Structural Characteristics and Properties of Polylactic Acid (PLA) and Cellulose Triacetate (CTA) Fibers for Heat-Not-Burn (HNB) Cigarettes

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Abstract. In this work, two commonly used filter fibers for heat-not-burn (HNB) cigarettes, polylactic acid (PLA) and cellulose triacetate (CTA) fibers, have been extensively investigated by characterizing their morphologies, thermal and wetting properties. It is found that plenty of small pores can be observed in PLA fibers, which can provide more effective surface areas for the adsorption of mainstream smoke than CTA fibers with smooth surface. At the same time, thermal properties results including differential scanning calorimetry data, thermogravimetry data, and thermal conductivities of PLA and CTA fibers indicate that CTA fibers have an amorphous phase, while PLA fibers present a mixture of amorphous phase and crystalline phase with better thermal properties. Additionally, wetting properties demonstrate that PLA fibers have better adsorption properties than CTA fibers.

1. Introduction

The urgent global problem of smoking-related hazards has received widespread attention. Conventional cigarette mainstream smoke (MS), which is generated by combusting tobacco at 700-950 °C, contains thousands of hazardous compounds, such as nicotine and polycyclic aromatic hydrocarbons, which generally affect the health of smokers [1-3]. Some very severe health risks, including cancer and heart disease, can be assumed to as a result from MS [4]. In order to strongly reduce the production of harmful substances in MS of cigarettes and effectively lower the toxic effects of the cigarettes, some attempts including development of novel tobacco-substitute sheets and alternative materials have been done [5]. New cigarette types, including heat-not-burn (HNB) tobacco and electronic cigarette (e-cigs), have been considered as the effective ways to reduce the production of MS because the cigarette aerosols of these new cigarettes are generated by different heating approaches [6-8]. However, e-cigs can generate new toxic compounds including formaldehyde, acetaldehyde, and acrolein via the oxidation of the e-cigs components (propylene glycol (PG) and vegetable glycerin (VG)) through heating and vaporization [9-11]. Since the HNB tobacco stick also contains PG and VG, some harmful gases including formaldehyde, acetaldehyde, and acrolein may also be generated in the MS of HNB [3, 12].

Recently, many attentions have been paid on the development of adsorbing materials for removal of toxic chemicals from MS. At the same time, nanomaterials such as activated carbon, zeolites,
metal-organic frameworks, carbon nanotubes, coordination polymers, fibers, have been usually used for the filtration to efficiently reduce the harmful compounds in the MS because of their excellent adsorbing properties [13-15]. However, the adsorption efficiency is difficult to be improved, and there are many limitations in processing and production, which cannot meet the requirements of materials safety, simple preparation process, low cost, and rich characteristics. There, it is highly in need to develop other alternative nanomaterials as adsorbing materials for HNB cigarettes.

Natural polymer fibers, such as cellulose triacetate (CTA) fibers and polylactic acid (PLA) fibers, are abundant renewable biomass polymer, which are highly attractive for HNM filter materials due to their advantages of low cost, lightweight, and apparently environmentally superior alternative to synthetic fibers [16-19]. It is proven that the application of natural polymer fibers in HNB tobacco can greatly eliminate the harmful pollutants form the environment, and presents strongly positive effects on the economy, human, and society.

In the present work, we studied the morphology, thermal properties and wetting properties of CTA and PLA fibers, and compared their properties by using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray diffraction (XRD), thermal gravimetric analyzer (TGA), thermal conductivity meters (TCM) and contact angle (CA) tester. It is found that PLA fibers have better adsorbing performance than CTA fibers.

2. Experimental

PLA fibers and CTA fibers used in this work are purchased from HUAWEI.

