.9	7.47	---
	120	4.85	-45.7	6.37	tendered	6.52	---
	150	4.81	-62.1	6.38	tendered	6.14	tendered
130	30	4.98	-53.5	6.17	-74.2	5.05	tendered
	60	4.89	tendered	4.06	tendered	4.19	tendered
	120	4.59	disintegrated	3.67	disintegrated	3.43	disintegrated
	150	4.35	dispersed	3.05	dispersed	3.42	disintegrated

(Greige: 14.7 cN/tex, Bleached: 11.8 cN/tex); *pH measured at the end of process.

caused excessive loss (63 %) in the tensile strength of PLA yarn. PLA was also simulated dyed under typical PET dyeing conditions of 130 °C and pH 5 for 30 minutes and it was observed that PLA was so sensitive to these conditions that processing for 30 minutes only resulted in 61.4 % loss in tensile strength. The processing at high temperature for extended time caused tendering followed by complete disintegration of the PLA fabric in the dyebath. Therefore PLA should not be dyed with disperse dyes at PET dyeing conditions. Dyeing at 100 °C and pH 5 were considered simulated dyeing conditions of wool with acid dyes in PLA-wool (PW) blends. PLA withstood process conditions without appreciable loss in strength. PC (polyester-cotton) blends are dyed usually with disperse-reactive dyes either by single-bath-single-stage (SBSS) or two-bath-two-stage (TBTS) techniques. The SBSS dyeing with suitable disperse dyes and reactive dyes – “Kayacelon React” was simulated by processing PLA at pH 7 and a temperature of 110 °C. It was evident from the data, Table 1, that PLA in PC blends might be processed without significant loss in tensile strength of yarn; however, lengthy processing damaged PLA excessively.

The extended processing up to 150 minutes led to tendering of the fabric and resulted in lowering of dyebath pH from 7.0 to 6.0. The TBTS dyeing is another popular technique in which each of the components of the blend is dyed separately. It is logical that if PLA possessed acceptable strength after disperse dyeing; it would withstand the severity of the following processes as well. On the other hand if PLA had already lost much of the strength which might be due to bleaching or multiple dye-additions, it would become impracticable to carry on to the

next stage of reactive dyeing. With the assumption that PLA possessed enough strength, it was subjected to simulated dyeing conditions of hot and warm reactive dyeing of cotton. The treatment at pH 11 and 60–80 °C presented the simulated dyeing conditions for warm and hot dyeing processes, respectively. It was evident from the Table 1 that PLA withstood these process conditions and that there was less damage to PLA at 60 °C and 80 °C.

Table 2 presents the tensile strength of bleached PLA yarn, taken from knitted fabric, treated under various process conditions *viz.*, pH, temperature and time. The results suggested that bleached PLA could be processed at pH 5 up to 110 °C for extended processing of 120 min, the longer processing up to 150 minutes might lead to excessive loss in tensile strength (62.1 %). On industrial scale PW blends are dyed with disperse-acid dyes. The processing of PLA at pH 5 and 100 °C represented the simulated conditions of dyeing wool with acid dyes and it might be inferred that PLA was “safe” under these process conditions. The treatment at pH 5 and 110 °C represented the simulated HT (High Temperature) dyeing of PLA with disperse dyes. The results showed that PLA withstood these conditions with acceptable strength losses. However, when PLA was subjected to HT simulated dyeing conditions of PET, it degraded appreciably. When comparing the tensile strength of scoured and bleached PLA yarns from Tables 2 and 3, it was evident that scoured PLA retained more strength at pH 5 than the comparable bleached fabric. PC blend may be dyed by SBSS or TBTS. In the SBSS technique, simulated dyeing was carried out at pH 7 and the results showed that PLA was stable up to 120 min, the extended processing caused tendering. In simulated TBTS dyeing, PLA was treated at

pH 5, reduction cleared followed by simulated dyeing of cotton portion with reactive dyes, the latter could be "warm" or "hot" reactive dyes. The results showed that treating PLA at pH 5 was acceptable and given that PLA possessed sufficient strength, it could be subjected to processing conditions required for cotton dyeing. The processing of PLA at pH 11 and in the temperature range of 60–80 °C were simulated conditions of dyeing cotton with warm and hot reactive dyes, respectively, and the results showed that PLA was stable to these process conditions.

