

PRODUCTION AND EVALUATION OF BIODEGRADABLE COMPOSITES
 BASED ON POLYHYDROXYBUTYRATE AND POLYLACTIC ACID
 REINFORCED WITH SHORT AND LONG PULP FIBERS

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In this study, two biodegradable polymers, polylactic acid (PLA) and polyhydroxybutyrate (PHB), were mixed with short and long fiber pulps using a torque rheometer. PLA/PHB-fiber composites consisting of up to 40 wt% paper pulp were produced through a unique procedure and evaluated using various techniques including thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD) and dynamic mechanical analysis (DMA). Changes in the matrix polymers and pulp fibers were analyzed using gel permeation chromatography (GPC) and Fiber Lab microscopy. The results showed that the composites reinforced with pulps showed significantly increased tensile stiffness and impact strength; the addition of a coupling agent did not improve the mechanical performance of PHB biocomposites. The degradation of PLA and PHB observed during the heating process is thought to be caused by the release of acidic organic compounds, such as crotonic and lactic acids, which chemically enhance the existing interface between the pulps and the matrix polymers. The storage modulus and loss modulus of the composites decreased as the pulp fiber content increased, and the damping capability (increase in dimensional stability) decreased with increasing pulp fiber content.

Keywords: polyhydroxybutyrate, polylactic acid, fiber pulps, mechanical properties

INTRODUCTION

UPM-Kymmene Corporation, one of several well known multinational corporations that use forest resources, has significant natural fiber reserves (e.g., 930,000 hectares of private forests producing 3.2 million tons of pulp out of an annual output of 9.7 million tons). As the global demand for paper decreases, the use of natural fiber raw materials to develop new products could serve as an alternative source of revenue for companies such as UPM.

Bio-based plastics have been available on the European market for a decade. Initially developed for medical purposes,¹ packing applications (e.g. biodegradable bags, loose fill and packaging of ecologically produced food) were later found,² and today bio-based plastics are commonly used in structural components. In several common composite materials, biopolymers can substitute for crude oil in matrix fabrication; however, such biogenous matrices must be reinforced in order to

achieve satisfactory mechanical performance. Full “biocomposites” can be produced using only natural fibers (NFs), one of their main advantages being their light weight. NFs (0.3-0.5 g/cm³) have significantly lower densities than glass fiber (GF) (2.5-2.7 g/cm³), which allows for the construction of parts that are comparatively lighter than those reinforced with GF or filled with minerals.

Polylactic acid (PLA) is a biodegradable and biocompatible crystalline polymer that can be produced from renewable resources; due to its availability and low cost, it is of great interest to the packaging industry.³⁻⁶ The properties of PLA are dependent on the ratio between the D and L enantiomers. Another typical biodegradable thermoplastic polymer is polyhydroxybutyrate (PHB), a highly crystalline polyester (80%) that is produced by microorganisms; it has a high melting point (173-180 °C) and a glass transition temperature (T_g) of approximately 1-5 °C.⁷⁻⁹

However, because of their unsatisfying impact resistance and low heat distortion temperature, neither PLA nor PHB has found meaningful market acceptance as an engineering resin, although there is current interest within the automotive and electrical industries for the development of high impact resistance, light-weight parts based on one or the other of these substances.

Owing to their low cost and acceptable mechanical properties, polypropylene (PP)-based composites continue to constitute the major engineering resins used in the automotive and electrical industries. If biocomposites are to become viable alternatives to existing materials, they will need to be competitively priced and to have comparable or improved mechanical properties.

Natural fiber (including cellulose and lignocellulosic fibers) has significant potential to fulfill such requirements. In general, cellulose fibers consist only of cellulose, whereas lignocellulosic fibers such as bamboo, abaca, jute, bagasse are composites of cellulose, hemicelluloses, and lignin and have fibers that are long and well-knit. Natural cellulose is a basic component of plants and is, accordingly, a nearly inexhaustible source of raw material; manufactured or "regenerated" cellulose fibers can be produced in chemical-technical viscose processes in which raw cellulose is modified into cellulose fibers and derivatives. The study centers on the use of natural fibers consisting of bleached Eucalyptus pulps (short fiber) or bleached Botnia-90 (long fiber) used by UPM at their Changshu Mill for paper making.

In recent years, there has been intensive research on reinforcing common polymers such as PP, polyvinyl chloride (PVC), or polyethylene (PE) with natural and cellulose spun fibers.^{10,11} Some of this research has focused on the idea of combining two inexpensive commodity materials, such as polypropylene and natural fibers or Rayontyre cord,¹² into a polymer composite in order to produce stronger components. The mechanical properties of PLA and PHB composites reinforced with natural fibers have also been investigated by fabricating composites in single and twin extruder steps.¹³ In this study, a mixed type torque rheometer (RJL 200, ShenZhen NewSans Materials Co. Ltd.) was used to prepare composites through mixing mill compounding. PLA/PHB-cellulose fiber composites with 20, 30, and 40% cellulose content were prepared and

their mechanical properties investigated.

EXPERIMENTAL

Materials

■Matrix (PLA): PolyL-lactic acid (PLA), PLA 4042D, from NatureWorks LLC (USA), D-lactid content 4-8%. The Melting Flow Index (MFI) for PLA is between 5.7 g/10 min (190 °C, 2.16 kg).

■Matrix (PHB): Polyhydroxybutyrate (PHB), Solvay Advanced Polymer. The MFI for PHB is between 2 and 3 g/10 min (170 °C, 2.16 kg).

■Additive: KH550 was bought from Sigma-Aldrich, molecular formula: $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$; molecular weight: 221; density: 0.941-0.950; it was tested for use as plasticizer for PHB.

■Pulp fiber reinforcements: oven dried bleached Eucalyptus short fiber (SF) pulps and oven dried bleached Botnia-90 long fiber (LF) pulps from UPM (Changshu Mill), which are used for papermaking.

