Gulzar A. Baig,
*Chris M. Carr

Surface and Structural Damage to PLA Fibres during Textile Pretreatments

University College of Textile Engineering, B Z U
60800 Multan, Punjab, Pakistan
E-mail: gabaig@bzu.edu.pk

*School of Design,
University of Leeds,
LS2 9JT, Leeds, UK

Abstract
PLA knitted fabric was treated with sodium carbonate in the presence of non-ionic detergent at various concentrations and temperatures in a short liquor bath. The scoured fabric was subsequently treated with industrially important bleaching agents such as hydrogen peroxide, sodium chlorite and sodium hypochlorite at various levels of concentration and pH. The bleached PLA fabric was then evaluated in terms of surface and bulk properties. The structural damage was assessed in terms of tensile strength, while the surface morphology was investigated using scanning electron microscopy (SEM). The surface chemistry of PLA was studied using infra-red (IR) and x-ray photoelectron spectroscopies (XPS). The alkaline-oxidative conditions were deleterious to the integrity of PLA polymer at high temperature, while at low temperature there was a little damage. The acidic-oxidative conditions did not appreciably affect bulk or surface properties even at high temperature.

Key words: *PLA, Renewable polymer, Scouring, Bleaching, Tensile properties, SEM, IR, XPS.*

romolecules have a helical structure with carbonyl groups having their positions reversed up and down [3]. Cargill Dow LCC (now Nature Works LLC) of USA is the largest manufacturer of PLA fibres, marketed under the trade name of Ingeo®. Since PLA is manufactured from sustainable resources, it does not depend on petrochemical resources as the industry standard PET (polyethylene terephthalate) does. PLA has some characteristics such as moisture regain, tensile strength, and crease resistance behaviour which 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 processing conditions as are employed for industry standard polyester i.e. PET and blends of PET with 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 at the end of wet processes such as bleaching and dyeing [8, 9].

Textile pretreatment comprises a series of wet processes aimed at removing impurities from textile materials [10]. Scouring is carried out in the presence of alkalies and detergents to remove oily and waxy substances [11]. The choice of chemicals and processing conditions during scouring depends on the chemical stability of synthetic fibres e.g. PET is more stable to sodium hydroxide than PLA, hence a weaker alkali such as sodium carbon-

ate should be chosen for the latter [12]. The scoured fabrics are bleached for dyeing light shades [13]. The bleaching is an important process, particularly for natural fibres. Although bleaching removes the pigmentation in natural fibres such as cotton and wool, sometimes synthetic fibres have to be bleached when extra whiteness is required; the material has developed yellowness during processing or when these fibres are blended with natural ones [14]. Although hydrogen peroxide is the industry standard, peracetic acid has also been used in the bleaching of synthetic fibres such as nylon, cellulose acetate and acrylic [15, 16].

Joziasse *et al.* studied the hydrolysis of PLA and reported that this process was autocatalytic due to the formation of carboxylic acid groups at the polymer chain ends [17]. Grizzi *et al.* and Nakamura *et al.* studied the hydrolysis of PLA at pH 7.4 and temperature 37 °C and reported that bulk hydrolysis was faster than the surface due to the accumulation of oligomers inside the PLA material [18, 19]. Vert *et al.* also discussed the autocatalytic and leaching effects mentioned earlier [20]. Mauduit *et al.* reported that the rate of degradation was directly related to the number average molecular weight (M_n); the lower the M_n the higher the hydrolysis rate [21]. Hyon *et al.* reported that PLA with lower M_n and with higher levels of oligomers degraded faster [22]. Iwata and Doi studied the changes in morphology and crystallinity of PLA and reported that the amorphous regions degraded faster than crystalline ones [23]. Tsuji and Nakahara tested PLA films at various pH values (2.0, 7.4 and 12.0) and

Introduction

PLA (polylactic acid) is a new renewable and biodegradable synthetic thermoplastic material derived from renewable resources [1]. From a chemistry viewpoint, PLA is linear alkyl polyester manufactured from the ring-opening polymerisation of cyclic dimers of lactic acid, with the latter being generated by the enzymatic action on corn etc. [2]. PLA mac-

concluded that the hydrolysis rate was in the following order: alkaline > acidic > neutral [24]. Tsuji *et al.* also studied the hydrolysis of PLA films in buffers at 97 °C and showed that hydrolysis took place preferentially in the amorphous regions [25]. Suesat *et al.* pretreated PLA and reported that scouring did not appreciably affect the mechanical properties; however, bleaching with hydrogen peroxide severely damaged the PLA fibres [26 - 28]. Huseyin *et al.* ozonated PLA fabric at various process conditions and reported little change in mechanical properties up to 10 minutes: however, long times of up to 60 minutes at room temperature decreased the strength down to 10%. They claimed that a treatment of 10 minutes was effective and a low cost alternative to hydrogen peroxide [29]. Baig scoured and subsequently bleached PLA fabric with various industrially important bleaching agents and found that scouring above 60 °C (T_g) decreased both the weight and tenacity of yarns, while bleaching with hydrogen peroxide caused hole formation in the fibre structure [30].

The present work was undertaken to investigate the effect of industrial scouring and bleaching processes on the mechanical stability, surface morphology and surface chemistry of PLA fibres. The knitted fabric was treated with sodium carbonate at a range of temperatures to investigate the effect of scouring on the tensile strength of yarns. Similarly the scoured fabric was bleached with various industrially important bleaching agents to evaluate the mechanical stability of PLA and to select the one that least damaged PLA textiles. SEM, XPS and IR spectroscopy were employed to investigate the surface morphology and chemistry of the pretreated fibres.