Effect of protein hydrolysates on the tensile properties of PLA yarn

Table 3 presents the tensile strength of scoured PLA yarn treated in the presence of various protein hydrolysates at 110 °C, pH 5 and 7 for 120 min (simulated multiple dye-additions) to determine the effect of protein hydrolysates on PLA tensile strength. The results showed that dyeing of PLA at 110 °C for extended time caused loss in mechanical strength. To possibly reduce these losses, protein hydrolysates were applied as protective agents to decelerate the degradation rate of PLA. It was evident from Table 3 that with the exception of Byco C, all other auxiliaries either exhibited little effect or increased degradation of the polymer. For example Hydrotriticum QS, Hydrotriticum QM and Croquat L increased the polymer

Table 3. Effect of protein hydrolysates on the tensile strength of scoured PLA yarn

Auxiliary	Concentration g/dm ³	pH 5		pH 7	
		pH*	tenacity %	pH*	tenacity %
Control	00	5.00	-	6.07	-
Hydrotriticum QS	01	5.00	-19.7	5.53	-12.3
	03	5.01	-28.1	5.13	-15.3
	05	5.02	-29.5	5.09	-17.0
	07	4.98	-29.5	5.07	-20.0
	10	4.98	-29.5	4.96	-26.1
Hydrotriticum QM	01	5.00	-14.0	5.73	-26.1
	03	4.99	-17.0	5.57	-32.3
	05	4.98	-31.0	5.28	-32.3
	07	4.98	-36.0	5.14	-32.5
	10	4.97	-38.0	5.10	-64.6
Byco C	01	5.00	+10.1	6.37	+8.4
	03	5.00	+11.2	6.38	+8.5
	05	5.00	+12.3	6.42	+11.0
	07	4.99	+9.0	6.49	+14.4
	10	4.99	+2.7	6.52	+8.5

(Control at pH 5: 7.1 cN/tex, Control at pH 7: 6.5 cN/tex);

*pH measured at the end of process.

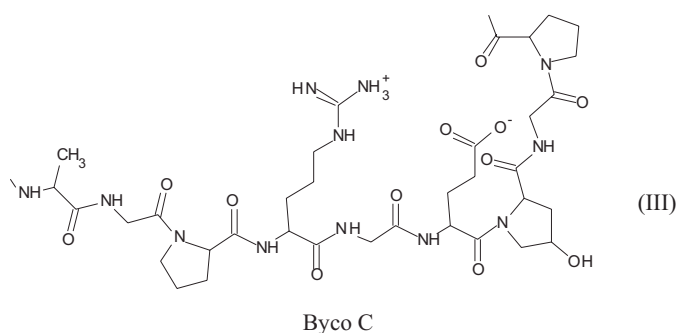
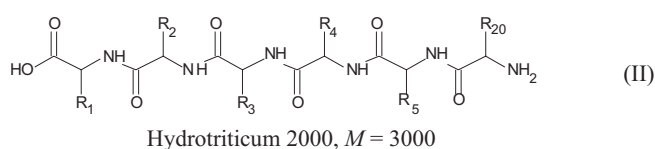
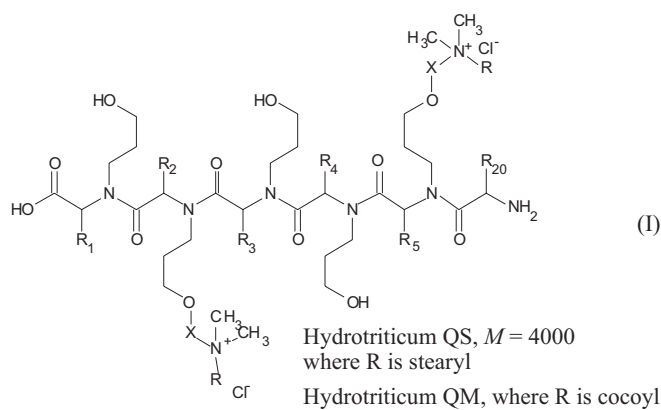
Table 4. Effect of protein hydrolysates on the tensile strength of bleached PLA yarn

