



## Wool powder: An efficient additive to improve mechanical and thermal properties of poly(propylene carbonate)



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### ABSTRACT

The synthesis of poly(propylene carbonate) (PPC) consumes carbon dioxide, which forms a promising route to fix greenhouse gas. Developing the applications of PPC could enhance the recycle of carbon dioxide. However, PPC typically has low mechanical strength and thermal stability, and its glass transition temperature ( $T_g$ ) is low as well, which restrict its use in practice. In this study, we have for the first time found that wool powder (WP) can be an efficient additive to modify PPC. By adding just 2.0wt% wool powder (WP) to PPC, the mechanical properties, glass transition temperature, and thermal decomposition temperature can be improved significantly. PPC containing 2.0wt% WP shows comparable tensile properties to commonly-used polymers such as poly(butylene succinate), polypropylene and high-density polyethylene. We further showed that PPC can form strong interfacial interaction with WP, responsible for the improvement in PPC mechanical properties. Addition of wool powder may offer a promising way to boost the applications of PPC.

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### 1. Introduction

Poly(propylene carbonate) (PPC) is an amorphous, biodegradable and biocompatible polymer, typically prepared by alternative copolymerization of carbon dioxide ( $\text{CO}_2$ ) with propylene oxide (PO) [1,2]. The consumption of gaseous  $\text{CO}_2$  during the synthesis makes it ideal to store greenhouse gas. Recent concerns over the impact of greenhouse gas on global warming have revived the interest in recycling  $\text{CO}_2$  into PPC and development of PPC's applications [3,4].

PPC possesses exceptional properties such as impact resistance, translucence, and innocuousness [1,2]. It shows potential applications in making package, binders, drug-releasing agents, tissue engineering scaffolds, coatings, barriers and electrolyte [5–9]. However, PPC typically has a low glass transition temperature ( $T_g$ ), and its poor mechanical strength and thermal stability are relatively low as well, due to the highly flexible molecular chains and

small inter-chain interaction [1,2]. Those weaknesses have restricted the wide use of PPC in practice.

To improve the thermal and mechanical properties of PPC, two main strategies have been developed, 1) structure modification of PPC through terpolymerization with other monomers during the synthesis, crosslinking or end-capping; 2) blending with an additive, such as polymers, inorganic fillers, or organic substances. The addition of additives is highly preferred for practical applications, because of the convenience, effectiveness and low cost. Non-toxic, biodegradable, natural additives will be beneficial for applications in the fields of food industry, biomedicine and daily life. Starch [10–16], *o*-lauroyl chitosan [17], wood flour [18–21], cellulose and cellulose derivatives [22–27] have been blended with PPC. At a composition level above 10wt%, these natural additives improve PPC thermal and mechanical properties. Wang et al. [22] reported that the incorporation of 10wt% cellulose nano whiskers (CNWs) into PPC increased the PPC tensile strength from 11.6 to 26.9MPa and storage modulus from 1680 to 2960MPa, however,  $T_g$  and maximum weight thermal decomposition temperature ( $T_{\text{max}}$ ) only had slight changes. The similar results were also obtained on PPC composited with microfibrillated cellulose (MFC) [24]. Hu et al. [25] described that loading 1.5wt% cellulose nanocrystals (CNCs) may lead to the increase of the PPC tensile strength from 1.8 to 37MPa

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and Young's modulus from 207 to 2192MPa. However, tedious physiochemical processes had to be involved in the preparation and dispersion of CNWs, MFC and CNCs.

Wool as a type of animal fibers is widely used for making textiles. It chiefly consists of keratin proteins. Because of the active groups brought, wool can form strong binding with many metal ions including mercury, manganese, cadmium, copper, iron, cobalt, nickel, aluminum, chromium, zinc, silver and gold [28–31]. It has been used for removal of metal ions from industrial effluents [30,31]. When wool fibers are ground into fine particles, the surface reactivity and absorbency are significantly increased as a result of the considerably increased surface area [32]. Considerably increased absorption ability to metal ions and dyes have been reported on wool powder [32–35]. Recently, wool particles were also reported as a filler to reinforce polyurethane [36] and polypropylene [37]. However, research on using wool particles to reinforce PPC has little been reported in research literature.

In this study, we have for the first time uncovered the considerable reinforcement ability of wool powder (WP) to PPC. By adding just 2% WP to PPC, the Young's modulus is improved from 546 to 1589MPa, tensile strength from 21 to 38MPa and storage modulus from 2.2 to 3.2GPa (at 25°C). The  $T_g$ , maximum weight thermal decomposition temperatures ( $T_{max}$ ) and Vicat softening temperature (VST) were increased from 28.3, 239 and 34.1°C to 34.2, 276 and 40.3°C, respectively. We further proved that WP can form strong interfacial interactions with PPC, responsible for the excellent properties of PPC/WP composites.