■ Experimental

Materials and machinery
Greige PLA knitted fabric of pique construction was obtained from Valuable Enterprises Co., Ltd, Taiwan. Staple yarn of count 19.7 tex S (Ne 30s) was used in the knitting of PLA fabric. The scouring and bleaching of PLA fabric were carried out in a pilot scale garment washing machine (Roaches, UK). The chemicals and fabric samples were weighed on a weighing balance L310 (Sartorius, UK) and the pH of the solution was measured using a PH-201 (Henna, UK). Tensile measurements of the yarn were taken

on an Instron 1122 interfaced to a dedicated personal computer. An S-3000N scanning electron microscope (Hitachi, Japan) was used in investigating the surface morphology of the PLA fibres. FT-IR spectroscopy was carried out using a Spectrum 2000 IR spectrometer (Perkin Elmer), while X-ray photoelectron spectroscopy (XPS) was carried out on an Axis Ultra (Kratos). All the chemicals were of laboratory grade, while auxiliaries were of commercial grade.

PLA pretreatments
Scouring
Alkaline scouring of the greige PLA fabric was carried out in a bath containing 0 - 5 g/l sodium carbonate and 0.5 g/l of Kieralon Jet B conc. (non-ionic surfactant, BASF) at 40 - 100 °C for 20 minutes at a liquor to materials ratio (LMR) of 10:1. After scouring, the fabric was rinsed with normal water and then dried at ambient conditions overnight.

Bleaching
H_2O_2 bleaching of the scoured fabric was carried out with 1 - 5 ml/l H_2O_2 (35% w/w), 0.5 - 3 g/l NaOH and 0.5 g/l Baystabil DB (organic H_2O_2 stabilizer; BASF) at 90 °C for 45 minutes, at a LMR of 10:1. The bleached fabric was rinsed with water (60 °C) for 15 minutes, followed by cold rinsing, and subsequently treated with 1ml/l of CH_3COOH solution to neutralise any residual alkali. The treated fabric was dried at ambient conditions overnight prior to further testing. For a cold pad batch (CPB), scoured PLA fabric was padded with a solution containing 10 - 50 ml/l H_2O_2 (35% w/w), 10 g/l NaOH, 1 g/l Kieralon Jet B. conc and 10 g/l Baystabil DB at 20 °C and wet pickup of 100% o.w.f. The fabric was wrapped in a polyethylene sheet and stored for 24 hours. The bleached fabric was washed with water (60 °C) for 15 minutes, rinsed with cold water, neutralised with 1ml/l CH_3COOH and finally dried at ambient conditions.

For $NaClO_2$ bleaching, scoured PLA fabric was treated in a bath containing 2 - 10% of o.w.f $NaClO_2$ (80% w/w), 3 g/l of $NaNO_3$, 4 g/l of NaH_2PO_4 and 0.5 g/l of Kieralon Jet B conc. The pH of the liquor was adjusted to 4 with HCOOH. Bleaching was carried out at 85 °C for 45 minutes, followed by washing (60 °C) for 15 minutes and rinsing with normal water. Anti-chlorination treatment was performed with 5 g/l of $NaHSO_3$ at 60 °C for 15 minutes, followed by rinsing with water, and finally dried at ambient conditions.

For NaOCl bleaching, scoured PLA fabric was treated in a bath containing 2 - 10 g/l of available Cl_2 (NaOCl 14% w/w), with the pH adjusted to 11.5 with Na_2CO_3. The treatment was performed at 40 °C for 60 minutes, followed by anti-chlorination with 5 g/l of $NaHSO_3$ at 60 °C for 15 minutes. Subsequently the fabrics were rinsed with normal water and left to dry at ambient conditions.

Measurements
Tensile strength
Yarns were conditioned at standard conditions of 25 °C and 65% RH. Tests were performed according to BS EN ISO 2062:1995, using an 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 a desktop computer interfaced to the testing machine. Data were received and analysed by computer software QT.

Infra-red spectroscopy
Attenuated total reflectance fourier transform infrared (ATR-FT IR) spectra of PLA fabric were recorded using a Perkins Elmer (Model Spectrum 2000). The spectrometer was used in the absorption mode with a resolution of 4 cm^{-1} in the range of 4000 - 500 cm^{-1}.

X-ray photoelectron spectroscopy
A Kratos Ultra instrument was used to record XPS spectra. The samples were analysed with monochromatic Al Kα

Table I. Effect of scouring on the tensile strength of PLA yarn.

