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The Influence of Biocomposite Processing and Composition on Natural Fiber Length, Dispersion and Orientation

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Abstract: In the study, the effect of process steps, melt viscosity and fiber type on the fiber length of biocomposites from triethyl citrate plasticized starch acetate and natural fibers was investigated. Composites were prepared by melt processing (compounding and injection molding). The lengths of fully processed fibers were determined by dissolving the starch acetate matrix and measuring the length of the remaining fibers by optical microscopy and image analysis. A clear reductive effect of the pelletising and melt processing on the fiber length was noticed. Also a reduction of fiber length along the increasing fiber content and the decreasing plasticizer content was detected. This reduction was originated from the increasing shear forces during compounding, which again depended on the increased viscosity of the material. When comparing the fully processed hemp and flax fibers, hemp fibers remained longer and fibrillated more than flax fibers, leading to higher aspect ratio. Thus, the reinforcement efficiency of hemp fibers by the processing was improved, on the contrary to the reduced reinforcement efficiency of flax fibers. In addition, the analysis of fiber dispersion and orientation showed a good dispersion of fibers in the matrix, and a predominant orientation of the fibers in the melt flow direction.

Key words: Starch acetate, natural fiber composite, fiber length, fiber distribution.

1. Introduction

An increasing interest towards the use of bio-based polymers instead of conventional petroleum-based plastic materials can be detected worldwide. Progressing technologies, rising prices of finite resources and new environmental legislation together with more environmentally concerned consumers are creating a need to compensate petroleum-based materials with bio-based plastics. However, the properties of bio-based plastics do not always meet the material requirements of certain applications. Fiber reinforcement of the plastic material can provide higher mechanical properties and thereby wider application possibilities. The most common fiber materials for reinforcement of plastics are glass, carbon and aramid [1]. To produce natural fiber reinforced biocomposites, various cellulosic fibers can be used. Fibers originated from flax, kenaf, cotton and pulp have been mixed with polylactic acid (PLA) to form natural fiber reinforced biocomposites [2]. Also other bio-plastics such as polyhydroxy butyrate (PHB), polycaprolactone (PCL) and polyvinyl alcohol (PVA) have been reinforced with natural fibers [6]. Within biopolymers, also starch-based bioplastics have been widely studied and used due to their low price and good availability. In thermoplastic starch composites, for example flax and ramie fibers have been used, resulting in four times higher tensile strengths than the neat plastics [9]. Starch

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acetates have earlier been reinforced with cellulosic fibers to give composites with enhanced mechanical properties, shock absorbance and processability [10, [11]. In the processing of the natural fiber composites, the variable and somewhat sensitive nature of the natural fibers needs to be taken into account. The fibers are inevitably reduced in length during the pelletising, compounding and molding processes [12]. In addition, the dispersion and orientation of the fibers in the composites are also influenced by processing conditions. These changes are actuated by shear forces during processing, which in turn depend on the melt viscosity. Plasticized starch acetates are suitable to be used as model matrix materials in order to analyze these changes, since the melt viscosity and the mechanical properties of the starch acetate can be adjusted by the plasticizer content [11]. An improved knowledge of the influence of biocomposite processing and composition on the fiber length, dispersion and orientation is needed in order to minimize iterative product design.

2. Experiment

2.1 Materials

For acetylation of the starch, a high amylose (62%) corn starch (Cerestar AmyloGel 03003) was purchased from Cargill-Cerestar BVBA (Mechelen, Belgium). The starch acetates were prepared according to a procedure by Lammers et al. [13] to a high degree of substitution (DS 2.6) at VTT Rajamäki. For plasticizing, triethyl citrate (TEC) by the product name of Citroflex® 2 was purchased from Morflex Inc. (North Carolina, USA) and obtained from OneMed (Finland). Flax and hemp fibers were delivered by Ekotex (Poland) and BaFa GmbH (Germany), respectively, both cut into approximately 12 mm length to ease the handling and afterwards pelletised for compounding trials.

2.2 Processing

Starch acetate was initially prepared in pre-plasticized form, containing 15 wt% of TEC. The material was further plasticized to TEC contents of 20, 25, 32.5 and 35 wt% using a twin-screw extruder (ZE 25 × 48D, Berstorff GmbH, Hannover, Germany) with co-rotating mixing screws. Composite compounds with fiber contents of 10 and 40 wt% were then prepared from pelletised flax and hemp fibers, using the same twin-screw extruder as described above. These samples were then injection molded with Engel injection molding machine (ES 200/50 HL, Engel Austria GmbH, Schwertberg, Austria) to ISO 3167 tensile test specimen.

