Composites: Part A 84 (2016) 377–385

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Advantages of regenerated cellulose fibres as compared to flax fibres in the processability and mechanical performance of thermoset composites ☆

H. Santamala [a,*], R. Livingston [a], H. Sixta [b], M. Hummel [b], M. Skrifvars [c], O. Saarela [a]

[a] Aalto University, School of Engineering, Department of Applied Mechanics, P.O.B 14300, FI-00076 Aalto, Finland
[b] Aalto University, School of Chemistry, Department of Forest Products Technology, P.O.B 16300, FI-00076 Aalto, Finland
[c] University of Borås, School of Engineering, Allegatan 1, 50190 Borås, Sweden

ARTICLE INFO

Article history:
Available online 22 February 2016

Keywords:
A. Biocomposite
A. Cellulose
B. Interface/interphase
D. Electron microscopy

ABSTRACT

Man-made cellulosic fibres (MMCFs) have attracted widespread interest as the next generation of fibre reinforced composite. However, most studies focused entirely on their performance on single fibre level and little attention has been paid to their behaviour on a larger application scale. In this study, MMCFs were utilized as reinforcement in unidirectionally (UD) manufactured thermoset composites and compared to several commercial UD flax fibre products. Specimens were prepared using a vacuum bag based resin infusion technique and the respective laminates characterized in terms of void fraction and mechanical properties. MMCF laminates had comparable or better mechanical performance when compared to flax fibre laminates. Failure mechanisms of MMCF laminates were noted to differ from those of flax-reinforced laminates. The results demonstrate the potential of MMCFs as a viable alternative to glass fibre for reinforcement on a larger scale of UD laminates. These results were utilized in the Biofore biomaterial demonstration vehicle.

1. Introduction

Natural fibres provide a viable alternative to glass fibres as reinforcement in polymer composite structures although a comparably high variation in properties, pronounced humidity absorption and laborious procedures to turn them into continuous structures have limited their widespread usage in mechanically stressed applications [1].

The properties of single flax and other natural fibres have been widely studied [2–7]. For structural applications, high mechanical properties on a single fibre level are needed. But in order to obtain high quality reinforcement the raw material often has to be processed to a continuous fibre product from which a composite structure can be manufactured. The fibre product should have suitable processing characteristics for the manufacture of the composite material, and it should provide high mechanical performance for the structure. To enhance the interface between fibre and matrix, the fibre's properties can be modified either chemically or mechanically. Most common pre-treatments remove residual particles, strengthen mechanical bonding by affecting fibre surface coarseness and improve fibre matrix adhesion and moisture resistance of the interface with chemicals applied onto the fibre surface. Considerable research effort has been devoted to this [8–12]. Van de Weyenberg et al. [9] studied effects of different retting processes, combined alkali and diluted epoxy treatment on mechanical properties of UD flax fibre epoxy composites. They demonstrated a notable increase, 40% of the longitudinal bending strength and stiffness by 60% as well as 200% and 500% for the respective transverse properties. Later the same group reported an improvement of UD flax fibre composite transverse strength by 30% after a treatment with 4 wt.% NaOH [10]. In addition to NaOH treatment, other chemical methods such as bleaching [12,13], UV radiation combined with $KMnO_4$ oxidation [14] and styrene treatment [15] have been introduced to increase the mechanical properties of natural fibres.

In order to produce continuous fibre products out of short fibres, such as flax, discontinuous fibres can be processed to yarns by twisting the fibres around each other. Twisting fibres orients them out of the longitudinal axis of the yarn and results in a reduction of mechanical properties when compared to single fibres. A high twist in yarns also contributes to reduced processing properties of the laminate, challenging yarn impregnation and lower

☆ This paper was submitted for the special issue Biocomposites.

* Corresponding author. Tel.: +358 40 334 1516.
E-mail address: harri.santamala@aalto.fi (H. Santamala).

http://dx.doi.org/10.1016/j.compositesa.2016.02.011
1359-835X/

compaction of the reinforcement [16]. Shah et al. [17] researched fibre compaction, fibre volume fraction and void volume fraction in composites by comparing laminates with differently twisted fibres. Fibre-yarn twist had an impact on the fibre volume and void content through fibre compaction. Due to problems related to twisted yarns, reinforcement products without twist have been studied extensively. One such method is spinning a thin string around the fibre yarn in a helix pattern. Better alignment of the fibre and unconstrained yarn packing should, in principle, increase the fibre yarn longitudinal modulus and strength as well as the compaction and wettability of the laminate. Another method to eliminate fibre yarn spinning is to tie fibres together with a chemical binder. In principle, the binder should eradicate the need for the fibre twist and optimally improve adhesion between the fibre and matrix without disturbing the processability of laminates. However, binder materials have still room for improvement, and new solutions are under research [18].

Man-made regenerated cellulose fibres potentially offer benefits of both natural and fossil based fibres. Their biggest advantage is their uniformity though the 1st generation of regenerated cellulose fibres, the viscose fibres, suffered from low mechanical strength making them unviable for reinforcement. The 2nd generation fibres, such as Lyocell (but also viscose tire cord), were able to overcome these deficiencies and are now utilized as reinforcement. Lyocell type fibres are manufactured by dry jet-wet spinning of cellulose solutions in a direct solvent. So far, the only commercial direct cellulose solvent is N-methylmorpholine N-oxide. In various studies, the mechanical properties of Lyocell fibres have been compared to viscose-type and other regenerated cellulose fibres [19–21]. The results have indicated that Lyocell-type cellulose fibres offer better mechanical performance than viscose and tensile properties comparable to flax fibres. Lyocell fibres have high failure strain, but generally their adhesion to matrix materials is inferior as compared to that of flax fibres. The latter can entail different failure mechanisms among the laminates.