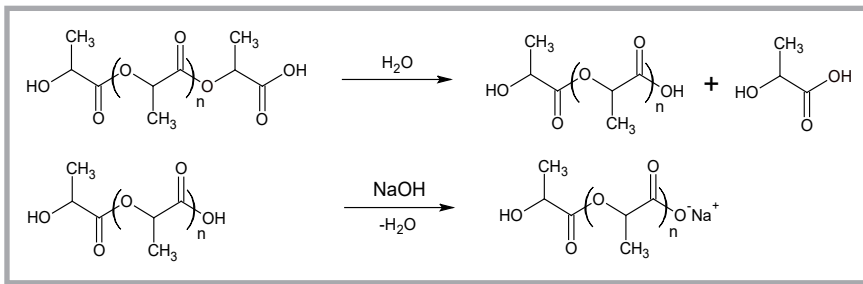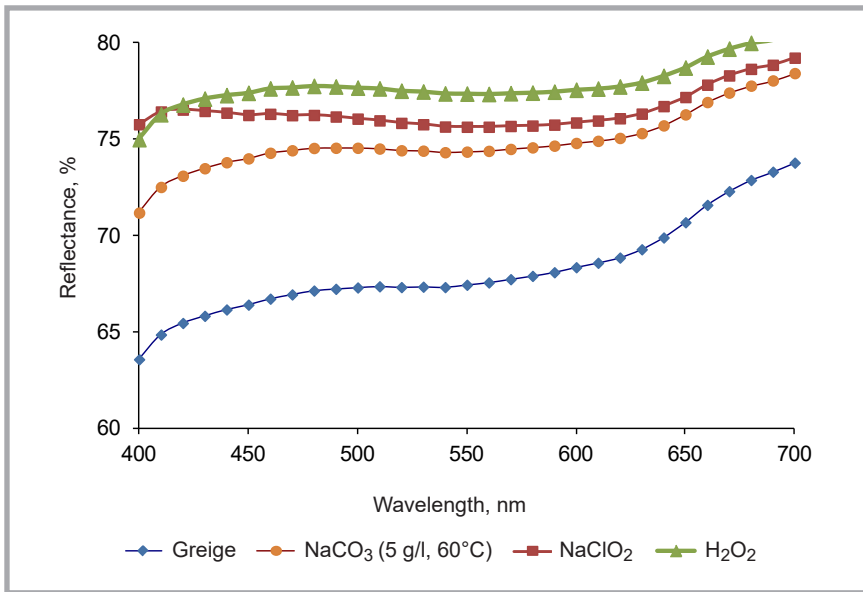| Sodium carbonate, g/l	Scouring temperature, °C			
	40	60	80	100
0	13.8 ± 1.0	13.1 ± 1.2	13.1 ± 1.0	11.2 ± 1.3
0.5	13.8 ± 1.1	13.0 ± 1.0	12.8 ± 1.0	11.1 ± 1.3
1	13.8 ± 1.1	12.8 ± 1.3	12.3 ± 1.0	11.0 ± 1.2
2	13.8 ± 1.1	12.7 ± 1.2	11.8 ± 1.2	10.9 ± 1.2
5	13.6 ± 1.0	12.6 ± 1.1	11.6 ± 1.1	10.8 ± 1.2

Figure 1. Schematic hydrolysis of PLA polymer.

Figure 2. Reflectance spectra of PLA knitted fabric after pretreatments.

Table 2. Effect of bleaching agents on the tensile strength of scoured PLA yarn

Bleach concentration	NaOH, g/l	NaClO, g/l Cl$_2$	NaClO$_2$, % o.w.f	H$_2$O$_2$, ml/l	H$_2$O$_2$, ml/l
0		14.0 ± 1.2			
2		13.7 ± 1.1			
6		13.7 ± 1.1	-		
10		13.6 ± 1.2			
0			13.2 ± 1.1		
2			12.4 ± 1.2	-	
6	-		12.4 ± 1.2		-
10			12.2 ± 1.2		
0				13.4 ± 1.2	
10				13.3 ± 1.2	
20				13.2 ± 1.1	
50				13.2 ± 1.1	
0	0.5				11.1 ± 1.0
	1.0				9.2 ± 1.2
	3.0				6.2 ± 1.0
1	0.5				11.3 ± 1.1
	1.0	-	-	-	10.3 ± 1.2
	3.0				8.4 ± 1.0
3	0.5				12.4 ± 1.2
	1.0				11.8 ± 1.2
	3.0				11.4 ± 1.3
5	0.5				12.9 ± 1.1
	1.0				12.3 ± 1.1
	3.0				11.9 ± 1.1

x-rays (1486.6 eV) at a base pressure of 4×10^{-7} Pa. Wide survey and high resolution spectra were recorded at pass energies of 100 eV and 20 eV, respectively. Curve-fitting to the data recorded was done using CasaXPS software. The binding energies (B.E) were calculated relative to the C(1s) photoelectron peak at 285.0 eV.

Scanning electron microscopy
An Hitachi SEM (Model S-3000N) was used to investigate the surface morphology of fibres sputter coated with Gold in a Polaron coating unit (Model E5100). Photo micrographs were taken at a gun-to-sample distance of 8 - 10 mm and voltage of 5 kV in the high vacuum mode. Electron beam focusing, image magnification and brightness were adjusted to take micro photographs using SmatSEM software.

■ Results and discussion

Tensile strength of PLA yarn
The tensile strength of PLA yarns scoured with sodium carbonate at various concentrations (0.5 - 5.0 g/l) and processing temperatures (40 - 100 °C) was measured, *Table I* (see page 53). The results showed that up to 60 °C, thealkali concentration did not appreciably affect the tensile strength of PLA yarn. At the glass transition temperature (T_g) the polymer chains in the amorphous region vibrate at such high amplitude that temporary voids are formed. Due to the high accessibility of the fibre structure at T_g (60 °C for PLA), the solute molecules ingress, resulting in a high rate of hydrolysis [23]. In the range of 80 - 100 °C, an increase in alkali concentration caused an ever higher loss of tensile strength. At high temperature, penetration of hot alkaline liquor inside the fibre was multiplied, thereby accelerating the hydrolysis of the polymer, *Figure 1*. From the discussion above, it was suggested that scouring should be carried out at around 60 °C to avoid undue hydrolysis of the polymer and, hence, preserve the mechanical strength. Sodium carbonate concentration as high as 5 g/l might be employed during scouring at 60 °C. A decrease in strength particularly above T_g might be attributed to the high rate of hydrolysis, which resulted in a decrease in the degree of polymerisation (DP) and, hence, the tensile strength [22].