2.3 Fiber Length Analysis

For each composite compound, pieces of (mm) 4 × 20 × 20 were cut from the tensile test specimens and dissolved in hot chloroform. The remaining fiber fraction was collected and the fiber length distribution was determined by optical microscopy and image analyzes.

2.4 Mechanical Properties

The tensile test specimens were kept in a room with standard conditions (23 °C, 50% relative humidity) for at least five days before testing. The ISO-527 and ISO-179 standards were used in the mechanical testing of the specimens. Tensile tests were performed using an Instron 4505 Universal Tensile Tester (Instron Corp., Canton, MA, USA.) and an Instron 2665 Series High Resolution Digital Automatic Extensometer (Instron Corp., Canton, MA, USA.) with 10 kN load cell and a 5 mm/min cross-head speed. Impact strengths were determined by using Charpy Ceast Resil 5.5 Impact Strength Machine (CEAST S.p.a., Torino, Italy). Impact strength tests were performed on unnotched specimens.

2.5 Fiber Dispersion and Orientation

Optical microscopy was used to study the dispersion and orientation of fibers by making and analyzing images of polished composite cross sections cut with different angles to the flow direction of the injection molded samples. The dispersion and orientation of the fibers were determined by image analysis using Image-Pro software.

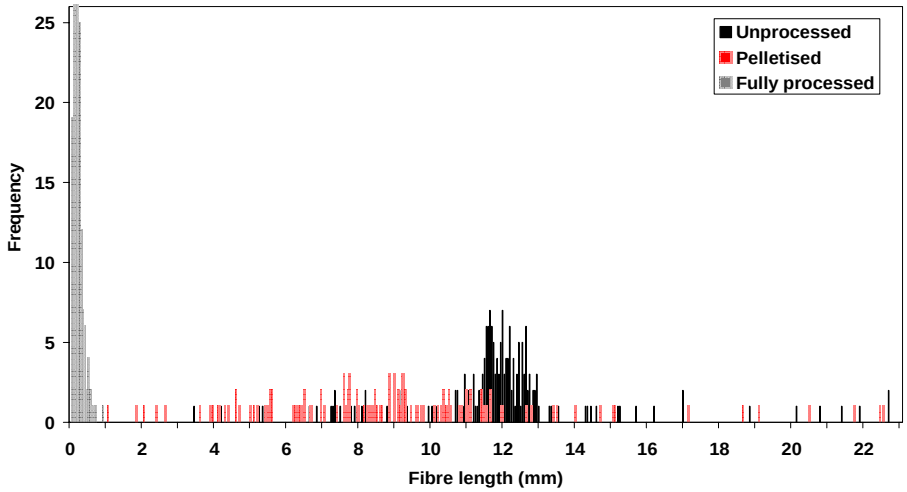


Fig. 1 Histograms of fiber lengths of unprocessed, pelletised and fully processed flax fibers. Frequencies of the fully processed fibers outside y-scale are 81 ($0.05 < x \leq 0.1$ mm), 83 ($0.11 < x \leq 0.15$ mm) and 42 ($0.151 < x \leq 0.2$ mm).

3. Results

3.1 Fiber Length

The change of the fiber length in the process of reinforcing starch acetate with natural fibers was studied from three different aspects: (1) process steps, (2) melt viscosity, and (3) fiber type.

3.1.1 Process Steps

Fig. 1 shows the histograms of flax fiber lengths of unprocessed, pelletised and fully processed fibers. The full processing includes pelletising, compounding and injection molding of the composite with 20 wt% of TEC and 40 wt% of flax fibers. From Fig. 1, the effect of processing on the reduction of fiber length can clearly be detected. The average length of the unprocessed flax fibers is 11.7 mm with standard deviation of 2.7 mm. Fiber pelletising has a slight effect on the fiber length: after pelletising, the average fiber length decreases to 10.4 mm with standard deviation of 6.1 mm. After full processing, the fiber length reduces extensively. The average fiber length of the fully processed fibers is 0.151 mm with standard deviation of 0.105 mm. The length reduction of the fully processed fibers is controlled by the conditions during compounding and injection molding of the composite: processing temperature, screw configuration and the resulting shear forces.

