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Electric field-induced alignment of nanofibrillated cellulose in thermoplastic polyurethane matrix

Shuman Xu, Dingyao Liu, Qin Zhang, Qiang Fu*

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, PR China

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ABSTRACT

Nanofibrillated fibers (NFC) has been largely used as reinforcing filler to improve the properties of polymer matrix because of their unique properties such as high aspect ratio, good aqueous stability, high specific strength and stiffness. However, the full potential of NFC as reinforcing agent has not been realized because of its poor dispersion and random distribution in polymer matrix. In this work, we demonstrate the importance of alignment of NFC to determine the mechanical properties of polymer via applying alternative current (AC) electric field and using thermoplastic polyurethane (TPU) as the matrix. The TPU/NFC nanocomposites were prepared via solution casting method and the effect of parameters of the applied electric field (amplitude, frequency as well as the duration of application) on the orientation degree of NFC and the final properties of TPU/NFC nanocomposites are systematically investigated. It was found that NFC could be easily oriented under effect of AC due to electric induced polarization. The prepared anisotropic TPU/NFC composites exhibit 2.07 and 1.82 times increase of tensile strength and elongation at break in the parallel direction than that in the vertical direction for the anisotropic samples, respectively. It was also interesting, to find that the samples with aligned NFC exhibit an increased dielectric constant with lower dielectric loss, which could provide an idea to fabricate high performance dielectric materials.

1. Introduction

In recent years, cellulose have attracted much attention because of their promising and impressive properties, as well as its renewable and biodegradable nature [1–5]. Nanofibrillated cellulose (NFC) with one-dimensional morphology structure is extracted from native cellulose fiber at nanoscale. Therefore, the obtained NFC remains many excellent properties of the primitive cellulose fiber, such as: large aspect ratio, high crystallinity, excellent mechanical properties and small density [6–8].Thus, extensive interest from the research community focused on the application of NFC acting as the reinforced agent of polymer matrix [9–12]. In general, the ultimate performance of composites, however, is not only associated with the initial properties of fillers, more to the supramolecular structure and the self-assembly behavior of fillers in polymer matrix [13]. Therefore, significant improvement of mechanical performance can be achieved by arranging the packing pattern and self-assembly behavior of fillers in composites. Owing to the high aspect ratio of cellulose nanofibril, it has been reported that the theoretical elastic modulus of cellulose nanofibril in axial direction is about 167 GPa, however, only 11–50 GPa in radial direction [14]. Such native properties should be took full advantage of when fabricating high performance NFC-reinforced composites with anisotropically tunable optical, mechanical properties for specific applications.

Many authors have devoted to aligning cellulose in polymer matrix using different methods, such as spinning [15–17], mechanical deformation [18–20] or under external field like magnetic [21,22] and electric field [23]. Although they could oriented the cellulose nanofiber in some extent, there remain some technically problems in these methods. For instance, Jalal et al. [24]. fabricated highly oriented cellulose nanocrystal (CNC) in poly(vinyl alcohol) matrix through gel spinning followed by a hot drawing. The drown fibers exhibit 1.27 and 1.4 times increase in tensile strength and Young' modulus at 5 wt% loading, revealing the circumscribed effect of this method. Except this, a good affinity between cellulose fiber and polymer matrix is indispensable for the alignment of cellulose fiber via spinning and drawing which is in favor of the efficient load transfer from the polymer matrix to cellulose

* Corresponding author.
E-mail address: qiangfu@scu.edu.cn (Q. Fu).

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nanofiber. In the case of using magnetic field to induce the orientation of cellulose fiber, due to the low magnetic susceptibility of cellulose fiber, ultra-strong magnetic fields are usually required which will greatly increase the complexity of the equipment to the extent that are unavailable in most research laboratories [25]. Compared with the magnetic field, the use of an electric field is a versatile and easily implemented method to align the anisotropic cellulose fibers. Up to now, a few studies have been dedicated to the alignment of cellulose fibers in suspension state. For example, Bordel et al. [26]. firstly obtained the oriented ramie fibers at microscopic and colloidal levels in cyclohexane and chloroform via applying an external AC electric field. However, this pioneer study was limited to a constant condition (200 V/mm, 1000 Hz). They did not investigate the effect of varied electric field (magnitude and frequency) on the fiber orientation and resultant property. Habibi et al. [13]. investigated the different oriented behavior of CNCs in water by using different amplitude and frequency of AC electric field. Kalidindi et al. [27]. and Kadimi et al. [28]. used AC electric field to induce the orientation of CNCs and NFCs in silicon oil, and again no resultant property was reported.