The tensile strength of PLA yarns treated with a range of bleaching agents at vari-
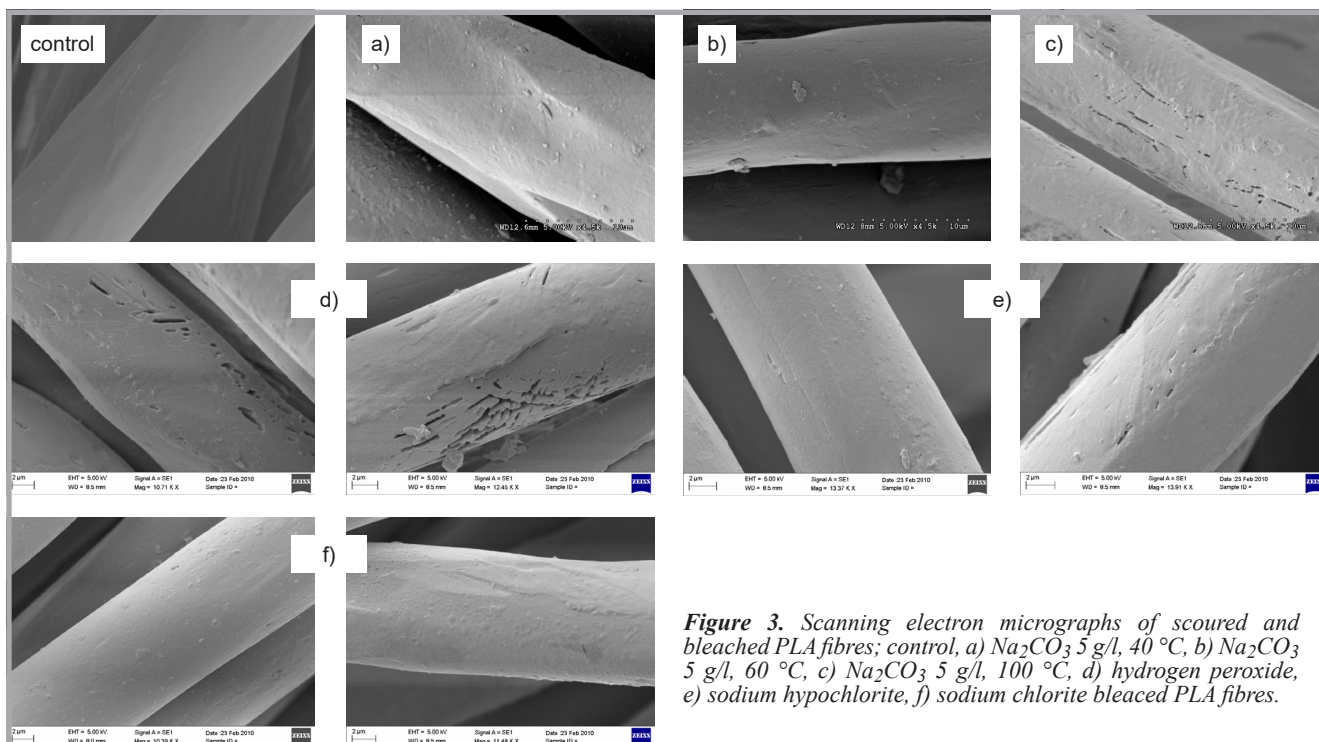
Figure 3. Scanning electron micrographs of scoured and bleached PLA fibres; control, a) Na$_2$CO$_3$ 5 g/l, 40 °C, b) Na$_2$CO$_3$ 5 g/l, 60 °C, c) Na$_2$CO$_3$ 5 g/l, 100 °C, d) hydrogen peroxide, e) sodium hypochlorite, f) sodium chlorite bleaced PLA fibres.

ous process conditions was measured, shown in **Table 2**. The results indicated that hydrogen peroxide bleaching in long liquor rendered the greatest damage to the yarn, and it was evident from the data that it was alkali which contributed to the deterioration of fibres. Since hydrogen peroxide is a weak acid, the alkali was consumed in the presence of hydrogen peroxide and produced ionized perhydroxyl ions. Accordingly, due to a lower amount of sodium hydroxide being present in the bleaching bath, there was better strength retention of PLA yarns. However, if the ratio of hydrogen peroxide and sodium hydroxide was maintained constant, there would be severe damage to the yarns. In the CPB treatment the tensile strength remained the same due to treatment being carried out at ambient conditions. In the case of other bleaching agents such as sodium hypochlorite and sodium chlorite, there were relatively negligible losses in tensile strength. The results suggested that hydrogen peroxide at low concentration was not deleterious to the fibre integrity. Sodium hypochlorite did not damage the fibres at all even at high concentration, while sodium chlorite treatment decreased the tensile strength slightly, but still acceptable. Sodium hypochlorite was applied in an alkaline medium (pH 11.5) at 40 °C, but since the bath temperature was low, there were negligible changes in the tensile strength of PLA yarns. In contrast, sodium chlorite was applied

at 85 °C (pH 4.5), and despite the high temperature; PLA retained its tensile strength at an elevated temperature when processed in an acidic medium. In short, alkaline-oxidative conditions were more dangerous to the integrity of PLA fibres than acidic-oxidative ones. The integrity of the PLA structure was affected in the following order: alkaline-oxidative-high temperature > alkaline-oxidative-low temperature > acidic-oxidative-high temperature.

Light reflectance from PLA yarn

Natural and synthetic polymeric fibres usually carry some impurities which mask their appearance and discolour the material. In synthetic fibres these impurities could be added or acquired [9]. The impurities added are mostly spinning oils and waxes, anti-static agents and sizes, while the fibres may also collect some dirt and dust particles from the surroundings. The organic impurities are mostly transparent but may develop some tint as a result of oxidation or undergoing other chemical reactions with exhaust gases from the atmosphere. It is evident from the reflectance curves that the greige fabric had lower light reflectance as compared to the scoured and bleached ones, as shown in **Figure 2**. With both scouring and bleaching treatments, an obvious significant benefit was evident in terms of raising the light reflectance.

