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An experimental investigation of modified and unmodified flax fibres with XPS, ToF-SIMS and ATR-FTIR

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Natural fibres are envisaged today as potential candidates for replacing glass fibres in composite materials. Although natural fibres have a number of advantages over glass fibres, the strong polar character of their surface is a limiting factor as, compatibility with strongly apolar thermoplastic matrices is very low. Such problems of incompatibility may be overcome with fibre pre-treatments, which can enhance compatibility although having a negative impact on the economics of using such materials. In this study two fibre pre-treatment methods, acetylation and stearic acid treatments, have been applied on flax fibres. The effect of these two pre-treatments has been examined by use of XPS, ToF-SIMS and FTIR spectroscopic methods. It was found that the fibre surface before treatment is very different to what may have been expected for cellulose materials. There is an appreciable coverage of the flax fibre surface with hydrocarbon compounds, possibly waxy substances, but no aromatic compounds were detected. All three spectroscopic methods revealed that the fibre surface chemistry has been altered after the treatments, and especially for acetylation it was found that ester bonds are present on the fibre surface after treatment. For the stearic acid treatment the situation still remains less conclusive. Finally, ToF-SIMS experiments revealed that the coverage of the fibre surface with acetyl groups and stearic acid is highly heterogeneous.

1. Introduction

Over the last few years there has been an increasing interest in using natural fibres as reinforcing agents in composite materials [1–7]. A combination of properties, such as low cost, low density, non-toxicity, high specific properties, no abrasion during processing, and recycleability, all contribute to a rising interest from the manufacturing industry of low cost, low weight composites. However, there are a number of problems associated with incorporating such fibres into thermoplastic matrices, most notably fibre-matrix incompatibility where apolar polymers are concerned, and thermal stability of the fibres where relatively high processing temperatures are required. The compatibility problem may be further complicated by dimensional instability of the resulting composites in humid conditions. When water is absorbed the matrix is placed under stress by the swelling of the fibres. Since no significant bonding exists between the fibres and the matrix, when the material is dried a rapid shrinkage of the fibres takes place that results in propagation of debonding cracks and severe deterioration of mechanical properties [8]. In addition, the poor interface contact between cellulose fibres and thermoplastic may contribute to phase separation under stress, especially at subzero temperatures, and lead again to the degradation of mechanical properties [9].

Fibre pre-treatments, although increasing the cost, are potentially able to overcome these limitations. In the past many attempts have been made to modify the surface properties of cellulose fibres in order to enhance adhesion with the matrix. Various methods such as corona treatment [10], plasma treatment [11], mercerisation [12], heat treatment [13], graft copolymerisation [14, 15], silane treatment [12, 16] and treatments with other chemicals [17–20], to mention just a few, have been reported to affect the compatibility

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in natural fibre composites, in most cases positively. However, the methods referred to possess many disadvantages, the most important of which are the use of expensive equipment or the use of expensive chemical reagents.

Acetylation is a rather attractive method of modifying the surface of natural fibres and making it more hydrophobic. It has been shown to reduce swelling of wood in water [21] and has been studied more than any other chemical reaction of lignocellulosic materials. The main principle of the method is to react the hydroxyl groups (—OH) of the fibre with acetyl groups (CH_3CO—), therefore rendering the fibre surface more hydrophobic. The hydroxyl groups that react are those of the minor constituents of the fibre, i.e., lignin and hemicelluloses, and those of amorphous cellulose [22]. The hydroxyl groups in the crystalline regions of the fibre are closely packed with strong interchain bonding, and are inaccessible to chemical reagents. Acetylation has been shown to be beneficial in reducing moisture absorption for natural fibres. Reduction of about 50% of moisture uptake for acetylated jute fibres and of up to 65% for acetylated pine fibres has been reported in the literature [23]. Liu *et al.* [24] studied the effect of acetylation in natural fibre composites (cotton, rayon, wood with polystyrene as matrix) and they showed by using the micro-debond test that acetylated fibres had an increased interfacial shear strength. Furthermore, they reported that acetylation increased the dispersive component of the surface energy of the fibres. Similar results to the ones reported by Liu *et al.*, have been also found by the authors of the present study [25]. Acetylation has also been found to enhance the interface in flax/polypropylene composites [26].

Another promising method of modifying the fibre surface of natural fibres is sizing with fatty acids such as stearic acid. Stearic acid has been used previously as a sizing agent in the papermaking industry, with photographic paper being one of the principal applications [27]. The principle of the method is similar to that of acetylation. The carboxylic group (—COOH) reacts with the hydroxyl groups of the fibre through an esterification reaction and, hence, they reduce the number of hydroxyl groups available for bonding with water molecules. Furthermore, the long hydrocarbon chain of stearic acid (C_{18}) provides an extra protection from water since it is itself quite hydrophobic. Another advantage of stearic acid is that it is not susceptible to oxidation at the processing temperatures of natural fibre/polypropylene composites [27]. The bonding of stearic acid onto cellulose has been investigated by infra-red spectroscopy (IR) [28] and by X-ray photoelectron spectroscopy (XPS) [29]. The sizing with stearic acid can be done via a solution process where the sizing agent is dissolved in an appropriate solvent.

In our laboratory, however, we have developed a vapour phase sizing process where there is no solvent involved. Vapour phase sizing is a very clean method that makes a more efficient use of sizing chemicals than is now practised with conventional sizing methods. It eliminates the requirement of a solvent and its subsequent evaporation. Furthermore, the current emphasis on environmentally friendly processes accentuates the need for more efficient processes as opposed to more and larger effluent treatment units. The application of stearic acid treatment on flax fibres has also been found to strengthen the interface in flax/polypropylene composites [26].

In this study an investigation of the surface chemistry via XPS (X-ray photoelectron spectroscopy), ToF-SIMS (time-of-flight secondary ion mass spectrometry), and ATR-FTIR (attenuated total reflectance Fourier transform infra-red spectroscopy) is reported.

2. Experimental

2.1. Materials

Six different types of flax fibres were used in this study. Green flax (GR), dew-retted flax (DR), acetylated green flax (ACGR), acetylated dew-retted flax (ACDR), stearic acid sized green flax (STGR), and stearic acid sized dew-retted flax (STDR). GR and DR flax were supplied by CERES BV, Holland. GR flax consists of fibres that have been mechanically extracted from the flax stem directly after harvesting. DR flax fibres have received a partial bacterial degradation by laying the plant stem in the field for a period of up to one month after harvesting. The fibres can then be extracted more easily from the weakened plant stem, and are less damaged than their green counterparts Further details of the extraction of flax and other vegetable fibres are described more fully elsewhere [30].

The acetic anhydride was of reagent grade and was supplied by BP Chemicals Ltd. Stearic acid was of 98% purity and purchased from BDH Chemicals Ltd., UK.

2.2. Flax fibre treatments

Acetylation was performed following Rowell's method [31]. The fibres were first "overdried," that is until no further loss of weight, for 24 h at 105°C. They were then placed in a stainless steel mesh container and dipped into a beaker containing acetic anhydride for 1 min. Afterwards they were drained for 3 min and placed in a preheated (120°C) oven for two hours. After the reaction was completed, the fibres were placed in a vacuum (0.003 MPa) for 2 h at 120°C and then overdried for 12 h (the fibres produced in this process are identified with the prefix 'AC').

The experimental procedure of the vapour phase sizing was as follows. A stainless steel tank containing stearic acid was placed in a preheated oven at 105°C. The fibres were first overdried and then placed on a fine mesh directly above the stearic acid. The duration of the treatment was 36 h, as this has been found to be the optimum treatment time for strength purposes [26]. Afterwards the fibres were overdried for 12 h (the fibres produced in this process are identified with the prefix 'ST').

