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Impact and tensile properties of PLA/Cordenka and PLA/flax composites

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Abstract

The interest for biodegradable polymers and natural fibre reinforced polymers has recently grown because of increasing environmental concerns. But the impact properties of bast fibres reinforced polymers cannot reach the levels of traditional fibre reinforced polymers.

PLA (polylactic acid) was reinforced with Cordenka rayon fibres and flax fibres, respectively. The mechanical properties of these composites which are examples for completely biodegradable composites were tested and compared. The samples were produced using injection moulding. The highest impact strength (72 kJ/m^2) and tensile strength (58 MPa) were found for Cordenka reinforced PLA at a fibre-mass proportion of 30%. The highest Young's modulus (6.31 GPa) was found for the composite made of PLA and flax. A poor adhesion between the matrix and the fibres was shown for both composites using SEM. The promising impact properties of the presented PLA/Cordenka composites show their potential as an alternative to traditional composites.

Keywords: A. Short-fibre composites; B. Impact behaviour; D. Scanning electron microscopy (SEM); E. Injection moulding; Natural fibre

Introduction

The use of traditional composites made of glass, aramid or carbon fibre reinforced plastics have recently been discussed critically because of increasing environmental consciousness [1]. Thus, the recent research and development efforts have led to new products based on natural resources. Some of these are biodegradable polymers like PLA (polylactic acid), cellulose esters, polyhydoxyalkanoates and starch polymers. Furthermore, natural fibre-reinforced polymers made with natural fibres like flax, hemp, kenaf, jute or cotton fibres are important research and development (R&D) achievements. Composites made of natural fibres and biopolymers are completely biodegradable and are called "green composites" because of their environmentally beneficial properties [2].

The lower price in manufacturing as well as the better performance of traditional, petrochemical plastics compared to polymers based on natural resources are the outcome of the R&D efforts of several decades, whereas only recently scientists have been trying to improve biopolymers which came to public only a few years ago so that they can become cheaper and more competitive [1]. Natural fibres as reinforcement for petrochemical polymers like PP (polypropylene) have already been established in the automotive industry [3]. Natural fibres themselves are fibre-reinforced structures in which the cellulose content and the angle of microfibrils influence their mechanical properties [4].

The only thermoplastic polymer based on natural resources which can be produced with a capacity of over 140,000 tons per year is PLA. Because of this and because of its properties it is one of the most promising biopolymers [5]. The low emission of greenhouse gases and the low amount of energy used for PLA production are also interesting factors [6]. Only its high price (1.80 - 4.00 Euro/kg) compared to the price of petrochemical thermoplasts lowers its competitiveness [5]. But a decrease of the price is expected with increasing demand and increasing R&D achievements in the next years [7].

PLA is a thermoplast which can either be synthesised by condensation of lactic acid or ring opening polymerisation of lactide which is the diester of lactic acid. Lactic acid is a chiral organic acid which mainly occurs in the L-form. It is produced by fermentation of dextrose which itself is gained from annually renewable resources like corn [8].

Mohanty *et al.* [1] give a good overview on the research on green composites up to the year 2000. But PLA has become an important part of R&D in the recent years because of the benefits listed above. Mechanical tests on natural fibre reinforced PLA have been performed with different types of fibres like kenaf [9, 10], jute [11], flax [12] abaca [13], hemp [7] and Cordenka rayon fibres [14].

Not much literature on the adhesion between the matrix and the fibres in “green composites” has been published, although it determines their mechanical properties significantly. Most publications are based on the interaction between fibres and polyoelfins. It is known that natural fibres have a poor adhesion to hydrophobic matrices like PP because of their hydrophilic nature [15]. Because of the hydrophilic nature of PLA, Heinemann and Fritz assumed a better interaction between PLA and natural fibres than between PP and natural fibres [5]. Nevertheless, Oksman *et al.* found long fibre pull-outs and clean fibre surfaces in the fracture surface of the PLA/flax fibre composite which proves a poor adhesion between the fibres and the matrix [12].

The insufficient impact strength of biodegradable composites, which plays an important practical role for example in housings of portable electronic devices, prevents a broader field of application. Thus, this work deals with the mechanical properties of PLA/flax and PLA/Cordenka (a rayon fibre that is usually used to reinforce tires) composites. The testing methods are the Charpy impact test and the tensile test. A relation between the fibre-mass proportion and the mechanical properties of the composites is analysed. Furthermore, the fracture surfaces of the composites are investigated using SEM.

