ice | science

Biodegradation as natural fibre pre-treatment in composite manufacturing

Maria Sotenko PhD
Research Fellow, Warwick Manufacturing Group, University of Warwick,
Coventry, UK

Stuart R. Coles PhD
Associate Professor, Warwick Manufacturing Group, University of Warwick,
Coventry, UK

Iain McEwen MEng
Master Student, Warwick Manufacturing Group, University of Warwick,
Coventry, UK

Rejane DeCampos PhD
Postdoctoral Student, Nuclear and Energy Research Institute, São Paulo,
Brazil

Guy Barker PhD
Associate Professor, School of Life Sciences, University of Warwick,
Coventry, UK

Kerry Kirwan EngD*
Reader, Warwick Manufacturing Group, University of Warwick, Coventry,
UK

Bacterial and fungal degradation of wheat straw has become intensively scrutinised in recent years because of the growing interest in procuring useful feedstocks and chemicals from lignocellulosic sources. Typically, after the extraction of valuable sugars and phenolics, significant quantities of solid biomass remain as waste. In this work, it has been shown that the leftover fermented wheat straw can be successfully used to reinforce epoxy resins, providing better strength properties compared to non-degraded straw. A 12% and a 22% increase in Young's modulus and ultimate tensile strength respectively were observed for degraded wheat straw/epoxy composites compared to composites containing non-degraded straw. The improvement in mechanical strength is explained in terms of the structural and morphological transformations that occurred in the fibres during the fermentation process. The opportunity to use degraded natural fibres in the manufacturing of composites, in addition to the production of chemicals from lignocellulosic feedstocks, looks promising for improving biorefinery economics further.

1.   Introduction

The concept of an enhanced biorefinery implies the intensification of a biomass-based process by reducing energy demand and waste streams, increasing product yield by way of a better reactor design and/or an optimised downstream processing.[1–3] One of the methods to enhance a biorefinery process is to turn wastes into useful feedstocks through an integrated approach. For example, the main by-products of pulp and paper-making industries, various industrial lignins, have attracted much attention during the last few years as promising additives for various applications[4–6] and as a substrate for the synthesis of useful chemicals[7] and polymers.[8] Commonly thought of as a waste product and generally burnt for energy recovery, lignin has gradually become a commercially attractive feedstock on its own, which can be used for the synthesis of valuable chemicals with aromatic functionality. New ways on how to obtain phenolic compounds from abundant lignocellulosic biomass have also been extensively researched in recent years. Bacteria[9] and fungi[10,11] have been proposed as less destructive, highly selective, cheaper, benign and more environmentally friendly catalysts for the degradation and the fractionation of biomass[12] in comparison to traditional chemical catalysts.[13–16] The concept of getting 'value prior pulping' with the help of fungi also emerged.[17] While initially proposed as an alternative to the chemical pre-treatment of

biomass in processes converting lignocellulose to ethanol, biocatalytic degradation has evolved into a separate platform within the biorefinery concept, which targets specific high-value chemical compounds from the lignin fraction. When this happens, the remaining biomass is a product rich in cellulose with the potential to be further refined and converted into industrially relevant products. This biologically pre-treated biomass can be converted to ethanol, as in the process of second-generation bioethanol, but it can also be used as reinforcement for the production of biocomposites, much like hemp, sisal and flax, natural fibres that have already been extensively used as reinforcements in thermosets and thermoplastics.[18–25] Wheat straw fibres are cheaper and more available compared to the aforementioned natural fibres, and there have been some reports on their use in materials production in recent years.[21,26–29] However, their reinforcing properties are worse compared to traditional natural fibres and need to be improved through appropriate pre-treatment in order to become more competitive.

In this work, the influence of a biological pre-treatment of wheat straw fibres on their reinforcing properties in an epoxy resin was studied. Epoxy resins, although expensive, are known to show high chemical and thermal resistance and mechanical strength compared to other polymer matrices.[30–32] With recent trends in

---

*Corresponding author e-mail address: kerry.kirwan@warwick.ac.uk

Green Materials
Volume 4 Issue GMAT1

**Biodegradation as natural fibre pre-
treatment in composite manufacturing**
Sotenko, Coles, McEwen *et al.*

the synthesis of epoxy resins from oil-based and lignin-containing feedstocks,[33] their reinforcement with natural fibres opens a great possibility for the production of truly sustainable biobased composites out of cheap and available feedstocks.

2. Experimental

2.1 General considerations

Deionised water was obtained by ELGA Purelab Option-S 7 water purification system. Folin-Ciocalteu reagent was sourced from VWR International. Anhydrous gallic acid was sourced from Merck. A solution of 3,5-dinitrosalicylic acid (1% w/v) was prepared by the following method: 3,5-dinitrosalicylic acid (0·4 g) was dissolved in sodium hydroxide (NaOH) (4 ml, 5 M) and distilled water (8 ml) and further combined with sodium potassium tartrate solution (28 ml, 30% w/v). SuperSap CLR resin was purchased from Entropy Resins. All other chemicals were sourced from Sigma-Aldrich and used as received without further purification.

2.2 Preparation of degraded and non-degraded wheat straw fibres

Two types of wheat straw were used in this work to reinforce epoxy resin: degraded and non-degraded wheat straw (WS). Initially, air-dried wheat straw was acquired from a local farm in Warwickshire, UK, and was a solstice winter wheat harvest of August 2013. Non-degraded WS fibres were obtained by milling the air-dried straw in a Christy Hunt mill, sieving the fibres to a size below 250 µm and drying them in an oven at 45°C for 24 h. The degraded wheat straw (DWS) fibres were obtained through biodegradation with chicken manure. The as-received air-dried straw (600 g) was mixed with fresh chicken manure (6·3 g) dissolved in water (30 ml). Deionised water (1 l) was added, and the straw was left to degrade in a closed plastic box in an oven at 65°C for 6 weeks. After this, the degraded straw was separated into small batches (25 g, 4·6% w/w moisture content) which were then autoclaved (120°C, 15 min) before being extracted with distilled water (750 ml) in a FerMac 310/60 2L batch reactor (40°C, 180 rpm, 2 h). After the extraction stage, the biomass

was squeezed through muslin netting and dried at 45°C, and a reduction of 15 ± 1% in dried weight was observed after the degradation/extraction procedure. The dried biomass was milled to a fine powder and sieved. The fraction of particles with a size of <250 µm was taken for further composite preparation.