It has previously been shown [25] that the fibres undergo a large weight percent gain after acetylation. This gain, of the order of 10–15% for treatment times of 2 h and above indicates that this process is not just a surface modification, but that a significant amount of sub-surface and bulk material is capable of participating in the reaction. It has been shown, however, that there is virtually no difference between the uptake of GR and DR fibres. On the other hand, stearic acid treatment of DR flax only results in weight gains of the order of 0.05–0.25% [25]. This indicates that the large stearic acid molecule is not capable of penetrating the surface pores of the natural fibre, and is therefore only likely to affect the surface of the fibre if a reaction occurs.

It has to be noted that for all experiments the fibres were used without any pre-drying, i.e., as received.

2.3. X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed with a ThermoVGScientific Sigma Probe using a microfocusing monochromatic Al K_α X-ray source at an operating pressure of not more than 10^{-8} mbar. All spectra were recorded using a spot size of 30 μm in order to maximise the analysis area incident with the fibre surface (fibre diameter approximately between 50 and 100 μm). The fibres were located using the video camera aid coincident with the field of view of the X-ray beam. Charge compensation was provided by a LEG 31 electron gun operated at 6 eV. Survey spectra were acquired using a pass energy of 50 eV (3 scans, channel width 1 eV), and high resolution spectra were recorded with a pass energy of 20 eV (15 scans, channel width 0.2 eV). The fibres were mounted by placing them on aluminium foil, and trapping them between a nickel backing plate and cover plate (aperture 7 mm). This assembly was then clipped to the sample platten of the spectrometer. Therefore, an aluminium signal would be observed in the resultant spectrum if the beam was not located accurately on the desired fibre.

2.4. Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

ToF-SIMS analysis were recorded using a VG Scientific Type 23 system equipped with a two-stage reflectron-type analyser and a MIG300PB pulsed liquid metal ion source. The primary ion beam used was a 20 keV $^{69}Ga^+$ ion beam rastered over an analysis area of either 0.5 mm by 0.5 mm, or 0.25 mm by 0.25 mm (depending on the spectral resolution attained by the former) at a rate of 5 kHz. The beam current used was 0.5–0.6 nA and the pulse width 25 ns, resulting in a primary ion dose well within the static SIMS regime for both analysis areas [32–34]. The spectrometer was run at operating pressure of approximately 10^{-9} mbar and the mass range recorded was m/z = 0–500 in both positive and negative modes. The use of a LEG 50 electron gun operated at 14 eV was also implemented to alleviate sample charging. Samples were mounted in a similar way to the XPS specimens, although in this case they were mounted on spring-loaded stubs prior to introduction to the spectrometer.

2.5. Attenuated total reflectance-fourier transform infra-red spectroscopy (ATR-FTIR)

The flax fibres were analysed with a Mattson Genesis II spectrometer equipped with $LiTaO_3$ and DTGS detectors. The spectra were obtained with an accumulation of 25 scans and with a resolution of 0.5 cm^{-1}. They were recorded in the transmission mode and in the range of 700–4000 cm^{-1}. The fibres were mounted on a 'Golden Gate' ATR accessory prior to scanning. The spectrometer was operated on a scanning velocity (laser clock frequency) of 20 kHz. The results were obtained and analysed with the Mattson WinFIRST data acquisition and analysis software for Windows 95.

3. Results and discussion

3.1. XPS of flax fibres

Flax fibres consist of a number of elementary fibres (approx. 40) that are bound together by a lignin/hemicellulose matrix [30]. The bulk fibre consists of approximately 70 wt% cellulose ($C_{12}H_{22}O_{10}$; O/C = 0.83), 18 to 19 wt% hemicellulose (polysaccharides with a range of monomers, where O/C $\approx$ 0.83), 2 to 2.5 wt% lignin (a complex polymer, where O/C = 0.35 [35], 2 to 2.5 wt% pectin (composition and O/C ratio similar to hemicellulose), and 1.5 to 2 wt% wax [31]. The greater proportion of cellulose lies within the elementary fibre in the form of crystalline and amorphous cellulose. Therefore, it can be expected that the fibre surface will be enhanced in lignin and hemicellulose material, which helps bind the fibres together, and wax, which acts as a natural barrier to the environment for the plant stem. In addition to this composition, there is an appreciable amount of water associated with the fibre (about 5 to 10 wt%), which can penetrate along the fibre direction through the hollow centre of the elementary fibres of the plant or be adsorbed through the fibre surface. The dew-retting process exploits the preferential degradation of lignin, pectin, and hemicellulose over cellulose to allow easier extraction of the fibres from the plant stem. Therefore, the surface of DR should possess greater polysaccharide character than the GR flax.

Fig. 1 shows the survey spectra acquired for all of the six types of flax fibres. As seen in the figure, all the fibres exhibit very simple spectra containing only carbon (BE = 285 eV) and oxygen (BE = 533 eV). This shows that after the extraction process, even where green fibres are concerned, there is no material containing significant amounts of N, P, Ca, K, or Na, as might be expected from natural materials. The O/C ratios for each type of fibre are presented in Table I. It can be seen that the O/C ratio for GR flax is 0.22, a value much lower than that expected for a purely polysaccharide surface (O/C $\approx$ 0.83). Therefore, it appears that the surface of the fibre is enriched in lignin-type material

TABLE I O/C ratios and peak-fitted C 1s ratios of flax fibres from XPS data

				C_1 (C–C)		C_2 (C–O)		C_3 (C=O)			
	C 1s at.%	O 1s at.%	O/C	eV	%	eV	%	eV	%	C_4 (O–C=O)	
DR	80.0	20.0	0.25	285	40.8	286.7	44.9	288.3	14.3	–	
ACDR	87.9	12.1	0.14	285	85.7	286.7	10.3	–		289.0	4.0
STDR	82.9	17.1	0.21	285	100	–		–		–	
GR	81.7	18.3	0.22	285	52.6	286.5	34.7	288.7	12.6	–	
ACGR	79.4	18.6	0.23	285	52.4	286.8	38.2	–		289.3	9.4
STGR	83.7	16.3	0.19	285	58.5	286.2	32.7	288.3	8.8	–	

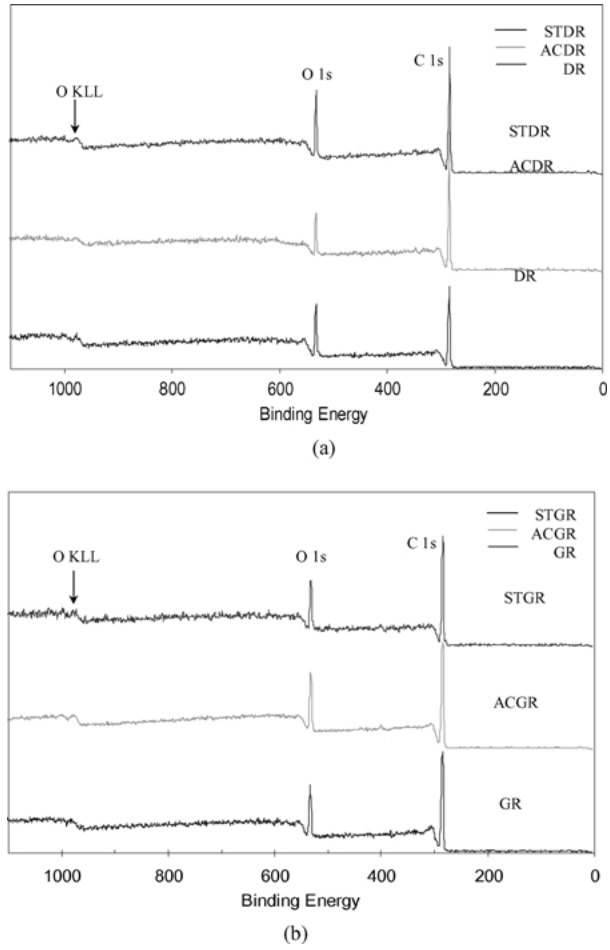


Figure 1 The XPS survey spectra for treated and untreated flax fibres.

