Anisotropy of paper and paper based composites and the modelling thereof

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Abstract
Anisotropic laboratory and industrially manufactured papers were use to reinforce an epoxy resin. The degrees of anisotropy of the papers as well as of the composites were evaluated by tensile properties. It was shown that the anisotropy of the Zero Span Tensile Index of the papers is close to that of the later composites, while the long span tensile properties of the papers are strongly affected by frozen in tensions that do not contribute to the composite properties. The Zero Span Tensile Index can be used to predict the composite strength of oriented paper reinforced composites.

1. Introduction

Compared to synthetic fibres like glass or carbon fibres, natural fibres posses a couple of advantages: they are low cost, available in large quantities, renewable, biodegradable and they have a low density. Therefore, a lot of research has been done about using natural fibres in composite materials. Natural fibres from annual plants like flax or hemp are extensively studied, mostly in combination with thermoplastic matrixes, but also with thermoset matrixes. In contrast to these annual plant fibres, wood fibres are available in abundance (compared to composite production): about 177 million tons of different pulp grades are produced annually, worldwide [1]. The by far largest share is consumed by the paper industry. Paper as reinforcement material was studied in early and mid 1940s as a potential material in aviation [2], [3], in the 70s and 80s [4–7] and increasingly since the year 2000 [8–21] as a material to potentially replace other composites. The investigations can be divided into two levels, the fibre level and the paper network level.

On the network level, fibre orientation, basis weight and wet pressing were investigated. Higher basis weight causes slightly higher strength and stiffness values [13]. Wet pressing densifies the paper and leads to an increased fibre volume fraction, strength and stiffness values [20]. Strength and stiffness values are higher in the direction of the fibre orientation [9], [11–13] and may be increased by higher orientation. Of course, these properties are reduced perpendicular to the direction of fibre orientation. However, none of the mentioned authors tried to relate the composite anisotropy caused by the anisotropic paper directly to paper properties.

The Kelly-Tyson equation (Eq. 1) gives the relationship:

$$\sigma_c = \eta_\theta\, \eta_l\, \sigma_f\, V_f + \sigma_m\,(1\text{-}V_f) \tag{1}$$

with composite tensile strength σ_c, orientation efficiency η_θ, fibre efficiency η_l, single fibre strength σ_f, fibre volume fraction V_f and the resin tensile strength σ_m. The fibre strength is usually calculated by the zero span tensile index (ZSTI) [22]:

$$\sigma_f = \rho_f * 1/\,\eta_\theta * ZSTI \tag{2}$$

The orientation factor η_θ is usually set to 3/8 for isotropic fibre mats or to 1 for unidirectional fibre reinforcements. In case of isotropic laboratory paper the factor 3/8 is used for the calculation of the fibre strength from the ZSTI value as well [22]. In conclusion equation (1) and (2) can be combined to [23] predict the composite tensile strength:

$$\sigma_c = ZSTI * c_f + (1\text{-}V_f)(\varepsilon_c/\varepsilon_m) * \sigma_m \tag{3}$$

with $(\varepsilon_c/\varepsilon_m)$ as correction for the contribution of the matrix, because the composite strain at break ε_c is much lower than the matrix strain at break ε_m.

In the industrial papermaking process, fibres are oriented in machine direction (MD) due to hydrodynamic forces. Fibre orientation leads to different mechanical properties in machine direction and in cross direction (CD). This anisotropy is also affected be the draws and shrinkage of the paper during drying. The shrinkage during drying can be as high as 10%. It is directly linked to the tensile strength, elastic modulus and the elongation at break of the paper. By different means in the paper machine the shrinkage in CD can be restrained in order to achieve a higher tensile strength and elastic modulus and a lower elongation at break. The change in these mechanical properties is caused by frozen in tensions and not by a re-orientation of the fibres, but fibres oriented in MD might have a higher elastic modulus due to the draws. For single fibres it is known, that their tensile strength and elastic modulus can increase if they are dried under tension [24]. It is not known whether these frozen in tensions or changed fibre properties affect the later composite properties.

There are different methods to characterize the anisotropy of paper. The most common ones are the ratio of the tensile indices or elastic moduli between machine and cross direction of the paper. Of course these measurements include the frozen in tensions, geometrical fibre orientation and possibly changed fibre properties.

The Zero Span Tensile Index is not usually used in industry to characterize the anisotropy of paper, although it is dependent on the geometric fibre orientation [25]. Furthermore it can be used to predict the composite strength of isotropic paper reinforced thermoset as recently shown by the authors.