### 2.3 Characterisation of degraded wheat straw extracts

The content of the total reduced sugars and soluble phenolics in the aqueous extracts was determined with Folin–Ciocalteu (FC)[34] and 3,5-dinitrosalicylic (DNS) colorimetry[35] accordingly. For the FC analysis, in a cuvette, each sample (20 µl) was mixed with distilled water (1·58 ml) and 10% FC reagent (100 µl). After a period of 8–10 min, a sodium carbonate (Na_2CO_3) (300 µl, 16% w/v) solution was added, and the mixture was left for 2 h to complete the reaction.

For the total sugar analysis, 250 µl of the aqueous extract from the degraded straw mixture was mixed with freshly prepared DNS solution (750 µl) in a plastic ultraviolet-visible (UV-Vis) cuvette and incubated in a water bath (15 min, 95°C) to allow the reaction to occur. The absorbance of the prepared solutions was measured at 765 and 540 nm using a Cary 50 Bio UV-Vis spectrophotometer (Varian Inc,) for phenolics and sugars respectively. The calibration curves were constructed using solutions of gallic acid and glucose with the final results expressed in equivalents of gallic acid and glucose for phenolics and sugars respectively. All assays were carried out in triplicate.

2.4 Preparation of wheat straw/epoxy resin composites

The composites were prepared using SuperSap CLR epoxy resin (Figure 1) and 1, 5, 10 and 20% w/w (by dry weight) of both the degraded and non-degraded WS (particle size <250 µm, dried at 45°C for 24 h to remove any residual absorbed water prior to manufacturing). The resin (10 g) was slowly mixed with the hardener (4·7 g) before the appropriate amount of straw was mixed in gently in order to avoid formation of air bubbles. Dog-bone-shaped samples with a gauge section 33 mm long, 5 mm wide and 2 mm thick (Figure 1) were prepared by pouring the

Characteristic	Value
Density: g cm^{-3}	1·17
Biocontent by mass: %	21–30
Tensile modulus: GPa	3·4
Tensile strength: GPa	0·065
Elongation at break: %	5
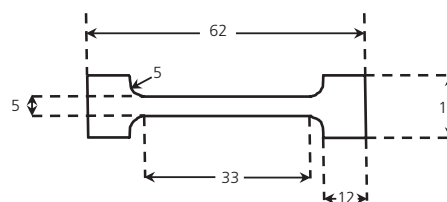
Figure 1. The main physical and mechanical characteristics of the virgin Super Sap epoxy resin (provided by Entropy resins Inc., ASTM D638 (ISO 527))[36] and a scheme of the dog bone-shaped sample used for tensile tests (all numbers are in millimetres)

mixture into moulds and leaving to cure for 24 h in air followed by 2 h post-curing in an oven at 50°C.

2.5   Characterisation techniques

Moisture analysis was carried out using an MB45 Moisture Analyser (Ohaus). The samples were dried at 105°C until a constant mass was achieved and the moisture content was assessed.

A Bruker VECTOR 22 infrared spectrophotometer was used to record Fourier transform infrared spectroscopy (FTIR) spectra in a spectral range of 4000–450 cm^{-1} with a resolution of 2 cm^{-1}. An X-ray diffraction (XRD) analysis was carried out using a PANalytical Empyrean X-ray diffractometer with cobalt (Co) Kα radiation ($\lambda = 1.789010$ Å) at 45 kV and 40 mA at a range of $2\theta = 5$–90° with a step of 0.78°/min.

The thermogravimetric analysis (TGA) of the fibres was carried out in an argon atmosphere at a temperature range of 25–600°C with a heating rate of 10°C/min using a TGA 1 Star System, Mettler Toledo. Scanning electron microscopy (SEM) analyses of the composites and fibres were obtained using a Zeiss Sigma microscope (Carl Zeiss Ltd, Welwyn Garden City, UK). The working distance ranged between 4 and 8 mm, the voltage applied was 5–15 kV, and both inlens (InLens) and second electrons (SE2) modes were used to obtain images. The samples (the wheat straw or the fracture surface of the composites after the tensile tests) were mounted on the SEM sample holders using carbon tape, and silver paint was applied to reduce the charging of the samples, followed by double coating with gold using an Agar Auto Sputter Coater (Stanstead, UK).

The tensile strength and the modulus were determined using dog bone-shaped samples on an Instron test machine with a ramp rate of 2 mm/min, at a room temperature of 21°C and a relative humidity of 40%. Eight to ten samples were tested for each composite, and the standard deviation was calculated. One-way analysis of variance was regarded as sufficient; one off repetition was carried out in order to verify the trend. A Tritec 2000 DMA (Dynamic Mechanical Analyzer) was used for the dynamic mechanical thermal analysis (DMTA) experiments. The testing was performed on a single cantilever arrangement with a frequency of 1 Hz to a displacement of 0.05 mm with a 2°C/min heat rate over a temperature span from −100 to 250°C. For the DMTA analysis, the samples were prepared in compliance with EN ISO 6721-1[37] with a rectangular geometry of 17.5 × 5 × 2 mm.

3.   Results

3.1   Study of the changes in wheat straw fibres induced by the solid-state fermentation with chicken manure

The degradation of biomass with chicken manure, followed by the aqueous extraction, was taken as an example of a cheap and simple biotechnological process for the production of useful compounds out of lignocellulosic feedstock. The UV-Vis analysis showed that the aqueous extract from the DWS contains 25.8 and 7.6 $mg/g_{dw\ straw}$ of sugars and phenols respectively. The sugars could be further used for the production of alcohols, acids or biogas, whereas the phenolic compounds could include valuable derivatives of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) lignols, the key compounds of which have been previously identified as vanillin, coumaric acid, 5-methoxy proto-catehuic acid, syringyl alcohol and ferulic acid.[38]

The remaining wheat straw was used as reinforcement for the composites. In order to study the changes in the chemical composition of the surface of the straw, which will eventually influence the interaction of the matrix with the fibres, FTIR, XRD and TGA analyses of both degraded and non-degraded WS fibres were carried out.