(O/C ≈ 0.35), and/or waxes. High resolution spectroscopy of the C 1s peak (not shown, reported in Table I) reveals that the carbon is present mostly in a hydrocarbon environment (C_1), with a significant amount present as alcohol or ether moieties (C_2), and a small amount of carbon possessing two bonds with oxygen atoms (C_3). Cellulose naturally possesses carbon atoms in an O–C–O environment, which arise as a result of the condensation reaction from the base sugar units. In pure cellulose, this would account for one-sixth of the carbon atoms in the cellulose backbone. Dew-retting has the effect of increasing the alcohol/ether content of the fibre surface, probably as a result of preferential degradation of hemicelluloses and removal of pectinous and waxy material from the fibre surface. Indeed it has been found through SEM examination that the DR fibre surface is considerably rougher than it is for GR fibres, which still have organic binding material (lignin, hemicellulose, wax) adhered to the surface [6, 25].

There is also an absence of a shake-up satellite at approximately 291 eV, suggesting that the surface treatments do not result in the formation of aromatic functional groups. This observation is of general importance to all the fibre surfaces, because the lignin macromolecule is rich in aromatic groups. Although the fibre is thought to contain only 2.2% lignin, if this was enhanced at the surface it would be an explanation for the relatively low O/C ratios recorded for all the fibres. However, the absence of any significant shake-up satellite (generally stated as approximately 10% of the C_x peak detected from the aromatic carbons present) points to a surface that is not enriched with lignin, but with waxy material. Therefore, this analysis suggests that the flax stem utilises waxes and/or lipids not only in the epidermis as it is generally thought, but also within the plant stem at the cell barrier between the technical fibres.

It is interesting to note that the O/C ratio, and both the C_1 and C_2 moieties for ACGR fibre remains unaltered after the acetylation procedure. However, the O–C–O component of the C 1s peak has been replaced with a peak that further shifted relative to the hydrocarbon peak. The peak has been reassigned as a result of this slight change in binding energy, because the O–C–O line is expected to fall in between 287.83 and 288.06 eV, whereas the O=C–O moiety is usually found to lie between 288.64 and 289.23 eV. Although these discrepancies are on the edge of experimental error, it does appear to be consistent with the presence of a carboxyl moiety indicating that part of the surface has reacted with the acetic anhydride.

The C–O moiety is increased slightly by the reaction, suggesting that either the reaction is inefficient or that a large proportion of the C_2 peak may be attributable to etheric carbon. Given that the O/C ratio does not change, and that the C_1 peak remains largely unaltered, it seems reasonable to conclude that the reaction with acetic anhydride can occur only on restricted parts of the fibre surface. Therefore, it appears that a proportion of the surface of GR fibres is not susceptible to the acetylation procedure, and coverage of the surface is heterogeneous. These results support the hypothesis that the surface of GR flax is enriched with waxy material that is largely unreactive towards acetic anhydride. However, the large weight gain (∼15% from immersion for 5 h) that is found from acetylation of green flax

[25] suggests that the reactant is capable of penetrating the surface and reacting with sub-surface and bulk material.

The scenario for DR fibres is somewhat different. Acetylation has the effect of decreasing the O/C ratio by approximately 50%, and the profile of the C 1s peak is radically altered. Although the alcohol/ether moieties are significantly reduced as expected from the acetylation procedure, the carbon present in a carboxyl environment is approximately 50% of that found in ACGR fibres. At this stage there is no solid explanation to account for this sharp difference of the effect of acetylation between DR and GR fibre. Possibly there is hydrogen bonded water molecules present within the fibre subsurface of DR fibres, which are removed on contact with acetic anhydride and converted to acetic acid. On the other hand the water in the GR fibre is probably present in the bulk rather than the surface or the subsurface. It has been found through X-ray diffraction that GR is less crystalline than DR [6, 25], hence, this assumption seems reasonable as it is more difficult for the water to penetrate in the bulk of the more crystalline DR fibre.

Table I also shows the O/C ratio and C 1s peak assignment for STGR and STDR fibres. The O/C ratio for GR flax is not altered greatly after exposure to stearic acid. The C 1s peak exhibits slightly enhanced hydrocarbon character, and a slight decrease in oxygen bound carbon. The results here indicate that there is a partial covering of the surface by the fatty acid, although there is no evidence that an esterification reaction has occurred. XPS is unlikely to detect the ester or acid introduced to the surface as a result of chemical reaction or physical adsorption, because the length of the hydrocarbon chain in stearic acid is greater than the escape depth of the expelled photoelectron.

The situation for STDR fibres is very different. There is still a significant amount of oxygen detected on the fibre surface (a slight decrease compared to DR fibres), although the C 1s peak is symmetrical, indicating carbon is present purely as hydrocarbon. It appears that the fibre surface has been totally covered in fatty acid, and the presence of oxygen suggests that there may be a significant amount of water still associated with the fibre surface. It is possible that this water has just condensed on the fibre surface and remained there, but once again there is no solid evidence for this assumption.

3.2. ToF-SIMS of flax fibres

ToF-SIMS fragmentation patterns can be very informative with regard to the chemical structure of the uppermost 2 nm of the sample surface. Therefore, alterations in the spectra are expected if either reaction has occurred successfully on the surface, because this technique is very sensitive to alterations in chemical structure. However, even though ToF-SIMS is a very powerful technique it has not been used to investigate the surface chemistry of natural fibres. To the best of our knowledge this is the first study reporting ToF-SIMS results for natural fibres. The positive ToF-SIMS spectra for DR, ACDR, STDR and for GR, ACGR, STGR fibres in the range $m/z = 0$–100 Da are shown in Figs 2 and 3, respectively. The cylindrical nature of the fibres results in relatively poor spectral resolution, so effectively the spectra are limited to unit mass resolution. The surprising observation is that there is no discernible difference between the spectra, despite the fact that XPS reveals an alteration in the C 1s envelope with surface treatment. There is also very little difference between the spectra recorded for the GR and DR fibres. In fact, all the ToF-SIMS spectra are typical of hydrocarbon-type surfaces, and do not display any prominent ions that are characteristic of cellulose. This general result is very difficult to explain in the light of the previous XPS results, which clearly indicated differences in O/C ratios and chemical modification to the carbon atom environment. Both sets of analyses show that the fibre surface does not consist of the cellulose-type material expected. It appears that there is still a hydrocarbon layer on the surface of the fibres after both dew-retting and acetylation, showing that bacterial action and submersion in acetic anhydride does not effectively remove the fatty substance present on the fibre surface. The absence of inorganic ions such as sodium ($m/z = 23$) and calcium ($m/z = 40$) is also notable, because the detection limit is very good for such ions with a low ionisation potential.

An examination of the positive spectra of DR-STDR and GR-STGR fibres in the range of $m/z = 200$–300 Da (Figs 4 and 5, respectively) reveals the appearance of two new peaks at 267 and 285 Da after stearation. These two new peaks are characteristic of the stearic acid molecule [36] and correspond to the ($C_{17}H_{35}C{\equiv}O^{+}$) ion and to the molecular ion ($C_{17}H_{35}CO_2H_2^{+}$), respectively. These two peaks are indicating that stearic acid has been deposited on the surface of the stearated fibres, although provide no information as to if an esterification reaction has taken place. There is also another peak associated with stearic acid in the negative mode. This peak should appear at $m/z = 283$ Da, but an examination of the negative mode spectra of STDR and STGR did not reveal such a peak. The absence of the 283 (negative mode) peak can be explained by the fact that after ion bombardment the fibre surface is charged positively. Hence, it is very difficult for large negatively charged ions to escape from the surface and probably this is the reason for not detecting the 283 Da peak.

Figs 6 and 7 show the negative ToF-SIMS spectra for modified and umodified DR fibres (DR, ACDR, and STDR) and for modified and unmodified GR fibres (GR, ACGR, and STGR). The spectra observed are very simple, and exhibit only ions of low mass. The only apparent difference is the presence of the peak at $m/z = 59$, present in the ACDR and the ACGR spectra of Figs 6b and 7b, attributed to the CH_3COO^{-} ion. The presence of this ion indicates the acetylation procedure has altered the surface as intended. As seen in Figs 6 and 7 the stearic acid treated fibres have a similar spectrum to the untreated fibres.