Compounding of composite materials

The composite materials were manufactured using a mixed type torque rheometer (RJL-200, ShenZhen NewSans Materials Co. Ltd.). The pulp fiber content was 20, 30, 40 wt%. The fiber and the matrix particles were fed into the mixing tank together, the fiber content in the composite was calculated according to the oven dried weight of the pulp, the moisture content in the pulps could be evaporated using the high mixing temperature. The processing parameters are machine speed 50 rpm, temperature zone 1: 190 °C, zone 2: 200 °C, zone 3: 190 °C, feeding and mixing time was 10 minutes in total.

Compression moulding

Test samples for mechanical testing were injection moulded with a conventional injection moulding press (Mini Injection Machine SZ-15, WuHan RuiMing Machinery Manufacturing Co. Ltd.) with a maximum injection capacity of 15 g. The mould temperature was 190 °C and the pressure was 0.3 MPa.

Mechanical testing

Tensile testing was performed according to ASTM 3039 standard for tensile testing on a WDW-1 Electronic Tensile Testing Machine, ShenZhen NewSans Materials Co.Ltd. Charpy impact testing was performed according to ISO 179 unnotched Charpy standard for fiber reinforced composite materials on a JB-300 Pendulum Lamented Impact Testing Machine, ShenZhen NewSans Materials Co. Ltd. At least 5 specimens were tested for every material.

Fiber size distribution

The fiber size was determined microscopically on a Metso FiberLab microscope supported with VHX analysis software. Approximately 500 measurements of the fibre length and 100 of the fiber diameter were taken. The fiber distributions in composites were also

measured using the same method after the fibers were dissolved out from composites using chloroform stirring for 6 hours.

Electron microscopy

Fractured surfaces of the materials were studied with a JEOL (JSM-6490A) scanning electron microscope (SEM) with an acceleration voltage of 30 kV. The cut down sample surfaces were sputter coated with gold to avoid charging.

X-ray diffraction

The diffraction patterns were obtained from radiation generated by the copper target of a Rigaku Ultima IV (Rigaku Corporation, Japan) set at 40 kV and 30 mA with the detector placed on a goniometer. Data was acquired on a 2θ scale from 5° to 70° .

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of PLA, PHB and their composites were conducted on a Mettler-Toledo TGA/SDTA 851e machine at a heating rate of $10^\circ\text{C}/\text{min}$ and over a temperature range of $30\text{--}600^\circ\text{C}$. A plot of weight percentage against temperature was obtained for each specimen.

Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of the composites were evaluated using a Perkin-Elmer DMA Diamond system. A 15 mm knife-edge, three-point platform with a 5 mm probe tip was used and DMA tests were performed in a temperature range from 30°C to 130°C with a heating rate of $4^\circ\text{C}/\text{min}$. Nitrogen was used as the purge gas. Assuming the physiological frequency was 1 Hz, all measurements were conducted at this frequency. Dimensions of DMA specimens were $22\text{ mm}\times 5\text{ mm}\times 1.5\text{ mm}$.

GPC

Number and weight average molecular weights before and after the injection moulding of the PHB and PLA were determined by gel permeation chromatography on a Waters GPC system with Styragel columns (HR₃THF, HR₄THF, HR_{4E}THF) and a refractive index detector. Tetrahydrofuran was used as effluent, and the analysis was done at room temperature. Universal calibration was used for the calculation of the molecular weights, using the polystyrene standard (4.3×10^4 , 1.1×10^5 , 1.8×10^5 , 4.3×10^5 , 7.8×10^5).

RESULTS AND DISCUSSION

Mechanical testing

Using an electronic tensile testing machine and a Charpy impact testing machine, statistical tensile and impact tests were carried out in which

the mechanical properties of PHB/SF, PHB/LF, PLA/SF, and PLA/LF composites were compared to those of both pure PHB and PLA.

Fig. 1 shows tensile strength and Charpy unnotched impact strength results for PHB reinforced with both short and long fibers. Both reinforcement types result in an increase in the tensile strength of PHB as the fiber content is increased to 40 wt%. The tensile E-modulus and tensile strength increase to the respective maxima of 175% and 158% relative to unreinforced PHB (Table 1). No significant difference in these properties can be seen between samples reinforced with long and short fibers. The increase in E-modulus indicates the transfer of stress to fibers, which have a much higher stiffness than the overall matrix. Fig. 1 also indicates that the impact strength of the composites with wood fiber content increases to up to 131% of unreinforced PHB, and the addition of coupling agent KH550 has no obvious effect on tensile strength and actually causes a decrease in the impact strength to only 122% of that of unreinforced PHB. The lack of a noticeable improvement from adding coupling agent is most likely caused by the fact that KH550 is not well-suited for this kind of composite, and although fiber smoothness may be improved by using the coupling agent, it is likely that the impact strength decreases owing to the reduction in chemical bonding between the fibers and matrix.

Fig. 2 shows the tensile strength and Charpy unnotched impact strength of PLA-wood fiber composites. Both short and long fiber-reinforced PLA composites show an increase in tensile strength as the fiber content increases to 40 wt%. Table 1 shows that the tensile E-modulus and tensile strength increase to 160 and 154% of the respective unreinforced PLA characteristics. Once again, there was no significant difference between long and short fiber characteristics, and the increased E-modulus indicates that stress is transferred to the fibers, which have a much higher stiffness than the matrix.

By adding 30 wt% of man-made cellulose, an increase in tensile strength of up to 50% can be achieved in PLA and PHBV [poly(3-hydroxybutyrate-co-3-hydroxyvalerate)] composite.¹³ For instance, Bax *et al.*¹⁴ achieved an improvement in tensile strength of approximately 30% in PLA/man-made cellulose fiber.

