

## Improving thermal stability of biodegradable aliphatic polycarbonate by metal ion coordination

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### ABSTRACT

Poly(propylene carbonate) (PPC), a typical aliphatic polycarbonate, has attracted much attention during the last two decades due to its biodegradability and commercializing perspective. However, the application of this material as thermoplastics has been limited by its poor thermal stability. Metal soaps, such as calcium stearate (CaSt<sub>2</sub>), are important processing additives in plastics industry. In the present work, PPC–CaSt<sub>2</sub> complexes were prepared, the thermal stability of which was investigated by thermogravimetric analysis (TGA). The results show that the complexes are more thermal stable than pure PPC material. Supramolecular lamellar mesomorphous structures of the complexes were corroborated by the combination of small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and polarizing optical microscopy (POM). Metal ion coordination of CaSt<sub>2</sub> to flexible PPC chains was determined by Fourier transform infrared spectroscopy (FT-IR). This coordination interaction plays the key role in improving the thermal property of PPC and constructing the self-organized structure of the complexes.

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### 1. Introduction

Poly(propylene carbonate) (PPC), the copolymer of carbon dioxide (CO<sub>2</sub>) and propylene oxide, was first synthesized by Inoue and coworkers in 1969 [1,2]. Over the past decades, considerable attentions have been paid to the development of high efficient catalysts to prepare this material due to the effective fixation and recycling of CO<sub>2</sub> [3,4]. The complete biodegradability and low cost of PPC make it potentially suitable for replacing universal plastics as one-off packaging materials to reduce the amount of polyolefin waste [5]. However, the weak carbonate linkage in the backbone and the noncrystallization of PPC lead to its relatively low glass transition temperature, low thermal decomposition temperature and poor mechanical properties, limiting the practical applications of this copolymer [6]. Although many modification methods including blending PPC with other polymers have been tried to enhance its performances [7,8], so far no substantial achievements have been made.

In recent years, the self-assembled polymer–amphiphile complexes based on specific noncovalent interactions such as hydrogen-bonding [9,10], ionic interactions [11], charge transfer [12,13] and coordination complexation [14,15], have attracted much interest due to the simple fabrication and special functions of the complexes [16]. Many of these complexes have flexible backbones and show pronounced tendency of forming thermotropic liquid crystals with lamellar microphase-separated nanostructures [9,12,13]. It was reported previously that the fatty acid, as a kind of common surfactant, can form comb-like liquid crystalline complexes without mesogenic units when associating with flexible polymers like poly(ethyleneimine) (PEI) [17–20]. These complexes exhibit typical smectic texture even with temperature rising above the melting point of the fatty acid, and this phenomenon has been observed by polarized optical microscopy (POM) and differential scanning calorimetry (DSC) [17,18,20,21]. The association mode of these complexes was further investigated by Fourier transform infrared spectroscopy (FT-IR), and it was found that the specific interactions between functional groups of PEI and fatty acid play a key role in stabilizing the mesomorphous structures at high temperatures [18,20,21].

In our recent publication, we reported the formation of complexes by PPC and octadecanoic acid via hydrogen-bonding

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interactions [22]. The polycarbonate–fatty acid complexes exhibited mesomorphic structure and good resistance to thermal degradation. Calcium stearate ( $\text{CaSt}_2$ ), as a derivative of octadecanoic acid, has been commonly used as surfactant in cosmetics and pharmaceuticals due to its ability to reduce surface tension and to absorb fats [23]. Moreover, this stearate also finds applications as various kinds of process additives such as thermal stabilizer, lubricant and acid scavenger to modify the properties of polymers in plastics industry [24]. Starting from the stabilizing effect of fatty acid and its derivatives such as carboxylates on the thermal stability of polymer matrices including biodegradable polycarbonate,  $\text{CaSt}_2$  was chosen in the present work as a candidate to change the aggregation structure and consequent thermal properties of PPC.

Here we used a facile route to prepare a series of supramolecular complexes of PPC and  $\text{CaSt}_2$ . The thermal stability of PPC was greatly improved after being complexed with  $\text{CaSt}_2$ , demonstrating that calcium stearate has unique capability to improve the thermal property of this aliphatic polycarbonate. More importantly, coordination interaction is proved to form between the noncharged flexible polycarbonate and the calcium ion-containing surfactant, which contributes to the enhancement of thermal stability of PPC and construction of self-assembly aggregates of the complexes.

## 2. Experimental

### 2.1. Materials

Totally biodegradable poly(propylene carbonate) (PPC) was supplied by Mengxi High-tech Materials Company (Inner Mongolia). The residual byproduct in the copolymer was eliminated by a repeated dissolution/precipitation procedure with acetone as solvent and methanol as precipitant. The weight-average molecular weight and the polydispersity index of the purified PPC were determined by gel permeation chromatography (GPC) to be  $1.8 \times 10^5$  and 2.44, respectively. The carbonate unit content of the purified copolymer is 97.2%, estimated from  $^1\text{H}$  NMR spectrum using the method described elsewhere [25,26]. Calcium stearate ( $\text{CaSt}_2$ ) was purchased from Alfa Aesar Co. and used as received. Other reagents were all commercially available and refined according to the standard procedures.