3.1.2 Melt Viscosity

Both the plasticizer and fiber content of the composite have an effect on the viscosity of the composite melt, which in turn influences the fiber length reduction during processing. Composites compounded with 10 or 40 wt% of fibers and plasticizer contents of 20, 25, 32.5 and 35 wt% were selected to study the effect of plasticizer and fiber content on the fiber lengths of the fully processed flax fibers. Table 1 shows the compositions of the selected composites in addition to mean fiber lengths, standard deviations and minimum and maximum lengths of the fully processed fibers.

Fig. 2 shows the mean fiber lengths of flax fibers in the composites with 10 and 40 wt% fiber content, as a function of plasticizer content. As seen in Fig. 2, an increase in the fiber content of the composite results in reduced fiber lengths. The fiber length reduction is also increased when plasticizer content is decreased. However, the effect of the plasticizer content is not affected by the fiber content, which can be concluded from the almost identical slopes of the two trendlines.

Both with plasticizer and fiber content, the fiber shortening originates from the increasing shear forces during compounding, which again depends on the viscosity of the material. Addition of fibers into the matrix polymer increases the viscosity of the melt and

Table 1 Mean fiber lengths, standard deviations, minimum and maximum lengths of the fully processed flax and hemp fibers in the composites.

Fiber	Fiber content (wt%)	TEC content (wt%)	Mean length (mm)	Standard deviation (mm)	Min. length (mm)	Max. length (mm)
Flax	10	20	0.347	0.257	0.043	1.506
Flax	10	25	0.317	0.268	0.024	1.566
Flax	10	32.5	0.334	0.262	0.028	1.282
Flax	10	35	0.498	0.473	0.016	2.686
Flax	40	20	0.151	0.105	0.028	0.697
Flax	40	25	0.252	0.196	0.024	1.100
Flax	40	32.5	0.293	0.256	0.020	1.572
Flax	40	35	0.297	0.247	0.033	1.218
Hemp	40	32.5	0.544	0.560	0.029	2.459

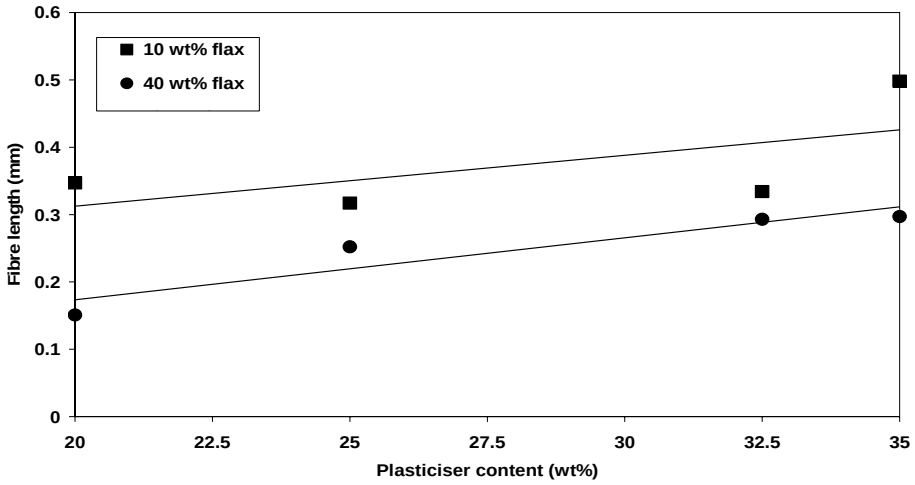


Fig. 2 Mean lengths of flax fibers after full processing at 10 and 40 wt% fiber content, and as a function of plasticizer content.

Table 2 Mechanical properties of flax and hemp fiber composites.

Fiber	Fiber content (wt%)	TEC content (wt%)	Tensile strength (MPa)	Elastic modulus (GPa)	Impact strength (kJ/m^2)
Flax	10	20	35.0	3.14	2.4
Flax	10	25	24.9	2.37	2.2
Flax	10	32.5	15.7	1.57	2.9
Flax	10	35	12.1	1.12	4.8
Flax	40	20	50.7	8.05	5.2
Flax	40	25	45.8	6.01	6.1
Flax	40	32.5	33.7	5.63	7.6
Flax	40	35	28.8	5.14	7.4
Hemp	40	32.5	26.6	4.45	8.8

therefore also the fiber cutting increases. The same phenomenon relates to adjustment of plasticizer levels. With less plasticizer, the melt is more viscous and therefore more susceptible to shear forces during compounding. Along the addition of plasticizer, less energy is absorbed by the composite melt from the mixing work done by the kneaders and mixers in the compounder and as a result, the fibers are split and cut to a smaller extent.