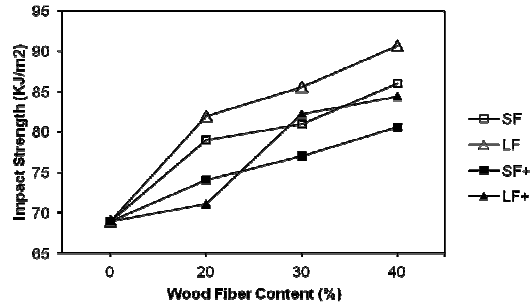


Figure 1: Mechanical properties of PHB composites reinforced with different pulp fiber contents; dark triangles: long fiber (LF) + 2%KH550; light triangles: LF without coupling agent; dark squares: short fiber (SF) + 2%KH550; light squares: SF without coupling agent

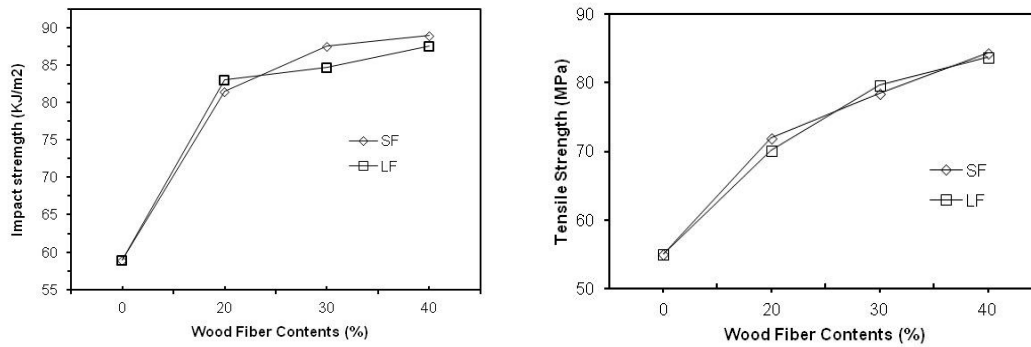


Figure 2: Mechanical properties of different pulp fiber contents reinforced PLA composites; light diamonds: short fiber (SF); light squares: long fiber (LF)

Table 1
Mechanical parameters of tested composites

Matrix	Fiber content	Tensile E-modulus (GPa)	Tensile strength (MPa)
PHB	-	1.02±0.08	52.30
	SF20%	1.73±0.12	70.51
	SF30%	1.76±0.05	80.25
	SF40%	1.78±0.09	82.52
	LF20%	1.75±0.03	69.44
	LF30%	-	80.10
	LF40%	-	81.46
PLA	-	1.31±0.17	54.98
	SF20%	-	72.01
	SF30%	1.99±0.15	78.52
	SF40%	2.10±0.12	84.44
	LF20%	1.75±0.23	70.21
	LF30%	-	79.75
	LF40%	2.07±0.15	83.81

In this study, it was shown that adding 40 wt% of pulp fiber can result in a significantly higher mechanical strength (Figs. 1 and 2), a finding that could have implications for industries in which such composites could be produced with pulp fibers instead of petroleum polymers on industrial scale. In addition, this study demonstrated that a

torque rheometer can be much more effective than an extruder in creating cellulose fiber-plastic composites.

In the findings above, there was no significant difference in the tensile strength of long and short fiber reinforced PHB and PLA. As reported in the literature,¹³ most natural fibers are composed of

so-called ‘fiber bundles’ whose properties differ depending on fiber bundle geometry. In this study, both the long and short fibers used were formed of pure cellulose fiber used for papermaking and therefore comprised bundles with relatively constant aspect ratios (fiber length/fiber width) (Fig. 3). As such, both types of fiber may have been dispersed into the matrix in similar patterns, resulting in similar stress transfer characteristics, which made it difficult to see significant differences between long and short fiber-reinforced composites. Nevertheless, the measured impact strengths of the long fiber-PHB composites were noticeably higher than those of the composites made with short fibers. As has been previously shown,¹³ the much lower diameter (higher aspect ratio) and smoother surface of pulp fiber determines the performance characteristics of a composite under impact stress. The fiber/matrix interaction is affected by fiber pull out and movement within the matrix. As is seen in Fig. 4, fiber pull-outs appear in each composite sample. Fiber movement causes enlarging in the path length of propagated cracks, which in turn increases the amount of energy needed to break a sample.¹⁵ The cell wall thickness (CWT) of long fiber is higher than that of the short fibers (Table 2); this means that the aspect ratios of the long fibers are higher and, in the case of fiber-PHB composites, the long fibers have higher impact strengths than the short fibers, although no significant difference is observed in PLA-fiber composites (this may be the result of

similarities in the distribution patterns of fibers within the matrix following the mixing process).

From our data, it can be seen that adding pulp fibers without coupling agent into PHB and PLA clearly improves the mechanical properties of the composites. Tensile strength is improved through the transfer of stress to the added fiber, and impact strength is improved by fiber pull-out and movement within the matrix, which propagate energy and increase ductility and flexibility. Fibers partially interwoven into the meshes within the composites can also absorb more impact energy.

