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Influence of surface modified cellulose microfibrils on the improved mechanical properties of poly (lactic acid)

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ABSTRACT

Cellulose microfibrils (CMF) were extracted from sisal fiber and characterized. Biocomposites of PLA reinforced with CMF were fabricated employing melt blending technique followed by injection moulding. The biocomposites were subjected to various characterization studies to investigate the effect of CMF within the PLA matrix. Differential scanning calorimetry (DSC) measurements confirmed that the addition of CMF accelerates the crystallization process of PLA matrix. Addition of 5 wt.% of CMF with and without compatibilizers and plasticizers such as maleic anhydride, polyethylene glycol and acetyltributyl citrate in PLA improved the crystallization of PLA up to 100 °C. MA grafting gave moderate effects on both the stiffness and ductility, exhibiting optimum properties.

1. Introduction

In the recent years, much more attention has been paid to sustainable, green and environmental friendly materials for various applications [1,2]. Because of concerns about disposal of plastics, polymer scientists have been strongly encouraged for the development of new biodegradable polymer composite materials. However, research on biodegradable polymers as composite matrices are limited because of the relatively poor performance characteristics vis-a-vis the petroleum based feedstokes. Several attempts here been focused on the influence of natural fibers on the properties of petroleum based polymers like PE, PP, epoxy etc rather than using biopolymer like PLA as a matrix. Numerous advantages are associated with the use of natural fibers, including low cost, abundance, low density, high specific properties and lack of residues upon incineration. Thus, the combination of natural fiber with PLA offers an answer to maintain the sustainable development of economical and ecological technology [3]. PLA is linear aliphatic thermoplastic polyester, produced from renewable resources, which has gained much attention in both research and applications. This polymer is produced either by ring opening polymerization of lactide or by poly condensation of lactic acid monomers. The monomer is obtained from the fermentation of corn or other renewable agricultural raw material [4]. However, low thermal stability, low water vapor and gas barrier properties as well as embrittlement have limited its use in certain applications such as high temperature environment. In order to overcome these inherent shortcomings, reinforcing fillers are now incorporated to improve these properties while maintaining its biodegradability for niche applications [5].

Cellulose, the most abundant biopolymer on earth, is the main constituent of wood and non-wood. It is a renewable and biodegradable material, low cost, widely available, low-energy consumption and has good mechanical properties as compared to the other inorganic reinforcing fillers [6]. Another advantage of cellulose is its fibrous nature, which can align and orient it easily. It's low weight, tough and fibrous nature supports to improve the mechanical properties compared to clay based fillers. Cellulose is composed of crystalline and amorphous phase at nano meter range.

Cellulose microfibrils (CMF) can be prepared from a huge variety of plant-based resources, among which, wood raw material was the earliest to be used [7]. Other sources of biomass, such as flax, hemp, sisal [8], soybean hull, sugar beet pulp [9], bagasse [10] have also been investigated. Recently, other agricultural by-products, such as rice straw, rapeseed straw and corn stalks, have also received increasing attention as potentially renewable raw material source for production of CMF [11]. They have shorter growing cycles and lower lignin contents compared to main woody fibers source, and can be disintegrated into CMF with easier delignification processes [12,13]. Sisal, an abundant lignocellulosic material with high

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Table 1
Formulations of PLA and its biocomposites.

Sample	Abbreviation	Amount (%)				
		VPLA	PLA/CMF	PLA/CMF/MA	PLA/CMF/PEG	PLA/CMF/ATBC
Virgin poly (lactic acid)	VPLA	100	–	–	–	
Poly (lactic acid)	PLA	–	95	90	90	90
Cellulose microfibrils	CMF	–	5	5	5	5
Maleic anhydride	MA	–	–	5	–	–
Polyethylene glycol	PEG	–	–	–	5	–
Acetyl tributly citrate	ATBC	–	–	–	–	5

cellulose content, also has strong potential to act as a biomass source for the production of CMF. Among all chemical treatment methods sulphuric acid has been extensively studied as it is generally inexpensive, convenient and effective for a broad spectrum of lignocellulosic biomass. Sulfuric acid can effectively hydrolyze hemicellulose which is present in fibers into monomeric sugars (arabinose, galactose, glucose, mannose, xylose, etc.) and soluble oligomers, thus improving the cellulosic conversion [14,15].

