



Hydrophilic CaCO₃ nanoparticles designed for poly (ethylene terephthalate)

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ABSTRACT

In this work, a new kind of the hydrophilic CaCO₃ nanoparticles modified by polyethylene glycol phosphate (PGP) was designed for the in-situ preparation of poly (ethylene terephthalate) (PET). It was confirmed that PGP induced the growth of calcite and coated the surface of calcite by the covalent bond. PGP not only adjusts the morphology and the size of CaCO₃ nanoparticles, but also solve the main problems in the in-situ preparation of CaCO₃/PET: (a) the reaction of CaCO₃ with TPA; (b) the agglomeration of CaCO₃ nanoparticles. Compared to the nanocomposite filled with the pure CaCO₃, the resulting nanocomposite filled with the modified CaCO₃ exhibits a better dispersion of the nanoparticles, a higher polymerization degree and a better thermal stability. The results related to the covalent bond formed by PGP on the surface of CaCO₃ and PET during the polymerization of the nanocomposite.

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1. Introduction

Due to the super mechanical properties and high thermal stability, CaCO₃ nanoparticles are filled in many kinds of polymers by the in situ polymerization method [1–4]. However, the research on the in situ polymerization of poly (ethylene terephthalate) (PET) in the presence of CaCO₃ is little.

PET, one of the main engineering plastics, has received extensive research for its wide use in bottles and fibres [5,6]. In modern industry, more and more PET is prepared by terephthalic acid (TPA) and ethylene glycol (EG), but the reaction between CaCO₃ and TPA leads to the difficulties of the in situ preparation of CaCO₃/PET. The second difficulty for the in-situ preparation is that the strong polarity of CaCO₃ surface and the weak particle-polymer affinity result in the agglomeration of nanoparticles and phase separation of the nanocomposite [7]. In the previous study, CaCO₃ was modified by the hydrophobic surfactant to solve these problems and filled into the polymer by blending [8–11]. However, hydrophobic CaCO₃ is incompatible with the monomer EG during the in situ polymerization. The in situ synthesis of CaCO₃/PET nanocomposite is still a significant barrier against efficient and rapid development of PET.

In this paper, we designed the hydrophilic CaCO₃ particles which are suitable for the use in the in-situ preparation of CaCO₃/PET. Polyethylene glycol phosphate (PGP) as surfactant is modified on the surface of CaCO₃ by the covalent bond through a carbonization route.

The morphology and the size of CaCO₃ nanoparticles are adjustable. The formation of the modified CaCO₃ nanoparticles is deduced. The dispersion of the modified CaCO₃ particles, the polymerization degree of PET, the thermal stability of the nanocomposite and the interaction between different components are studied.

2. Experimental procedure

2.1. Materials

All of the chemical reagents used in this study were analytical grade except terephthalic acid (TPA, industrial grade) and ethylene glycol (EG, industrial grade). Distilled water was used throughout the experiments. EG and TPA were both obtained from Petrochina Company Limited Liaoyang Petrochemical Company. Calcium oxide (CaO) was made by Menghe Chemical Reagent Factory. Polyethylene glycol phosphate (PGP) was made in our lab by polyphosphoric acid and polyethylene glycol (PEG) purchased from Sinopharm Chemical Reagent Co. Ltd. Antimony trioxide (Sb₂O₃) was obtained from Fuchen Chemical Plant. Phenol was obtained from Beijing Chemical Reagent Factory. Tetrachloroethane was obtained from Longxi Chemical Plant.

2.2. Preparation of PGP

The preparation procedure for polyethylene glycol phosphate (PGP) was described in our previous paper [12]. A mixture of PEG and polyphosphoric acid was introduced into a 100 mL three-necked flask. After constant stirring for 0.5 h at room temperature, the temperature was increased to 90 °C and maintained for 3 h.

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2.3. Preparation of PGP functionalized CaCO₃ nanoparticles

68 g of CaO was digested in 1000 ml distilled water at 100 °C to form Ca(OH)₂ slurry. After 12 h, the slurry was filtered through a 200 meshes sieve. PGP in a certain quality range was added into 150 ml slurry with vigorous stirring for 0.5 h. Then the carbonization reaction monitored by pH value of the slurry was carried out at 19 °C in water bath. The gas mixed by CO₂ and N₂ with a molar ratio of 1:2 was bubbled into the mixture through a tube at a flow rate of 3 L/min. When pH of the slurry reached 7, the reaction was stopped. The precipitates were collected after filtration and washing with water for three times. The final white powders were dried at 80 °C overnight in an oven. To investigate the effect of PGP, the weight ratio of PGP/CaCO₃ was varied from 0 to 0.4%. And for the test of DTA and TG, the weight ratio of PGP/CaCO₃ was increased to 1.5%.

2.4. Preparation of CaCO₃/PET nanocomposite

PET nanocomposite filled with the functionalized CaCO₃ nanoparticles (1 wt.% of PET) was prepared. 198 ml EG, 7.55 g of the functionalized nanoparticles ($m_{\text{PGP}}/m_{\text{CaCO}_3} = 0.2\%$), 0.52 g of Sb₂O₃ and 520 g of TPA were mixed in a 250 ml three-necked flask with the vigorous stirring. At the first stage, the mixture was maintained at 120 °C for 0.5 h to remove water from the system. At the second stage, the esterification of the mixture was conducted at 190 °C for 1 h and at 240 °C for 4 h, with the pressure of N₂ controlled at 0.4 MPa. At the third stage, the mixture was polymerized at 270 °C for 4 h with the vacuum varied from 4000 Pa to 100 Pa to remove excess EG. The product was released from the round discharge hole with a diameter of 1 cm under the press of N₂ controlled at 0.2 MPa. Then the product was collected in cold water and dried at 80 °C overnight to obtain PET hybrids. The preparation procedure for the pure PET and the pure CaCO₃/PET is similar.