Fiber size distribution

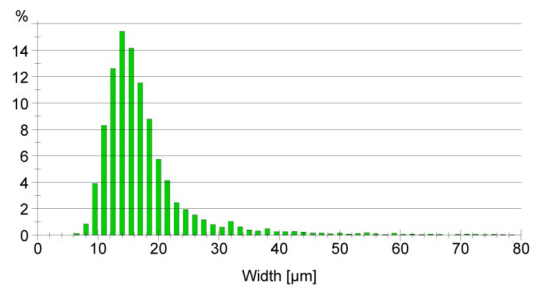
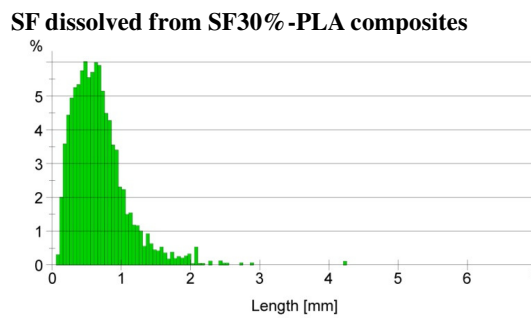
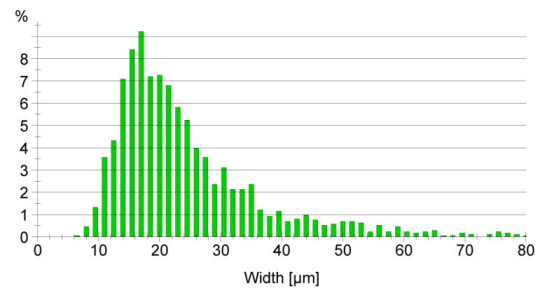
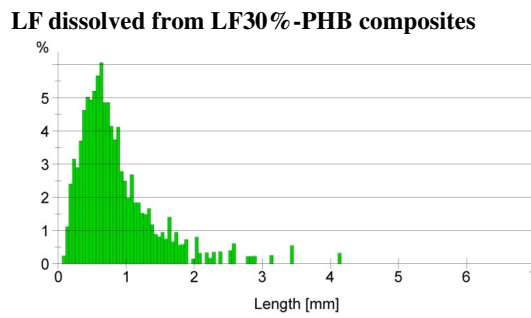
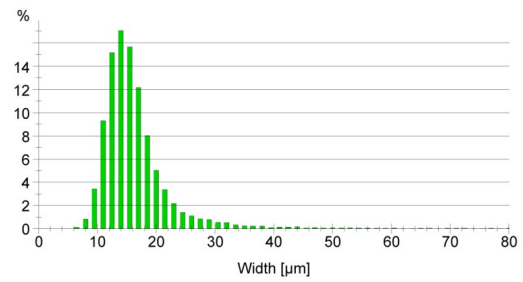
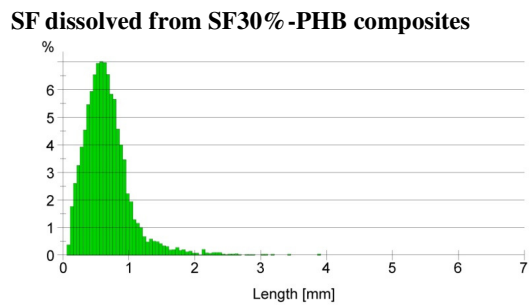
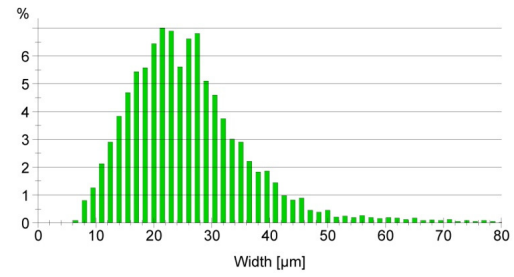
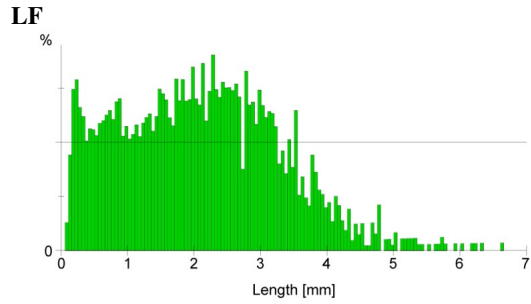
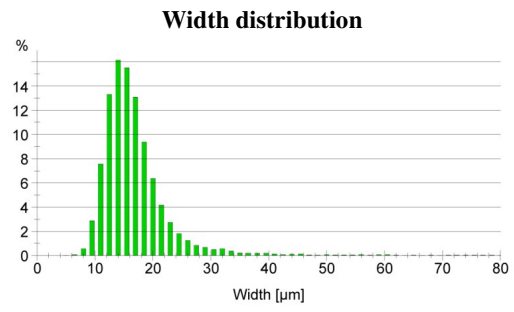
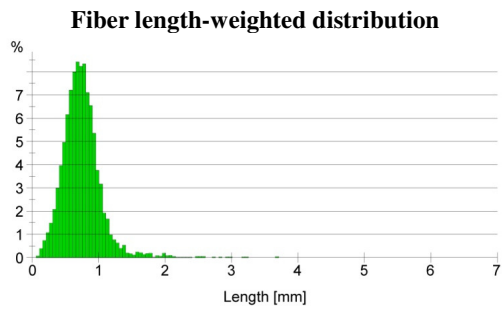
An investigation of the long and short fiber parameters prior to their mixing into the matrix was performed. Fiber features are shown in Fig. 3 and Tables 2 and 3, from which it is clear that the length distribution of the long fibers is much broader than that of the short fibers. Although the spectrum of long fiber width (Fig. 3) is also much broader than that of short fiber, there is no large difference between the two absolute data ranges. The slightly lower calculated fiber aspect ratio for short fiber helps explain the slightly lower mechanical values obtained for PLA/short fiber composites. Furthermore, because the fiber bundles have not undergone complete defibrillation, no significant difference is seen between the short and long fiber reinforced composites which indicates that, although single fibers are different, the sizes and distributions of the fiber bundles are relatively unvarying.

Table 2
Fiber width and cell wall thickness (CWT) of original and dissolved fibers

	SF	LF	SF30%-PHB	LF30%-PHB	SF30%-PLA	LF30%-PLA
Fiber width (μm)	14.4	23.6	13.8	21.9	15.0	22.5
Fiber CWT (μm)	4.6	8.0	4.4	6.1	5.0	7.9

Table 3
Length weighted fractions of original and dissolved fibers

Length (mm)	Fraction percentage (%)					
	SF	LF	SF30%-PHB	LF30%-PHB	SF30%-PLA	LF30%-PLA
0.00-0.20	3.50	5.38	11.37	8.51	14.66	19.39
0.20-0.50	38.99	9.39	48.75	34.79	46.37	39.49
0.50-1.20	56.01	19.75	38.04	47.04	36.97	36.79
1.20-2.00	1.31	25.27	1.66	7.59	1.82	4.33
2.00-3.00	0.19	27.54	0.13	2.07	0.18	0.00
3.00-7.60	0.00	12.66	0.06	0.00	0.00	0.00



