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Preparation, structure and mechanical properties of all-hemp cellulose biocomposites

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ABSTRACT

All-hemp (*Cannabis Sativa* L.) cellulose composites were prepared by a mechanical blending technique followed by hot pressing and water–ethanol regeneration. The alkali treated fibres were ground and sieved to a size ranging from 45 μm to 500 μm. Introduction of fibres into 12% w/v cellulose *N*-methyl-morpholine-*N*-oxide (NMMO) solution was performed with low solution viscosity at 100 °C. The solid mixtures were cut and heat pressed between heated glass and PTFE plates at 85 °C to obtain a flat smooth-surfaced composite sheet of approximately 0.2 mm thickness. The cellulose was regenerated in a 50:50 water–ethanol mixture that subsequently removed NMMO and stabilizer (Irganox 1010, Ciba) from the composite. FTIR and X-ray diffraction measurements were performed to investigate the structural change of cellulose from fibre into partially regenerated composite. Composition and thermal stability of composites were investigated using thermogravimetry. A broadening of the scattering of the main crystalline plane (0 0 2) and a depression of the maximum degradation temperature of fibre were observed. The observations revealed a structural change in the fibres. The mechanical properties of composites depended on size, surface area, crystallinity and the structural swelling of fibres.

1. Introduction

There is increased interest in sustainable biocomposites obtained from renewable resources driven by the potential for reduction of petrochemical feedstock and by the hazards of traditional fibreglass composite waste management [1]. Widely-used semi-biocomposites, i.e. polypropylene (PP) or polyethylene (PE)-cellulose are not sufficiently eco-friendly because of their petroleum-based and non-biodegradable matrix. Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) and poly(hydroxyoctoate) (PHO) composites containing cellulose are examples of 'green' composites [2–8]. Nevertheless, modification of cellulose is still required to improve the interfacial adhesion in composites. Differing proportions of polymer and matrix caused variation of biodegradation times [2]. Usually good interfacial adhesion between fibre and matrix is the expected requirement for composites. This requires compatibility between both materials, so composites derived from fibre and matrix of similar chemical structure are of increasing interest. The main rationale is the anticipated better interfacial adhesion. Consequences of using the same component but with different physical properties for composite production such as all-PP, all-PE fibre–matrix composites has been reported [9–11], where interfacial adhesion was improved without surface modification requirement. This initiated the idea to prepare a composite (matrix and filler) comprised of materials from a sustainable resource without an interfacial problem and totally biodegradable.

Cellulose is the most abundant biomass resource. It has potential to be an alternative feedstock for composite manufacturing. Cellulose is not meltable however it can be dissolved in several solvents [12]. Instead of a melt mixing process, a composite containing all cellulose could be prepared by an addition of cellulose fibres into a cellulose solution or vice versa. An example of a composite that has all components derived from cellulose was prepared by the impregnation of 3% pulp cellulose in DMAc (LiCl) solution into a rami fibre [13], and the partial dissolution of microcrystalline cellulose powder in a similar solution [14]. The mechanical properties of this composite relied upon the similarity between the matrix and the fibre.

An alternative process to prepare a cellulose solution by using *N*-methyl-morpholine-*N*-oxide (NMMO) was claimed to be environmentally friendly and the most economic method for producing regenerated cellulose. The basic closed loop process with full recovery of solvent was an advantage of this process. Moreover the waste water produced from this process was less harmful

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and completely treated by the ozonisation and activated sludge method [15,16]. The main product of the NMMO process is Lyocell or Tencel fibre with outstanding properties [17]. Interestingly, the process can be adopted to manufacture regenerated cellulose in film form [18].

Generally the mechanical properties of cellulose or carbohydrate films could be improved by fibre reinforcement [19,20]. Hence it is possible to prepare a composite which has fibres embedded in cellulose matrix via the NMMO process. The raw materials used in this process are mainly from wood pulp. Cellulose fibres from crop plants such as hemp have advantages compared with wood pulp because of their short growing period. Within the same time-period, the crop-sourced fibre yielded ten-times the cellulose of wood over the land area. In addition, the strength of hemp fibres is suitable for reinforcement of cellulose films derived from the NMMO process.

In summary, all-cellulose composites may obtain several advantages from an environmental point of view. Firstly, hemp fibre is a sustainable reproducible crop fibre that has a suitable strength for composite applications. Secondly, solvent used in the NMMO process is almost totally recovered and waste from the process can be treated efficiently. Thirdly, the formation of composites with the same chemical structure can improve interfacial adhesion. Moreover the waste management of composites of the same material causes less problems and useful recyclability.