Semi-quantitative data may also be obtained by normalising the peak in question to the total number of

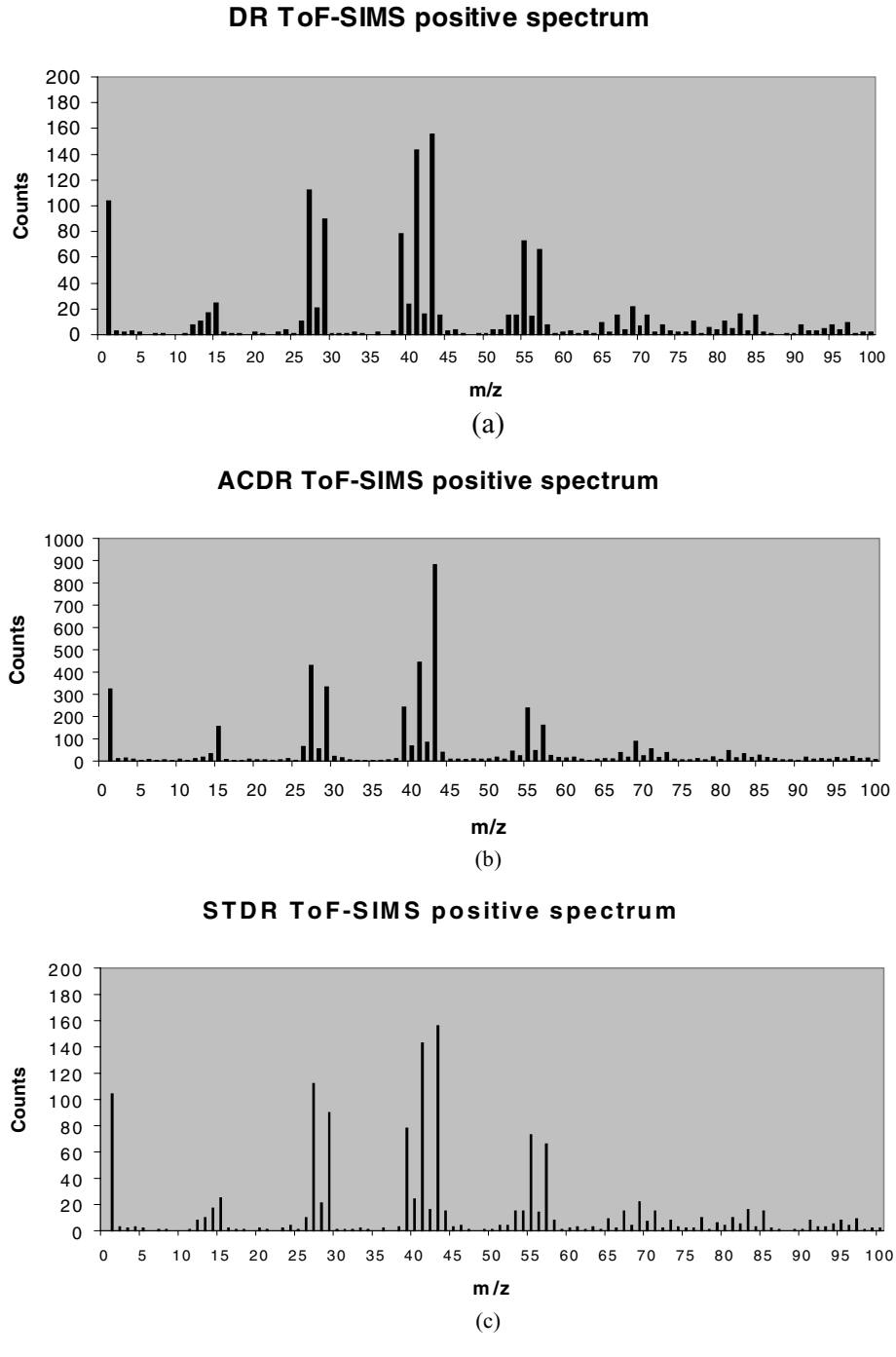
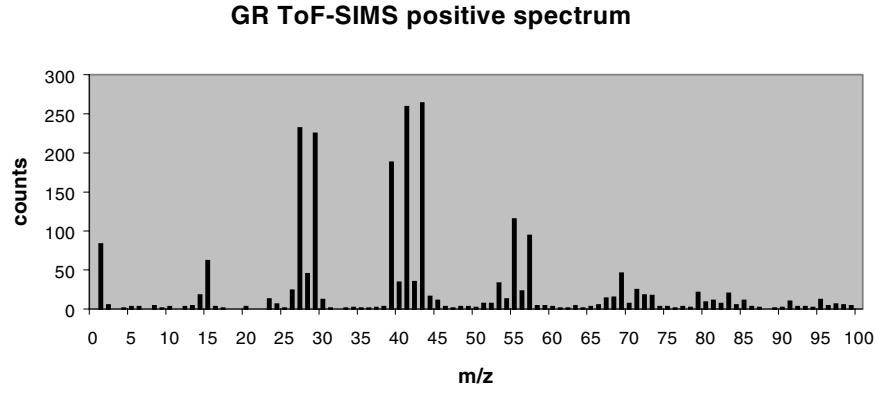


Figure 2 ToF-SIMS positive spectra of DR (a), ACDR (b) and STDR (c) fibres (m/z = 0–100 Da).

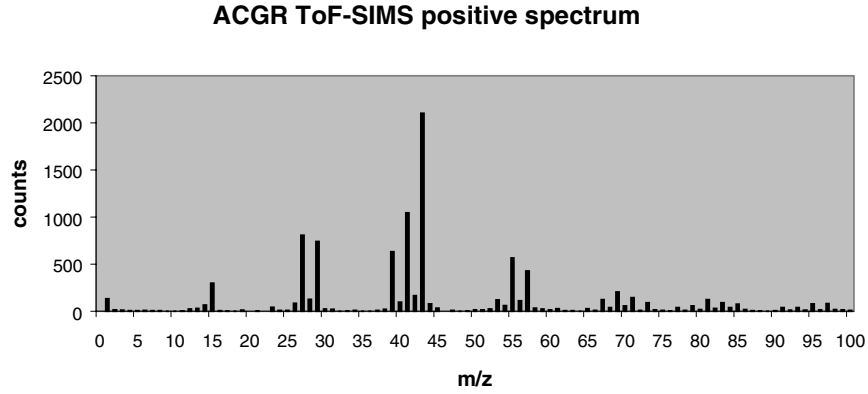
counts recorded in the spectrum. Fig. 8 shows a plot of the normalised intensity of the $CH_3CO_2^-$ ion for ACDR and ACGR flax fibres. The analysis points were taken from the same sample, at different points along the fibres. It is clear that there is a great deal of scatter in the relative intensities from the different analysis points of the acetylated fibres. It therefore appears (as with XPS) that the acetylation procedure is a heterogeneous one, suggesting that some areas of the surface are more strongly acetylated than others. In similar fashion Fig. 9 shows the normalised intensities for the ions at m/z = 267 (Fig. 9a) and at m/z = 285 (Fig. 9b). Once again there is a great deal of scatter in the relative intensities from the different analysis points of the stearated fibres, suggesting that the stearic acid treatment is producing an inhomogeneous surface similarly to acetylation.