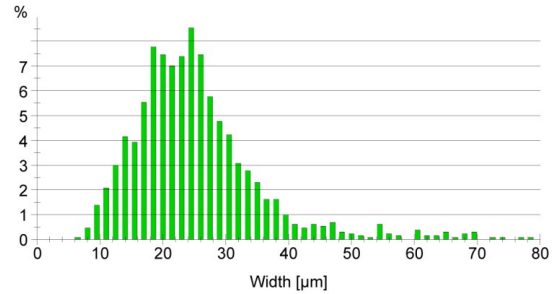
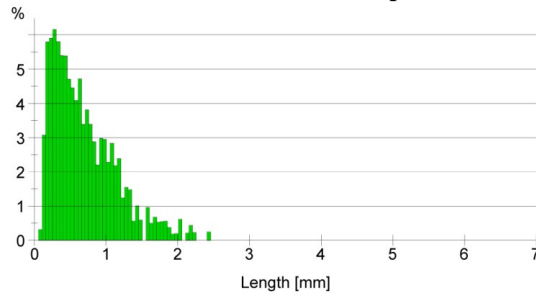
LF dissolved from LF30%-PLA composites

Figure 3: Fiber size distribution of original short fiber (SF), long fiber (LF) and dissolved SF from composites

Along with initial fiber distributions, the distributions of fibers dissolved from PHB-30%SF and PHB-30%LF composites are shown in Fig. 3 and Table 3. In the PHB-30%SF, the fiber length-weighted distribution $L(l)$ decreases from 0.56 to 0.48 mm and the fine content increases from 13.66 to 34.62%. Although fiber width decreases from 14.4 to 13.8 μm , the cell wall thickness (CWT) of fiber decreases only slightly, from 4.6 to 4.4 μm . In the PHB-30%LF, the fiber length-weighted distribution $L(l)$ decreases from 1.75 to 0.65 mm and the fine content decreases from 39.48 to 30.30%. The fiber width decreases from 23.6 to 21.9 μm , but the CWT of fiber decreases from 8.0 to 6.1 μm . The data in Table 3 indicate that the fibers are slightly degraded by the acid released during the mixing process, the interphase is likely fortified by the formation of chemical connections between fibers and matrix. In both composites, the LF and SF contribute 0-1 μm to the overall length, confirming that the fibers are dispersed uniformly within the matrix in both cases and that there are no significant differences in mechanical strength between the LF and SF-reinforced composites.

Scanning Electron Microscopy Analysis

Scanning electron microscopy (SEM) images of the microstructures are shown in Fig. 4. It is seen that, both in this study and the published literature,¹³ the PHB composites have interphasial adhesion of similar quality to that of manufactured PHBV cellulose and a similar interphasial pattern to that of the PLA composites. The largest difference can be seen in the pull-out frequency of fibers; the PHB- and PLA-pulp composites have similar patterns and lower pull-out frequencies than those of the manufactured PHBV cellulose. Because pull-outs contribute to an increase in fracture energy during Charpy test,

the pull-out frequency is proportional to the impact strength. Although the impact strengths of the materials used in this study are higher than those of the original plastics, they are lower than that of the PHBV-cellulose, which is consistent with conclusions drawn from SEM observation. In addition, relatively good interphasial adhesion is seen between the fibers and the matrix in both PHB and PLA. Because the component chains in these materials were partly degraded during the mixing process under elevated temperature, organic acid such as crotonic acid¹⁶ and polylactic acid might have formed, which in turn induced partly hydrolyzed cellulose components in the fibers to form chemical bonds that resulted in a high degree of dispersion of cellulose within the plastics matrix. It was also observed that the number of pull-out cellulose fibers and remaining pores decreases as the fiber content increases; this is believed to result from the formation of a strong skeleton-like network with increasing fiber content, which reduces the number of pull-out fibers on the fracture surfaces, a conclusion that is consistent with the observed mechanical properties of the reinforced composites.

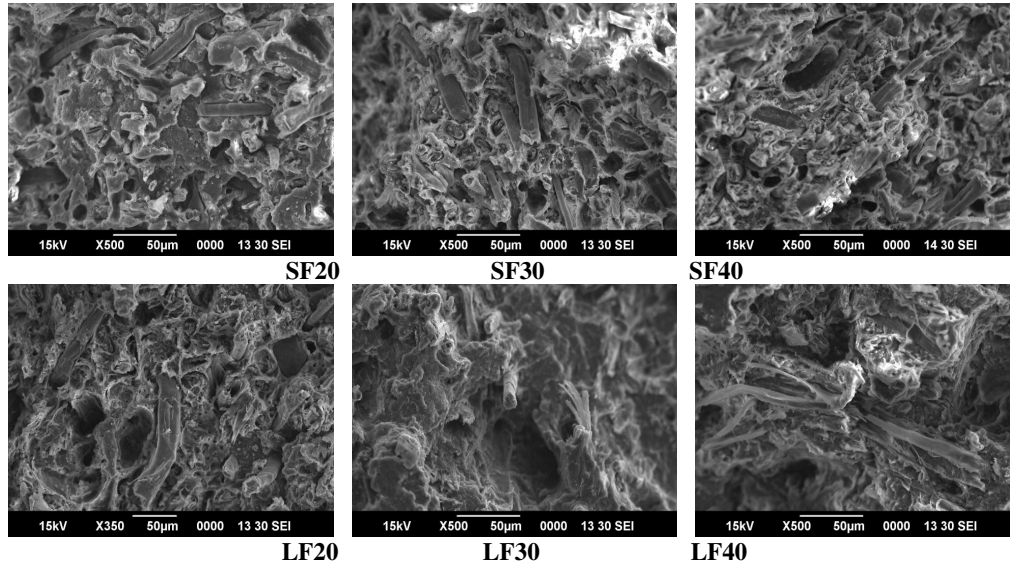
X-Ray Diffraction Analysis

X-ray diffraction (XRD) analysis was used to determine the crystalline structure and the degree of crystallinity of the blends. PHB is a highly ordered polymer that is known to crystallize in orthorhombic cell^{17,18} with reflection peaks at 13.5° and 16.8° and three weaker peaks at 19.1°, 22.2°, 25.5°. The first two peaks are typical of the orthorhombic structural form.³ Fig. 5 shows the XRD spectra of the PHB-fiber composites. The reflection peaks at 13.5° and 16.8° are observed for the control sample, but the three other peaks are not seen, probably because unlike the PLA particle samples, injection molding was used to create the control samples, leading to fewer changes during the injection process. The figure

shows that the patterns of all the composites mixed by a torque rheometer differ from those composed of pure PHB; it is seen that the diffraction at both $2\theta=13.5^\circ$ and 16.9° shows intensity decreases, with two sharp peaks becoming one shoulder peak and a new peak

appearing at $2\theta=22.5^\circ$. This result implies that the interactions between the cellulose fiber and the PHB matrix significantly alter the crystal structure of PHB, with recrystallization occurring during the mixing and injection processes.