Electron microscopy of PLA yarn

Scanning electron microscopy (SEM) of PLA yarns subjected to a range of process conditions indicated that scouring with sodium carbonate did not bring about any major change in the smooth surface morphology of PLA fibres up to 60 °C, as shown in **Figures 3.a** & **3.b**. However, scouring at high temperature imparted damage to the fibres, in particular at 80 °C, where small localised holes appeared on the fibre surface. Furthermore at 100 °C there was more widespread severe damage to the fibrous structure and slits along the fibre axis were observed, shown in **Figure 3.c**. These observations correlated with the tensile data in **Table 1**, where it was proposed that above T$_g$, hot-alkaline liquor penetrated into the polymer matrix and increased hydrolysis. Long liquor high temperature bleaching, shown in **Figure 3.d**, caused significant damage to PLA fibres, but again it was attributed to the strong alkaline conditions. SEM analysis of bleached PLA showed that long liquor hydrogen peroxide treatment caused cracking and holes to appear in the PLA filaments, and it was these holes and slits which contributed to the decrease in tensile strength of PLA yarns, details of which are shown in **Table 2**. Similarly, although PLA bleached by CPB peroxide bleaching showed little surface degradation, there was some sheet-like polymer observed on the yarns, suggesting some localised surface dam-
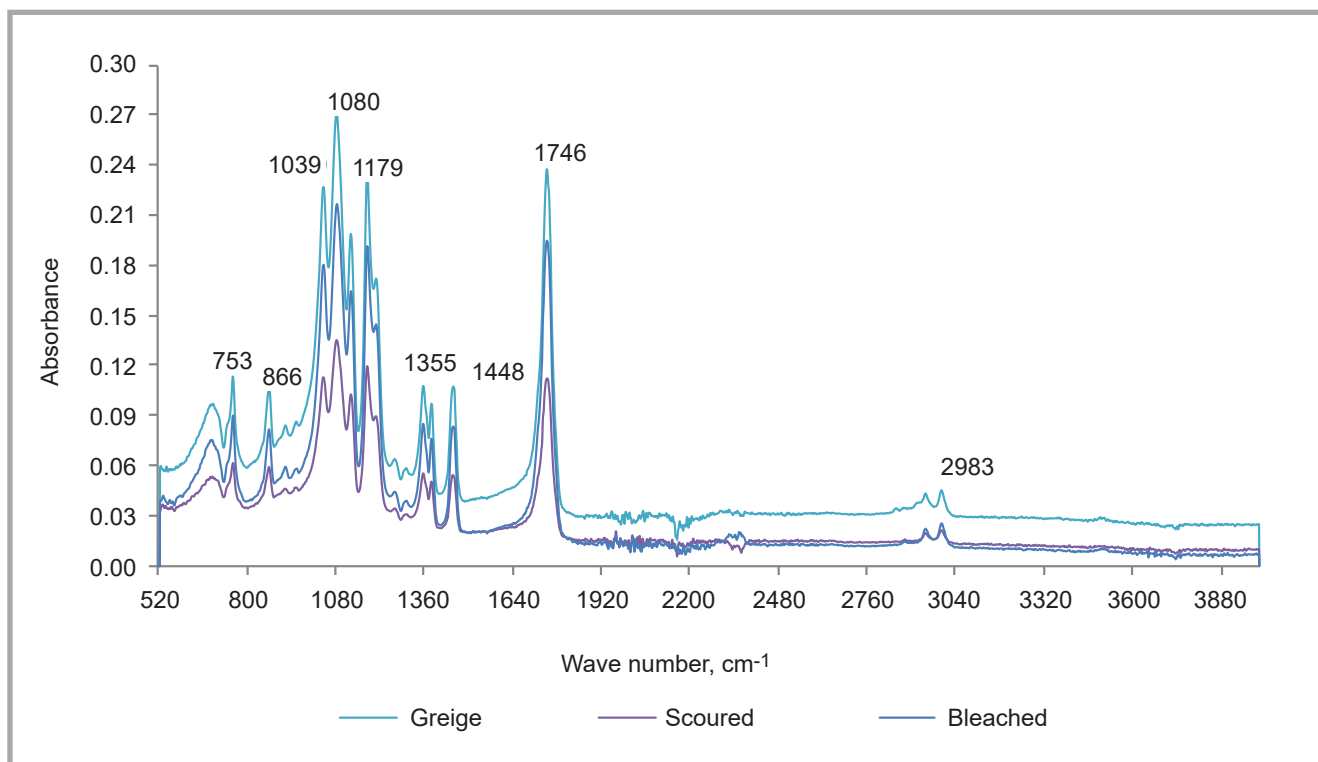
Figure 4. Fourier transform infra-red spectra of pre-treated PLA fabric.

age. For CPB bleaching with hydrogen peroxide, acceptable PLA strength retention and whiteness could be achieved due to relatively low temperature conditions. SEM analysis of the sodium hypochlorite treated PLA indicated that surface damage was minimal, although some holes and cracking were observed (***Figure 3.e***). However, the loss of strength could further be reduced by carrying out sodium hypochlorite bleaching at 25 - 30 °C. Analysis of the sodium chlorite treated PLA fibres indicated no surface degradation, shown in ***Figure 3.f***. It was concluded that alkaline-oxidative conditions at high temperature caused damage to fibres, while sodium chlorite exhibited the least damaged surface morphology, which was attributed to better stability of PLA fibres to acidic pH at high temperature and alkaline pH at lower temperatures.
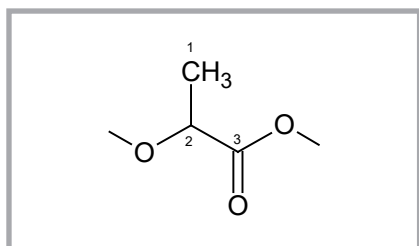