The interpretation of the FTIR spectra of lignocellulose is hampered by the high similarities in the FTIR spectra of lignin, cellulose and hemicellulose which contain the same functional groups.[39,40] For example, a high-intensity peak at around 3300 cm^{-1} could be attributed to O–H stretching in the hydroxyl groups in lignin, hemicellulose or cellulose and is therefore not suitable for monitoring the changes in lignin content only. Nevertheless, some changes in the FTIR spectra of the straw before and after the degradation/extraction process can be observed in Figure 2, where a differential spectrum was also presented in order to better visualise the changes in the peak intensities. The degradation of the straw causes a reduction in the peak size at 1606, 1514 and 1422 cm^{-1}, which corresponds to vibrations in aromatic rings, which are present only in lignin.[41,42] The difference at 1422 cm^{-1} can also be attributed to the methylene (CH_2) scissoring motions in cellulose.[43] The reduction
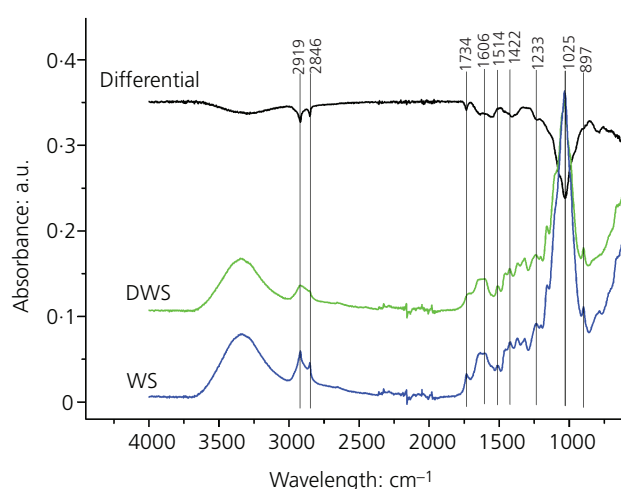
Figure 2. FTIR spectra of the wheat straw before and after solid-state degradation with chicken manure at 65°C for 6 weeks and following aqueous extraction

in the following peak intensities was observed: 1462 cm^{-1} (aromatic methyl vibrations) and 1233 (aromatic C–O stretching) in lignin, 1641 cm^{-1} (H–O–H bending in absorbed water) and 1553 cm^{-1} (carboxylate), which all are attributed to lignin.[42,44] The peaks at 897 (characteristic of β-glycosidic linkages between sugar units), 1025 and 1156 cm^{-1} represent C–O–C pyranose ring skeletal and C–O stretching and deformation in cellulose and hemicelluloses.[45,46] They decreased in intensity after the degradation/extraction process suggesting lowers the cellulose/hemicellulose content in the treated fibres. The peak at 1734 cm^{-1} is usually attributed to the C=O bond in the acetyl and uronic ester groups of the hemicellulose, but it could be also of the C=O linkage of the ferulic and p-coumaric acids of lignin and/or hemicelluloses.[40,47] The intensity of this peak decreases after degradation pointing towards a lower content of lignin and hemicellulose in DWS fibres. Thus, the lower intensities of the peaks attributed to lignin and hemicellulose in degraded/extracted straw compared to that in non-degraded suggest a reduction in lignin and hemicellulose contents. There is also some evidence that cellulose may have been partially degraded.

Lignin and hemicellulose are amorphous; however, the crystallinity of cellulose, which influences the fibres strength, could be monitored by an XRD analysis.[48] The crystallinity index (C_{rI}) for the fibres was evaluated according to the following equation[48]

1. $C_{rI} = [100 \times (I_{200} - I_{am})]/I_{200}$

where I_{am} is the intensity above baseline at 2θ = 21° corresponding to amorphous cellulose (for cobalt Kα or 18° for copper (Cu) Kα) and I_{200} is the maximum intensity for the peak

of (200) crystalline plane (2θ = 22·5° for copper Kα or 26° for cobalt Kα).

The XRD spectra of the wheat straw before and after degradation (Figure 3) show a sharp peak at 2θ = 26°, a broad peak at 2θ = 19 and a small peak at 2θ = 41°, which can be attributed to the crystallographic planes (200), (1-10) and (110) and (004) of crystalline cellulose I.[49,50] As it can be seen, the degradation/extraction process does not induce the structural transformation of cellulose I (parallel orientation of chains) to cellulose II (anti-parallel orientation of chains), unlike the mercerisation process for example,[51] suggesting that the fermentation of the biomass appears to be a mild pre-treatment technique. The estimated crystallinity index changes from 68% for non-degraded straw to 75% for degraded/extracted straw. This could be a result of a reduction in the amorphous fraction of cellulose, which is more susceptible to degradation compared to crystalline regions. With a higher crystalline fraction of cellulose, one might expect better mechanical properties of the fibres due to the higher rigidity of the crystalline regions compared to disordered amorphous regions.