The aim of this investigation is to find out whether one of the above methods to characterize the anisotropy of paper can be used as an estimation of the anisotropy of paper based composites. Therefore oriented papers are used to reinforce an epoxy resin. The oriented paper samples include industrial manufactured paper that should posses frozen in tensions because of the draws in machine direction and shrinkage in cross direction and oriented laboratory papers that were dried without draws. Furthermore it should become obvious whether frozen in tension do contribute to the composite mechanical properties.

2. Materials and Methods

2.1 Used Papers

Two industrial manufactured papers were used: a tea bag paper and a highly oriented specialty paper. The basis weight of the teabag paper was 12.67 gm^{-2} the basis weight of the speciality paper was 60.36 gm^{-2}. The papers are described more detailed in [26].

The oriented laboratory papers were produced on the formette dynamique at the PTS in Munich. For these papers an unbleached eucalyptus pulp was used. The pulp was used as it is (Schopper Riegler value 22) and beaten to a Schopper Riegler value of 43. For the sheetforming different drumspeeds of 400 rpm and 700 rpm were use to vary the degree of anisotropy. With a higher drumspeed the degree of orientation was increased. The basis weight of the papers used for the composites was 160 gm^{-2} while 80 gm^{-2} papers were used for the Zero Span measurements. The specimen are labelled as a combination of two numbers (22-400, 22-700, 43-400, 43-700) with the first number indicating the Schopper Riegler value and the second number indicating the drum speed.

2.2 Paper and Fibre Measurement

The paper Tensile Stiffness Index (TSI) was measured with an L & W Ultrasonic tester in both MD and CD. The long span tensile test was done for the industrial papers according to DIN EN ISO 1924-2:09.

The zero span tensile index (ZSTI) was measured with a Pullmac device according to Tappi standard T 231 cm-96 for the industrial papers. Because of the limited scale of the Pullmac tester, the high strength laboratory papers could not be measured with this device. Instead a Zwick testing machine with Zero Span Clamps was used. The agreement between the measurements of the Pullmac and the Zwick testing equipment is very good (in the range of the standard deviation of single tests).

2.3 Composite Manufacturing

An epoxy resin (EP, Larit L-285, Lange + Ritter GmbH) as a cold curing system was used in this study. The manufacturing process is subdivided by several processing steps. The specimens were manufactured by a hand lay-up process. This process is rather simple and commonly used for prototypes, batch production or large parts. At first, the number of papers had to be determined. The paper stack had to reach a total thickness of approx. 1.8 mm. This thickness was chosen to ensure a thickness of approx. 2 mm in the later specimens. After this, the EP resin was mixed with the hardener (Larit 287 – blau, Lange + Ritter GmbH). Once both components were added in one jar, they were mixed by a wooden spatula. The mixture was carefully stirred to avoid air bubbles. Then, every single paper sheet was impregnated with the EP resin. After impregnating a single paper sheet, a new paper sheet was laid onto the impregnated paper and pressed onto it with a roller. This is done to guarantee contact between the two layers and especially the resin. In the next step the impregnated stack of papers was inserted into a plastic film which was sealed by tacky tape. To prevent over-

pressing, metal plates were put around the laminated papers. After the positioning of the laminated papers, the press was closed and the actual pressing process started. The plates were heated to 50°C and the pressing force was set to 50 kN. The composites were pressed for five hours.
The next step was the tempering. Therefore the plastic film was removed from the laminated papers. The paper plates were then put into a climate chamber for ten hours at 60 °C and 50 % relative humidity.

Rectangle shaped flat specimens were cut out of the laminated paper plates using a diamond belt saw. To prevent overheating of the specimens the blade was cooled by water. The amount of water was minimized because the contact with natural fibres may cause some processing issues. Also the specimens were dried instantly for at least five hours. Before the specimens were tested the sides and edges were polished.

2.4 Composite Testing

The composite testing was conducted according to DIN EN ISO 527-4 “Test conditions for isotropic and orthotropic fibre-reinforced plastic composites”. All specimens were plain and provide no force transmission elements. The material was characterized by its Young’s modulus, tensile strength and tensile strain at break.

3. Results and Discussion

3.1 Paper Properties

In table 1 the TSI, the tensile strength and the ZSTI of the paper are shown in MD and CD for the papers used in this study. In all cases the strength and stiffness values are larger in MD than in CD, an expected result. The ratio of anisotropy of the industrial paper is larger than that of the laboratory papers for the classical measurements used to characterize the anisotropy (TSI, tensile strength). In contrast to that the anisotropy ratios of the ZSTI are in the same range for both sets of paper. Higher anisotropy ratios for the TSI and breaking length are most likely caused by the draw in MD and the shrinkage in CD in the industrial paper machine.