### 2.2. Preparation of PPC– $\text{CaSt}_2$ complexes

Methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) solution (5% w/v) of PPC and  $\text{CaSt}_2$  were mixed at 25 °C in desired weight proportions of  $\text{CaSt}_2$ /PPC:

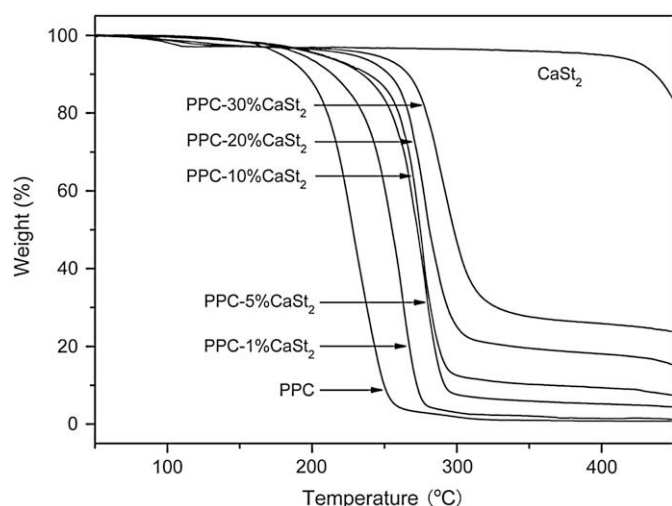


Fig. 1. Thermal stability comparison of PPC– $\text{CaSt}_2$  complexes, PPC and  $\text{CaSt}_2$ .

**Table 1**  
Thermal degradation data of PPC– $\text{CaSt}_2$  complexes, PPC, and  $\text{CaSt}_2$ .

Sample	$T_{5\%}^a$	$T_{\text{max}}^b$
$\text{CaSt}_2$	399.3	450.6
PPC	179.0	205.1
PPC–1% $\text{CaSt}_2$	193.1	238.0
PPC–5% $\text{CaSt}_2$	205.1	256.8
PPC–10% $\text{CaSt}_2$	206.8	259.2
PPC–20% $\text{CaSt}_2$	227.5	262.4
PPC–30% $\text{CaSt}_2$	242.2	271.1

<sup>a</sup>  $T_{5\%}$  is defined as the temperature with 5% weight loss.

<sup>b</sup>  $T_{\text{max}}$  is defined as the temperature with the maximum weight-loss velocity.

1/99, 5/95, 10/90, 20/80 and 30/70. The mixed solutions were stirred for 2 h and then cast onto Petri dishes. Most of the solvent was evaporated at room temperature. For further removal of the residual solvent, all the pre-complexes were dried under vacuum at 65 °C until constant weight. The final complexes were kept in a desiccator before use.

### 2.3. Characterizations

Thermal properties of  $\text{CaSt}_2$ , PPC and PPC– $\text{CaSt}_2$  complexes were evaluated by thermogravimetric analysis (TGA). The thermal degradation process was recorded with a Perkin–Elmer Pyris 1 TGA thermal analyzer. The samples were heated from 20 to 600 °C at a rate of 20 °C/min in a dynamic nitrogen atmosphere. The aggregated structure of the PPC– $\text{CaSt}_2$  complexes was revealed by small-angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and polarizing optical microscopy (POM) technique. SAXS measurement was performed with an Anton Paar SAXSess system using Cu K $\alpha$  radiation ( $\lambda = 0.1541$  nm) at room temperature. The scattering vector  $s$  is given by  $s = (2/\lambda)\sin \theta$ , where  $2\theta$  is the scattering angle. TEM observation was carried out using a JEOL JSM-2200FS model operated at 200 kV. The samples were prepared by adding one drop of 0.3% w/w methylene chloride solution of the complexes on the carbon-coated copper grids and then stained with ethanol solution of uranyl acetate to enhance contrast. The oriented texture of the complexes was observed with a Nikon Eclipse E600 polarizing microscope equipped with a Linkam CSS450 hot stage. The samples were first heated to 140 °C and held for 3 min to eliminate heat history, then sheared into films with a thickness of ca. 30–40  $\mu\text{m}$  and finally quickly cooled down to room temperature. The as-prepared thin films were subjected to

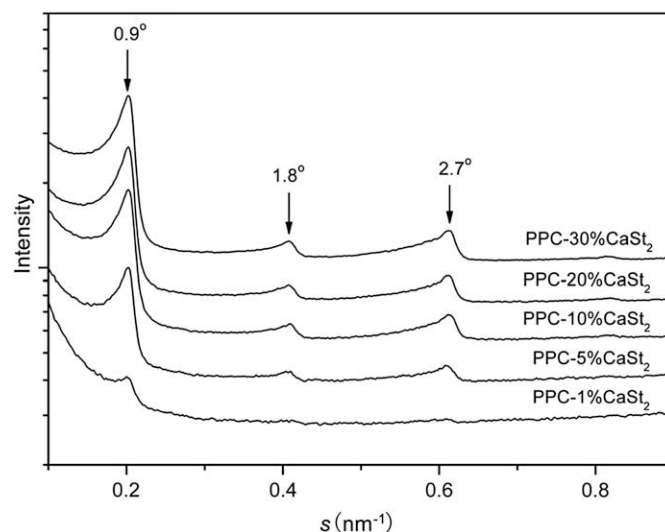


Fig. 2. SAXS measurements of PPC– $\text{CaSt}_2$  complexes at room temperature.

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