PHB



PLA

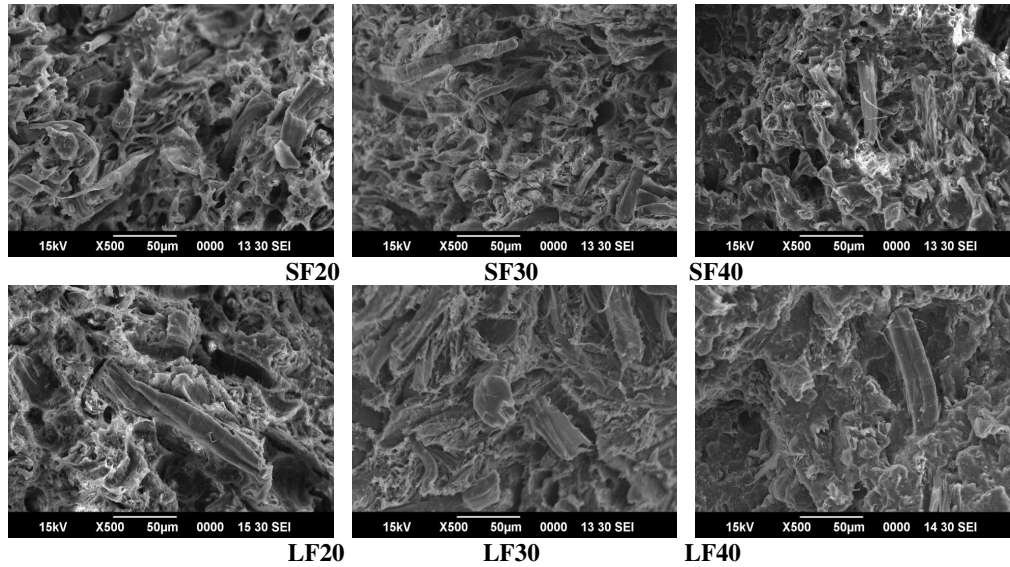


Figure 4: Scanning Electron Microscope photos of the fracture face of PHB/PLA-pulp fiber composites; SF20, 30, 40: short fiber contents in composites were of 20%, 30%, 40% respectively, composites were mixed using a torque rheometer; LF20, 30, 40: long fiber contents in composites were of 20%, 30%, 40% respectively, composites were mixed using a torque rheometer

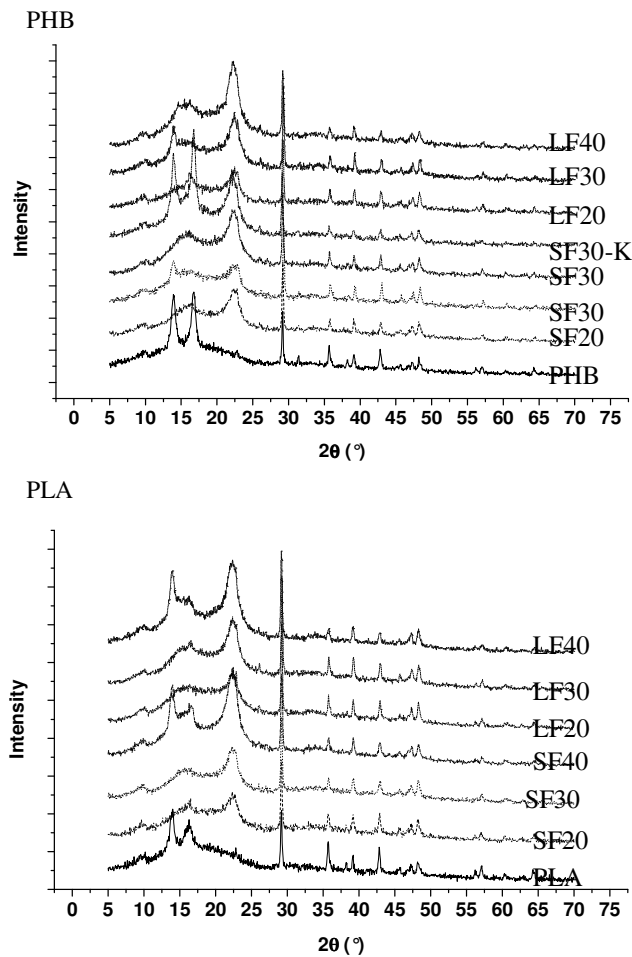


Figure 5: X-ray diffraction patterns of PHB and PLA composites; SF30-K: short fiber 30% and PHB were mixed using a kneader; SF20, 30, 40: short fiber contents in composites were of 20%, 30%, 40% respectively, composites were mixed using a torque rheometer; LF20, 30, 40: long fiber contents in composites were of 20%, 30%, 40% respectively, composites were mixed using a torque rheometer

The fourth image from the top in Fig. 5 (1) is taken of a PHB-30% short fiber sample mixed with a kneader. It is seen that the crystallinity of this sample is not as altered as those of the samples mixed using a torque rheometer, as in the former case the fibers can only rest on the surface during mixing rather than becoming fully immersed in the matrix. As a result of this, the mechanical strength is not as high as in other samples.