Materials and methods

Materials

Polymer / Polylactide

NatureWorks™ PLA Polymer 6202D by the company Cargil Dow LLC was used as the matrix material. This thermoplast has a density of 1.24 g/cm^3, a melt temperature of 160-170 °C and a glass transition temperature of 60-65 °C. A tensile strength of 44.46 MPa, a Young's modulus of 3.11 GPa and an impact strength of 16.13 kJ/m^2 was measured for this material in a former publication [7]. The used PLA was in fibre form. Ingeo fibre type SLN2660D (company: Far Eastern Textile Ltd., Taipei, Taiwan) is a medium denier (0.67 tex) round cross-section polylactic acid (PLA) staple fibre (64 mm) for nonwoven applications (strength 37 cN/tex; elongation at break 55 %) [19].

Reinforcement Fibre / Flax (Linum usitastissimum L., Linacea)

Flax of the type Holstein flax HO-0401b, planted in 2003 was used. For this type the fibre strength is 874 N/mm² (59.9 cN/tex), Young's modulus is 14583 N/mm² and the strain is 6.6 %. Bundle width mean value is 31 µm [20].

Reinforcement Fibre / Cordenka

Cordenka 700 rayon fibres (company: Cordenka, Obernburg, Germany) was used as reinforcement for the different composites. Fibres out of yarn type RT700 1840/1000 were used. In this connection RT700 specifies the type, 1840 the polyfil fineness in dtex and 1000 the number of fibres in the yarn [21].

According to Ganster and Fink fineness of Cordenka fibre is 0.18 tex, strength is 56±4 cN/tex (833 N/mm²), elongation is 13±2 %, and Young´s modulus is 1300 cN/tex (20 GPa) [14].

Composite production

Samples with three different fibre-mass proportions (10%, 20%, 30%) for the PLA/flax composite and samples with four different proportions (10%, 20%, 30%, 40%) for the PLA/Cordenka composite were produced. For each of these seven different composites, seven tensile specimens according to DIN EN 61 and seven impact specimens according to DIN EN ISO 179 were produced.

Multilayer webs with random in-plane reinforcement fibres were fabricated using a carding machine. For this experiments a lab roller card (manufactured by Anton Guillot, Aachen, Germany) with a working width of 30 cm was used. The rollers are clothed with flexible card clothing. The produced multi layer webs have a web-weight of about 800 g/m². According to NatureWorks PLA Polymer 6202D data sheet these webs were dried for 4 hours at 80°C before they were pressed with a hydraulic press by the company Rucks Maschinenbau GmbH, Glauchau, Germany (type: KW 214.1). The composites were pressed at a temperature of 170°C and at 18 MPa for 5 minutes. Pellets were made of the resulting plates using a shredder. These pellets were dried again before injection moulding under the conditions given above. A machine by the company Battenfeld, Bad Oeynhausen, Germany (type: UNILOG 4000) was used for injection moulding. The temperatures in the screw were set to 170°C, 175°C and 180°C; the temperature in the injector was set to 180°C. A dwell pressure of 10 MPa was used for all composites except for the composite with a fibre proportion of 40% for which a pressure of 12 MPa was used.

Mechanical testing

All mechanical tests took place at 50% relative humidity and 23 °C. The specimens had been conditioned under the same circumstances for at least 24 hours before testing. The cross sectional area of each specimen had been measured with a gauge at 3 locations within the testing area before testing.

The Charpy impact strength of the composites was tested according to DIN EN ISO 179. A Thwing-Albert FRANK (Waldbüttelbrunn, Germany) testing machine (type 53302) with a pendulum of 4 J energy was used to measure the unnotched, rectangular specimens (80 mm * 10 mm * 4mm). Seven specimens were tested for each material.

The tensile strength and the Young's modulus were determined according to DIN EN 61. A Zwick/Roell (Ulm, Germany) 250 kN test machine operated at a crosshead speed of 10 mm/min was used for testing the dogbone-shaped specimens (testing area: 80 mm * 10 mm * 4 mm; total length 150 mm). The strain of the samples was recorded by the testing machine itself; no extensometer was used. The Young's modulus was calculated within 50-600 N.