Figure 5. *Chemical repeat unit of PLA.*

Infrared spectroscopy of PLA yarn

Figure 4 shows the Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FT-IR) spectra of pre-treated PLA yarns. Since in the attenuated total reflectance mode, infra red waves penetrated only a few nanometres from the fibre surface, the chemistry of polymer surface was studied [31, 32]. The objective of the IR study was to investigate changes in the surface chemistry of PLA fibre that might have taken place during pretreatment processes. However, no new peaks were observed in IR spectra of the greige and pretreated PLA suggesting, little change in the surface chemistry of the polymer. The assignments used in this study were derived from the literature, with the peak at 1746 cm-1 assigned to the asymmetric stretching of carbonyl bonds in ester groups (-COOC-) [33 - 37]. A pair of peaks at 2983 cm-1 and 2930 cm-1 was assigned to the stretching vibration of –CH2 bonds, while the peak at 1179 cm-1 was assigned to -C-O-C- stretching of ester groups.

During scouring, the hydrolysis of PLA occurred, which resulted in the cleavage of ester bonds and the formation of carboxylic acid and hydroxyl groups at the polymer chain ends. The hydroxyl group (-OH) peaks in the IR spectra usually lie in the range of 2500 – 3300 cm-1 (carboxylic acid) and 3200 – 3600 cm-1,

but no peaks were recorded in the region of 2500 – 3600 cm-1. Therefore it was inferred that presence of hydroxyl groups was too little to be detected by the ATR-IR set up. The IR spectrum of PLA treated with hydrogen peroxide is also shown. Once again, like scoured fabric no new absorption peaks were detected in the IR spectra. It was therefore concluded that no new functional groups were generated during the bleaching of PLA. The intensity of various peaks in the IR spectra was found to be nearly the same. In conclusion, there was little information gained about the changes in the chemistry of PLA polymer due to scouring and bleaching processes using FT-IR spectroscopy.

X-ray photoelectron spectroscopy of PLA yarn

The literature review indicated that various workers fitted the varying number of peak assignments to the C1(s) spectra [38 - 41]. Zhao *et al.* fitted four peaks to C 1(s) of PLA, the peaks being –C-C-, -C-O-, -C=O and O=C-O [38]. Wardman *et al.* fitted five peaks to C1(s) of PLA, the peaks being –C-C-/-C-H, -C(∗)-COO-, -COOH, -C-O-C- and –(CO)-O-(CO)- [39]. Waliporn *et al.* fitted three peaks to C1(s) spectra of PLA. In the present work only three peaks were fitted to the C1(s) XPS spectra of PLA and were

regarded as the most representative of the surface species present.

The C(1s) and O(1s) XPS spectra of greige PLA fabric exhibited a number of peaks. In addition to the three major peaks characteristic of PLA, there were two minor peaks as well. Commercial textile fabrics contain impurities both added as well as acquired. The minor peaks might be due to the presence of various sizing chemicals, oils, lubricants, waxes etc. The O(1s) XPS spectrum contained two peaks characteristics of PLA. These peaks were due to single and double oxygen atoms bonded to the carbon atoms, *Figure 5*. There were only three spectral peaks the C(1s) XPS spectra of scoured and bleached PLA fabric. The peak at approximately 284.0 eV was attributed to the carbon-carbon/carbon-hydrogen bonds in the PLA polymer. Since the electronegativity of carbon and hydrogen is nearly the same, the chemical shifts are not resolved. The other two peaks were attributed to the -C-O- and –C=O groups in the polymer at the binding energies of approximately 286.0 and 288.0 eV, respectively.

Figure 6 shows the C(1s) spectrum of PLA fabric scoured with 5 g/l Na_2CO_3 at 40 °C. The graph shows the CPS (counts per second) on the y-axis vs. the B.E (binding energy) on the x-axis. *Figure 7* shows the C1(s) spectra of scoured PLA fabric bleached with various bleaching agents. The XPS C(1s) spectra of bleached PLA fabric indicated that the least surface damage was done during sodium hypochlorite bleaching due to little change observed in the chemical composition of the PLA polymer i.e. the spectral percentage contribution of

Table 3. *% C 1(s) components of PLA fabrics after scouring.*

Sample		C (1s) components, %		
		-C-C-/-C-H	-C-O-C-	>C=O
Greige		53.7	26.3	20.0
40 °C	0.5 g/l	50.8	27.4	21.8
	5.0 g/l	44.8	29.8	25.4
60 °C	0.5 g/l	50.5	27.8	21.8
	5.0 g/l	39.4	28.5	26.5
80 °C	0.5 g/l	50.7	28.0	21.2
	5.0 g/l	40.7	30.8	28.5
100 °C	0.5 g/l	44.5	31.0	24.5
	5.0 g/l	38.6	31.5	29.9