The higher crystallinity of cellulose in the treated wheat straw could also improve the thermal stability of the fibres,[52,53] which was confirmed by TGA analysis. Indeed, differential thermogravimetric curves (Figure 3) showed that an intense peak, attributed to cellulose degradation,[54,55] shifts from 322°C for non-degraded straw towards 353°C for DWS. Because of the higher degradation temperature for cellulose, a shoulder peak at 285°C on the graph for DWS, which is attributed to hemicellulose, appears to be more profound compared to that for the non-degraded WS. Also, the weight of the residue after the thermal decomposition reduced from 37% to 31% of the initial weight for
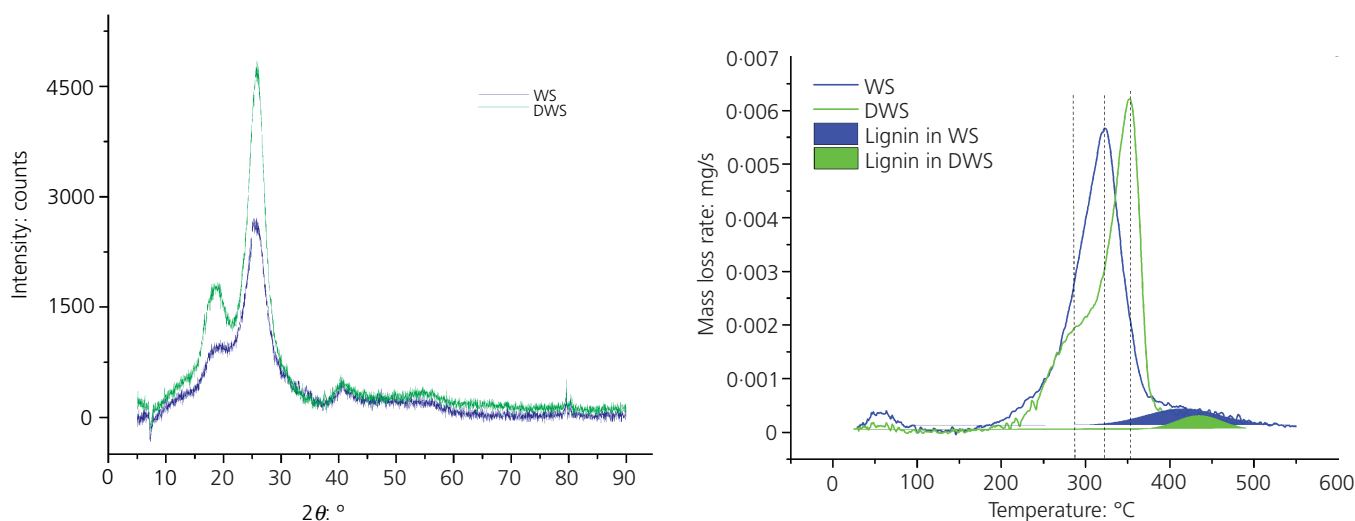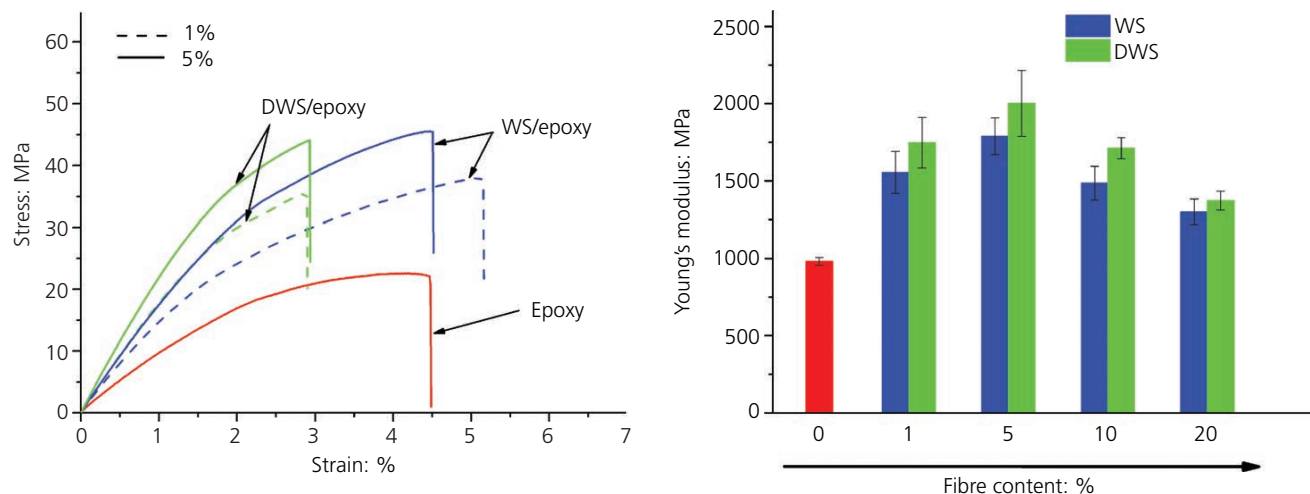

Figure 3. XRD diffractograms (left) and TGA differential curves (right) for WS and DWS

Figure 4. Stress-strain curves for the epoxy resin and the composites with non-degraded WS and DWS fibres (left). Tensile modulus against wheat straw fibres content for the DWS and non-degraded WS/epoxy composites (right)

the treated fibres compared to for the non-treated ones. Thus, fermentation and consecutive aqueous extraction removed some salts and silicates present in the straw. A peak-fitting procedure allows an observation of a low-intensity peak at around 375°C corresponding to the degradation of lignin, which reduced in area for treated fibres compared to non-treated fibres.

3.2 Composite preparation and tensile strength testing

Prior to the preparation of the composites, the fibres were dried, milled and sieved, and the particles with a size <250 µm were used. This reduced the variation in the composite properties due to the large variation in particle size. The wheat straw dispersed well in the hydrophobic epoxy/hardener mixture, despite concerns about potential problems with the hydrophilic nature of the feedstock. As the filler loading was increased in the composite (>5%), the viscosity of the mixture increased which meant that the removal of air bubbles became problematic. This could be

overcome by using techniques such as vacuum-assisted resin transfer moulding.