Tescan MIRA 3 was used to measure the morphology of CTA and PLA fibers by recording their SEM images. The phase change properties were performed by using a DSC (Q2000, TA Instrument) under 30 mL min⁻¹ N₂. 10 mg fibers were placed in aluminum crucible and then sealed hermetically before being scanned from 30 to 200 °C for heating cycles and from 200 to 30 °C for cooling cycle with a heating and cooling rate of 10 °C min⁻¹. The thermal reliability of CTA and PLA fibers was investigated by TGA (HCT-1, Hengjiu Instruments). An amount of 10 mg of each sample were analyzed from 40 to 200 °C with a heating rate 10 °C min⁻¹ under ambient atmosphere.

To investigate the phase composition, thermal conductivities and wetting properties of PLA and CTA fibers, CTA and PLA fibers were pressed into disks with a diameter of 25 mm and a thickness of 5 mm. The phases composition of CTA and PLA fibers were carried out using a PANalytical X’pert Pro X-ray diffractometer, and the XRD data were collected in the 2 theta range of 20-80°. The hot disk TPS 2500S was used to perform the thermal conductivity measurements at 30 and 55 °C. The sessile-drop method was used to measure the wetting properties of CTA and PLA fibers by using CA meters (JC2000C, POWEREACH) and dropping water, glycerol, or 1,2-propanediol on the surface of the disks.

3. Results and Discussion

Microstructure and morphology of PLA and CTA fibers are characterized by SEM images and shown in figure 1. It can be clearly seen from figures 1a-1b that lots of small pores along the direction of the fibers can be observed on the surfaces of the fibers. On the contrast, the CTA fibers have smooth surfaces without any observable pores (figures 1c-1d). These results suggest that PLA fibers could offer more effective surface areas for MS adsorption than CTA fiber, and PLA fibers are a more promising candidate material of HNB cigarette fibers [19].

At the same time, CTA and PLA fibers are characterized by DSC measurement to determine the thermal transition of the samples resulting from melting, glass transition, crystallization or other exothermic and endothermic transition. As is shown in figure 2, the heat flow is monitored as a function of temperature in both heating and cooling operations. When the CTA fibers are heated from room temperature to 200 °C, two transitions of curing are observed in the CTA sample at temperature range of 25-35.3 and 35.3-79.91 °C, which are possibly related to dehydration and softening, respectively. However, PLA sample occurs a sharp thermal transition at temperature ranging from 169.11 to 177.6 °C due to the melting of PLA fibers. On the other hand, when PLA fibers are cooled
from 200 °C to room temperature, a positive peak is observed 121.69 to 111.77 °C, which corresponds to the recrystallization transition. As the temperature is cooling to this point, PLA material may rearrange from the amorphous state into a crystalline polymer, along with releasing heat. However, the CTA exhibits a flatten DSC plot during the cooling operation with no obvious exothermic or endothermic peak. The results reveal that PLA is in a crystalline form while CTA has an amorphous structure.

Figure 1. (a), (c) 1000× and (b), (d) 5000× SEM images of (a)-(b) PLA and (c)-(d) CTA fibers.
To confirm the crystallization characteristic of PLA and CTA fibers, XRD data of CTA and PLA fibers are also collected. Figure 3 shows the XRD patterns of the PLA and CTA fibers recorded at room temperature. An amorphous bump centered at 23.22° can be clearly observed in the two theta range of 15-30°, further confirming the CTA fibers are amorphous phase [20]. However, two additional sharp diffraction peaks at 16.52 and 19.01° are present around a small amorphous bump, indicating that the PLA material may be a mixture of amorphous phase and crystalline phase. The results are highly consistent with the thermal transition behavior in the DSC curves (figure 2).