2.5. Characterization

Transmission electron microscopy (TEM) images of CaCO₃ samples were performed on a Hitachi H-800 electron microscope operated at 200 keV. Field-emission scanning electron microscopy (SEM) (JEOL JSM-6700F electron microscope) was used to observe the dispersion of CaCO₃ nanoparticles in the nanocomposite. Energy spectrum of the nanocomposite was also measured by this instrument. Fourier transform infrared spectrometer (FTIR) was characterized on an Omnic system 2000 with KBr pellet method. X-ray diffraction (XRD) technique, using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) on an SHIMADZU-6000 X-ray

diffractometer. A Netzsch STA 409C thermal analyzer carried out the thermogravimetric (TG) and differential thermal analysis (DTA) measurement which was performed from 350 to 550 °C in air, at a heating rate of 10 °C/min. To determine CaCO₃ content of the nanocomposite, 1 g of the sample was broken into solid powder and

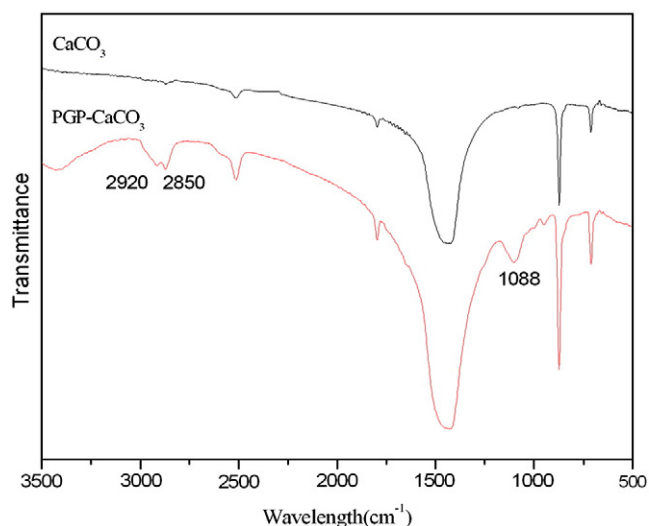


Fig. 1. FTIR of the pure CaCO₃ and the modified CaCO₃.

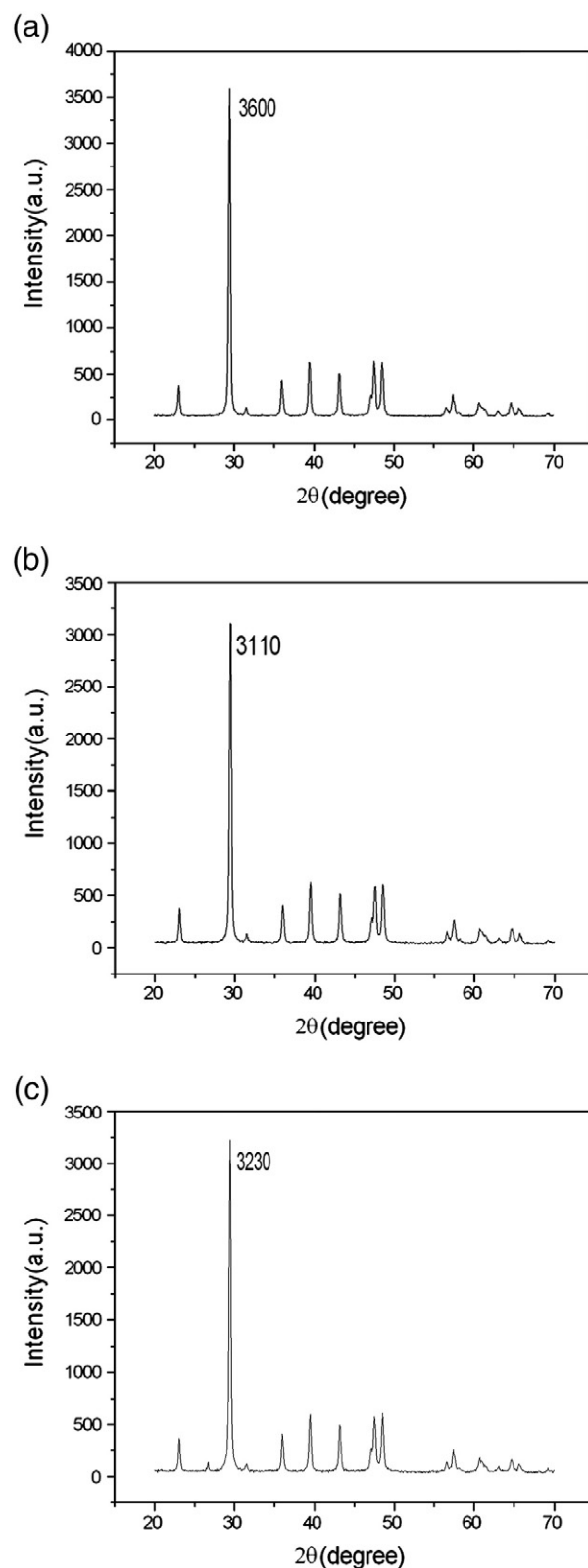


Fig. 2. XRD patterns of (a) the pure CaCO₃, (b) CaCO₃ modified by 0.2% PGP, and (c) CaCO₃ modified by 0.4% PGP.

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