3.3. ATR-FTIR of flax fibres

The FTIR spectra of DR-ACDR and GR-ACGR are shown in Figs 10 and 11, respectively. It may easily be seen that in both ACDR and ACGR cases two new peaks appear at around 1733 cm^{-1} and 1228–1235 cm^{-1}. These two peaks are associated with the C═O stretching (1733 cm^{-1}) and with the C─O stretching (1228–1235 cm^{-1}) of the carboxyl group. The appearance of these two peaks indicates the presence of the acetyl groups in the fibres and also that these acetyl groups are involved in an ester bond with the fibre



(a)



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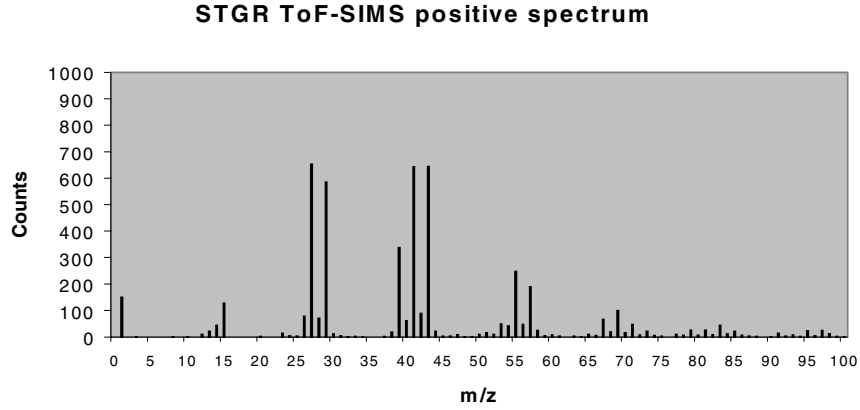
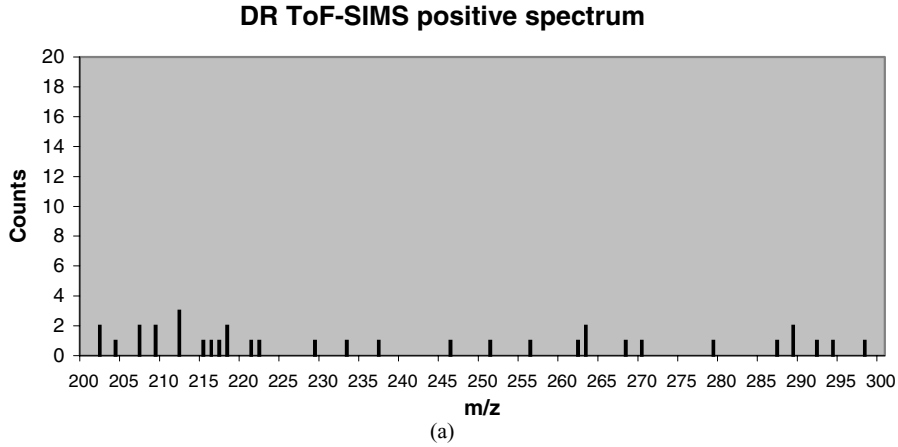


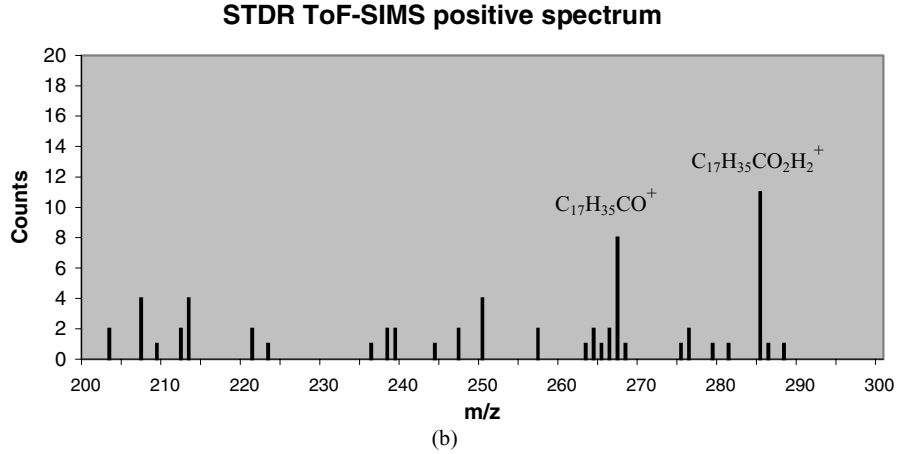
(c)

Figure 3 ToF-SIMS positive spectra of GR (a), ACGR (b) and STGR (c) fibres ($m/z = 0$–100 Da).

constituents. If the acetyl groups were in free form (acetic acid) then the stretching of C═O should have been at a position below of 1725 cm^{-1} as is indicated by the reference tables of IR spectra [37]. Furthermore, if the acetyl groups were present as acetic anhydride (highly unlikely because of the reactivity of acetic anhydride), two peaks should have appeared for the C═O stretching, one around 1805–1830 cm^{-1} and another one at around 1780–1800 cm^{-1}, accounting for the presence of two ketonic carbons. In addition, the C─O stretching peak should have appeared below 1200 cm^{-1} if it was present in this environment. The absence of these peaks from Figs 10 and 11 show that the acetyl groups in the fibre can be attributed to presence of ester bonds, which are bound to the surface of the fibre. In combination with the XPS and SIMS results, it is clear that the acetyl groups present on the surface of the fibres must also be in an ester environment. It may also be seen from Figs 10 and 11 that there are no peaks present above 3000 cm^{-1} (C─H stretching in aromatic rings), with the exception of the broad peak around 3280 cm^{-1} that may be attributed to O─H stretching for hydrogen-bonded hydroxyl groups. This is further evidence that there are no aromatic compounds in the fibre subsurface. The absence of peaks in the region of 700─850 cm^{-1} (out-of-plane C─H deformation), characteristic of aromatic compounds, also support this analysis. The peak at around 1600 cm^{-1} is probably associated with absorbed water in crystalline cellulose [37] rather than with C═C stretching in aromatic rings. Therefore, it appears that the fibres are free of lignin, a compound rich in aromatic rings, or more precisely there is no lignin at such a level that it could be detected by FTIR.

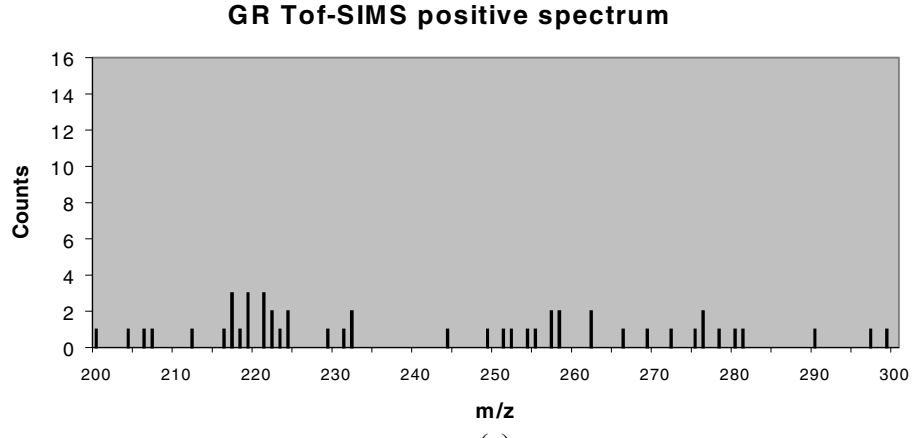


(a)

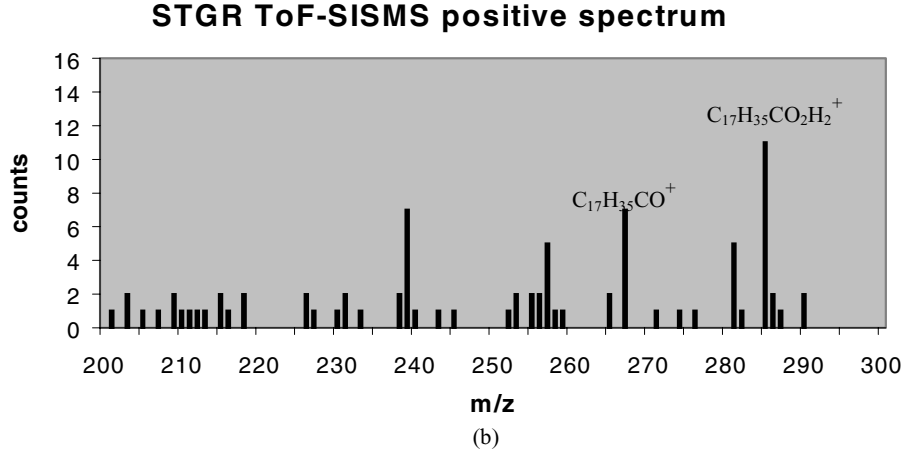


(b)

Figure 4 ToF-SIMS positive spectra of DR (a) and STDR (b) fibres ($m/z = 200$–300 Da).