Scanning electron microscopy

The fracture surfaces which emerged during mechanical testing were examined using a scanning electron microscope (SEM) type CS 24 from Obducat CamScan with an acceleration voltage of 20 kV. For each test series the specimen with an impact strength value closest to the average was chosen for microscopy. The specimens had been coated with platinum iridium over a span of six minutes.

Results and Discussion

Microscopy

SEM images of the fracture surfaces of impact specimens can be seen in figures 1-3. Pulled out fibres and the corresponding holes are visible in both composites. Furthermore, it can be seen that the surfaces of the pulled out fibres are clean. Both observations can also be found in the literature for the PLA/flax composite [12] and suggest a poor adhesion between the fibres and the matrix. They are more distinct in the case of the PLA/Cordenka composite: the fibre pull-outs are much longer and the fibre surfaces are cleaner which indicates an even worse adhesion between PLA and Cordenka than between PLA and flax.

There are gaps between the fibres and the PLA which could either occur because of debonding during mechanical testing or because of poor approximation during composite production. Either would also indicate a poor matrix/fibre adhesion.

As a comparison, the composite of flax fibres in a MAPP (maleic anhydride-grafted polypropylene) matrix can be seen as an example for a good matrix/fibre adhesion: in SEM images only very small fibre pull-outs which were coated with matrix material were found [16].

Heinemann and Fritz [5] predicted a good adhesion between natural fibres and PLA because of its hydrophilic nature. PLA has slightly polar oxygen atoms which could form hydrogen bonds to the hydroxyl groups of the natural fibres. But because of the results of this work and former works it can either be assumed that these hydrogen bonds only have a small influence on the fibre/matrix adhesion or that an approximation between the polar groups cannot occur during processing because of the macromolecular structure of cellulose, hemicellulose and lignin which are the main components of natural fibres.

The stronger adhesion between MAPP and natural fibres in comparison to PLA results from additional covalent bonds between the maleic acid anhydride and the hydroxyle groups of the natural fibres [17].

Impact strength

The results of the Charpy impact test are shown in table 1 and figure 4. All values are normally distributed (α=5%, David-test). It is apparent that the impact strength of the PLA/flax composites increases with increasing fibre-mass proportion. But the highest value is still 31% lower than the value for pure PLA. This result converges well with the result of Oksman *et al*. [12]. Small differences can be explained by the use of different types of PLA and different ways of processing.

The impact strength of Cordenka reinforced PLA increases significantly and reaches a maximum value of 72 kJ/m^2 at a fibre-mass-ratio of 30% which is approximately 4.5 times higher than the value for pure PLA. A comparison of the rates of improvement which can be reached using different types of fibres to reinforce PLA can be found in table 2.

As jute reinforcement, the use of flax fibres leads to a decrease of impact strength [11]. Kenaf can also improve the impact properties of PLA but a clear improvement can only be reached by the use of aliphatic copolymers [10]. In a publication by Ganster and Fink [14] the impact strength of a PLA/Cordenka composite with a fibre-mass proportion of 25% was examined with a value of approximately 70 kJ/m^2.

Thus, the impact strength of the PLA/Cordenka composite is more promising than all other biodegradable composites. It is even higher than the impact strength of flax reinforced PP or MAPP whose impact strengths are approximately 30 kJ/m^2 [16] and which are two of the most important natural fibre reinforced polymers in the automotive industry [3].

Debonding, pull-out and fracture of the fibres are the three mechanisms of energy absorption during impact. It is assumed that the strain energy which is released by fibre debonding and fracture is proportional to the debonded length. Consequently, a poor adhesion between matrix and fibres leads to a higher energy absorption [18]. Thus, the better fibre/matrix adhesion in the PLA/flax composite could be an explanation for the worse impact strength compared to the PLA/Cordenka composite.

The decrease of impact strength between the fibre-mass proportions of 30% and 40% in the PLA/Cordenka can be explained by comparing figure 2 and 3: there are many fibres which are not completely surrounded by matrix material and are in contact with other fibres. Consequently, less energy can be absorbed during debonding. Above a certain fibre proportion, which is different for every composite, the mechanical properties cannot be improved anymore. This point appears to be between 30% and 40% for this composite.