The plasticizer and fiber contents affect also the mechanical properties of the composites. Table 2 shows the tensile strength, elastic modulus and impact strength values of the composites with varying compositions. Increasing plasticizer content leads to

decreased tensile strength and elastic modulus, but improved impact strength properties. On the other hand, the increase in fiber content results in overall higher mechanical properties of the composites. The effect of plasticizer and fiber contents on the mechanical performance of the composites is addressed in details elsewhere [11].

3.1.3 Fiber Type

The effect of fiber type on the fiber length change during processing was studied by determining the fiber lengths in the composites containing 40 wt% hemp and flax fibers and 32.5 wt% TEC. The histograms of the lengths of fully processed hemp and flax fibers are shown in Fig. 3 and the mean fiber lengths, widths, standard deviations and aspect ratios of unprocessed and fully processed fibers in Table 3. As seen from the data, full processing seems to result in higher level of length reduction of flax fibers than of hemp fibers. The length of unprocessed flax fibers are about the same as hemp fibers. The fully processed hemp fibers are remained longer than flax fibers: the mean lengths of fully processed flax and hemp fibers are 0.293 and 0.544 mm, respectively.

Although the length of the fibers is crucial for the reinforcing effect, the more important parameter is the fiber aspect ratio (length to diameter ratio). Therefore, simultaneously to preserving the fiber length, the width (diameter) of the fiber should ideally be decreased in order to increase the fiber aspect ratio which governs the reinforcement efficiency of the fibers in the composites [16]. The most effective fiber reinforcement is achieved if the length of the fiber exceeds the critical fiber length, which is also depended on the diameter of the fiber [17]. In glass fiber-reinforced polyamide 6,6 composites, tensile strength has been found to increase linearly with decreasing fiber diameter [18]. In addition, fibrillation of the fiber bundles into single fibers is essential to increasing both the longitudinal and transverse strengths of the material. In non-separated fiber bundles low transverse strengths is observed due to the weak interaction between the individual fibers. Therefore, if material contains non-separated fiber bundles, the failure of the composite will occur prematurely by initiation from cracks within the material (within fiber bundles). On the other hand, if the fiber bundles are fibrillated into single fibers, the weak interfaces inside the bundles disappear and are

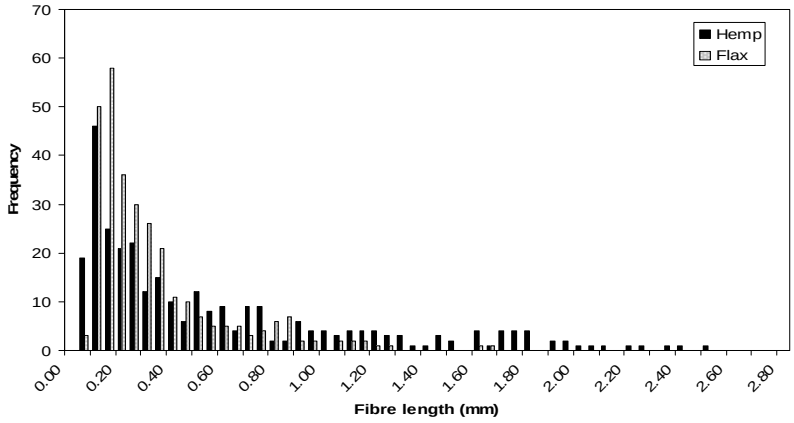


Fig. 3 Comparison of fiber length distributions of fully processed hemp and flax fibers.

Table 3 Mean lengths, widths, standard deviations and aspect ratios of unprocessed and fully processed hemp and flax fibers extracted from composites with fiber content of 40 wt% and plasticizer content of 32.5 wt%.