So far most of works related to the orientation of cellulose nanofibers orientation are carried out mainly in solvent under electric field. To our knowledge, most of the published literature on electric field—assisted orientation are mainly associated with CNC. For example, Ten et al. [29]. prepared aligned poly(3-hydroxybutyate-co-3-hydroxyvalerate) (PHBV)/CNC composites under a very high direction current (DC) voltage (56.25 kV/m). It was found that the mechanical properties in the oriented direction was much better than that of the vertical direction as well as the viscosity of the suspension strongly influenced the degree of CNC alignment. There are two things should be considered in their work. The first one is that they used DC electric field instead of AC. There are some restrictions when DC electric field was applied on particles with abundant negatively charge, the particles may move to the anode and will be absorbed on the electrode neutrally via transferring the charge to the electrode. Therefore, DC electric field is not appropriate method to align the negative charged particles, while AC electric field could overcome the problem effectively. The other is that CNC was used in their work to reinforce PHBV rather than NFC. Compared with CNC, there is still amorphous region on NFC, thus lower crystallinity were obtained for NFC. Iwamoto et al. [30] reported that the elastic modulus of NFC and CNC are 145.2 ± 31.3 and 150.7 ± 28.8, respectively. They are experimentally in agreement with the elastic modulus of native cellulose crystals. But in general, NFC possesses higher aspect ratio thus higher reinforcement efficiency is expected. So far, we did not find any study in the literature devoted to fabricating oriented NFC in polymer/NFC nanocomposites via using electric field, not to mention the relationship between the degree of alignment of NFC in polymer matrix. Thus the parameters of the applied electric field (i.e., amplitude, frequency as well as the duration of application) and the final properties of anisotropic nanomaterials containing oriented NFC should be thoroughly investigated.

In this work, we chose thermal-plastic polyurethane (TPU) as polymer matrix and TEMPO-catalytic-oxide NFC as the reinforcing nanofiller, to prepare aligned NFC in TPU matrix via applying AC electric field. The effect of parameters of the applied electric field (amplitude, frequency as well as the duration of application) on the orientation degree of NFC and the final properties of TPU/NFC nanocomposites are systematically investigated. The results show that the magnitude of voltage has positive correlation with the orientation degree of NFC and the effect of frequency is also related to the viscosity. Longer duration is benefit for alignment of NFC and overlong duration will result in agglomeration. The obtained anisotropic TPU/NFC nanocomposites in the parallel direction exhibit better mechanical performance and dielectric property than that for the isotropic samples.

2. Experiment section

2.1. Materials

Thermos-plastic polyurethane (TPU, Irogran PS455-203), bought from Huntsman Corp, was used as polymer matrix of the composites. Micro-fibrillate cellulose (MFC) (Celish KY100-S, derived from wood pulp) was provided by Daicel Chemical Industries, Ltd, Japan. TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) and Sodium bromide (NaBr) are obtained from Sigma-Aldrich. Other reagents referred by this work were provided by Chengdu Kelong Chemical Reagent Company (China) and used as received.

2.2. Fabrication of nano-fibrillated cellulose

NFC was fabricated through TEMPO- mediate oxidation process by MFC as the raw material as our previous work [31,32]. 0.16 g TEMPO and 1 g NaBr were added to 1 L deionized water containing 10 g MFC with magnetic stirring. Then NaClO solution (10 mmol per gram of cellulose) was added in the obtained suspension gradually to initiate the TEMPO-mediate oxidation. 0.5 M NaOH was used to ensure the pH of the system stay around 10–10.5. The oxidation process was kept at room temperature for 5 h. Then 10 ml ethyl alcohol was added to terminate the reaction. The obtained product was thoroughly washed with distilled water by filtration. Subsequently, centrifugation (8000 rpm, 15min) was used to separate the NFC from the product. Finally, the obtained NFC was transferred into DMF via solvent exchange method.

2.3. Preparation of anisotropic TPU/NFC nanocomposite films via applying AC electric field

The fabrication procedure for aligned TPU/NFC nanocomposites was as follows: take the 3 wt% TPU/0.5NFC sample as an example, 60 ml DMF was added into the 10 ml NFC/DMF suspension containing 10 mg NFC and pre-ultrasonic for 15min with ice bath. Then 2 g TPU was added into the NFC suspension with magnetic stirring at room temperature until complete dissolved to obtain homogenous TPU/NFC suspension. Then an AC electric field was applied on the obtained homogenous TPU/NFC suspension to obtain the anisotropic TPU/NFC composite and the experimental setup as shown in Fig. 1. The homogenous TPU/NFC suspension (6 ml) was added into the polytetrafluoroethylene (PTFE) mould equipped with two piece of copper sheet on both sides. The AC signals were supplied by Agilent 33210A function waveform generator. A TREK2220 high voltage amplifier was integrated with the generator to obtain high voltages. The magnitudes of the electric field applied for the alignment experiments are 100, 500, 1000, 1500 and frequencies are 10, 100 and 1000 Hz. The duration of the electric field varied from 5 to 60min. Finally, the PTFE moulds were heated to 60 °C to accelerate the evaporation of DMF to obtain the anisotropic TPU/NFC films. As for reference samples, isotropous TPU/NFC was also prepared using the same method without applying any electric field. In this work, we defined the sample as TPU/xNFC, where x represents the content of NFC in the composite, for example, TPU/0.5NFC is the sample with 0.5% NFC loading. The materials for neat TPU, TPU/0.3NFC, TPU/0.5NFC and TPU/0.7NFC are listed in Tab.S1.

2.4. Characterization

Transmission electron microscopy (TEM, JEOL JEM-100CX, Japan) was used to observe the morphology of the NFC. Diluted