Figure 4 shows the original stress-strain curves obtained for the neat epoxy, epoxy with 1 and 5% of DWS powder and non-degraded WS powder, whereas all the data are summarised in Table 1. Overall, the reinforced composites showed the same stress-strain behaviour as the initial epoxy resin, where elastic deformation is followed by plastic deformation and fracture. The wheat straw/epoxy composite has a strain at break (3–5%) close to the one of the virgin epoxy resin (4·5%). The composite reinforced with DWS fibres has somewhat lower strain-to-failure properties values, showing that the DWS/epoxy samples became more embrittled. The ultimate tensile stress is higher for both reinforced materials (35–45 MPa) compared to the neat resin (20 MPa), which proves that the resin, reinforced with the fibres, withstands higher loading.

| Sample	Fibre content: %	Young's modulus: MPa	Ultimate tensile strength: MPa	Elongation at break: %
Neat epoxy	0	982 ± 99	25·0 ± 4·0	4·4 ± 0·5
Non-degraded WS	1	1555 ± 136	33·7 ± 5·7	4·3 ± 0·9
	5	1790 ± 119	31·3 ± 4·2	4·0 ± 1·2
	10	1485 ± 109	23·3 ± 4·0	2·6 ± 0·5
	20	1299 ± 83	16·0 ± 0·8	1·7 ± 0·4
DWS	1	1746 ± 164	41·3 ± 4·1	3·3 ± 0·6
	5	2002 ± 213	38·2 ± 5·2	3·1 ± 0·4
	10	1711 ± 69	29·8 ± 1·3	2·6 ± 0·3
	20	1372 ± 61	17·1 ± 1·2	1·7 ± 0·5

Table 1. Young's moduli and ultimate tensile strength for the composites with DWS and non-degraded WS fibres

By comparing the Young's moduli deduced from the above curves (Table 1), it can be seen that at a fibre loading of only 1%, Young's modulus increased by 50% compared to that of the non-reinforced epoxy resin. The modulus almost doubled for a composite with 5% wheat straw, which can be regarded as the optimum loading for manufacturing epoxy/wheat straw composites with improved stiffness. If the loading is increased to 10–20%, Young's moduli decrease, although it is still higher than for the neat epoxy matrix. At higher fibre volume fractions, agglomeration of the fibres occurs, weak fibre–fibre interactions become dominant over stronger fibre–matrix interactions and therefore higher loading does not lead to higher stiffness of the composites.

DWS fibres appeared to be a better reinforcing agent compared to non-degraded WS, as the Young's modulus for 1%, 5% and 10% in DWS/epoxy are 12–15% higher compared to that in WS/epoxy. A similar enhancement in stiffness was observed for starch-based composites modified with chemically and mechanically treated wheat straw fibres.[47] The observed enhancement in comparison to non-treated natural fibres suggests either better fibre–matrix adhesion or higher strength of the treated fibres themselves due to higher crystallinity of the cellulose; however, more investigation is required to prove this. At higher DWS fibre content of 20%, however, the beneficial effect of degradation on lignocellulosic fibre mechanical properties is negated by the effects of fibre agglomeration.

Table 1 summarises the data for the Young's moduli and the ultimate tensile strength for the prepared composites and the neat epoxy resin. It can be seen that at a loading as low as 1% of fibres in the composites, the ultimate strength increases by 35% and 65% for WS/epoxy and DWS/epoxy composites accordingly. Overall, the addition of 1–10% of wheat straw increases the ultimate strength compared to the unmodified epoxy resin. The optimum loading, which provides the highest stiffness, is 5% of the fibres, with 10% being the maximum content at which the properties of the neat epoxy are preserved, whereas a higher loading of 20% leads to greater brittleness of the material. This was caused by a combined effect of both higher stiffness and agglomeration of the fibres at their higher content in the matrix and has been observed elsewhere.[28]

The damping parameter (tan δ) obtained by DMTA analysis shows the ratio of the loss to the storage moduli, and it is related to molecular motions and phase transitions. Here again, the fibres interact with the matrix and therefore reduce the mobility of the polymer molecules; hence, a reduction in the damping parameter can be observed for the composites in comparison to the pure epoxy (Figure 5). At a low fibre content, this effect is more profound for the DWS compared to that for the non-degraded fibres. At higher fibre loading, the decrease in tan δ can be also attributed to the effect of the matrix dilution with the filler.[56] A small change (1–5°C) in the glass transition temperature for the composites compared to the neat epoxy resin (T_g = 55°C) also
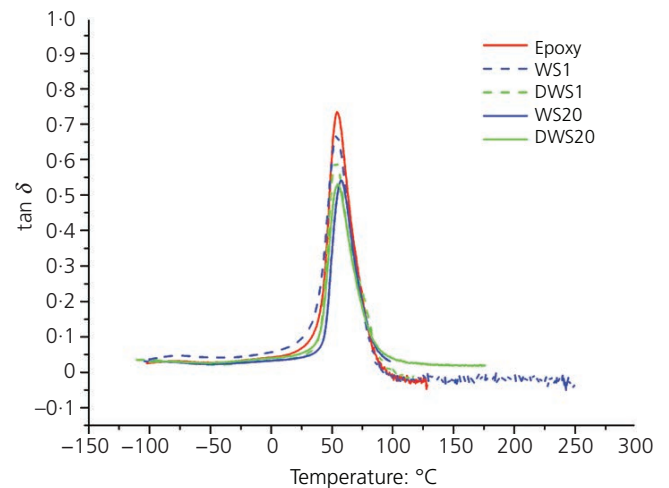

Figure 5. The dependence of damping parameter tan δ on the applied temperature for the neat epoxy and the 1 and 20% WS and DWS composites (DWS20, DWS1 – 20 and 1% DWS/epoxy; WS20, WS1 – 20 and 1% non-degraded WS/epoxy)

confirms that curing/cross-linking was not significantly affected by the addition of the fibres even at high loadings.

Studies of the fracture surfaces of the composites under a SEM microscope showed brittle failure with broad smooth islands of the epoxy matrix (Figure 6). It can be observed (also on the fibres before compounding) that the DWS has a rougher surface and therefore higher surface area compared to non-degraded straw (the surface of which looks smooth and undamaged). Also, the degraded fibres look damaged and more disintegrated in comparison to non-treated fibres. Thus, the SEM analysis proves that the degradation process changes the surface of the straw fibres. Larger pores and deeper grooves were also observed on the surface of rice straw that underwent biodegradation for long periods of time (28 d).[45] Some changes in corn stover and soybean straw morphology, such as erosion of the surface and appearance of numerous cavities and cracks, were also reported after a hot water treatment combined with fungal degradation.[57]

The overall fibre–matrix interaction, however, is not strong enough to yield a clean break on the surface. Indeed, the fibres pull out, and a visible void between the fibres and the matrix could be observed for both DWS and non-degraded WS fibres (Figure 6).