	Unprocessed			Fully processed		
Fiber	Fiber length (mm)	Fiber width (mm)	Aspect ratio	Fiber length (mm)	Fiber width (mm)	Aspect Ratio
Hemp	12.62 ± 4.30	0.458 ± 0.143	28	0.544 ± 0.560	0.013 ± 0.008	42
Flax	11.74 ± 2.70	0.403 ± 0.128	29	0.293 ± 0.256	0.019 ± 0.007	15

replaced by the (assumed) stronger interfaces between single fiber and the matrix. Table 3 shows the mean lengths and widths of unprocessed and fully processed flax and hemp fibers. Differences between the appearances of the fibers before and after processing can be observed in the images of the fibers in Fig. 4. As it can be noticed, the fiber length reduction of hemp fibers during processing is not as extensive as with flax fibers. In addition, the hemp fibers tend to fibrillate more easily, and therefore the fiber width reduces more compared to flax fibers. Distinct behavior of the two fiber types during processing affects the aspect ratios of the fibers, which are calculated in Table 3. For the hemp fibers, the fiber aspect ratio is increased from 28 to 42 during processing which will lead to better stress transfer from matrix to fiber according to the shear lag model [16]. Therefore, in this case, the reinforcement efficiency of the fibers is actually improved by the processing. For the flax fibers, the fiber aspect ratio is decreased from 29 to 15, subsequently reducing the reinforcement efficiency of the fibers. The influences of the fiber aspect ratios (in addition to effects of plasticizer, fiber content and fiber orientation) on the mechanical properties of the composites are analyzed in the forthcoming publication [15].

3.2 Fiber Dispersion and Orientation

The degree of fiber dispersion and orientation was investigated by optical microscopy of polished cross-sections of composites with 20 wt% flax fibers and 20 wt% plasticizer. Two representative images of cross-sections along and perpendicular to the melt flow direction are shown in Fig. 5. Both images show that the fibers are well dispersed in the matrix with no large

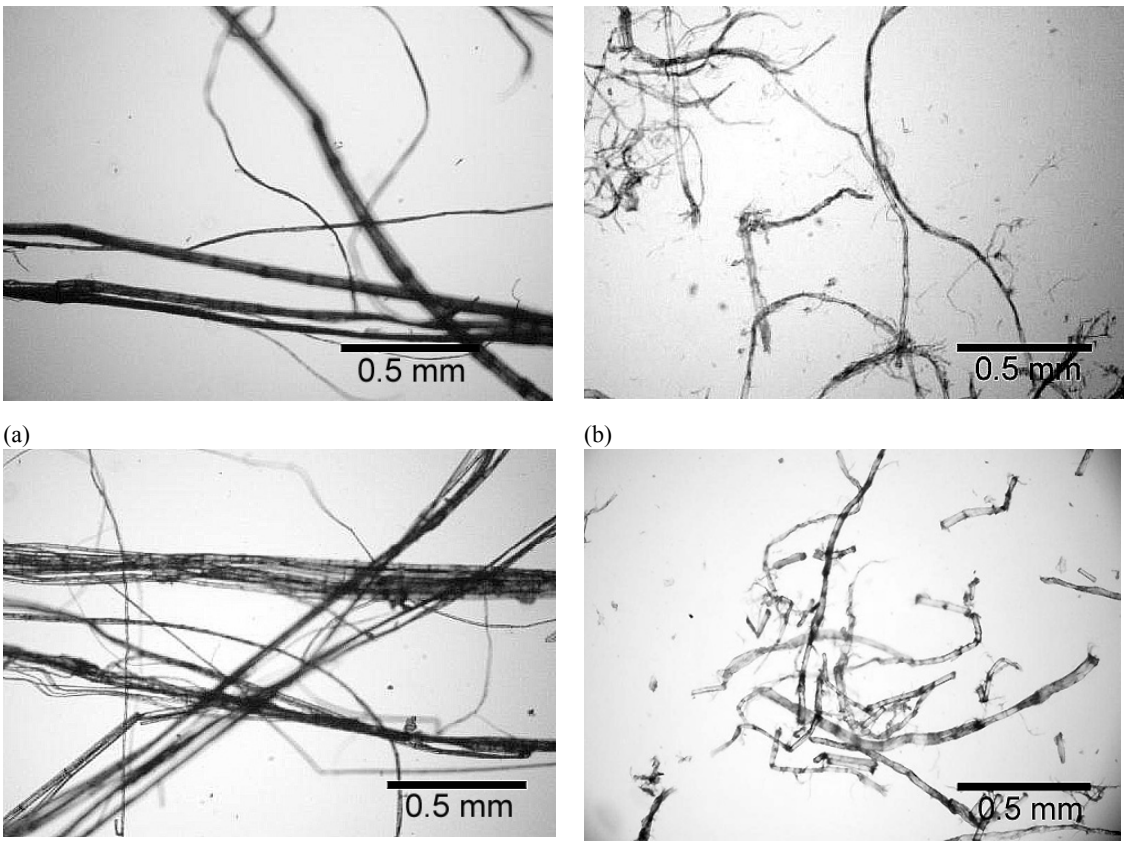
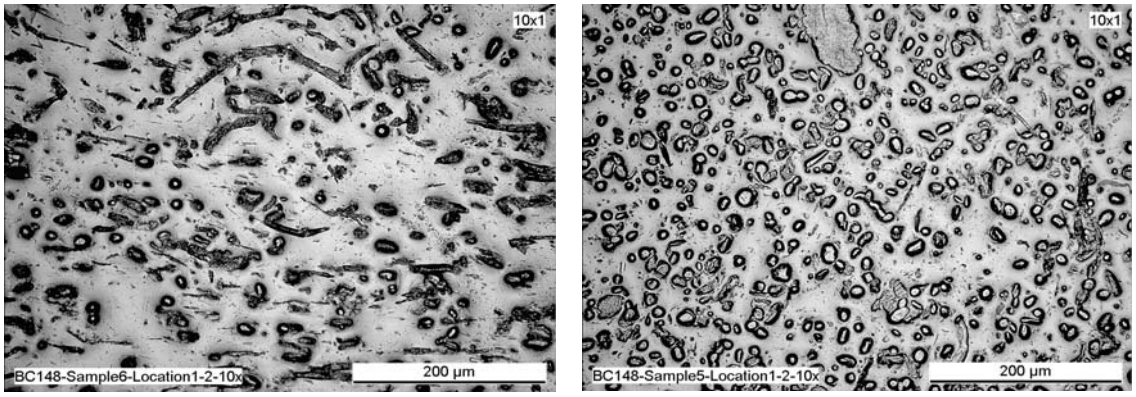