(a)



(b)

Figure 5 ToF-SIMS positive spectra of GR (a) and STGR (b) fibres ($m/z = 200$–300 Da).

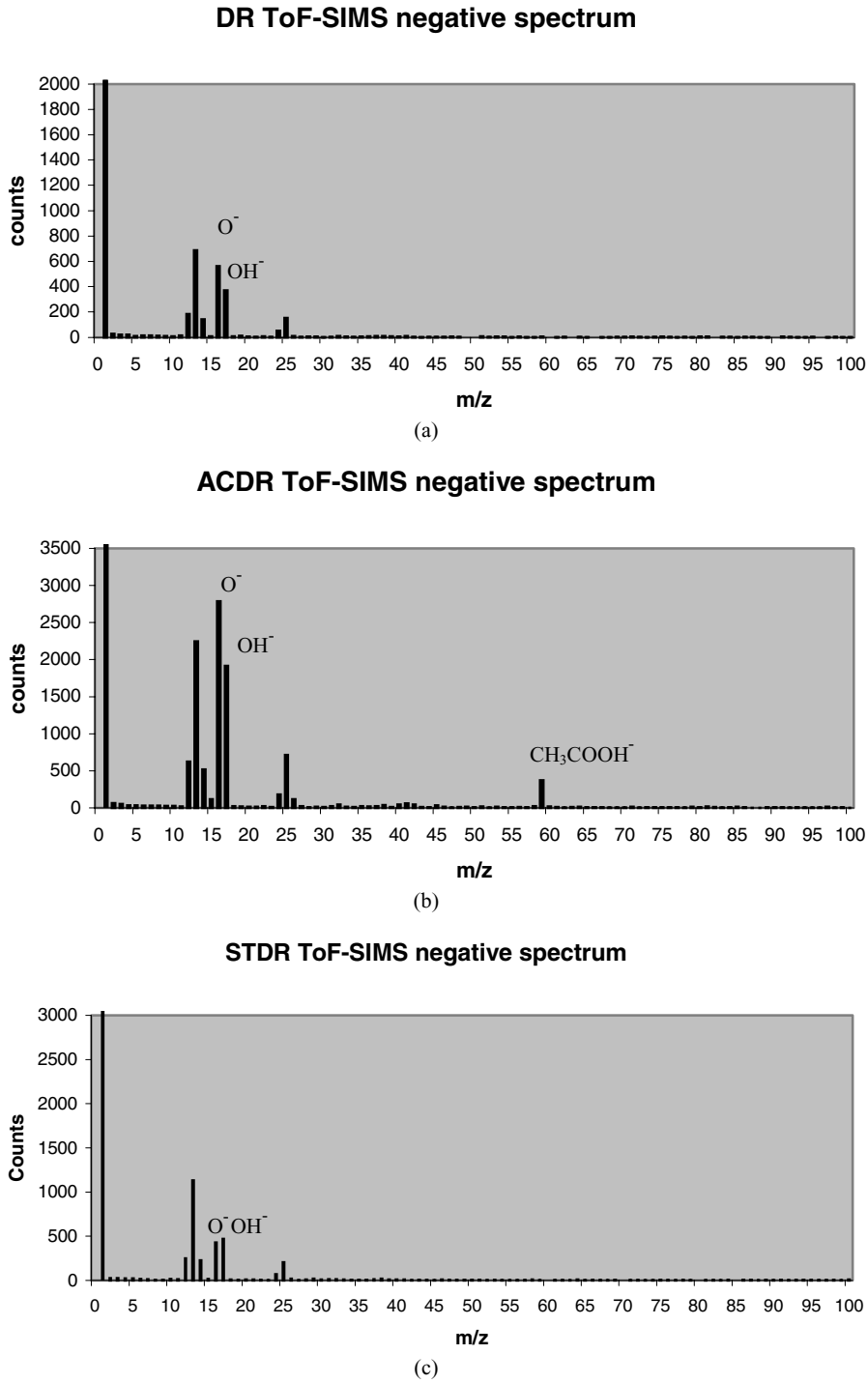
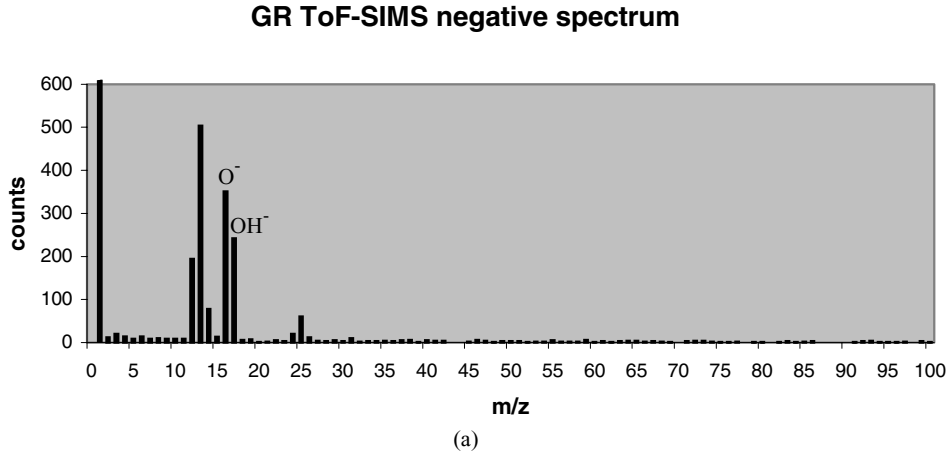


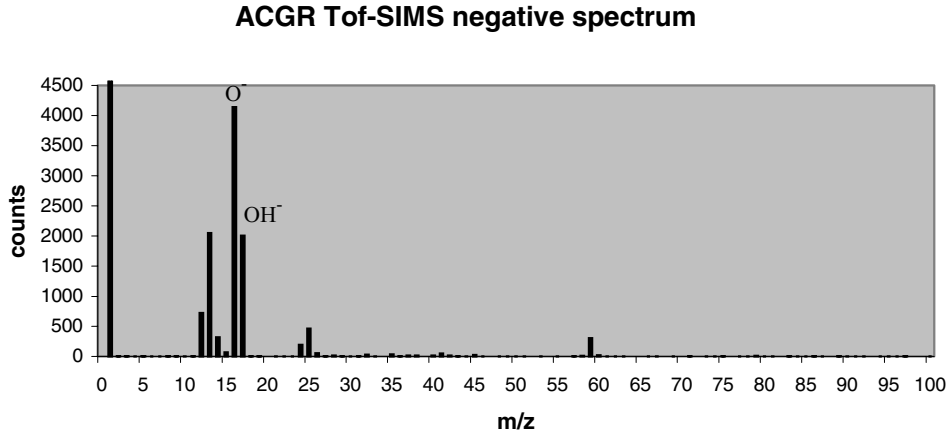
Figure 6 ToF-SIMS negative spectra of treated and untreated DR fibres (DR (a), ACDR (b), STDR (c)).

Another very interesting feature that can be seen in Fig. 10 is that the two peaks at around 2920 and 2850 cm^{-1}, both associated with C─H stretching of non-aromatic compounds, have increased after the acetylation of DR flax fibres. Although no quantitative treatment of data took place, it is in good agreement with the XPS results that showed a 50% reduction of the O/C ratio for ACDR in comparison to DR fibres. A possible explanation again may be that many methyl groups (associated with the acetyl groups) have been inserted as a result of the acetylation process into the fibre. The opposite effect can be seen in Fig. 11 for GR-ACGR fibres. In this case the two C─H stretching peaks have decreased after acetylation of the GR fibres. Again this is in a good agreement with the XPS data where the O/C ratio was found to slightly increase after acetylation. A possible explanation in this case is that the treatment has caused a removal of an outer layer of the fibre surface rich in hydrocarbon, which compensated for the insertion of the new methyl groups.