The XRD spectra of the PLA-composites are also shown in Fig. 5, from which it is seen that injected neat PLA has two main peaks at $2\theta=14^\circ$ and 16° . Again, the XRD patterns of the composites differ greatly from that of the control sample, with intensity decreases in the two sharp peaks and a new peak at $2\theta=22.5^\circ$, indicating that interactions between the PLA and the fibers have

changed the crystallinity of PLA, with recrystallization occurring during the mixing and injection processes. When the fiber content of both short and long fibers is increased to 40%, the crystallinity of the composites changes externally and the peaks at $2\theta=14^\circ$ and 16° reappear, although these changes had no negative effect on the composite strength.

Thermogravimetric analysis

Because the polymerization degree of fibers and fiber bundles is lower than that of the matrix, the thermal degradation temperature of PHB- and PLA-fiber composites decreases gradually as the fiber content is increased (Fig. 6). When heated, therefore, fibers and fiber bundles act as plasticizers of the composite, resulting in increased polymer plasticity.

Dynamic Mechanical Analysis

Dynamic mechanical tests were run to characterize the composites. Fig. 7 shows the dynamic modulus and tan delta curves of PLA/PHB and their composites. Because PLA and PHB are viscoelastic materials, they both have the capability of storing mechanical energy without dissipation (measured using the storage modulus, E') and the ability to dissipate energy without storage (measured using the loss modulus, E''). In a polymeric material, the dissipation of energy manifests as internal friction or damping, and in a polymer matrix composite energy dissipation may also arise from inter-material friction at the filler-matrix interface. This internal friction can be quantified by $\tan\delta$, the ratio of the energy dissipated per cycle to the energy stored during the cycle (i.e. E''/E'), and a

high dissipation factor is accompanied by a decrease in dimensional stability. Our results seem to show that, in the 40-80 °C temperature range, the addition of pulp fibers increases the mobility of the amorphous phase of the matrix polymer and thus reduces damping in the composites (the degree to which this effect is seen depends upon pulp fiber weight percentage). It is seen that as fiber content is increased, E' and E'' both decrease, as the smoothness of the pulp fiber surfaces allows the interfacial bonds between the fibers and matrix to tend to move together. The energy dissipation ratio, $\tan\delta$, is also observed to decrease owing to the network of fibers dispersed in the polymer matrix improving the hardness of the composites. Because both PHB and PLA are highly viscoelastic materials, the addition of fibers decreases their viscosity and increases their dimensional stability.

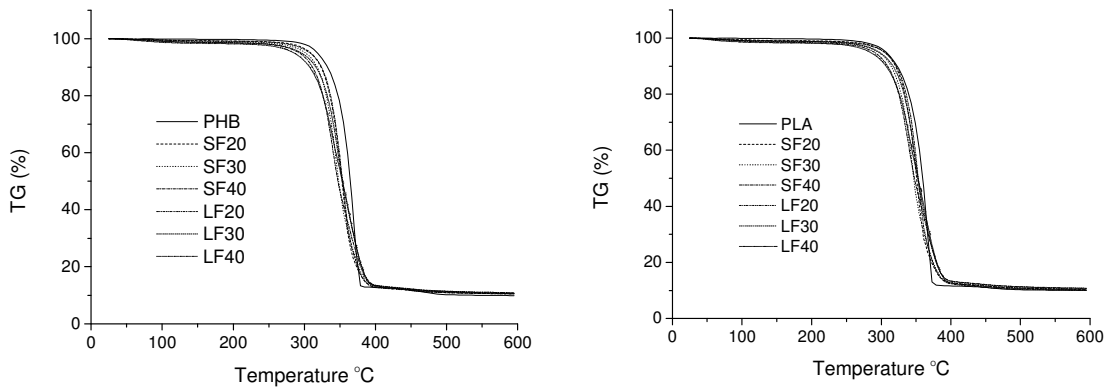
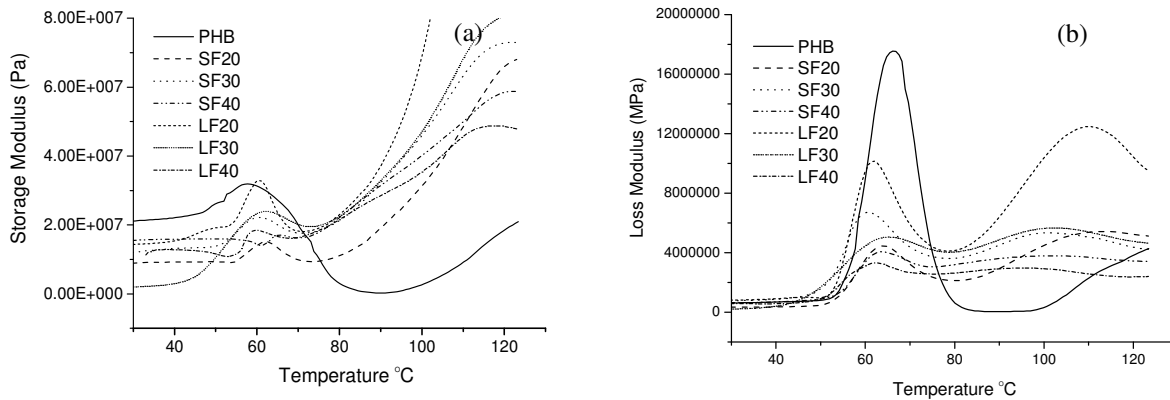


Figure 6: Thermogravimetry charts of PHB and PLA composites; SF20, 30, 40: short fiber contents in composites were of 20%, 30%, 40% respectively, composites were mixed using a torque rheometer; LF20, 30, 40: long fiber contents in composites were of 20%, 30%, 40% respectively, composites were mixed using a torque rheometer