The thermal reliability of PLA and CTA fibers is also studied from the TG curves. As is shown in figure 4, the TG curves of CTA fibers could be distinguished into two obvious stages. The first region ranges from 40 to 60 °C, where no typical weight loss occurs, while the second stage starts from 60 °C and extends to 180 °C, where the CTA sample has 40% weight loss. Similar value of 41% is achieved for the PLA sample from 40 to 169 °C, which is possibly associated with evaporation of moisture or other substance, such as the adsorbed gas and low-weight grease. However, when the temperature is higher than 169 °C, the remaining products of PLA fibers continue to lose weight rapidly, the residuals mass weight has dramatically decreased from 41% at 169 °C to 60% at 173 °C, which is possibly attributed to melting of PLA fibers starting at 169 °C, which is confirmed from the melting temperature observed by the DSC curves (figure 2).

Figure 5 presents the thermal conductivities of PLA and CTA fibers, which are pressed into shape of pellets for thermal conductivity measurement. When the temperature is operated at 30 °C, PLA and CTA fibers has a thermal conductivity of 0.1319 and 0.1378 W m⁻¹ K⁻¹, respectively. When the temperature increases to 55 °C, the thermal conductivity value has increased to 0.1342 and 0.1407 W m⁻¹ K⁻¹, respectively, indicating that increasing temperature can promote the thermal transfer properties. Moreover, it is also shown that PLA fiber exhibits a higher thermal conductivity compared to CTA at both 30 and 50 °C, demonstrating that PLA fibers have better thermal transfer properties than CTA fibers.

Since the adsorption properties of CTA and PLA fibers are strongly affected by their wetting properties to water, glycerol, and 1,2-propanediol, their corresponding surface wetting properties have been investigated by performing CA measurements [21]. It can be seen in figure 6 that the CTA material has a contact angle of 76.9, 84.8 and 71.0° when 3 μL water, glycerol, and 1,2-propanediol are dropped on the surfaces of the disk sample, respectively. On the contrast, at the same condition, the PLA material presents a contact angle of 64.4, 70.8, and 65.9°, respectively, which is effectively lower than that for CTA fibers. The results indicate that PLA exhibits a better surface wetting behavior than CTA fibers, reasonably leading to an efficient promotion of absorption to water, glycerol, and 1,2-propanediol, and certainly resulting in an enhancement of cooling effect.
Figure 3. XRD patterns of PLA and CTA fibers.

Figure 4. TG curves of PLA and CTA fibers measured at temperature of RT-200 °C with a heating rate of 10 °C min⁻¹.

Figure 5. Thermal conductivities of PLA and CTA fibers measured at 30 and 55 °C.

Figure 6. Summary of contact angles for PLA and CTA fibers.

Consequently, it can be concluded from the experimental results including morphology observed by SEM, thermal properties derived from DSC, XRD, TG and TC data as well as wetting properties
indexed by CA data that PLA fibers would have a better cooling effect for MS as it has a porous surface with a higher adsorption site, a crystalline structure contributing to better thermal conducting properties and lower contact angles to water, glycerol, and 1,2-propanediol. As a result, PLA material is more suitable to be used as an alternative filter materials candidate for HNB cigarette.

4. Conclusion
Herein, the morphologies, thermal properties as well as wetting properties of PLA and CTA fibers have been intensively studied. It is shown that PLA fibers show a porous surface with lots of small pores observed along the direction of the fibers, which is strongly different with the smooth surface for CTA fibers, reasonably providing more actives areas for cigarette mainstream smoke adsorption. DSC results demonstrate that CTA fibers have an amorphous phase, while PLA fibers present a mixture of amorphous phase and crystalline phase due to the obviously observed endothermic peak located at the temperature range of 169.11-177.6 °C, which are also confirmed by amorphous bump for CTA fibers and diffraction peaks for PLA fibers collected by XRD. Thermal conductivity results demonstrate that PLA fibers have better thermal transfer properties than CTA fibers. Moreover, lower contact angles exposure to water, glycerol, and 1,2-propanediol for PLA fibers than CTA fibers indicate the better adsorption properties for PLA fibers. Our findings in this work demonstrate that PLA material is a more promising filter material candidate for HNB cigarettes than CTA fibers. In summary, PLA material is a promising filter material candidate for HNB cigarettes.

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