Fig. 4 Optical microscopy images of hemp and flax fibers: (a) unprocessed; (b) and fully processed hemp fibers; (c) unprocessed; and (d) fully processed flax fibers.



(a) (b)

Fig. 5 Optical microscopy images of cross-section of composite sample (a) along and (b) perpendicular to the flow direction.

fiber agglomerates which would tend to restrict matrix impregnation and increase the porosity content. The observed good fiber dispersion is supported by measurements of low porosity in the composites [11]. The two images in the figure show very clearly that the fibers are predominantly oriented in the melt flow direction of the composite samples since the cross-sections of the fibers are in general more elongated in Fig. 5a than in Fig. 5b.

Images of composite cross-sections with different angles (0, 30, 60 and 90°) to the flow directions were analyzed. An angle of 0° corresponds to a cross-section perpendicular to the flow direction (Fig. 5b). Elliptical outlines were fit to the fiber cross-sections by image analysis, and the aspect ratios (minor diameter/major diameter) of the ellipses were recorded. An aspect ratio of 1.0 designates at circular fiber cross-section, where larger aspect ratios designate more elongate fiber cross-sections, and as such the fiber aspect ratios can be used to quantify the fiber orientation. Fig. 6 shows the cumulative frequency distributions of fiber aspect ratios measured from images of composite cross-sections cut at different angles to the flow direction. All cross-sections are from the same type of composite (20 wt% flax fibers, 20 wt% plasticizer). As expected, the curves in Fig. 6 are shifted downward as a function of angle, which supports the above qualitatively assessed finding of Fig. 5 that the fibers are predominantly oriented in the flow direction. In Fig. 7, the median aspect ratio (at a cumulative frequency of 0.50) of the fibers is plotted as a function of the angle, and this gives a linear relationship with a positive slope. The same preferred fiber orientation has also been shown previously in a study of injection molded glass fiber/polyamide composites where the fiber orientation factor was estimated to be about 0.80 [18]. In the same study, the fiber content was found to have no influence on the fiber orientation. For the natural fiber/starch acetate composites investigated in the present study, future work will be addressed to obtain data for composites with variable fiber and plasticizer content in order to be able to quantify how this will effect the fiber orientation.

