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Chemical modification of regenerated cellulose fibres by cellulose nano-crystals: Towards hierarchical structure for structural composites reinforcement

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ABSTRACT

A simple and innovative new route, with less negative impact on the environment, for depositing and hope-grafting cellulose nano-crystals onto the surface of regenerated cellulose fibres (Cordenka 700 Super 3), using γ-methacryloxypropyltrimethoxysilane as coupling agent, is presented. Hierarchical cellulosic structure involving micro-scale fibres and nano-scale cellulose crystal network was created as verified by the scanning electron microscopy. The fibres were initially oxidised by optimized concentration of cerium ammonium nitrate to generate radicals on the cellulose backbone in order to polymerize the coupling agent at the surface. Infrared spectroscopy and scanning electron microscopy confirmed the chemical polymerisation of MPS onto regenerated cellulose fibres without enabling to show the chemical bonding between silane and nano-crystals. However, tensile test which was performed to study the impact of different treatments on mechanical properties of regenerated cellulose fibres, revealed that the modification by silane decreased the stiffness and strength of fibres (22% and 10% decrease, respectively) while the strain at failure was increased. These changes were attributed to the treatment conditions which may have induced the disorder and the misalignment of the structure of cellulose fibres (e.g. axial orientation of molecular chains and crystalline phase of the fibre has been reduced). This assumption is supported by the results from successive loading-unloading test of the fibre bundle. However, after depositing cellulose nano-crystals onto the fibre's surface, the stiffness was recovered (20% increase in comparison to MPS treated fibres) while the strength and strain at failure remained at the same order of magnitude as for fibres treated only by the coupling agent.

1. Introduction

Due to high mechanical properties combined with chemical/environmental resistance and low weight, synthetic polymer composites reinforced with continuous synthetic fibres are widely used in structural applications such as aerospace and aeronautics, marine, oil/gas industries, energy, transportation, sporting equipment, construction. However, because of environmental concerns and public awareness of potential problems associated with growing consumption of oil and petroleum based materials (such as polymers, for example) there is rising demand for sustainable and eco-friendly materials. In latest years this demand massively boosted research on natural fibre composites and bio-based polymers. In particular plant fibres with high content of cellulose are of great interest due to their high stiffness and strength. Cellulose is the most abundant renewable resource polymer on Earth where the nature produces more than 7.5×10^{10} tons a year (Habibi, 2014). The remarkable physical and chemical properties allow this sustainable polymer to be used in various forms for different applications that cover huge domains ranging from products that do not require high mechanical properties (e.g. papers, cellophane films, etc) up to the applications that require load bearing capabilities, for instance structural polymer composites (e.g. precursor for carbon fibres, regenerated cellulose fibres).

It is well known that composites usually exhibit excellent in-plane properties (e.g. tensile stiffness and strength) which are controlled by fibres that may be assembled in various 2-D reinforcements (e.g. uni-directional fabric, weave, non-crimp fab-

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ric). However, through-thickness properties are relatively weak because they are governed by the properties of the resin and in large extend by the strength of fibre/matrix interface (Tong et al., 2002). In general, the reinforcing function of fibres is mostly governed by the fibre/matrix interaction (interfacial adhesion) that can be enhanced through chemical or physical modification of the polymer and/or the fibre. Natural fibres bear hydroxyl groups from cellulose as well as lignin and there are numerous papers published regarding the modification and the use of coupling agents to promote the adhesion between the fibre surface and the matrix. Such modifications use coupling agent depending on the physico-chemical nature of the matrix. Maleic anhydride graft PP homopolymers or copolymers have been widely used as coupling agent for thermoplastic composites (Angles et al., 1999; Bendahou et al., 2008; Caulfield et al., 1999). On the other hand, silicon alkoxides such as alkyl triethoxysilanes (Devi et al., 1997; Gassan and Bledzki, 1999; Pothan et al., 1997; Raj et al., 1990), pure organic coupling agents (Felix and Gatenholm, 1991; Hassan and Nada, 2003; Kaddami et al., 2006; Sbiai et al., 2008; Singh et al., 1998) or simple oxidation of the fibres (Dai et al., 2013; Moharana et al., 1990; Sbiai et al., 2011; Sbiai et al., 2010; Wei et al., 2016) have been frequently used to modify lignocellulosic fibres to improve the composites processing with thermoset matrices. Moreover, and even if these modifications usually decrease the own mechanical properties of the fibres, they upgrade the adhesion fibre/matrix and then enhance not only the mechanical properties of composites and reduce the water uptake.