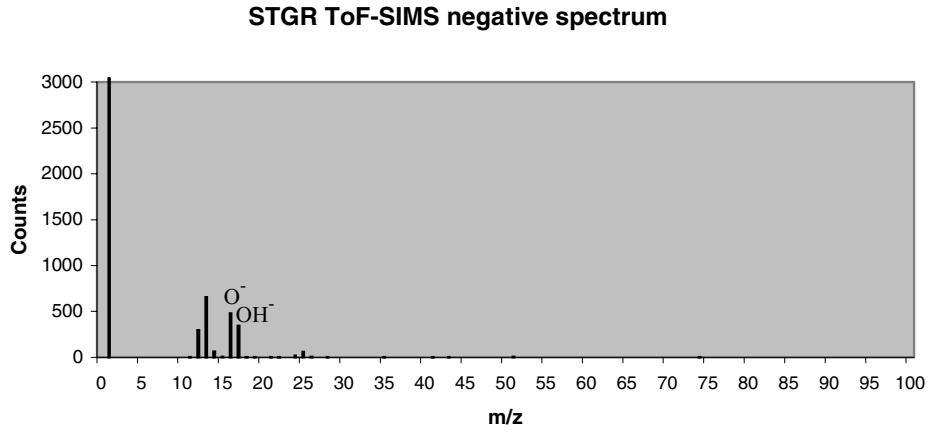
In Figs 12 and 13 the FTIR spectra of the DR-STDR and GR-STGR fibres are shown, respectively. In these cases no significant difference can be seen between the spectra of untreated and stearic acid treated fibres. There are no peaks that could be associated with a carboxyl group as there were for acetylated fibres and few differences may be observed



(a)



(b)



(c)

Figure 7 ToF-SIMS negative spectra of treated and untreated GR fibres (GR (a), ACGR (b), STGR (c)).

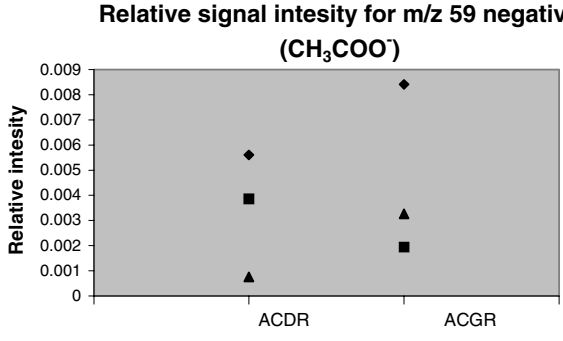
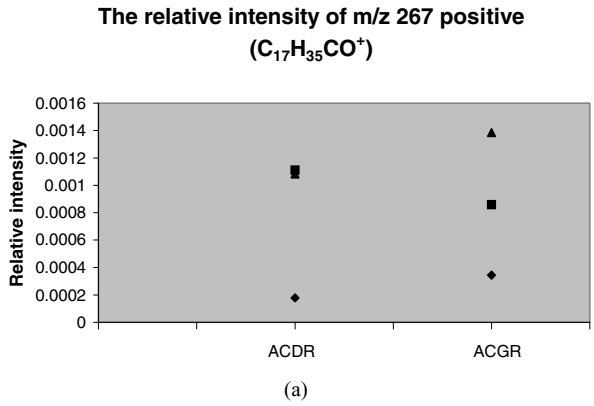
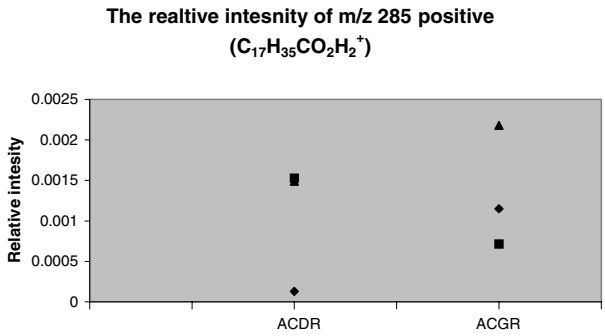


Figure 8 Normalised intensity for the CH_3COO^- ion.

for the two C–H peaks at 2920 and 2850 cm^{-1}. There is only a slight decrease of these two peaks for STGR fibres, which does not agree with the XPS results. The absence of carboxyl group related peaks from the spectra is not necessarily indicative that no ester bonds are present between stearic acid and the fibre surface constituents since the amount of stearic acid deposited on the fibres is very small and it may very well be outside the sensitivity range of the technique. Hence, the question of whether or not stearic acid has reacted with the fibre to form ester bonds remains still unresolved.



(a)



(b)

Figure 9 Normalised intensities for the $C_{17}H_{35}CO^+$ (a) and $C_{17}H_{35}CO_2H_2^+$ (b) ions.

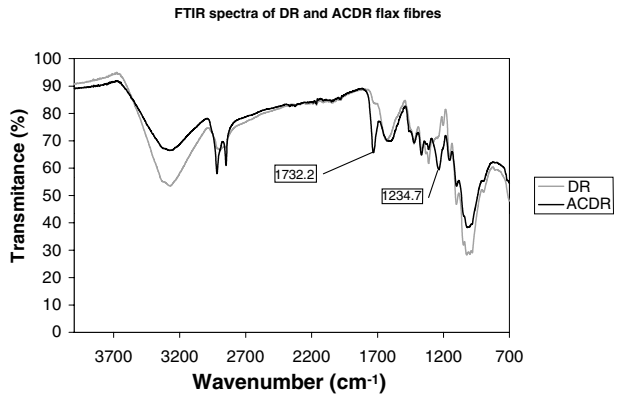


Figure 10 FTIR spectra of DR and ACDR flax fibres.

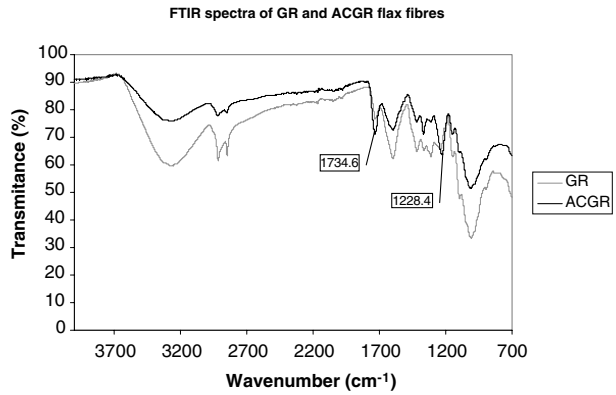


Figure 11 FTIR spectra of GR and ACGR flax fibres.

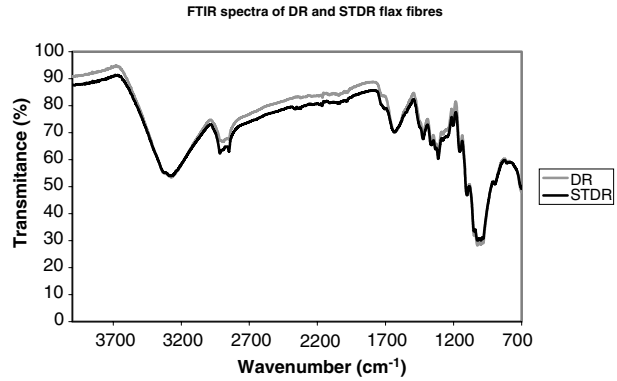


Figure 12 FTIR spectra of DR and STDR flax fibres.

