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Effect of thermal treatment on properties of ramie fibers

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ABSTRACT

The properties of ramie fibers treated by thermal treatments at 200 °C under nitrogen and air atmospheres, including thermal stability, crystalline properties, chemical structure, longitudinal thermal deformation behavior and surface performance, were studied. When the ramie samples had been treated, both the lateral order indices (LOI) and infrared (IR) crystallinity ratios were increased, whereas the crystallinity indices of X-ray diffraction analysis were decreased. The absorbed water had a great impact on the properties of the treated ramie samples, promoting the LOI and the crystallite sizes and reducing IR crystallinity ratios, crystallite d-spacings and crystallinity indices. Oxidation in thermal treatments led to the decrease of crystallite sizes and crystallinity indices. The longitudinal thermal deformation behavior of ramie fibers were further measured by thermo mechanical analyzer. The results showed that 2 treated samples with moisture absorption were of thermal expansion properties, the one without moisture absorption and treated under dried air exhibited thermal shrinkage in the temperature range below 100 °C and thermal expansion above 100 °C, while the one without moisture absorption and treated under dried nitrogen displayed thermal shrinkage in the whole temperature range. These different behaviors were attributed to the diversity of chemical structure and crystalline structure in fiber samples resulted from the absorbed water, oxidative decomposition and thermal degradation. The fracture morphology of ramie fibers/epoxy resin composites was observed by scanning electron microscopy, which disclosed that the compatibility between fibers and resin matrix was enhanced through thermal treatments, and the failure tips of fiber samples without moisture absorption are coarser and looser than those with moisture absorption because of the influence of absorbed water on cellulose structure. It can be seen that the atmospheres of thermal treatments and moisture absorption are the main factors to affect the properties of the treated ramie fibers.

1. Introduction

Natural fibers are presently receiving increasing attention as environmentally friendly biomaterials for they are renewable, biodegradable, widely distributed, easily available locally, cheap, versatile and light [1–5]. The use of natural fibers as reinforcements in polymer composites to replace synthetic fibers is greatly focused because of the advantages, including good longitudinal mechanical properties, high specific strength, low density, cost effectiveness, as well as their availability as renewable resources [6–9]. However, the main disadvantages of natural fibers in composites are their susceptibility to moisture uptake [10–12], incompatibility between hydrophilic natural fibers and hydrophobic matrix materials [13–16], low thermal resistance, and inconsistency in quality [17–21]. To overcome these drawbacks, significant efforts of modifying natural fibers have been made by many researchers via physical treatment methods, such as thermal treatment [22,23], corona discharge [24] and plasma [25], and chemical treatment methods, such as alkali [26], acetylation [27], silane coupling agent [28,29] and bleaching [30]. Among them, the thermal modification is an ecological process that avoids the use of toxic chemical products to preserve the fibers and contributes to decrease the impacts of chemical treatment technologies on the environment. Nowadays, works on the thermal treatment of natural fibers have shown that the performance of fibers can be improved in several aspects [31,32]. The modifications of chemical structure in natural fibers occurring at high temperature are accompanied by several favorable changes in physical properties: reduced shrinkage and swelling, low equilibrium moisture content, enhanced weather resistance and decoration, better decay resistance. At the same

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time, the degradation of hemicelluloses and recombination of lignin during thermal treatment [5,33–35], lead to an increase of the crystallinity degree of cellulose and nonpolar surface energy of natural fibers, which enhances the adhesion between the reinforcing fibers and the matrix and rectifies the final mechanical properties of composites. The study on properties of natural fibers after thermal treatment is generally concentrated on several aspects such as chemical structure, thermal stability, moisture absorption, and crystalline properties. However, the longitudinal thermal expansion, another important performance of fibers, is often neglected. During the processing and utilization of composites, natural fibers are usually subjected to different temperature fields. Commonly, there is a great difference in thermal expansion between reinforcing fibers and polymer matrix, inducing strong residual stress and interface failure in composites. Therefore, it is necessary to understand the longitudinal thermal expansion of natural fibers.

The natural fiber studied in this work was ramie [36–39], one of the most important non-wood fibers, native to China, and widespread in Asia. The ramie fibers are considered as the longest and most durable natural fibers, and in particular, its higher cellulose content (65–75 wt%) compared with bast fibers such as hemp, flax and jute. Ramie fibers are commonly used for the production of textiles due to the comfortable characteristics of the final product. Even in technical applications, such as the production of composites, ramie has excellent performance, as demonstrated by many studies [40–43].