The use of CMF as a novel green filler in polymer matrices using polypropylene, poly (ethylene terephthalate)-poly (trimethylene terephthalate) blends to develop environmental friendly composites have been reported [17]. The suitability of cellulose fibers for thermoplastics in general and biopolymers in particular were investigated because of ecological advantages, high mechanical properties in terms of Young's modulus and tensile strength, low density and dimensional stability [18–20]. Chuayjuljit et al. shows increase in tensile strength and Young's modulus when CMF used as reinforcement in poly (vinyl chloride) [16]. Mathew et al. reported the use of CMF as filler to fabricate PLA biocomposites using twin screw extrusion process. They reported lower mechanical properties of PLA biocomposite as compare to the pure PLA. However the dynamic mechanical thermal analysis (DMTA) showed that the storage modulus was increased with the addition of CMF [21].

The main goal of this work was to extract CMF from sisal fiber and to evaluate its reinforcing ability on morphological, thermal, and mechanical properties of the PLA and its biocomposites. A low concentration of CMF was preferred to modify the brittle nature of PLA biocomposite. Chemical grafting onto the cellulose microfibrils has been carried out to improve the compatibility between the CMF and the matrix. The functional group analysis was studied using Fourier transform infrared spectroscopy (FT-IR), morphological analysis from scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Both thermogravimetric analysis (TGA) and thermal analysis (TA) were carried out in order to investigate the thermal properties of the produced biocomposites. The visco-elastic properties of the biocomposites were also evaluated employing dynamic mechanical analysis.

2. Experimental

2.1. Materials

Poly-lactic acid (PLA 4042 D) with a density of 1.24 g/cc and average molecular wt. of 1,65,000 g/mol was purchased from M/s. Cargil Dow (Bair, US-NE) which consisted of 95% L-Lactide, 5% D-Lactide units. The MFI of PLA is 1.5- 5.0 g/10 min (190 °C, 2.16 kg). Sisal fibers (Agave sisalana) obtained from M/s Sheeba fibers and handicrafts, Poovancode, Tamilnadu, India, with density of 1.5 g/cc. Common chemicals such as sodium hydroxide, sulphuric acid, H_2O_2, acetone of AR grade were purchased from M/s Merck Specialities Pvt. Ltd., Mumbai, India. Other chemicals such as Polyethylene glycols (PEG, MW, 4000 g/mol), Acetyltributyl citrate (ATBC) (98%), Maleic anhydride (MA) were obtained from M/s Merck Specialities Pvt. Ltd., Mumbai, India.

2.2. Preparation of cellulose microfibrils (CMF)

Sisal fibers which are abbreviated as UTS are inherently bonded into bundles by lignin, pectin and other natural substances. The extraction of CMF from UTS has been carried in stepwise procedure in accordance with the process described by Zuluaga et al. [22]. The alkali treatment of UTS was to soak the crushed cellulose powder into 8 wt.% NaOH aqueous solution, the mixture was heated to 55 °C and kept for 2 h under mechanical stirring. The NaOH treated crushed cellulose fiber (MSF) was filtrated and washed with deionized water for several times to neutralize it and dried at 60 °C. Again the MSF was acid hydrolysed with 50 wt.% sulphuric acid for 3 h at 45 °C to get CMF followed by washing, filtration, neutralization of suspension and ultrasonication and drying at 60 °C to obtain 40 wt.% yield of CMF.

2.3. Fabrication of PLA/CMF biocomposite

PLA was melt blended with 5 wt.% CMF followed by injection moulding. Prior to compounding, CMF and PLA were pre dried at 60 °C and 80 °C in a vacuum for 12 hrs. The compounding was carried out at 180 °C with a rotor speed of 50 rpm for 4 min. The obtained melt mixes were used to prepare specimens using micro-compounder (DSM Xplore 15 ml, Netherland) at a pressure 7–8 bar and mould temperature of 35 °C for various characterizations. Similar parameters was followed in case of PLA grafted with 5 wt.% MA and loaded with 5 wt.% CMF biocomposite and plasticized biocomposites, PLA/5 wt.% CMF/5 wt.% PEG and PLA/5 wt.% CMF/5 wt.% ATBC respectively to observe their plasticizing effect. The dicumyl peroxide (DCP) was set to be very low (0.2%) to avoid the side reactions and the degradation of the PLA. The formulations of PLA and its biocomposites are depicted in Table 1.

3. Characterization

3.1. Wide angle X-ray diffraction analysis (WAXD)

The X-ray diffraction patterns of fibers and extracted microfibrils were obtained from radiation generated by copper target of Schimadzu X ray diffractometer 7000 L, Japan, (CuKα, radiation with $\lambda = 0.15406$ nm) at a scanning rate of 0.50°/min and scanning range of 5–40°. The percentage of crystallinity (%Cr) calculated by using the following formula [23].

$$\%\mathrm{Cr} = \frac{I_{22.5}}{I_{22.5} + I_{16}} \times 100 \quad (1)$$

where, $I_{22.5}$ and I_{16} are the crystalline and amorphous intensities at 2θ scale close to 22.5 and 16°, respectively.