	TSI			**Breaking Length**			**ZSTI**		
	MD	**CD**	**Ratio**	**MD**	**CD**	**Ratio**	**MD**	**CD**	**Ratio**
	kNm/g	**kNm/g**	**MD/CD**	**m**	**m**	**MD/CD**	**kNm/kg**	**kNm/kg**	**MD/CD**
Speciality	11.9	4.9	2.43	7762	3264	2.38	150.2	109.4	1.37
Teebag	12.11	2.45	4.94	8283	2320	3.57	162.8	76.3	2.13
22-400	8.67	4.33	2.00				152.4	100.6	1.52
22-700	11.59	5.32	2.18				196.3	92.9	2.11
43-400	12.75	8.18	1.56				203.2	134.7	1.51
43-700	14.811	7.21	2.05				225.3	90.0	2.50

Table 1. Paper properties

3.2 Composite Properties

The tensile strength of the composite is shown in MD and CD in figure 1. For all papers the strength in MD is higher than in CD. The MD/CD ratio ranges from 1.27 to 1.49. A higher circumferential speed of the formette dynamique leads to a higher anisotropy. A share of the tensile strength, both in MD and in CD is caused by the resin according to equation (3). For the comparison of the anisotropy ratios of paper with that of the composites, it is necessary to subtract the isotropic part of the matrix from the anisotropic part of the reinforcement, both for the strength and elastic modulus values.

The contribution of the matrix to the composite strength was calculated as described in [23] and equation (3). The contribution of the fibres was calculated by the difference between the composite strength/elastic modulus and the corresponding matrix contribution. The contribution of the matrix to the elastic modulus was the matrix elastic modulus weighted by the volume fraction of the matrix. The values of the composite strength, elastic modulus the share of fibre and matrix to both properties and the MD/CD ratios are shown in table 2.

The anisotropy ratios of the composite strength and the composite elastic modulus are very close together. This could be evidence that the composite strength and elastic modulus are affected in the same way by the fibre orientation.

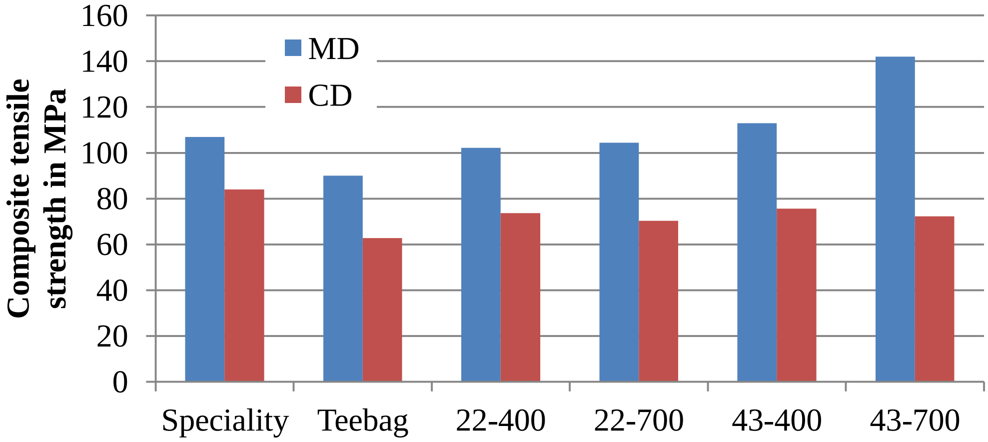

Figure 1. Tensile strength of the composites

	Tensile strength, matrix contribution		Tensile strength, fibre contribution			Elastic Modulus		Matrix contribution		Fibre contribution		
	MD	CD	MD	CD	Ratio	MD	CD	MD	CD	MD	CD	Ratio
	MPa	MPa	MPa	MPa	MD/CD	MPa	MPa	MPa	MPa	MPa	MPa	MD/CD
Specialty	16.6	23.4	90.3	60.6	1.49	9355	6694	753	755	8602	5939	1.45
Tee bag	20.4	23.3	69.6	39.4	1.77	7281	4465	972	973	6309	3492	1.81
22-400	23.8	13.3	78.3	60.3	1.30	7799	6271	811	657	6988	5614	1.24
22-700	16.5	18.9	87.9	51.5	1.71	9144	5396	793	793	8351	4603	1.81
43-400	14.1	12.5	98.9	63.1	1.57	10106	7209	696	696	9410	6513	1.44
43-700	15.1	20.2	126.9	52.1	2.44	12695	5828	704	691	11991	5137	2.33

Table 2. Composite properties

Figure 2 sets the degree of anisotropy of the paper properties in relationship to the degree of anisotropy of the composite. There is a good correlation between the composite anisotropy and the ZSTI anisotropy. The TSI anisotropy is very close to the ZSTI anisotropy for the oriented laboratory sheets, while for the industrially manufactured papers the TSI anisotropy is much larger than the ZSTI anisotropy. This indicates that anisotropy in the paper caused by draws and shrinkage in the paper machine does not affect the anisotropy of the composite.