In this work, thermal treatments of ramie fibers were carried out under air and nitrogen atmospheres, respectively. The chemical structure, crystalline properties, surface performance, and in particular, longitudinal thermal expansion of treated ramie fibers were analyzed, and their interrelations were discussed.

2. Experimental

2.1. Materials

The natural fibers used for this experiment was crude ramie fibers supplied by Hunan Canary Bast Fiber Textile Co., Ltd., China. Ramie fibers were yellowish in appearance, dried naturally, fluffed mechanically, and avoided further physical and chemical treatments, whose chemical composition is showed in Table 1. Epoxy resin (E51) and amine curing agent (R2266) were produced by Baling Company, SINOPEC and Guangzhou Rich Chemical Co., Ltd, respectively. High purity nitrogen and compressed air were purchased from Changsha Zhongyi Gas Co., Ltd. A dehydration procedure of gases, washing firstly with concentrated sulfuric acid (Hunan Kelong chemical Co., Ltd) and subsequently with activated carbon (Hunan Liyuan Activated Carbon Co., Ltd), was employed to prepare dried nitrogen and dried air.

2.2. Thermogravimetric analysis (TGA)

The thermogravimetric analysis was carried out on an instrument (NSK DTG7300). Approximate 5–10 mg of sample cut into about 1.0 mm length was placed in a platinum crucible with a diameter of 4.0 mm under a constant gas flow with a flow rate of 20 ml/min. In order to evaluate the thermal stability, the crude ramie fibers were exposed to a temperature range between 25 and 700 °C at a constant heating rate of 5 °C/min under nitrogen and air. The weight losses were generated by thermal degradation during thermal treatment were also recorded and samples were heated from 25 °C to six representative temperatures (150, 175, 200, 250, 275, 300 °C) respectively at a heating rate of 5 °C/min under a nitrogen or air atmosphere, and then held for 40 min.

2.3. Infrared (IR) spectroscopy

The ramie fiber powders were diluted to 1% using KBr and pellets were prepared using a Hydraulic press. The Fourier Transform Infrared (FT-IR) spectra of the untreated and treated samples were recorded in 4000–500 cm^{-1} region on a Perkin Elmer 16PC FTIR instrument with 32 scans in each case at a resolution of 4 cm^{-1}.

2.4. X-ray diffraction (XRD) characterization

The XRD of fiber samples were measured by a wide angle X-ray diffractometer (D/max 2027, Rigaku Co. Japan) from 5° to 30° at a scan speed of 2°/min. The experimental data were treated by using XPS PEAK4.1 and a linear background was first subtracted from all data. A broad reflection at 18.5°, representing the non-crystalline cellulose component was simulated for all analyses, whose full width at half maxima (FWMH) was fixed as 8.0°. The intensity of non-crystalline feature was freely adjusted during the fitting exercise. The sharper reflections of the [−110], [110] and [200] crystallographic planes of cellulose I were also simulated, with FWMHs, intensities and positions of the peaks freely adjusted during the fitting exercise.

The crystallinity index (Eq. (1)) of the samples was calculated from the areas of the crystalline and non-crystalline simulated peaks, proposed by Hermans [44–47]:

$$\mathrm{CrI}(\%) = 100 \times \mathrm{area}([-110] + [110] + [200])/\mathrm{total\ peak\ area} \tag{1}$$

Another approach used to determine the crystallinity index (Eq. (2)) was the empirical method proposed by Segal [48–50]:

$$\mathrm{C.I.}\ (\%) = 100 \times (I_{200} - I_{am})/I_{200} \tag{2}$$

The apparent crystallite size (L) (Eq. (3)) was calculated using the Scherrer equation [46,51]:

$$L = K \times \lambda/(\beta \times \cos\theta) \tag{3}$$

where K is a constant of value 0.94, λ is the X-ray wavelength (0.1542 nm), β is the half-height width of the diffraction band and θ is the Bragg angle corresponding to the (200) plane.

2.5. Thermo-mechanical analysis (TMA)

The ramie fiber bundles for TMA analysis selected under optical microscope were about 40 μm in diameter, whose longitudinal thermal deformation as a function of temperature were measured using a NSK SS7300 thermo-mechanical analyzer. For the crude fiber sample (named F0), its longitudinal thermal deformation from

Table 1
Chemical composition of the crude ramie fiber used in this study.

Composition	Cellulose	Hemicellulose	Lignin	Pectin	Waxes	Extractives	Moisture content
Value (wt%)	68.0–75.0	13.0–16.0	0.8–1.5	3.0–4.0	0.5–1.0	4.0–8.0	7.0–8.5