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Cotton cellulose nanofiber-reinforced high density polyethylene composites prepared with two different pretreatment methods

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ABSTRACT

The reinforcing effect of cellulose nanofibers (CNF), individualized from cotton fibers subjected to a chemical process and a grinding process, has been investigated using high density polyethylene (HDPE) as matrix. In order to solve the agglomeration problem of cotton nanofiber in non-polar HDPE, two pretreatment methods have been used prior to the extrusion process, one method was relative to the physical pretreatment, and the other corresponded to the polyoxyethylene (PEO) dispersion agent method. The dispersion of cotton CNF in HDPE and reinforcing effect of cotton CNF on HDPE with the two preparation methods were made a comparison. From the SEM images observation, a good dispersion effect and an ideal network structure of the cotton CNF/HDPE composites could be achieved via two preparation methods. However, PEO dispersion agent method could improve the CNF dispersion much better than the physical pretreatment method, but unfortunately reducing the aspect ratio of the cotton CNF. Addition of cotton CNF clearly increased the bending strength (MOR) and bending modulus (MOE) of HDPE. The MOR and MOE of cotton CNF/HDPE composites with the physical pretreatment method were much higher than those of the nanocomposites with the PEO dispersion agent method. A comparative study was also made to find out the effect of two cellulose based nanofillers (CNF and nanocrystalline cellulose (NCC)) on the rheological, thermal, and mechanical properties of HDPE. The results demonstrated that cotton CNF had a better reinforcing effect on HDPE than NCC, while NCC could decrease the thermal expansion of the nanocomposites more significantly.

1. Introduction

Cellulose has gained considerable research interest due to its environmentally attractive origin and properties. Cotton is an important commercial crop playing a key role in economic, political and social affairs of the world (Bhatt, 1992; Kairon et al., 2004; Singh, 1997). It accounts for nearly 40% of global fiber production (Kaura et al., 2012). The cotton fiber is mainly comprised of cellulose (about 95%) (Zhao et al., 2013). Cellulose is a linear homopolysaccharide of β-1.4-linked anhydro-D-glucose units with a degree of polymerization (DP) of approximately 10,000 for cellulose chains in nature and 15,000 for native cellulose cotton (Azizi Samir et al., 2005). According to Habibi et al. (2010), about 36 individual cellulose molecules are brought together into larger units known as elementary fibrils, which are packed into larger units called microfibrils. The diameter of elementary fibrils is about 5 nm whereas the microfibrils has diameters ranging from 20 to 50 nm. The microfibrils have highly ordered regions (i.e., crystalline phases) alternating with disordered domains (i.e., amorphous phases) (Klemm et al., 2005). The crystalline regions of the microfibrils have a high Young's modulus of 138 GPa (Sakurada et al., 1962) and a very low thermal expansion coefficient (10^{-7} K^{-1} in the longitudinal direction) (Nishino et al., 2004). Nanocrystalline cellulose (NCC) is crystalline cellulose and is typically derived from the acid hydrolysis of the cellulose materials. NCC is rod-like nanoparticles presenting an average length of 100 nm to a few microns and a diameter of 5–15 nm depending on the cellulose source (Goffin et al., 2011). Unlike NCC, cellulose nanofibers (CNF) exhibit both amorphous and crystalline parts and present a higher aspect ratio with a web-like structure than NCC (Lu et al., 2008a,b). A number of methods have been studied to isolate cellulose nanofibers from cellulosic materials (Chen et al., 2011). These methods include grinding, cryocrushing, TEMPO-mediated oxidation, sulfuric acid hydrolysis, and enzyme-assisted hydrolysis. All

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these methods lead to different types of nanofibers, depending on the starting material and the disintegration process.

Using cellulose as reinforcing material in thermoplastic composites is a novel application of nature derived materials and it has numerous advantages for the environment, such as reducing CO_2 emissions into atmosphere during their cycle of production, processing and use. NCC reinforced plastics have mechanical advantages over conventional automotive plastics, being 30% lighter and 3–4 times stronger than the currently used materials (Ten et al., 2010). They are also less susceptible to be damaged from heat, chemicals, and spilled gasoline and are considered for use in car parts such as dashboards, bumpers, and side panels. However, the strength of polymer composites reinforced with cellulose nanofibers remains far below the theoretical properties. This is due to the limited compatibility between the hydrophilic cellulose nanofibers and the hydrophobic polymer matrixes. Poor dispersion of the nanofibers and the insufficient adhesion between the cellulose nanofibers and the matrix also induce unsatisfactory mechanical properties of the composites (Li et al., 2010). To overcome the compatibility difficulties, cellulose has been subjected to physical treatments (i.e., plasma), chemical modification (i.e., esterification, etherification, oxidation, silylation, and polymer grafting by click chemistry) and direct silanol-cellulose condensation with prior hydrolysis treatment (Tang et al., 2013). To solve the dispersion problem, the usage of an organic medium (such as, a surfactant) is the most common way. Wang and Sain (2007) apply solid phase melt-mixing followed by compression molding to produce CNF-reinforced composites. In their study, nanofiber is directly incorporated into PE and PP matrix using ethylene-acrylic oligomer emulsion as a dispersant. As a consequence, the mechanical properties of nanocomposites are not improved significantly.