## 2. Experimental

### 2.1. Materials

Commercial grade PPC resin, with molecular weight of  $M_n$  82,000 and polydispersity of 5.8, was supplied by Henan Tianguan Enterprise Group Co., Ltd. (Henan, China). WP was kindly provided by Deakin University (prepared as described in Ref. [32]). The average particle size of WP was about 4.02 $\mu$ m in diameter and the size distribution was 1.0. Dichloromethane ( $CH_2Cl_2$ ) was purchased from Kemiou Chemical Reagent Co., Ltd. (Tianjin, China).

### 2.2. Preparation of PPC/WP composites

PPC/WP composites were prepared by mixing the two materials in a solution, followed by solvent evaporation. In brief, 10g PPC was dissolved in 100mL  $CH_2Cl_2$  under vigorous stirring to get a clear solution. A required amount of WPs was dispersed in 50mL  $CH_2Cl_2$  by sonicating for 10min to yield WP/ $CH_2Cl_2$  suspension. The two solutions were then mixed, and the obtained mixture was further stirred for 2h. The solvent was evaporated from the solution through vigorous stirring at room temperature, and the composite solid was finally dried in vacuum at 60°C to a constant weight. The composites were then compression molded for testing at 110°C. Using the same procedure, a series of PPC/WP composites containing 0, 0.5, 1.0, 2.0, and 4.0wt% WP were obtained and the corresponding samples was named as PPC, PPC/WP-0.5%, PPC/WP-1%, PPC/WP-2% and PPC/WP-4%, respectively.

### 2.3. Isolation of WP from PPC/WP composites

To analyze the interfacial interactions between WP and PPC, WP was isolated from the composites using a Soxhlet extractor. The sample PPC/WP-4% was cut into small pieces and then extracted in Soxhlet for 36 and 72h using dichloromethane as solvent. In this

way, physically adsorbed PPC on WP can be removed. The insoluble part was dried at 60°C in vacuum to a constant weight. For convenience, the insoluble part was labeled as WP-E-36h and WP-E-72h, respectively.

### 2.4. Characterizations

The size and size distribution of WP were detected by dynamical light scattering (DLS) using a Malvern ZS90 Nanosizer instrument. XPS were performed on a VG Scientific ESCALab220I-XL spectrometer using mono-AlK $\alpha$  radiation. The C1s photoelectron line was used for energy calibration and the C1s binding energy was taken to be 284.4eV. The morphology of WP and the fractured sections of the PPC/WP composite films were observed with a field-emission scanning electron microscope (JEOL JSM-7610F) at 5kV accelerating voltage. WP was firstly dispersed in  $CH_2Cl_2$  at a low concentration, and then dropped onto a silica wafer, finally was dried in a vacuum at room temperature. All the samples need to be coated with gold for scanning electron microscopy (SEM) analysis. Fourier transform infrared (FTIR) spectra were recorded in a Bruker VERTEX 70 FTIR spectrometer with a resolution of 4 $cm^{-1}$  and 32 scans. The  $CH_2Cl_2$  solutions of PPC was cast onto a potassium bromide (KBr) disk and dried at room temperature in vacuum for 24h. WP and WP-E were pressed with KBr into pellets prior to FTIR measurements, respectively. Differential scanning calorimetry (DSC) measurements of the samples were carried out on a Mettler-Toledo 822e thermal analyzer in a dry nitrogen environment. Typically, 5–6mg sample was heated from 25°C to 70°C at a scan rate of 20°C/min and held for 5min to erase the thermal history, it was then quenched to –30°C and finally reheated to 70°C at a rate of 10°C/min.  $T_g$  was evaluated from the midpoint of the second scan to minimize the thermal history effect. The thermal stability of the samples was measured on a Mettler-Toledo TGA/SDTA851e analyzer in nitrogen flow. The samples were heated from 25 to 500°C at a heating rate of 10°C/min. The static tensile properties were determined at 23 $\pm$ 2°C and relative humidity of 50 $\pm$ 5% using an Instron 1185 tensile tester according to the ASTM D 638-14 standard. The crosshead speed was set at 50mm/min. At least five samples were tested in order to ensure accuracy and repeatability. The average values were reported. Young's modulus was determined from the slope of a least-squares regression line fit to the linear elastic part of the stress-strain curve (below 5% strain). Dynamic mechanical analysis was carried out using a dynamic mechanical analyzer (DMA Q800, TA instrument). The temperature was calibrated according to ASTM E 1867-06 standard test method and the controlling accuracy reached  $\pm$ 0.1°C. A heating rate of 3°C/min and a frequency of 1Hz were employed under film tension mode. The measurement temperature range was from –25°C to 80°C. At least two tests were carried out for each case. The vicat softening temperature (VST) of PPC and the composites was carried out according to GB/T1633-2000 using the VST tester (WKY-3, Jinnan Instrument Co., Ltd., China).

## 3. Results and discussion

Fig. 1a illustrates the procedure for preparing PPC/WP composite films, and the photos of PPC resin, WP, and PPC/WP films are shown in Fig. 1b. PPC film was colorless and transparent. When WP was added to PPC, the PPC/WP film looked translucent because of light scattering stemmed from WP. When the content of WP is 4wt%, the transparency was largely decreased and the film turned light yellow.

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