Regenerated cellulose filaments show fewer defects and less variation than bast fibres such as flax. Different cellulose fibre processes have given elastic moduli between 9.4 and 41.71 GPa with the upper and lower limit being Bocell and viscose fibre, respectively [22,20]. Bocell is a fibre spun from an anisotropic solution of super-phosphoric acid. However, Bocell fibres have never been developed to a commercial stage. A commercial cellulose product claims to achieve 35 GPa elastic modulus with 675 MPa strength and 6% strain [23]. The highest mechanical properties of commercial Lyocell fibres (cellulose II) are significantly lower than those of a cellulose I which constitutes natural cellulose fibres. For cellulose I and II maximum elastic moduli of ca. 135 and 90 GPa, respectively, have been calculated from X-ray analysis [24]. Cellulose types and test methods naturally have an impact on the nanoscale test results. Elastic moduli differences of Lyocell fibrils and fibres are partly connected to a strain-hardening effect that is hypothesized to be caused by the orientation of the fibrils under loading. For example, Gindl and Keckes [19] measured a significant increase of 47% in elastic modulus of Lyocell fibres in tensile deformation. Later they also [25] analysed Lyocell all-cellulose and epoxy matrix composites and found similar properties, except for improved extensibility of all-cellulose composites compared to epoxy-Lyocell composites. Adusumalli et al. [26] investigated adhesion of Lyocell and ramie fibres with epoxy and polypropylene matrices. They reported that ramie exhibits improved adhesion characteristics due to its rougher surface.

In comparison to glass fibre, natural fibre composites have their differences in their composite manufacturing methods [1]. The relatively low temperature resistance of natural fibres, poor adhesion to matrix and wettability are sometimes regarded as major issues in processing. Common production methods today are injection moulding, extrusion, compression moulding, sheet moulding and resin transfer moulding (RTM) [27]. For thermosetting processes, vacuum assisted resin infusion presents a cost effective alternative to RTM for relatively low production volumes.

Several studies on the performance of UD flax fibres as reinforcement in thermoset composites are available [28,6] but to the best of our knowledge past studies lack a comparison of UD flax and Lyocell reinforced thermoset composites on an industrial application level. Comparative studies of cellulose fibres as composite reinforcement have mostly focused on their performance on single fibre composite level or utilizing them as short fibre reinforcement in thermoplastic composites [29,25,26]. For the development of new fibre materials single fibre composite level is important. Yet several studies on single fibre test level methods conclude that methods such as fibre pull-out, fragmentation and microbond tests show high scatter in results and their reproducibility is limited especially with cellulose fibres with high strains [30].

Thus, more attention should be devoted to how these fibres perform at the macroscale of composite industrial applications. In addition, the influence of flax fibre processing methods, pretreatments and fibre combinations on the overall potential for reinforcement on the laminate scale still lacks a thorough understanding. To fill these gaps, this study compares cellulose reinforced thermoset composites to three state-of-the-art flax fibre products and to literature values of typical E-glass composites. Different parameters of the flax fibre structures affecting processing, mechanical performance and failure mechanisms of respective laminates manufactured are compared. Unidirectional test laminates from Lyocell type cellulose and three flax fibre reinforcements were manufactured for further testing. The main parameters to evaluate the processing characteristics of the fibre products included wettability, fibre volume fraction and void content. Standard mechanical tests were performed to measure the mechanical performance of laminates made from the fibre products. This study concentrates essentially on the identification of failure mechanisms through scanning electron microscope (SEM) observations.

2. Materials and methods

Lyocell type UD fibres were kindly supplied by Porcher Industries (France) from their pilot production. The flax fibre products, which have been sourced from different commercial providers and origins, are available on the market in a unidirectional fabric form that offers the best potential for structural applications. Table 1 lists the fibre fabrics included in this study. They have an aerial weight ranging from 150 to 275 (g/m^2). Aerial weight values in the table are provided by the manufacturer with the exception of Flax2 which was measured by us. Flax1 yarns are formed by traditional low-twisting technology. The manufacturer claims that the fibres have been treated with a surface treatment to enhance their adhesion and decrease humidity absorption. Flax1 yarns are tied together by stitch-bonding using single transverse flax yarns spaced every 3 mm on average. Flax2 is formed using a binder to keep the UD fibres aligned. The binder is epoxy-matrix compatible. Flax3 fibres in yarns are held together with a small string that is spun helically around the fibre yarn. These Flax3 yarns are tied together by stitch-bonding a single transverse cotton string spaced every 8 mm, on average. Cellulose fibres are man-made and therefore endless filaments, having no surface treatment. Cellulose yarns are bound together by stitch-bonding a single transverse cellulose yarn every 2 mm, on average.

Gurits Prime 20 LV epoxy resin and slow hardener was used as matrix (Gurit, United Kingdom) [31]. This resin system is sold for vacuum resin infusion method, having several different hardeners