Polyethylene is a widely used thermoplastic found in everyday life with high hydrophobicity. With easy availability, low cost, and good processability, polyethylene is a promising matrix material for nanocomposites. Moreover, it is worth noting that these lower-price plastics (PP, PE and PVC) constitute about 70% of the total amount of thermoplastics consumed by the plastics industry (Azizi Samir et al., 2005). So it has a great significance using cellulose nanofibers to reinforce the high density polyethylene (HDPE) matrix and the nanocomposites can be used in many value-added products instead of those traditional applications. But until now, most of the literature is focused on the NCC or MCC (microcrystal cellulose) reinforced thermal plastics (Ashori and Nourbakhsh, 2010; Elanthikkal et al., 2013; Mamun and Bledzki, 2013; Okubo et al., 2009; Pöllänen et al., 2013; Sabo et al., 2013; Samir et al., 2004), and there has been few research on the nanocomposites made of CNF/HDPE due to the feeding difficulty of the ultralong CNF.

In this paper, chemical and grinding treatments were combined to extract cellulose nanofibers from cotton fibers. Before the cotton CNF/HDPE composites were extruded, two methods were used to solve the cotton CNF dispersion problem, separately. One was called "the physical pretreatment method", which corresponded to preblending treatment of HDPE powder in a cotton CNF water suspension before extruding. After the preblending treatment, the mixture of HDPE powder and CNF was dehydrated and freeze dried, and then compounded and extruded by a HAKKE minilab. This process could avoid the usage of chemical dispersing agent, which was a time-saving and environmentally-friendly method. The other method was to use polyoxyethylene (PEO) as a dispersion agent, which was called "the dispersion agent method". PEO is a highly biocompatible, biodegradable, hydrophilic, and flexible polymer which has found many different applications, e.g., drug delivery, mucoadhesive, dispersant, surfactant, hydrogel, electrolyte solvent in lithium polymer cell, flocculation and rheology control agents (Brown and Laborie, 2007). After coated with the PEO dispersion agent, the cotton CNF were added into the HAKKE minilab with HDPE granules and then extruded. Maleic anhydride grafted polyethylene (MAPE) was used as coupling agent to improve the compatibility between the cotton CNF and the HDPE matrix. The effect of cotton CNF on the capillary rheological properties, mechanical properties, morphology, thermal expansion, and viscoelastic properties of HDPE with two different preparation methods was compared and investigated. In order to evaluate the dispersion effect of these two preparation methods, the freeze-dried cotton CNF were directly added into the HAKKE minilab with HDPE granules and then extruded as control. To investigate the possible contribution of the network-forming behavior of cotton CNF, the cotton NCC/HDPE nanocomposites were also prepared via the direct extrusion method.

2. Materials and Methods

2.1. Materials

Cotton fibers used as the raw material in this study is the absorbent cotton, medical grade, purchased from Beijing Tianheng Bohao Medical Equipment Co., Ltd. (Beijing, China). The H_2SO_4 hydrolyzed NCC was obtained from Daicel Chemical Industry (Japan). HDPE used as matrix has a melt flow index (MFI) of 3 g/10 min measured at 190 °C and 2.16 kg, density of 0.94 g/cm^3, melt point (T_m) of 135 °C, bought from Nanjing Jufeng Advanced Materials Co., Ltd. (Nanjing, China). Polyoxyethylene (PEO) used as the dispersion agent, with the molecular weight distribution of 2.5–3 million, viscosity of 830 mPa s, T_m of 70 °C, was purchased from Shanghai GongBiKe New Materials and Technology Co., Ltd. (Shanghai, China). Maleic anhydride grafted polyethylene (MAPE) used as coupling agent with a MFI of 6.4 g/10 min, grafting ratio of 0.8%, was purchased from Nanjing Deba Chemical Industry Company (Nanjing, China). All chemicals were purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China).

2.2. Preparation of cotton CNF/HDPE composites

2.2.1. Preparation of cotton CNF

Firstly, a certain amount of absorbent cotton was placed into a beaker. Lignin in the samples was removed using an acidified sodium chlorite solution with 1% (w/w) at 75 °C for 2 h; then washed by distilled water until neutral. Afterwards, the samples were soaked in a potassium hydroxide solution with 2% (w/w) at 90 °C for 2 h to remove hemicelluloses then washed with distilled water until neutral. Finally the samples were treated with a hydrochloric acid solution with 1% (v/v) at 80 °C for 2 h to break up the fibers bundles then washed with distilled water until neutral. After successive chemical treatments, a water suspension with 5% (w/w) CNF was passed through a grinder (MKCA6-2, Masuko Sangyo Co. Ltd., Japan) for 20 times with the grinding stone at 1800 rpm.

2.2.2. Preparation of cotton CNF/HDPE composites with the physical pretreatment method

Before the extrusion process, different content of HDPE powder (60–80 mesh) were added into the cotton CNF water suspension under continuous stirring by a magnetic stirrer at 80 °C for 1 h. The samples formulation is listed in Table 1. After the preblending process, the suspension was dehydrated by vacuum filtration with a Buchner funnel and then was freeze dried until the moisture content of the mixture became stable.

The freeze dried samples were placed into a blender, mixed uniformly, then added to a HAKKE minilab (HAKKE minilab II, Thermo Fisher Scientific, Germany) for capillary rheological test. MAPE was added as coupling agent for each formulation. The compounding