Among other methods to increase adhesion between fibre and matrix the development of multi-scale hierarchical composite is rapidly growing. This approach joins nano-scale reinforcement with micro-scale fibres and has been tried out on various combinations of substrates (micro-scale fibres) with different nano-reinforcement (Qian et al., 2010). For instance, carbon nanotubes (CNT) have been deposited on various types of fibres (carbon fibres, quartz, alumina), the deposition can be achieved by growing CNT directly on fibres, by electrophoretic deposition or by incorporating CNT into sizing applied on fibres (Qian et al., 2010). In the recent work concerning CNTs grown on woven fabrics of quartz and alumina fibres (Li et al., 2015) it was demonstrated that addition of nano-phase on the surface of reinforcement resulted in an increase of the in-plane shear strength of epoxy based composite.

Similar approach of improving adhesion between natural fibres and polymer matrix can be employed in bio-based composites. However, the use of nano-reinforcement, such as CNT, is not possible with bio-based materials because it would diminish environmental friendliness of these materials. Therefore, in case of micro-sized cellulosic fibres one should also consider use of bio-based nano-reinforcement, such as cellulose nano-crystals for instance. Pure cellulose can be extracted from cellulosic materials and be highly valorized and transformed under an acid hydrolysis into rod-like crystalline particles: cellulose nanocrystals (CNC) (Habibi, 2014; Lin et al., 2012) with an elastic modulus between 120 and 150 GPa (Šturcová et al., 2005). Regarding the surface chemistry of CNC, where a large number of hydroxyl groups are present, they represent a unique substrate for significant surface modification to graft molecules with different functional groups by applying various chemical processes outspreading therefore their use in wide range of applications (Habibi et al., 2010; Peng et al., 2011; Zhou et al., 2011).

Earlier two routes of chemical modification of the surface of cellulose nano-crystals extracted from palm tree (Bendahou et al., 2014) have been developed. It was also demonstrated in previous work (Hajlane et al., 2013) that cellulose nano-crystals extracted from date palm tree can be successfully deposited onto micro-sized continuous regenerated cellulose fibres (RCF) in order to create hierarchical structure. It resulted in composite with improved fibre/matrix adhesion which delayed initiation of transverse cracks in material and increased the transverse properties of a unidirectional (UD) laminate. The approach to design composites with hierarchical structure to enhanced intralaminar and interlaminar performance is currently developed by number of researchers. Within the same framework of creating hierarchical structure, this paper describes another route to deposit cellulose nano-crystals onto RCF with less negative impact on the environment by using water as solvent in the chemical process and optimized concentrations of reagents. This makes it more suitable for industrial process. On the other hand, the introduction of “polymerizable” coupling agent will generate interface with new properties that will certain improve the mechanical properties by more pronounced delay of cracks initiation in the resulting structural composites.

2. Experimental

2.1. Materials

The micro-scale reinforcement used in this study was RCF Cordenka 700 Super 3 twisted Z100 (CORDENKA GmbH, Germany). Fibres were supplied in a form of bundles on bobbin, the summary of the materials characteristics are given in Table 1 (Wang et al., 1988).

Cellulose nano-crystals (CNC) were extracted from date palm tree in the laboratory according to the procedure described in previous work (Bendahou et al., 2009). These nano-crystals were deposited using Methacryloxypropyltri-methoxysilane (MPS) as a coupling agent (purity ≥ 98%). This later was purchased from Sigma Aldrich along with Sodium hydroxide, Nitric Acid and Ethanol. The initiator Cerium Amonium Nitrate (CAN) was purchased from Fluka. All these chemicals were used as-received without any further purification. The water was distilled in laboratory in order to be used as co-solvent with ethanol.

2.2. Chemical modification of fibres

2.2.1. Silane treatment

A 1600 ml mixture of ethanol and water (50/50 v%) was poured into a reactor and heated up to 65 °C. After stabilizing the temperature, NaOH and Nitric acid solutions were added in order to adjust the pH to 7. When the pH was stabilised (takes approximately 2 h), 16 g of fibres previously wound on a holder and fixed on mechanical stirrer were introduced in the reactor. The ratio of fibres to solvent was adjusted to be 1% (w/v). The graft polymerisation of MPS was carried out by adding first cerium ammonium nitrate (CAN) 10^{-3} mol L^{-1} in the reactor and stirred for 30 min. Meanwhile, the mixture was purged with Nitrogen gas for 15 min to remove any dissolved oxygen gas. At this stage, the free-radicals are supposed to be created at the surface of the cellulose backbone and ready to react with vinyl monomers (MPS). To initiate the graft polymerization, 10^{-3} mL L^{-1} of MPS was added to the reactor and the nitrogen gas flow was maintained until the end of the reaction (5 h); the mixture was stirred at medium constant rate. It’s worthy noticing that the pH and the concentrations of CAN and MPS used were chosen after optimization of the reaction conditions by varying the ceric ion concentration, reaction time, pH as well as MPS concentration. Fibres were then washed two times by ethanol and once by water to remove unreacted products and other impurities trapped in the grafted fibres.

2.2.2. NCC deposition

After polymerization of MPS onto the surface of cellulose fibres, different concentrations of cellulose nano-crystals were prepared in order to create hierarchical structure combining the micro-sized