In comparison to man-made carbon fibres, natural fibres are known to exhibit non-homogeneous strength distribution due to the numerous intrinsic defects in the form, the shape and the structure of the fibres.[19,58] This non-homogeneity increases after the mechanical treatment of fibres, worsening their total reinforcing properties.[58] In this work, the opposite effect was observed – the DWS fibres appeared to have better reinforcing properties compared to the non-degraded fibres. This can be attributed to the changes in both the chemical composition and
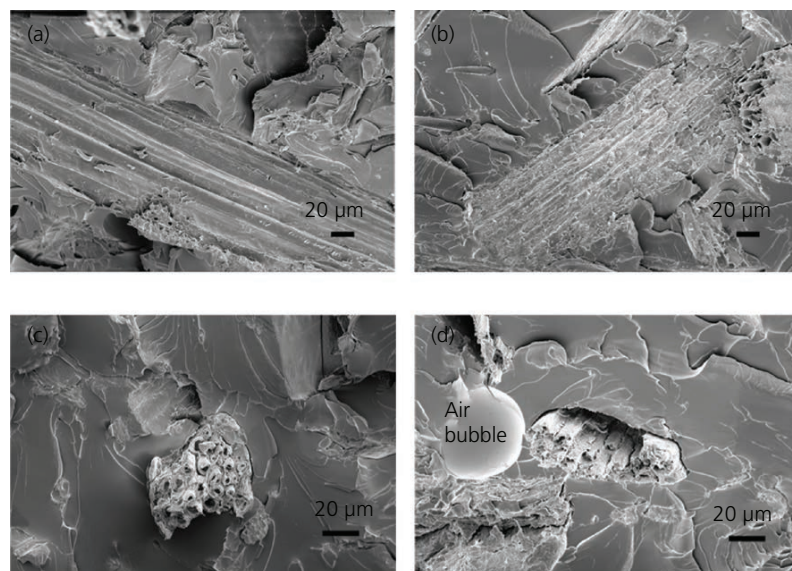
Figure 6. In the lens, the SEM images of the fracture surface for the (a) non-degraded WS and (b) DWS fibres in the epoxy resin after a tensile break (5% fibres content). In the lens, the images of the fibre pull out for (c) non-degraded and (d) degraded fibres

the surface structure of the degraded lignocellulosic fibres providing better fibre–matrix adhesion. The degradation process worked as a mild pre-treatment of biomass, which led to the decrease in lignin, hemicellulose and amorphous cellulose content, leaving the crystalline cellulose fibres mainly intact. It is known that lignin and hemicellulose polymers randomly cover and cement together the cellulose fibrils. Therefore, their degradation will lead not only to fibrillation, but also to higher thermal stability and better intrinsic structural properties of the degraded biomass due to higher regularity and higher content of cellulose crystals. Higher overall crystallinity (because of the higher content of cellulose and lower content of lignin obtained as the result of fibres treatment) was previously reported to increase the mechanical strength of the natural fibres.[47,58]

Higher disintegration and surface area provide better load sharing capability and stress dispersion between the matrix and the fibre and, with good fibre–matrix interaction, result in better mechanical properties. Therefore, the higher surface area and the irregularity of the degraded fibres provided somewhat better interaction between the fibres with the resin matrix in comparison to that of the non-degraded fibres. Compositional changes were accompanied by morphological changes of the surface and the structure of the natural fibres during the degradation and extraction processes. The higher surface roughness and the lower surface uniformity and homogeneity were observed after the degradation and extraction processes. The same changes in surface morphology were reported for mechanically treated wheat straw fibres.[58] A better interaction between the polymeric matrix and the rough surface would eventually lead to better mechanical properties of the obtained

composites. It is worth noting that the main problem of variation in biomass properties due to varying environmental conditions of growth[44] could be potentially overcome by biocatalytic degradation, after which, one would expect more uniform properties within different batches of the same type of biomass.

4. Conclusion

In this work, wheat straw fibres were pre-treated by way of a solid state fermentation with chicken manure as a biocatalyst. Solid-state fermentation is advantageous compared to a traditional aqueous fermentation in a stirred tank reactor because it demands less energy (no mixing, quite low temperature), capital and consumables costs (no need for a reactor; chicken manure provides both nitrogen source and biocatalyst), and it can also be easily adopted by local producers of agricultural wastes. Various lignocellulose degradation products, such as sugars and phenolics, could be recovered by a simple aqueous extraction following the degradation stage. The aqueous solution of the products is the main intermediate stream product in bioenergy processing in which biomass is used as a feedstock to produce targeted aromatic compounds (from lignin), C_5 (from hemicellulose) and C_6 sugars (from glucose mainly).

The remaining biomass can be easily turned into a source of reinforcing fibres and used in composite manufacturing. In this work, composites were made out of SuperSap epoxy resin reinforced with DWS and non-degraded WS by a simple and low energy curing process and proved that the composites with degraded natural fibres have better mechanical properties compared to non-degraded biomass. Currently, a further study on

how the pre-treatment influences the reinforcing properties of the wheat straw fibres and how their properties are comparable to other types of fibres, such as cellulose and carbon, is under way, and the outcomes will be published soon.

Thus, it has been shown that the waste biomass remaining after fermentation has great potential to be used as reinforcement for the production of sustainable composites. It is suggested that the degradation process, followed by aqueous extraction, can be regarded as a mild pre-treatment method. It induces morphological changes on the surface of the fibres and reduces the content of lignin, amorphous cellulose and hemicellulose. This has led to better reinforcing properties of the DWS fibres compared to the non-degraded variants. With the growing interest in procuring valuable chemicals from lignocellulosic feedstock by way of bacterial or fungal degradation, the proposed utilisation of the remaining biomass in the manufacturing of reinforced composites will bring significant environmental and economical benefits.