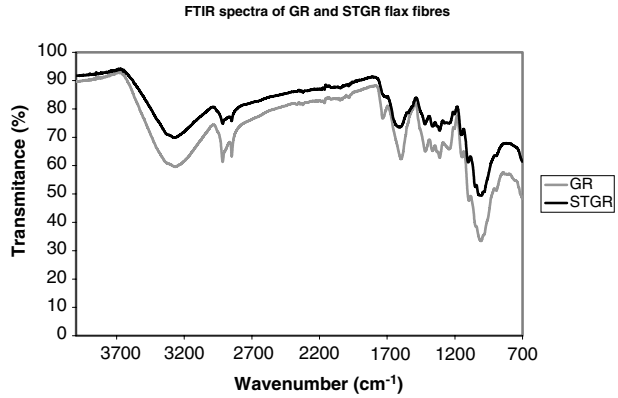


Figure 13 FTIR spectra of GR and STGR flax fibres.

4. Conclusions

Three spectroscopic methods have been applied in an attempt to investigate the effect of acetylation and stearic acid treatments on the fibres. In all cases the surface of the fibres was found to have a rather different structure to that expected. All three spectroscopic methods indicated that there are no aromatic compounds on the surface or in the bulk, which implies that there is no lignin or there is only a very small amount in the fibres, in contrast with the reported values from the literature (≈2.5% [31]. However, even if there is lignin in the fibres, it is definitely not present on the fibre surface (it is noted that the sensitivity of XPS and especially ToF-SIMS is far higher than that of FTIR).

It was found through XPS and ToF-SIMS that the fibre surface is rich in compounds that are of hydrocarbon nature, such as waxes and wax like substances. Cellulose and hemicellulose are mostly contained in the bulk rather than on the surface of the fibres. XPS, ToF-SIMS and FTIR revealed the presence of acetyl groups that are involved in an ester bond with the fibre constituents for acetylated fibres. ToF-SIMS indicated that the fibre surface is very heterogeneous and that there are areas rich in acetyl groups and areas with less acetyl content. This implies that there are areas that are more reactive with acetic anhydride than others. For stearic acid treated fibres the evidence was less conclusive. XPS revealed that there is an increase of carbon in treated fibres compared to untreated ones as expected, and also for STDR the C 1s envelope could not be deconvoluted, which implies that the oxygen present in

the fibres is possibly due to water rather than being associated with carbon atoms. ToF-SIMS revealed that stearic acid molecules are present on the surface of the stearated fibres, and that the coverage of the fibre surface is not homogeneous. The FTIR examination of STDR and STGR fibres revealed that these fibres had almost identical spectra with the DR and GR fibres, respectively. In these cases no peaks were observed that could indicate the presence of an ester bond between the stearic acid molecule and the fibre constituents. There were also no peaks that could be associated with the carboxyl of the stearic acid molecule. Hence, no conclusion can be drawn as to whether or not the stearic acid has reacted with the fibre. It has to be noted though that the amount of stearic acid deposited on the fibre is very small and probably undetectable through FTIR. Hence, although the stearic acid is present on the fibre surface it is still not clear whether or not it has reacted with fibre surface constituents to form ester bonds.

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References

1. P. R. HORNSBY, E. HINRICHSEN and K. TAVERDI, *J. Mater. Sci.* **32** (1997) 443.
2. R. HEIJENRATH and T. PEIJS, *Adv. Comp. Lett.* **5** (1996) 71.
3. M. O. W. RICHARDSON, T. J. MADERA-SANTANA and J. HAGUE, *Prog. Rubb. Plast. Tech.* **14** (1998) 174.
4. N. E. ZAFEIROPOULOS, A. H. BARBER, C. A. BAILLIE and F. L. MATTHEWS, in Proceedings of the 5th International Conference on Deformation and Fracture of Composites, London, March 1999 (IOM Communications) p. 282.
5. R. GAUTHIER, C. JOLY, A. C. COUPAS, H. GAUTHIER and M. ESCOUBES, *Polym. Comp.* **19** (1998) 287.
6. N. E. ZAFEIROPOULOS, C. A. BAILLIE and F. L. MATTHEWS, *Composites* Part A **32** (2001) 525.
7. S. S. TRIPATHY, L. DI LANDRO, D. FONTANELLI, A. MARCHETTI and G. LEVITA, *J. Appl. Poly. Sci.* **75** (2000) 1585.
8. P. ZADORECKI and P. FLODIN, *ibid.* **31** (1986) 1699.
9. D. BESHAY, B. V. KOKTA and C. DANEAULT, *Polym. Comp.* **6** (1985) 261.
10. M. N. BELGACEM, P. BATAILLE and S. SAPIEHA, *J. Appl. Poly. Sci.* **53** (1994) 379.
11. J. M. FELIX, C. M. G. CARLSSON and P. GATENHOLM, *J. Adh. Sci. Tech.* **8** (1994) 163.
12. E. T. N. BISANDA and M. P. ANSELL, *Comp. Sci. Tech.* **41** (1991) 167.
13. S. SAPIEHA, J. F. PUPO and H. SCHREIBER, *J. Appl. Poly. Sci.* **37** (1989) 233.
14. J. M. FELIX and P. GATENHOLM, *ibid.* **42** (1991) 609.
15. D. MALDAS, B. V. KOKTA and C. DANEAULT, *ibid.* **37** (1989) 751.
16. K.-P. MIECK, A. NECHWATAL and C. KNOBELSDORF, *Die Angew. Makro. Chem.* **224** (1995) 73.
17. T. STERZYNSKI, B. TRIKI and S. ZELAZNY, *Polimerzy* **40** (1995) 468.
18. R. G. RAJ, B. V. KOKTA, D. MALDAS and C. DANEAULT, *Polym. Comp.* **9** (1988) 404.
19. P. ZADORECKI and P. FLODIN, *J. Appl. Poly. Sci.* **30** (1985) 2419.
20. L. HUA, P. ZADORECKI and P. FLODIN, *Polym. Comp.* **8** (1987) 199.
21. R. M. ROWELL, in "The Chemistry of Solid Wood" (Advances in Chemistry Series No. 207, American Chemical Society, Washington DC, 1984) Chapt. 4.
22. E. SJORSTROM, in "Wood Chemistry: Fundamentals and Applications" (Academic Press, London, 1981) p. 169.
23. K. BLEDZKI and J. GASSAN, *Prog. Polym. Sci.* **24** (1999) 221.
24. F. P. LIU, M. P. WOLCOTT, D. J. GARDNER and T. G. RIALS, *Comp. Inter.* **2** (1994) 419.
25. N. E. ZAFEIROPOULOS, D. R. WILLIAMS, C. A. BAILLIE and F. L. MATTHEWS, *Composites* Part A **33** (2002) 1083.
26. N. E. ZAFEIROPOULOS, C. A. BAILLIE and J. M. HODGKINSON, *ibid.* **33** (2002) 1183.
27. T. ARNSON, B. CROUSE and W. GRIGGS, in "The Sizing of Paper," 2nd ed. (Tappi Press, Atlanta, 1989) Chapt. 5.
28. R. E. SWANSON, *Tappi* **61** (1978) 77.
29. S. TAKEYAMA and D. G. GRAY, *Cell. Chem. Tech.* **16** (1982) 133.
30. H. KIRBY, in "Vegetable Fibres" (Interscience Publishers Inc., London, 1963).
31. R. M. ROWELL, A.-M. TILLMAN and R. SIMONSON, *J. Wood Chem. Tech.* **6**(3) (1986) 427.
32. I. S. GILMORE and M. P. SEAH, *Surf. Int. Anal.* **24** (1996) 746.
33. D. BRIGGS and M. J. HEARN, *Vacuum* **36** (1986) 1005.
34. G. J. LEGGETT and J. C. VICKERMAN, *Anal. Chem.* **63** (1991) 561.
35. M. P. STEVENS, in "Polymer Chemistry: An Introduction" (Oxford University Press, Oxford, 1990).
36. D. BRIGGS, in "Surface Analysis of Polymers by XPS and Static SIMS" (Cambridge University Press, Cambridge, 1998).
37. W. KEMP, in "Organic Spectroscopy," 2nd ed. (Macmillan, Hong Kong, 1989).

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