The aim of this research was to prepare composites with matrix and fibres derived from the same cellulose resource (hemp fibres) but different in crystalline structure (cellulose I and cellulose II). The hemp fibres were treated with 8% NaOH solution, then were ground and sieved to a uniform size to ensure that non-cellulosic components have been removed and fibres could be dispersed homogeneously in the composites. Composites containing 40% variation in fibre sizes were prepared. Subsequently, they were fabricated and regenerated to form films or composite sheets. Presence of the fibres in the film matrix was expected to enhance shape stability, modulus and strength. An investigation of the structure, composition and mechanical properties of the composite were performed by using wide-angle X-ray diffraction (WAXD), FTIR and DMA techniques, respectively. Thermal decomposition of composites was studied using thermogravimetry (TGA). Morphology of fibres and films were investigated using optical microscopy (OM), scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) gas adsorption techniques. The results obtained for composites and pure cellulose films have been compared. Furthermore, composite properties depending on the initial fibre physical properties (surface area, crystallinity) were explored and discussed. A mixture of Tencel fibre and cellulose powder (Ajax chemicals) were also prepared and used as a reference system for quantitative evaluation of the mixtures between cellulose I and cellulose II in composites.

2. Experimental

2.1. Materials

Hemp (*C. Sativa* L) was obtained from Australian Hemp Resource and Manufacture (AHRM) with an average fibre length of 10 cm. *N*-methyl-morpholine-*N*-oxide (NMMO) from Aldrich Chemical Company was used as received. Irganox 1010 (Ciba Specialty Chemicals) was used as the stabiliser. Standard grade, ashless cellulose powder was purchased from Ajax Chemicals (Sydney, Australia). Tencel fibre (Acordis Group) was obtained from school of Fashion and Textiles, RMIT University.

2.2. Pre-treatment

2.2.1. Acetone extraction and alkalisation

The fibres were subjected to Soxhlet extraction with acetone for 3 h to remove any waxes present and then air-dried. Dried fibres (2.5 g) were mixed with 8% w/v NaOH aqueous solution (100 mL) then placed in an oven at 30 °C for 1 h to remove lignin associated with the fibres. The alkaline treated fibres were subsequently washed with running tap water followed by distilled water until no alkali was present in the wash water.

2.2.2. Fibre grinding and sieving

The fibres were cut in an IKA MF10 cutting mill and sieved to provide a size range between 45 and 600 μm. Firstly all cut fibres were placed in a sieve of mesh number 36. A gentle shaking of sieve was conducted until no more fibre falling into sieve number 72. The same procedure was applied for smaller sieve opening size. Since the fibre was laid parallel to the surface of sieve. Fibres with length (L) (or diameter (D)) shorter than the sieve opening size passed through. The average fibre diameter and length measured from SEM images were used for the L/D ratio calculation.

Therefore the fibre retained on the sieve mesh number 36, 72, 140 and 325 would provide a minimum L/D ratio.

2.3. Dissolution of fibre using NMMO solution

The cellulose-NMMO solution containing 12% w/v cellulose and 0.6% w/v stabiliser was prepared using the ground 200 μm hemp fibres. A three neck 500 mL round bottom flask was equipped with a mechanical stirrer, a nitrogen purge gas inlet and a water-cooled condenser. NMMO powder (15.5 g), hemp fibres (2.1 g) and water (0.4 g) were transferred into this reactor separately then mixed gently without heating. An oil bath was used to heat the mixture to 140 °C. with stirrer speed of 200 rpm and a nitrogen purge used. The mixture became viscose at 135 °C. The stirring speed was then increased to 300 rpm and a vacuum was applied to remove any water from the reactor. The reactor temperature was maintained at 135–140 °C until the fibres dispersed in the viscous solution was completely dissolved. This could be observed from the presence of a residue of clear brown paste. The total time for the dissolution of fibres was 12–15 min. The heating bath was removed and the reactor was allowed to cool for 5 min.

2.4. Composites preparation

Fibres were then added to the viscous paste and mixed for 3 min to provide 40% w/w fibre in dissolved cellulose. In order to control the fibre content in the composite, an inclusion of calculated amount of fibres (0.8 g) into regenerated cellulose matrix was all conducted in a similar manner, i.e. 3 min mixing time and stirring speed of 300 rpm.

The composites were prepared by spreading NMMO–cellulose–water solution on a heated glass sheet at 85–90 °C, since the solutions were solid at ambient temperature, then covered with a PTFE sheet [21]. The melted solution was manually spread outward from centre to form a round flat sheet by an applied compression force from roller above the PTFE covered sheet. The thickness of composites was gradually reduced and was restricted by the diameter of the embedded fibre resulted in approximate 0.2 mm thickness sheet. An ever pressuring caused a separation of melt solution and a discontinuous sheet was obtained. Generally the thickness of unfilled composite was lower than the fibre-filled one.

The films were kept under compression to achieve a flat and smooth surface. After the composite films were cooled they were