Acknowledgements

REFERENCES

1. Liu S, Lu H, Hu R *et al.* (2012) A sustainable woody biomass biorefinery. *Biotechnology Advances* **30(4)**: 785–810.
2. FitzPatrick M, Champagne P, Cunningham MF and Whitney RA (2010) A biorefinery processing perspective: treatment of lignocellulosic materials for the production of value-added products. *Bioresource Technology* **101(23)**: 8915–8922.
3. Zhu QL, Shao R, Dong R and Yun Z (2014) An integrated approach for obtaining biodiesel, sterols, gossypol, and raffinose from cottonseed on a biorefinery concept. *Energy* **70**: 149–158.
4. Lora J (2008) Industrial commercial lignins: sources, properties and applications. In *Monomers, Polymers and Composites from Renewable Resources* (Belgacem MN and Gandini A (eds)). Elsevier, Amsterdam, the Netherlands, pp. 225–241.
5. Wood BM, Coles SR, Maggs S, Meredith J and Kirwan K (2011) Use of lignin as a compatibiliser in hemp/epoxy composites. *Composites Science and Technology* **71(16)**: 1804–1810.
6. Ghaffar SH and Fan M (2014) Lignin in straw and its applications as an adhesive. *International Journal of Adhesion and Adhesives* **48**: 92–101.
7. Kang S, Li X, Fan J and Chang J (2013) Hydrothermal conversion of lignin: a review. *Renewable and Sustainable Energy Reviews* **27**: 546–558.
8. Laurichesse S and Avérous L (2014) Chemical modification of lignins: towards biobased polymers. *Progress in Polymer Science* **39(7)**: 1266–1290.
9. Taylor CR, Hardiman EM, Ahmad M *et al.* (2012) Isolation of bacterial strains able to metabolize lignin from screening of environmental samples. *Journal of Applied Microbiology* **113(3)**: 521–530.
10. Koncsag CI, Eastwood D and Kirwan K (2011) Recovering low molecular weight extractives from degraded straw by oyster mushroom at the farm scale for high value use. *Biomass and Bioenergy* **35(7)**: 3276–3279.
11. Yao W and Nokes SE (2014) Phanerochaete chrysosporium pretreatment of biomass to enhance solvent production in subsequent bacterial solid-substrate cultivation. *Biomass and Bioenergy* **62**: 100–107.
12. Hasunuma T, Okazaki F, Okai N *et al.* (2013) A review of enzymes and microbes for lignocellulosic biorefinery and the possibility of their application to consolidated bioprocessing technology. *Bioresource Technology* **135**: 513–522.
13. Menon V and Rao M (2012) Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept. *Progress in Energy and Combustion Science* **38(4)**: 522–550.
14. Behera S, Arora R, Nandhagopal N and Kumar S (2014) Importance of chemical pretreatment for bioconversion of lignocellulosic biomass. *Renewable and Sustainable Energy Reviews* **36**: 91–106.
15. Geng W, Huang T, Jin Y *et al.* (2014) Comparison of sodium carbonate–oxygen and sodium hydroxide–oxygen pretreatments on the chemical composition and enzymatic saccharification of wheat straw. *Bioresource Technology* **161**: 63–68.
16. Naseeruddin S, Yadav KS, Sateesh L *et al.* (2013) Selection of the best chemical pretreatment for lignocellulosic substrate *Prosopis juliflora. Bioresource Technology* **136**: 542–549.
17. Singh P, Sulaiman O, Hashim R, Rupani PF and Peng LC (2010) Biopulping of lignocellulosic material using different fungal species: a review. *Reviews in Environmental Science and Bio/Technology* **9**: 141–151.
18. Yan ZL, Wanga H, Lau KT *et al.* (2013) Reinforcement of polypropylene with hemp fibres. *Composites: Part B* **46**: 221–226.
19. Yan L, Chouw N and Jayaraman K (2014) Flax fibre and its composites – a review. *Composites: Part B* **56**: 296–317.
20. Ramzy A, Beermann D, Steuernagel L, Meiners D and Ziegmann G (2014) Developing a new generation of sisal composite fibres for use in industrial applications. *Composites Part B: Engineering* **66**: 286–298.
21. Montano-Leyvaa B, da Silva GGD, Gastaldia E *et al.* (2013) Biocomposites from wheat proteins and fibers: structure/mechanical properties relationships. *Industrial Crops and Products* **43**: 545–555.
22. Saba N, Paridah MT and Jawaid M (2015) Mechanical properties of kenaf fibre reinforced polymer composite: a review. *Construction and Building Materials* **76**: 87–96.
23. Azwa ZN, Yousif BF, Manalo AC and Karunasena W (2013) A review on the degradability of polymeric composites based on natural fibres. *Materials and Design* **47**: 424–442.

24. Meredith J, Coles SR, Powe R *et al.* (2013) On the static and dynamic properties of flax and Cordenka epoxy composites. *Composites Science and Technology* **80**: 31–38.

25. Meredith J, Cozien-Cazuc S, Collings E *et al.* (2012) Natural fibre composite energy absorption structures. *Composites Science and Technology* **72(2)**: 211–217.

26. Pfister DP and Larock RC (2010) Green composites from a conjugated linseed oil-based resin and wheat straw. *Composites: Part A* **41(9)**: 1279–1288.

27. Pradhan R, Misra M, Erickson L and Mohanty A (2010) Compostability and biodegradation study of PLA-wheat straw and PLA-soy straw based green composites in simulated composting bioreactor. *Bioresource Technology* **101(21)**: 8489–8491.

28. Ahankari SS, Mohanty AK and Misra M (2011) Mechanical behaviour of agro-residue reinforced poly(3-hydroxybutyrate-co-3-hydroxyvalerate), (PHBV) green composites: a comparison with traditional polypropylene composites. *Composites Science and Technology* **71(5)**: 653–657.

29. Reddy CR, Sardashti AP and Simon LC (2010) Preparation and characterization of polypropylene-wheat straw-clay composites. *Composites Science and Technology* **70(12)**: 1674–1680.

30. Takeichi T and Toyohashi N (2012) Epoxy resins and phenol-formaldehyde resins. In *Polymer Science: A Comprehensive Reference. Volume 5: Polycondensation* (Schmidt HW and Ueda M (eds)). Elsevier, Amsterdam, the Netherlands, pp. 723–751.

31. Fink JK (2013) Epoxy resins. *Reactive Polymers Fundamentals and Applications*. Elsevier, Amsterdam, the Netherlands, pp. 95–153.