Auxiliary	Concentration g/dm ³	pH 5		pH 7	
		pH*	tenacity %	pH*	tenacity %
Control	00	4.99	-	6.59	-
Hydrotriticum QS	01	5.00	-33.3	6.36	-0.1
	03	4.99	-33.3	5.57	-12.2
	05	5.00	-39.6	5.32	-40.3
	07	4.98	-50.7	5.26	-40.5
	10	4.97	-54.0	5.16	-41.2
Croquat L	01	5.00	-3.1	6.16	-21.0
	03	4.98	-4.7	5.69	-22.8
	05	4.97	-50.7	5.63	-22.8
	07	4.97	-50.7	5.52	-24.5
	10	4.97	-52.3	5.45	-25.1
Byco C	01	5.00	+1.5	6.63	+13.6
	03	5.00	+7.3	6.67	+16.1
	05	4.99	+7.4	6.70	+16.2
	07	4.99	+10.0	6.78	+16.2
	10	5.00	+7.3	6.78	+13.6

(Control at pH 5: 6.3 cN/tex, Control at pH 7: 5.7 cN/tex);

*pH measured at the end of process.

degradation, though the latter two protein derivatives were more deleterious than the former. Formulas (I)–(III) show the schematic chemical structures of va-



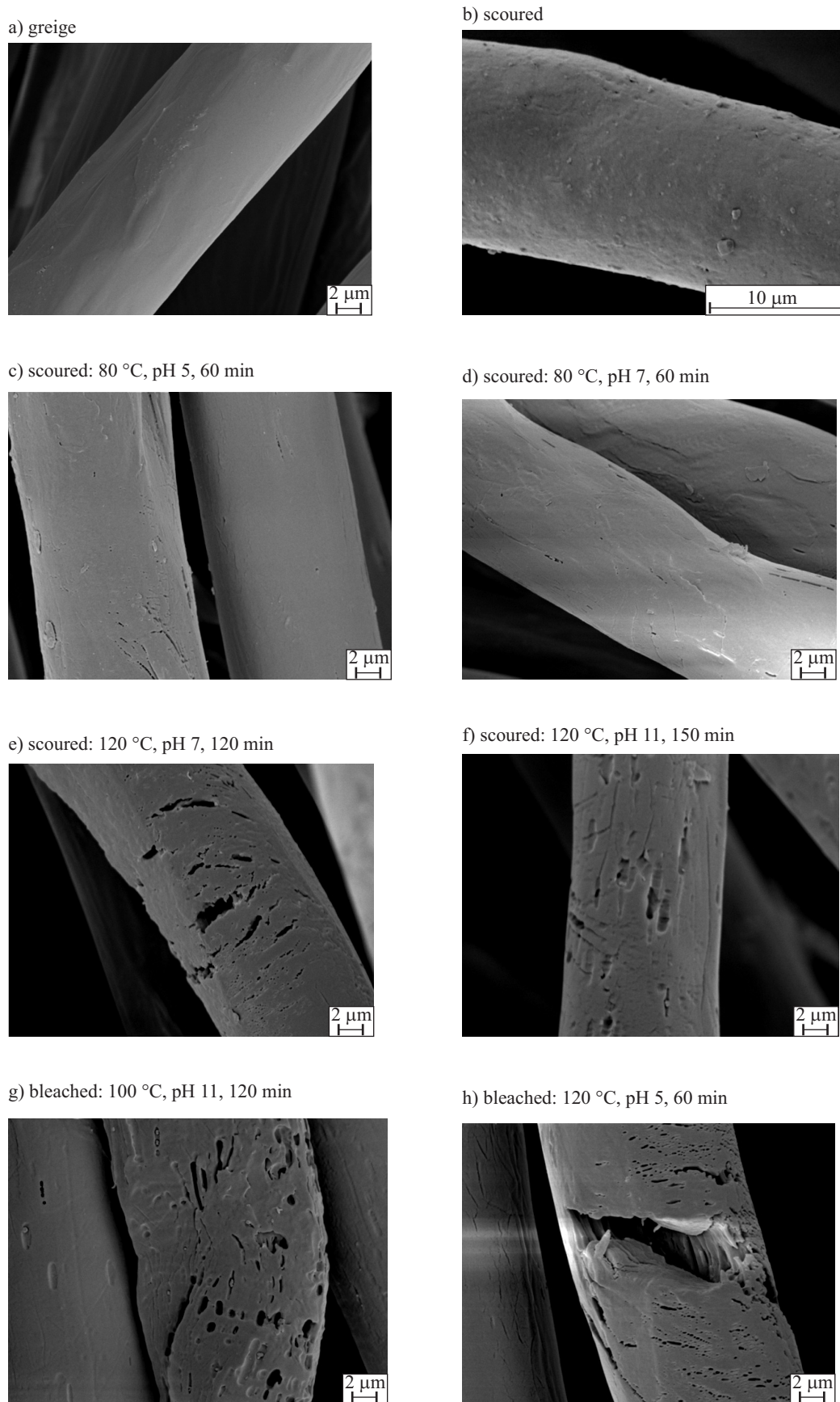


Fig. 4. SEM micrographs of scoured and bleached PLA fibers

rious protein derivatives. From the chemistry viewpoint Hydrotriticum QS, QM and Croquat L are all quaternary

ammonium compounds and it was the cationic nature of these auxiliaries that catalyzed the hydrolysis of PLA.

Byco C exhibited some beneficial effects in retaining the tensile strength at 110 °C and pH 5. The control PLA yarn had strength of 7.1 cN/tex while yarn treated in the presence of Byco C exhibited tensile strength increase up to 12 %. Similarly at pH 7 fabric treated in the presence of Byco C demonstrated enhanced strength retention, up to 14 %, with the cationic derivatives increasing strength loss. Since bleached fabric possessed low initial strength, the effect of the protein derivatives on strength retention was also examined and the same trend was observed with the neutral Byco C offering beneficial effects at both pH 5 and 7, Table 4. In contrast the cationic protein hydrolysates accelerated the strength loss. The dyebath pH did not change significantly from buffered value of 5 while for fabric treated at pH 7 it decreased in the presence of cationic auxiliaries which catalyzed polymer hydrolysis.

SEM of PLA yarn

