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Synthesis of kenaf cellulose carbamate and its smart electric stimuli-response

Sinyee Gan[a], Shang Hao Piao[b], Hyoung Jin Choi[b,*], Sarani Zakaria[a,*], Chin Hua Chia[a]

[a] *School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia*
[b] *Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Republic of Korea*

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ABSTRACT

Cellulose carbamate (CC) was produced from kenaf core pulp (KCP) via a microwave reactor-assisted method. The formation of CC was confirmed by Fourier transform infrared spectroscopy and nitrogen content analysis. The degree of substitution, zeta potential and size distribution of CC were also determined. The CC was characterized with scanning electron microscopy, X-ray diffraction and thermogravimetry analysis. The CC particles were then dispersed in silicone oil to prepare CC-based anhydrous electric stimuli-responsive electrorheological (ER) fluids. Rhelogical measurement was carried out using rotational rheometer with a high voltage generator in both steady and oscillatory shear modes to examine the effect of electric field strength on the ER characteristics. The results showed that the increase in electric field strength has enhanced the ER properties of CC-based ER fluid due to the chain formation induced by electric polarization among the particles.

1. Introduction

Electrorheological (ER) fluids are smart suspensions of electric field-responsive particles dispersed in an insulating fluid of which the mechanism of ER phenomenon is determined from the formation of particle chains by an applied electric field (Choi, Park, & Lee, 2002). The rheological properties of the suspensions can change quickly from a liquid-like to a solid-like state with an external electric field. Consequently, the shear viscosity of ER fluid can be controlled by an external electric field, which reveals a reversible phase transition between liquid-like and solid-like, along with the strong endurance against shear under high electric field strength although only small amount of particles is being used. This typical characteristic of ER fluid potentially provides one of the most efficient engineering approaches in controlling mechanical responses from the adjustment of electric field strengths (Liu et al., 2014a; Park, Hwang, Choi, Kim, & Jhon, 2003; Tilki, Yavuz, Karabacak, Çabuk, & Ulutürk, 2010). Thereby, ER fluids have considerable potential in various applications such as optical finishing, dampers, clutches and haptic devices due to its controllable properties (Kamelreiter, Kemmetmüller, & Kugi, 2012).

The active materials used in ER fluids most probably are polarizable or semiconducting particles, for examples, dielectric inorganics (such as TiO_2, SiO_2, and $BaTiO_3$), conducting polymers with a suitable conductivity range from 10^{-6} to 10^{-9} S/m and their composites. These particles are being polarized and arranged into interconnected chain structures with respect to the direction of the applied electric field. Therefore, the applied electric field can affect the rheological properties of ER fluids remarkably. Various researches have been carried out on ER-active materials such as different type of materials, structure and particle shapes on ER effects (Liu, Quan, Hwang, Kwon, & Choi, 2014b). Recently, silica, corn, starch, zeolite and cellulose have been extensively used as the dispersed phase in the formulation of hydrous (wet base) ER suspensions. Their ER performances are relied on small amount of low molecular solvent activation and water contained in dispersed phase in an external electric field (Choi et al., 2002). The main difference between dry and wet based ER fluids is the carrier species of polarized particles. For the wet based ER fluids, the fibrillar structure is formed from the migration of the ionic particles in absorbed water. While the for dry based ER fluids, the electronic migration inside the dispersed particles molecules inducing dielectric polarization is the driving force of the particle chain structure (Tilki et al., 2010).

On the other hand, cellulose with a structural formula $(C_6H_{10}O_5)n$ for each chain and bound together by β-1 chain, 4 glikosidik has been also adopted as an ER material. Cellulose known as organic polymer has been used most abundant on earth

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* Corresponding authors. Tel.: +82 328607486.
E-mail addresses: hjchoi@inha.ac.kr (H.J. Choi), szakaria@ukm.edu.my (S. Zakaria).

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with natural production at approximately 1.5×10^{12} t in a year. Cellulose is a biodegradable polymer ($1000 < DP < 15{,}000$) and a raw material in a wide range of applications such as cellulose acetate, rayon, cellophane and so on. Thus, cellulose can reduce the use of the limited fossil resources with its environmental friendly properties and has been used in industrial applications. The celluloses are processed massively in industrial to the regenerated material (such as films, sponges, food casings, fibers, membranes, paper and so forth) and cellulose derivatives (which include ether and ester) (Cao et al., 2009; Vitz, Erdmenger, Haensch, & Schubert, 2009). Kenaf is a species of plant with scientific name *Hibiscus cannabinus* and gradually becomes one of the most important commercially fiber sources which has a world production at approximately 970,000 t (Eichhorn et al., 2001). Kenaf core consists of about 46.1% cellulose, 29.7% hemicellulose and 22.1% lignin (Ashori, Harun, Raverty, & Yusoff, 2006).