32. Brostow W, Goodman SH and Wahrmund J (2014) Epoxies. In *Handbook of Thermoset Plastics*, 3rd edn (Dodiuk H and Goodman SH (eds)). Elsevier, Amsterdam, the Netherlands, pp. 191–252.

33. Hirose S, Hatakeyama T and Hatakeyama H (2014) Novel epoxy resins derived from biomass components. *Procedia Chemistry* **4**: 26–33.

34. Ainsworth EA and Gillespie KM (2007) Estimation of total phenolic content and other oxidation substrates in plant tissues using Folin–Ciocalteu reagent. *Nature Protocols* **2(4)**: 875–877.

35. Chua M, Chan K, Hocking TJ *et al.* (2012) Methodologies for the extraction and analysis of konjac glucomannan from corms of *Amorphophallus konjac* K. Koch. *Carbohydrate Polymers* **87(3)**: 2202–2210.

36. ASTM (2014) D638: Standard test method for tensile properties of plastics. ASTM International, West Conshohocken, PA, USA.

37. ISO (International Organization for Standardization) (2011) ISO 6721-1:2011: Plastics – Determination of dynamic mechanical properies – Part 1: General principles. ISO, Geneva, Switzerland.

38. Koncsag CI, Eastwood D, Collis AEC *et al.* (2012) Extracting valuable compounds from straw degraded by *Pleurotus ostreatus*. *Resources, Conservation and Recycling* **59**: 14–22.

39. Yang H, Yan R, Chen H, Lee DH and Zheng C (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **86(12–13)**: 1781–1788.

40. Lisperguer J, Perez P and Urizar S (2009) Structure and thermal properties of lignins: characterization by infrared spectroscopy and differential scannin calorimetry. *Journal of the Chilean Chemical Society* **54(4)**: 460–463.

41. Xu F, Yu J, Tesso T, Dowell F and Wang D (2013) Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: a mini-review. *Applied Energy* **104**: 801–809.

42. Ghaffar SH and Fan M (2013) Structural analysis for lignin characteristics in biomass straw. *Biomass and Bioenergy* **57**: 264–279.

43. Kumar A, Negi YS, Choudhary V and Bhardwaj NK (2014) Characterization of cellulose nanocrystals produced by acid-hydrolysis from sugarcane bagasse as agro-waste. *Journal of Materials Physics and Chemistry* **2(1)**: 1–8.

44. Lindsey K, Johnson A, Kim P, Jackson S and Labbe N (2013) Monitoring switchgrass composition to optimize harvesting periods for bioenergy and value-added products. *Biomass and Bioenergy* **56**: 29–37.

45. Zhang S, Jiang M, Zhou Z, Zhao M and Li Y (2012) Selective removal of lignin in steam-exploded rice straw by *Phanerochaete chrysosporium*. *International Biodeterioration & Biodegradation* **75**: 89–95.

46. Nguyen HD, Mai TTT, Nguyen NB *et al.* (2013) A novel method for preparing microfibrillated cellulose from bamboo fibers. *Advances in Natural Sciences: Nanoscience and Nanotechnology* **4(1)**: 015016.

47. Alemdar A and Sain M (2008) Biocomposites from wheat straw nanofibers: morphology, thermal and mechanical properties. *Composites Science and Technology* **68(2)**: 557–565.

48. Segal L, Creely JJ, Martin AE and Conrad CM (1959) An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Textile Research Journal* **29(10)**: 786–794.

49. Liu Z, Sun X, Hao M *et al.* (2015) Preparation and characterization of regenerated cellulose from ionic liquid using different methods. *Carbohydrate Polymers* **117**: 99–105.

50. Yuan Z, Fan Q, Dai X *et al.* (2014) Cross-linkage effect of cellulose/laponite hybrids in aqueous dispersions and solid films. *Carbohydrate Polymers* **102**: 431–437.

51. Mansikkama P, Lahtinen M and Rissanen K (2007) The conversion from cellulose I to cellulose II in NaOH mercerization performed in alcohol-water systems: an X-ray powder diffraction study. *Carbohydrate Polymers* **68(1)**: 35–43.

52. Yang H, Yan R, Chen H *et al.* (2006) In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. *Energy Fuels* **20(1)**: 388–393.

53. Poletto M, Júnior HLO and Zattera AJ (2014) Native cellulose: structure, characterization and thermal properties. *Materials* **7(9)**: 6105–6116.

54. Zeng J, Singh D and Chen S (2011) Thermal decomposition kinetics of wheat straw treated by *Phanerochaete chrysosporium*. *International Biodeterioration & Biodegradation* **65(3)**: 410–414.

55. Monteiro SN, Calado V, Margem FM and Rodriguez RJS (2012) Thermogravimetric stability behavior of less common lignocellulosic fibers – a review. *Journal of Materials Research and Technology* **1(3)**: 189–199.

56. Tzounis L, Debnath S, Rooj S *et al.* (2014) High performance natural rubber composites with a hierarchical reinforcement structure of carbon nanotube modified natural fibers. *Materials and Design* **58**: 1–11.

57. Wan C and Li Y (2011) Effect of hot water extraction and liquid hot water pretreatment on the fungal degradation of biomass feedstocks. *Bioresource Technology* **102(20)**: 9788–9793.

58. Panthapulakkal S, Zereshkian A and Sain M (2006) Preparation and characterization of wheat straw fibers for reinforcing application in injection molded thermoplastic composites. *Bioresource Technology* **97(2)**: 265–272.

WHAT DO YOU THINK?

To discuss this paper, please submit up to 500 words to the managing editor at journals@ice.org.uk.

Your contribution will be forwarded to the author(s) for a reply and, if considered appropriate by the editor-in-chief, will be published as a discussion in a future issue of the journal.

ICE Science journals rely entirely on contributions sent in by professionals, academics and students coming from the field of materials science and engineering. Articles should be within 5000–7000 words long (short communications and opinion articles should be within 2000 words long), with adequate illustrations and references. To access our author guidelines and how to submit your paper, please refer to the journal website at www.icevirtuallibrary.com/gmat