Scanning electron microscopic analysis of the surface of PLA fibres subjected to various wet processing conditions was taken, Fig. 4. In greige state PLA fibres exhibited a very smooth surface with scouring producing little surface damage. Bleaching with hydrogen peroxide caused severe damage to the fibre structure. Jantip *et al.* and Baig also reported that hydrogen peroxide caused severe damage to the fibre and appreciably reduced the fibre strength [22, 23, 35, 36]. The electron micrographs showed the effect of extended wet processing on scoured and bleached PLA fibres and it was evident that acidic and alkaline conditions rendered damage to the PLA fibres. In the less severe cases only the surface was peeled off while in other cases surface was eroded. Further in the severe cases, some holes were observed in the fibres and accordingly the HT PET dyeing conditions must not be employed for PLA as the fibre was severely damaged at 130 °C.

CONCLUSIONS

In the temperature range of 80–100 °C at pH 5 and 7 there was negligible loss in weight and tensile strength of PLA yarns, while at pH 11 the loss was higher but still within acceptable limits. The high temperature processing at 110–130 °C caused excessive loss in weight and tensile strength of PLA yarn. The higher the temperature and pH, the higher was the degradation rate. At 130 °C the fabric was completely disintegrated after 30 min only with little physical integrity. Some protein hydrolysates exhibited beneficial effects in terms of aqueous processing while others proved deleterious, the latter being cationic in nature. The optimum concentration for Byco C was identified as approximately 5 % o.w.f. (on-weight-of-fiber). Scoured fabric withstood high temperature for extended processing as compared to bleached one due to initial higher strength of the former and not being “sensitized” to further wet processing at elevated aqueous tem-

perature. PLA exhibited better hydrolytic stability when subjected to simulated two-bath dyeing conditions than single-bath dyeing. Again scoured PLA fabric exhibited better hydrolytic stability at pH 5 than at pH 7 when subjected to simulated single-bath dyeing conditions.

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