Table 4. *% C 1(s) components of PLA following bleaching.*

Sample		C (1s) components, %		
		-C-C-/-C-H	-C-O-C-	>C=O
Greige		53.7	26.3	20.0
Scoured		50.5	27.8	21.7
H_2O_2, ml/l	1	46.5	27.8	25.7
	5	43.3	28.8	27.9
$NaClO_2$, % o.w.f	1	46.5	29.1	24.4
	5	46.4	28.9	24.7
NaClO, g/l Cl_2	1	47.3	28.5	24.3
	5	47.3	27.9	24.8

various C(1s) components were approximtely unchanged. The results showed that the surface damage was higher due to bleaching with hydrogen peroxide in comparison to sodium chlorite and sodium hypochlorite. When comparing the results of XPS and SEM it was seen that hydrogen peroxide during long liq-
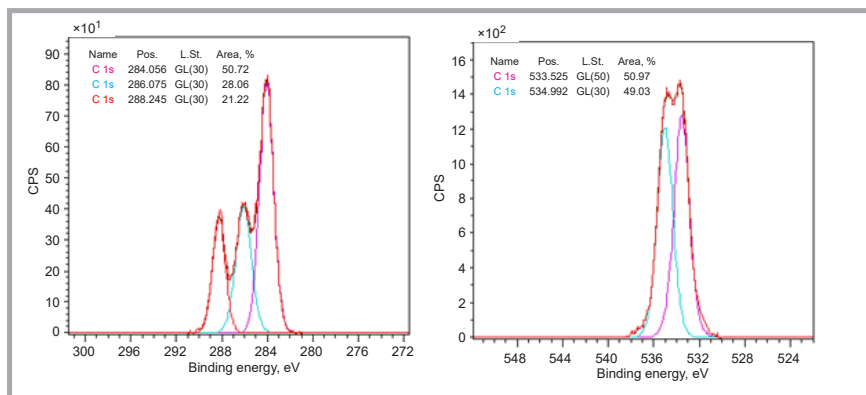

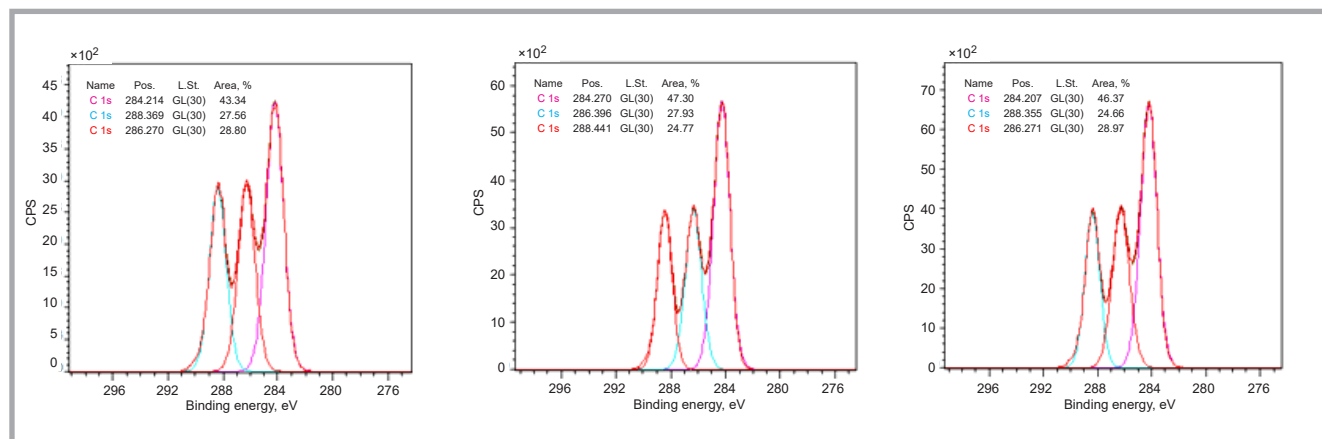**Figure 6.** *C (1s) and O(1s) of scoured PLA fabric (Na_2CO_3 5 g/l, 40 °C).*

Figure 7. *C (1s) Spectrum of peroxide bleached PLA fabric; a) H_2O_2, b) $NaClO_2$, c) NaOCl.*

uor application imparted greater bulk and surface damage/modification. The spectral contributions of the various C(1s) components of scoured PLA are presented in **Table 3** (see page 57) and indicate that there was a decrease in the -C-C- species and increase in -C-O-C- and >C=O spectral contributions. The increase in the latter two components might be due to the oxidation of the PLA polymer and/or removal of surface contaminants. The increase in polar groups, such as carboxyl, at the fibre surface improves fibre adhesion to various coatings and reduces static charge build-up. The XPS results correlated with the above-mentioned tensile strength measurements and SEM.

The spectral contributions of the various C(1s) components of bleached PLA are presented in **Table 4** (see page 57), which indicate that sodium hypochlorite did not appreciably damage the PLA, as the percentage of various C(1s) components remained the same even after treatment at 5 g/l available chlorine. These results were in accordance with tensile strength measurements, where bleaching was performed at low temperature and there were negligible changes in the structure of PLA fibres. The bleaching with sodium chlorite also did not greatly affect the tensile strength, and the XPS results showed that during bleaching with sodium chlorite, PLA did not undergo appreciable degradation due to little change in the chemical composition of the polymer. However, bleaching with hydrogen peroxide proved to be deleterious, as evidenced by the higher levels of surface oxidation.