Tensile properties

The results of the tensile tests are shown in table 1 and figure 5 and 6. All values are normally distributed except for the PLA/Cordenka composite with a fibre-mass proportion of 10% (α=5%, David-test). The specimens of the composite with a fibre-mass proportion of 40% did not fail in the testing area but in the area where they were fixed to the testing machine and consequently can not be used for further discussion. The Young's modulus as well as the tensile strength of both composites increase with increasing fibre-mass proportion. The flax reinforcement leads to a better improvement of the modulus while the Cordenka reinforcement leads to a better improvement of the tensile strength.

The value of the tensile strength of flax reinforced PLA with a fibre-mass proportion of 30% (54.15 MPa) is very close to the value found in literature (53 MPa) but the modulus (6.31 GPa) is smaller than the value found in the same publication (8.3 GPa) [12]. To find out if this difference is due to the fact that no extensometer was used in this work, another experiment was done: the Young's moduli of six specimens of the PLA/flax composite with a fibre proportion of 30% were measured using an Instron extensometer. The average value (7.05 GPa; S.D.: 0.09 GPa) was slightly larger than the one found in the first experiment. This leads to the assumption that the different values between literature and experiments presented here are influenced by the way of measuring.

The values for the Young's moduli of the PLA/Cordenka composite are close to those found by Ganster and Fink [14]. But the tensile strength differs significantly to the one found in literature. The tensile strength in that work is given by a value of approximately 110 MPa while the highest value found in this work is only 57.7 MPa. But the higher values for pure PLA in that work, which was around 70 MPa, has to be taken under consideration when comparing the tensile strengths. It can generally be said that it is hard to compare the values for the tensile strength of the different biodegradable composites because the authors have found completely different values for the pure PLA matrix which reach from values of 21 MPa [9] up to values above 110 MPa [13]. Nevertheless, the relative improvement caused by the reinforcement fibres can be compared (table 2). The best improvements have been reached using jute fibres [11] and kenaf fibres [9]. The Cordenka fibres in this work caused an increase in tensile strength of 30%.

Conclusion

The composite made of PLA and Cordenka fibres shows promising mechanical properties, especially impact properties (72 kJ/m^2). Possible fields of application could be the automotive or the electronic industry. But further research and development of this composite is necessary. Optimised parameter for composite production, fibre length and fibre proportion have to be found. Furthermore, exact tests on the moisture, thermal and chemical resistance have to be made. The ecological benefits must also be investigated in long time tests.

But the PLA/Cordenka composite has the potential to become an ecologically beneficial alternative to natural reinforced composites with petrochemical matrices in the future.

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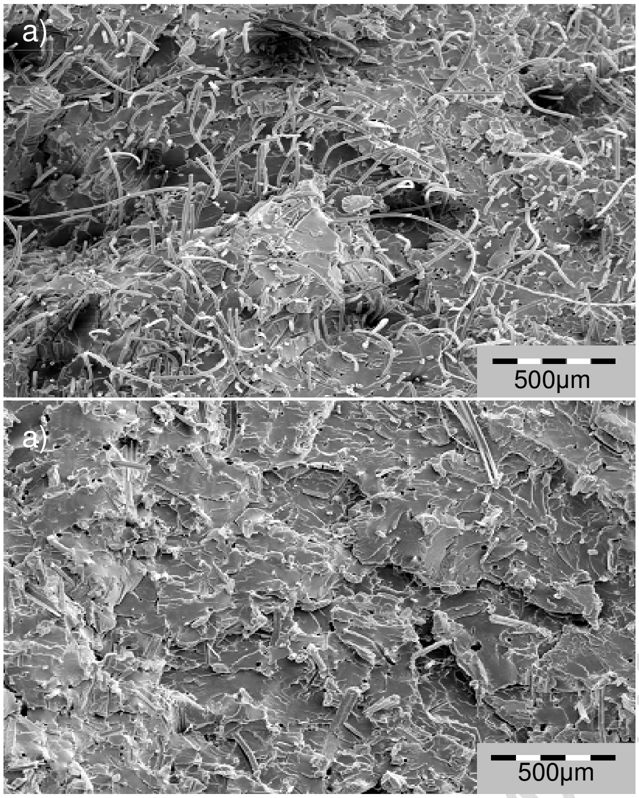

Fig. 1. Overview of the fracture surface of composites with a mass proportion of 10% after impact testing: (a) PLA/Cordenka composite, (b) PLA/flax composite.