4. Conclusions

The effect of processing-pelletising, compounding and injection molding-on the reduction of fiber dimensions in composites of triethyl citrate plasticized starch acetate with hemp and flax fibers was determined by optical microscopy. A correlation between the fiber length and the plasticizer and fiber content of the composite was found. The shear force level in the compounding and injection processes is proportional to the composite melt viscosity, which again is a result of the fiber and plasticizer content. A reduction of fiber lengths of both hemp and flax along the increasing fiber content and the decreasing plasticizer content was observed. The comparison of the lengths of fully processed hemp and flax fibers revealed that the hemp fibers remained longer than flax

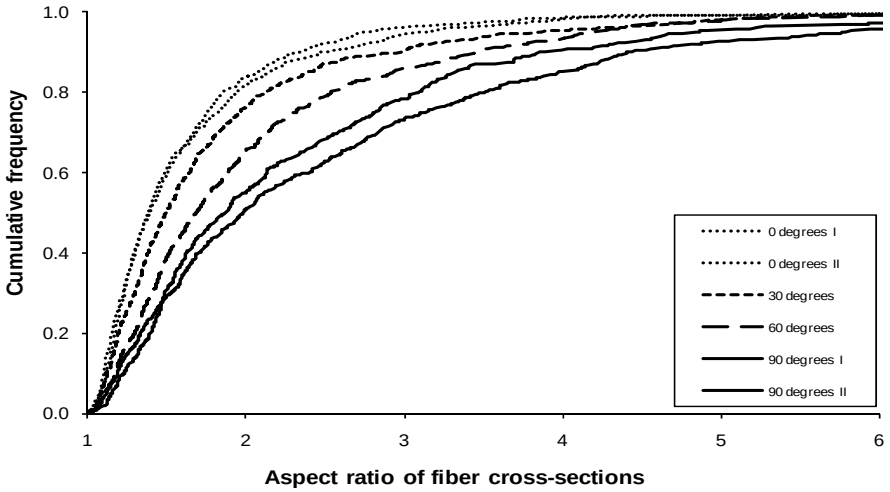


Fig. 6 Cumulative frequency distributions of fiber aspect ratios.

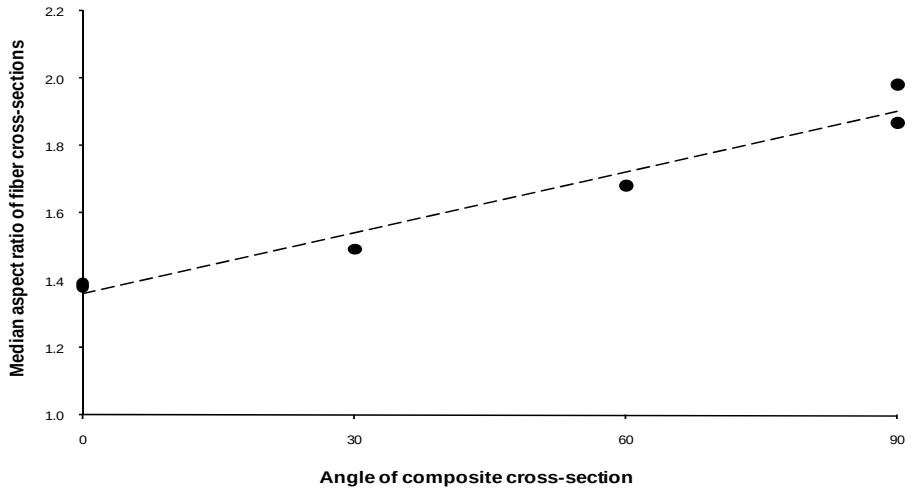


Fig. 7 Median aspect ratio of fiber cross-sections as a function of angle of composite cross-section.

fibers. Moreover, higher level of fibrillation occurred with hemp fibers, producing lower fiber widths than those of the flax fibers. Therefore, in case of hemp fibers, the fiber aspect ratio increased from 28 to 42 by the processing, whereas the fiber aspect ratio of flax fibers was reduced from 29 to 15. This indicates that the reinforcement efficiency of hemp fibers was improved by the processing, on the contrary to the reduced reinforcement efficiency of flax fibers. In a composite containing 20 wt% flax and 20 wt% triethyl citrate, good dispersion of fibers was detected by image analysis of the composite cross-sections. It was found that the fibers were predominantly orientated in the melt flow direction of the composite samples.

Acknowledgments

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