Numerous methods have been carried out to synthesize cellulose carbamate (CC) and have been reported in many literatures. The CC can be obtained by heating up the cellulose and urea at temperature roughly 140 °C (Iller, Stupińska, & Starostka, 2007). This is due to the melting point of urea is around 140 °C and it will be decomposed into isocyanate acids to react with cellulose in order to form CC (Shen et al., 2005). The conventional carbamate synthesis process needs long reaction time, high temperature, organic solvents and catalysts. An alternative path for the fabrication of CC has been reported by the mixing of cellulose with ammonia solution that contains urea. However, this alternative faces some limitations in technical applications due to the strict conditions imposed and high involvement of chemicals (Vo, Široká, Manian, & Bechtold, 2010; Yin & Shen, 2007). Furthermore, Guo, Zhou, Song, and Zhang (2009) and Guo, Zhou, Wang, Zhang, and Lin (2010) have also reported the microwave-assisted synthesis of CC. Note that the CC is considered as an environmentally friendly material which might serve as a potential alternative to petroleum based polymers since it has natural compatibility properties and biodegradable, while it is soluble in conventional solvents (Yin & Shen, 2007).

In this study, we synthesized CC via a microwave irradiation technique and characterized its physical properties with scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), elemental analyzer, thermogravimetry analysis (TGA), zeta potential and particle size analyzer and X-ray diffraction (XRD). The ER properties of the CC when dispersed in silicone oil were also investigated using a rotational rheometer.

2. Materials and methods

2.1. Materials

Raw kenaf core was supplied by the Malaysian Agricultural Research and Development Institute (MARDI). The analytical grade of lithium hydroxide monohydrate (LiOH H_2O), urea and 98.8% sulfuric acid were purchased from Sigma Aldrich. Urea and other reagents used in this study were of analytical grade and were used without further purification. The raw kenaf core was soda pulped in Forest Research Institute Malaysia (FRIM) in a digester with 25% NaOH concentration at 170 °C for 2.5 h. The kenaf core pulp was bleached using four stages bleaching method (DEED) where process D composed of 1.7% sodium chlorite at 80 °C for 4 h and process C is an alkaline treatment on KCP (referring the bleached kenaf core pulp) with 4–6% NaOH solution at 80 °C for 3 h. After every single stage performed, the sample was washed until neutral to remove the bleaching chemicals and dissolved lignin from the sample prior to entering the next stage. Then, the sample was dried at 105 °C for 24 h.

2.2. Viscosity measurement and molecular weight calculation for KCP

The intrinsic viscosity measurement of cellulose in cadoxen solution is a common method as reported previously by Brown and Wikstrom (1965). The obtained intrinsic viscosity was then used to calculate molecular weight of cellulose.

2.3. Preparation of CC

In a typical reaction procedure, KCP was immersed into a urea aqueous solution with 200 ml H_2O and mass ratio of KCP and urea was 1:1. The mixture was stirred at an ambient temperature for 30 min and placed in the desiccators that connected to a vacuum pump giving rise to a vacuum condition for 30 min. The vacuum pump was then turned off and allowed atmosphere forces the urea aqueous solution to penetrate into KCP for 30 min. The mixture was later poured into a reaction flask and was heated in a microwave reactor at the power set at 380W at 20 min. The microwave reactor is a multimodal microwave apparatus (Electrolux—EMM1908S) that has been equipped with a condenser to prolong the microwave irradiation. After 20 min, the mixture in the reaction flask was immersed instantly in an ice bath to stop the reaction. The obtained CC was washed with deionized water using both vortex shaker and centrifuged to remove the excessive urea. The CC was vacuum-dried at 80 °C for 24 h to make sure the water is completely removed.

2.4. Preparation of CC-based ER fluid

The dried CC was then ground using a mixer to pass through a 200 μm sieve shaker to control the particle size distribution. The density of the CC is $1.74\,g/cm^3$, while the density of KCP is $1.72\,g/cm^3$. The 0.5 vol% of CC-based ER fluid was prepared by dispersing the CC particles in silicone oil (density; $0.956\,g/cm^3$, kinematic viscosity; 20 cSt), which was dried in a vacuum oven and stored with molecular sieves before use. The prepared ER fluid was stored in a desiccator prior to use and redispersed before used for the measurement.

2.5. Characterizations

The samples were characterized by Fourier transform infrared spectroscopy (FT-IR) (Perkin Elmer Spectrum) to observe the functional groups in the CC. The percentage of the nitrogen (N) element in CC was determined using elemental analyzer, Interscience Flash EA 1112 series (Thermo Finnigan) with TCD detector, CHNS—Porapack PQS column, 50–190 °C oven temperature. The values of nitrogen content were used to calculate degree of substitution (DS) of hydroxyl groups on cellulose by carbamate groups following the equation (Vo et al., 2010):

$$DS = \frac{162 \times N}{14 \times 100 - 43 \times N} \tag{3}$$

where N (%) is the nitrogen content of modified cellulose determined by elemental analysis, 162 is the molecular weight of the anhydroglucose unit (AGU), 14 is the molecular mass of nitrogen atom and 43 is the net increment in the AGU for every substituted carbamate group. The morphology of KCP and CC has been analyzed under a Scanning electron microscopy (SEM) (JSM-6390, JEOL). Phase and crystallinity index (CrI) for both KCP and CC were characterized using X-ray diffraction (XRD) (Bruker Axs D8 Advance). The XRD was performed using radiation of Cu $K\alpha = 1.5458\,\mathring{A}$ at a diffraction angle (2θ) range of 10 to 50°. Diffraction profiles were carried out with a Gaussian function to determine the crystallinity index (CrI) of the samples. The CrI of the samples was examined