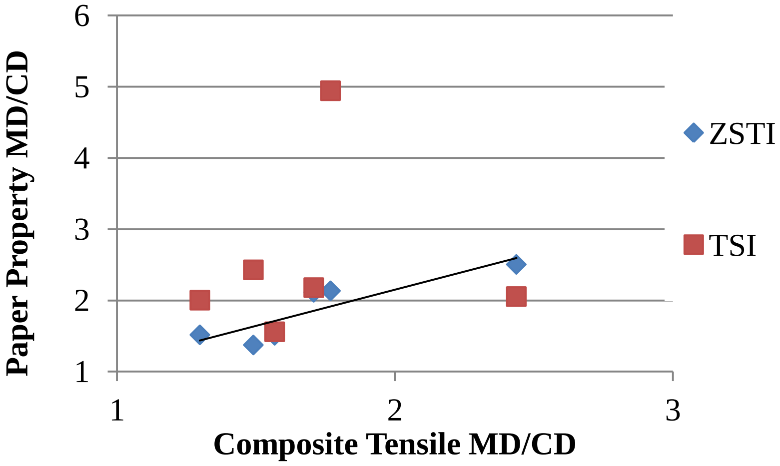

Figure 2. Comparison of anisotropy ratios

The recently proposed equation (3) for the prediction of the tensile strength of paper based composites is able to estimate the composite performance for oriented papers, regardless whether they are manufactured industrially or in the lab. In addition to the values from this study, the composite strength values for isotropic Rapid Köthen sheets from [23] are plotted in the graph as well. The values predicted by the strength model for the tea bag reinforcement are to low compared to the measured composite strength. A reason might be that the ZSTI values for the tea bag paper are too low. Usually abaca fibres that are used to produce tea bag papers are very strong. A possible explanation might be that in tea bag paper a considerable proportion of the fibres is damaged by the clamps during Zero Span testing, because the basis weight is only about 12.67 g/m².

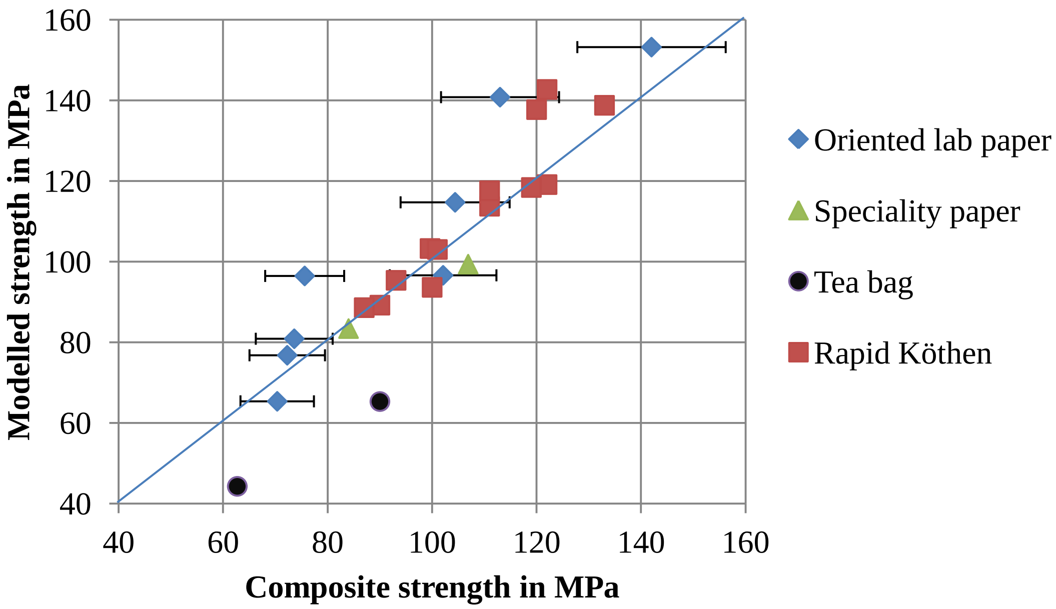

Figure 3. Use of the strength model for oriented papers

4. Conclusion

Both industrial and laboratory manufactured anisotropic papers were used to reinforce an epoxy resin. As expected the composite mechanical properties were better in direction of the main fibre orientation. The degree of anisotropy of the tensile strength and the elastic modulus in the composite is close to that of the Zero Span anisotropy in the paper. The ultrasonic TSI and the long span tensile anisotropy of the paper can be used to estimate the composite anisotropy only if there are no frozen in tensions from paper manufacturing caused by draws or shrinkage in the paper machine. Most important, the Zero Span Tensile Index can be used to predict not only the degree of anisotropy in such composites but actual strength values.

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