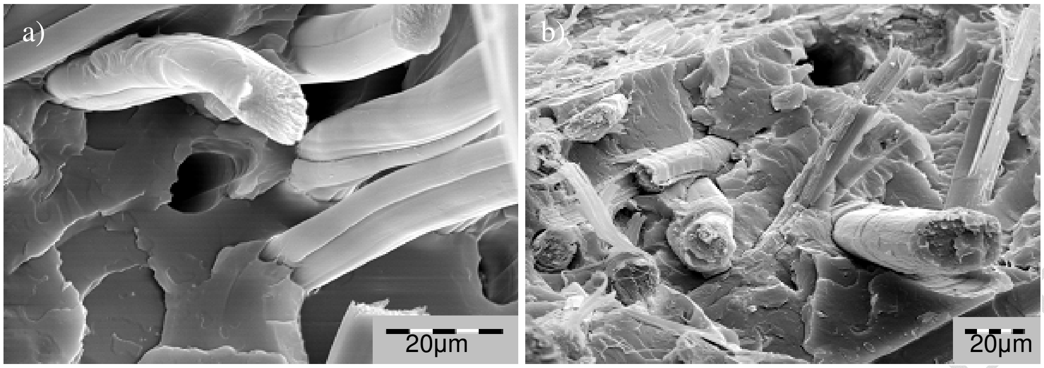

Fig. 2. Detailed pictures of the fracture surface of composites with a mass proportion of 30% after impact testing: (a) PLA/Cordenka composite, (b) PLA/flax composite.

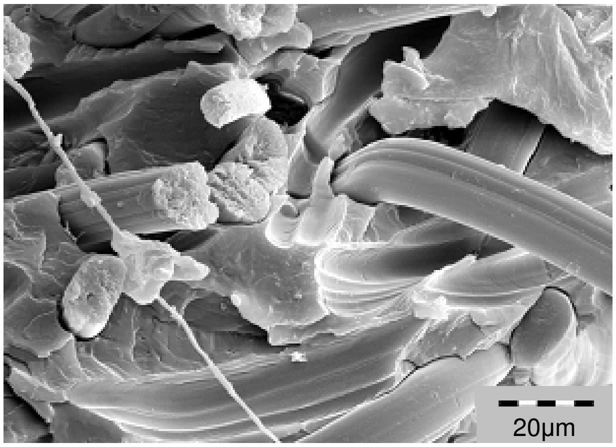

Fig. 3. Detailed pictures of the fracture surface of the PLA/Cordenka composite with a mass proportion of 40% after impact testing. There are many fibres which are in direct contact to other fibres and are not completely surrounded by matrix material.

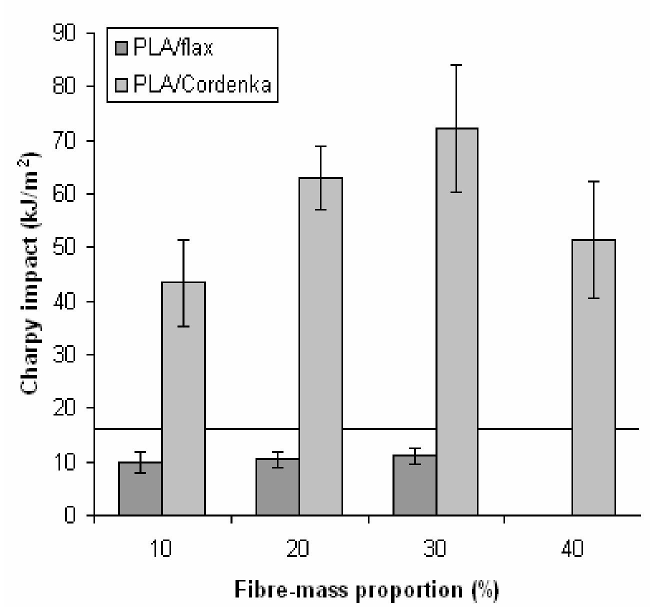

Fig. 4. Impact strength of the composites versus their fibre-mass proportion. The horizontal line represents the value for pure PLA.