■ Conclusion

PLA was not damaged during scouring by a non-ionic detergent and sodium carbonate up to 5 g/l. A processing temperature up to 60 °C (T_g) should be used for PLA and the pH must not exceed 11. The SEM analysis indicated that scouring above T_g caused the formation of pin holes in the structure of fibres; the formation of surface holes was high at 100 °C. Bleaching with sodium hypochlorite at 40 °C for 30 minutes in the presence of 10 g/l of available Cl_2 did not affect the tensile strength, while sodium chlorite concentration as high as 10% o.w.f at 85 °C was acceptable. CPB bleaching with hydrogen peroxide up to 50 ml/l at ambient conditions did not affect the PLA

tensile strength. Alkaline-oxidative conditions were more deleterious to PLA polymer than acidic-oxidative conditions; the lower the temperature, the lower the fibre damage. SEM results showed that hydrogen peroxide bleaching caused pinhole and slit formation in fibres and, therefore, resulted in strength losses. ATR-FT-IR spectroscopy of scoured and bleached PLA indicated that few or no new functionalities were introduced into the polymer. The XPS of pretreated PLA revealed that during scouring and bleaching newer surfaces were exposed and that bleaching with sodium hypochlorite and sodium chlorite was less damaging than hydrogen peroxide. Polar groups such as hydroxyl and carboxyl generated during pretreatment might improve the adhesion of textiles to various coatings and reduce static charge build-up.

References

1. Drumright RE, Gruber PR and Henton DE. *Advanced Materials* 2000; 23: 1841.
2. Cargill, Inc., US Patent No. 5142023.
3. Hoogsteen W, Postema AR, Pennings AJ, Brinke GT and Zugen P. *Macromolecules* 1990; 23: 634.
4. Dugan, JS. *Novel Properties of PLA Fibres.* In Research Fiber Innovation Technology, Inc. 26 – 28 September 2000. Dallas, Texas, USA.
5. Avinc O. Ph.D Dissertation, UMIST, Manchester, UK, 2007.
6. Schmitt EA, Flanagan DR, and Linhardt RJ. *Macromolecules* 1994; 27: 743.
7. Baig GA. *Polish J. Chem. Tech.* 2014; In press.
8. Baig GA. *Fibers and Polymers* 2013; 14: 1912.
9. Ahmad G. Ph. D Dissertation, University of Manchester, UK, 2012.
10. Betrabet SM. *Bleaching & Mercerising*, BTRA, India, 1985.
11. Karmakar SR C*hemical Technology in the Pre-treatment Processes of Textiles*, Elsevier Science B.V., Netherlands,1999.
12. Avinc O and Khoddami A. *Fibre Chemistry* 2010; 42: 68.
13. Tomasino C. Chemistry & Technology of Fabric Preparation & Finishing, NCSU, USA, 1992.
14. Carr CM. Chemistry of the Textiles Industry, Blackie Academic & Professional, UK, 1995.
15. Chesner L. Woodford. G. C. *J.S.D.C.* 1958; 74: 531.
16. Hickman WS. *Coloration Technology* 2002; 32: 13.
17. Joziasse CAP, Grijpma DW, Bergsma JE, Cordewener FW, Bos RRM and Pennings AJ. *Colloid Polym. Sci.* 1998; 276: 968.

18. Grizzi I, Garreau H, Li S and Vert M. *Biomaterials* 1995; 16: 305.
19. Nakamura T, Hitomi S, Watanabe S, Shimizu Y, Jamshidi K, Hyon SH and Ikada Y*J. Biomed. Mater. Res.* 1989; 23: 115.
20. Vert M, Li S, Garreau H, Mauduit J, Boustta M, Schwach G, Engel R and Coudane J. *Ange. Makromol. Chem.* 1997; 247: 239.
21. Mauduit J, Perouse E and Vert M*J. Biomed. Mater. Res.* 1996; 30: 201.
22. Hyon S, Jamshidi K and Ikada, Y. *Polym. Int.,* 1998; 46: 196.
23. Iwata T and Doi Y. *Sen'i Gakkaishi* 2001; 57: 172.
24. Tsuji H and Nakahara K *J. Appl. Polym. Sci.* 2002; 86: 186.
25. Tsuji H, Nakahara K and Ikarashi K. *Macromol. Mater. Eng.* 2001; 286: 398.
26. Suesat J. Ph. D Dissertation, UMIST, Manchester, UK, 2004.
27. Phillips D, Suesat J, Wilding M, Farrington D, Sandukas S, Sawyer D, Bone J. and Dervan S. *Color. Technol.* 2004; 120: 35.
28. Phillips D, Suesat J, Wilding M, Farrington D, Sandukas S, Sawyer D, Bone J and Dervan S. *Color. Technol.* 2004; 120: 41.
29. Eren H A, Avinc O, Uysal P and Wilding M. *Tex. Res. J,* 2011; 8: 1091.
30. Carr CM, Vynias D, Baig GA and Volooj S. *10th Asian Textile Conference,* Ueda, Japan, 2009
31. Vigo TL. *Textile Processing and Properties*, Elsevier, 1994
32. Skoog DA, Holler FJ and Nieman TA. *Principles of Instrumental Analysis*, 5th ed., Harcourt Brace & Company, UK, 1998
33. Kister G, Cassanas G and Vert M. *Polymer* 1998; 39: 267.
34. Kister G, Cassanas G and Vert M *J. Raman Spectroscopy* 1995; 26: 307.
35. Kister G, Cassanas G and Vert M. *Polymer* 1998; 39L 3335.
36. Lee S H and Song W S *J. Korean Soc. of Cloth. & Tex.* 2011; 35: 670.
37. Vey E, Rodger C, Booth J, Claybourn M, Miler AF and Saiani A. *Poly. Degradation & Stability* 2011; 96: 1882.
38. Zhao G, Gao J, Gao Q and Chen Y. *Plasma Science & Technology* 2011; 13: 230.
39. Wardman RH. and Abdrabbo A. *AUTEX Res. J.* 2010; 10, 1.
40. Inagaki N, Narushima K, Tsutsui Y. and Ohy Y. J. *Adhesion Sci. Technol.* 2001; 16: 1041.
41. Beamson G and Briggs D. High Resolution XPS of Organic Polymers, Wiley, New York, USA, 1992.