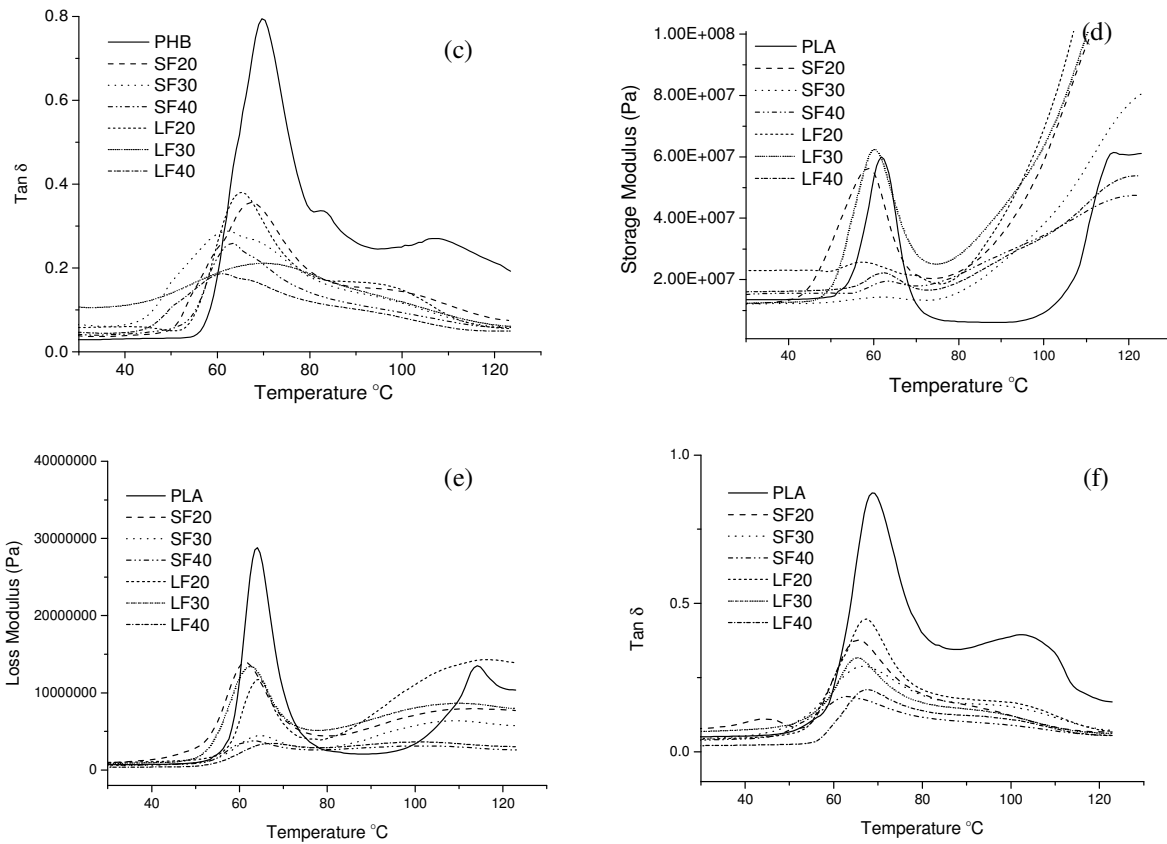


Figure 7: Dynamic mechanical analysis runs for PHB-fiber composites; (a) storage modulus, (b) loss modulus, (c) tan delta, PLA-fiber composites, (d) storage modulus, (e) loss modulus, (f) tan delta; SF20, 30, 40: short fiber contents in composites were of 20%, 30%, 40% respectively, composites were mixed using a torque rheometer; LF20, 30, 40: long fiber contents in composites were of 20%, 30%, 40% respectively, composites were mixed using a torque rheometer

Gel Permeation Chromatography Analysis

The melting point instability of PHB and its copolymers owing to thermal degradation is well documented.¹⁹ The molecular weight of pure polymers and pulp fiber filled composites were investigated with gel permeation chromatography (GPC). Table 4 shows the molecular weight of

pure polymers and of the composites with different fiber content, the results indicating that the pure polymers clearly degraded during the mixing process, while the composites with increased fiber content showed a less obvious degree of degradation.

Table 4
Molecular weight of matrix polymers

Matrix	Fiber contents	Mw	Mn	Mw/Mn
	0	102967	46721	2.20
PHB	SF30%-Kneader	98991	49090	2.02
	SF20%	84205	42107	1.99
	SF30%	72761	28793	2.53
	SF40%	79056	43960	1.79
	LF20%	74025	35001	2.11
	LF30%	69061	26780	2.58
	LF40%	71196	29135	2.44

	0	95142	43423	2.19
	SF20%	60211	24785	2.43
	SF30%	60649	24786	2.44
PLA	SF40%	51927	18987	2.73
	LF20%	57862	23041	2.51
	LF30%	53075	19942	2.66
	LF40%	59684	28357	2.10

This difference likely occurred because both samples were heated to a higher temperature (190 °C) and maintained in the mixing container, while the PHB-30%SF was mixed in a kneader tank at 180 °C with a non-uniform fiber distribution on the rotary gear. Based on mechanical principles, the composite strength of a matrix polymer was affected by its degree of degradation, with a higher degree of degradation resulting in a stronger composite. It is believed that the release of acidic compounds, such as crotonic acid and lactic acids, during the mixing process strengthens the existing interface between the fibers and the matrix polymers through the formation of chemical connections.²⁰

In conclusion, this study reveals a preparation method of a new type of composite materials with good mechanical properties, without using any coupling agent. The obtained composites can be completely biodegraded and present good application prospects in the fields of food containers, medical and health care, cosmetic boxes, toy and stationery materials.

CONCLUSION

This study demonstrated that PHB/PLA cellulose fiber composites with strong mechanical properties can be created by a torque rheometer at 190 °C with very short mixing times. The tensile and impact strengths of the PHB and PLA composites were improved by factors of up to 1.5 and 1.3, respectively, relative to their original (unreinforced) strengths. GPC data indicated that PHB and PLA partially degrade during the composite forming process, an effect that is believed to occur when the existing interface between pulp fiber and matrix polymers is fortified by crotonic and lactic acids released during the formation process. This study demonstrates a novel potential method for creating biodegradable composites using pulp fibers without coupling agent.

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