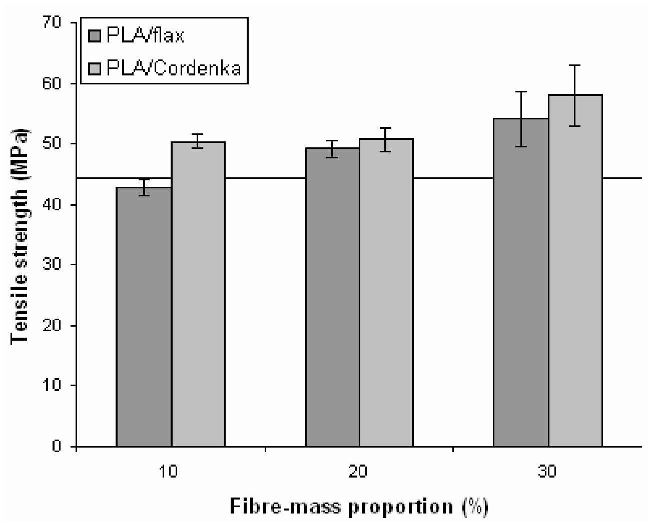

Fig. 5. Tensile strength of the composites versus their fibre-mass proportion. The horizontal line represents the value for pure PLA.

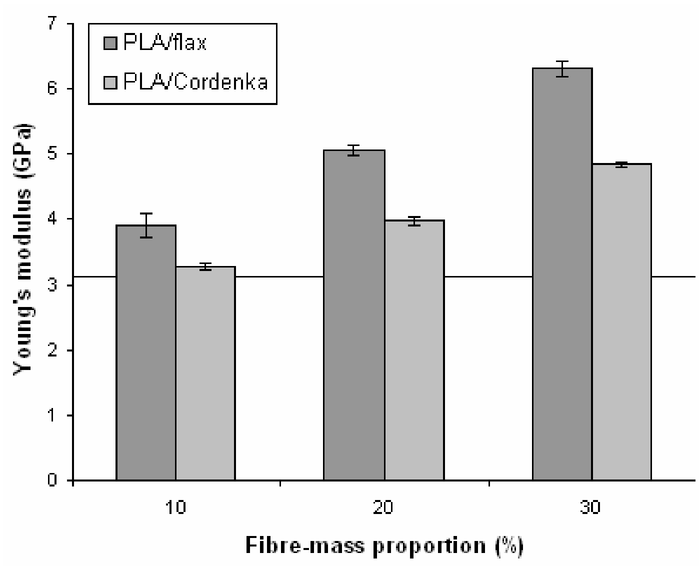

Fig. 6. Young's modulus of the composites versus their fibre-mass proportion. The horizontal line represents the value for pure PLA.

Table 1. The mechanical properties of PLA/flax and PLA/Cordenka composites.

Fibre content (%)	Charpy Impact (kJ/m^2)				Tensile Stress (MPa)				Young's modulus (GPa)			
	flax		Cordenka		flax		Cordenka		flax		Cordenka	
	average	S.D.	average	S.D.	average	S.D.	average	S.D.	average	S.D.	average	S.D.
10	9.97	2.05	43.44	8.11	42.73	1.29	50.40	1.19	3.90	0.18	3.27	0.04
20	10.45	1.53	62.97	6.01	49.23	1.40	50.75	1.90	5.06	0.07	3.97	0.07
30	11.13	1.55	72.24	11.79	54.15	4.57	57.97	5.08	6.31	0.12	4.85	0.03
40			51.34	10.95								

Table 2. Comparison of the mechanical properties of PLA composites with different reinforcement fibres. Because the values for mechanical properties for pure PLA presented in different papers differ significantly from each other percentage values compared to the value for pure matrix material given in every particular work are presented. Values marked with an asterisk are calculated by using information which was not given in numeric values but in figures.

Fibre type	Fibre proportion	Charpy Impact	Tensile Strength	Young's modulus	Source
abaca	20%	-	*104%	*170%	[13]
Cordenka	25%	*188%	*157%	*146%	[14]
Cordenka	30%	447%	130%	155%	This study
flax	30%/40%	*63%	106%	244%	[12]
flax	30%	69%	121%	202%	This study
jute	40%	93%	182%	271%	[11]
kenaf	70%	-	286%	492%	[9]