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In-Situ Formation of BHET/Titanium Compound Nanocomposite and its Catalysis for Polyester

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Summary: The tetrabutylorthotitanate (TBOT) was hydrolyzed by H_2O produced during the esterification of pure terephthalic acid (PTA) and ethylene glycol (EG), and the bis(2-hydroxyethyl) terephthalate (BHET)/titanium compound nanocomposite was in-situ formed. The effect of TBOT on the esterification and its product property has been investigated. The results show that the butyl alcohol from the hydrolysis of TBOT is almost distilled out with H_2O and there has no effect on the chemical structure of BHET caused by the introducing of TBOT. A kind of novel titanium compound is manufactured during the esterification under the existence of TBOT, which shows slice-like morphology from SEM micrographs and special XRD pattern with new diffraction peaks between $2\text{-}\Theta = 6.9^\circ$ and 10.2°. It is found that the BHET/titanium compound nanocomposite can act as the catalyst of polymerization of poly(ethylene terephthalate) (PET). The PET resins synthesized by in-situ formed catalyst have almost the same physicochemical properties with the commerced resins and have good spinnability.

Keywords: BHET/titanium compound nanocomposite; catalysis; In-situ formed titanium compound nanocomposits; sol-gel

Introduction

Recently, there is a great interest in organic–inorganic hybrid materials[1–5] since they could exhibit better mechanical, thermal, biological, magnetic, optical, electronic and optoelectronic properties[6–9] compared with the corresponding pure organic or inorganic materials. A lot of organic–inorganic hybrids could be prepared by blending, in-situ polymerization and sol–gel process. Han and co-workers[10] had successfully synthesized poly(ethylene phthalate)/titanium compound nanocomposite fabrics in situ polycondensation which exhibited excellent UV-blocking properties. Matsuura et al.[11] had successfully prepared polysilane–titanium dioxide hybrid thin film with higher photo-durability than polysilane or polysilane–silica hybrid thin film. A new ceramic coatings based on blown soybean oil with titania network had been prepared by Teng and co-workers.[12]

Sol–gel process has proved to be a very good opportunity for the synthesis of variety of organic–inorganic hybrid materials at macro or micro-s cale even at molecular level.[13–14] As we know, the molecular water is produced during the esterification and water is needed by the sol-gel process for preparation of nanomaterials. However, there are few reports on the in situ sol-gel process during esterification. In present work, the esterification process at the

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existence of TBOT has been investigated in detail, and the structure of novel titanium compound formed by in situ sol-gel process of TBOT has been examined by FTIR, SEM and WAXD. The BHET/TiO_2 nanocomposite has originally been used as catalysts for polyester polycondensation and its catalysis as well as the spinnability of the resulted PET resin have been discussed.

Experimental Part

Materials

Pure terephthalic acid (PTA), Ethylene glycol (EG) and 1,4-Butylene glycol (BG) were supplied by Yizheng Chemical Fibre Company Limited of China, Tetrabutylorthotitanate (TBOT) was purchased from Shanghai Chemical Agent Company of China.

Synthesis of BHET/Titanium Compound Nanocomposite

BHET/titanium compound nanocomposite was prepared by adding 3 mol of PTA, 5.4 mol of EG and 0.07 mol of TBOT at 230–260 °C,0.3–0.5 MPa into the 2.5 L polycondensation reactor. The reaction was kept until more than 90% (corresponding to 106.7 mL) of theoretical amount of water was distilled off.

Synthesis of PET with BHET/Titanium Compound Nanocomposite as Catalyst

The PET resins were prepared by adding 3 mol of PTA, 5.4 mol of EG and given amount of BHET/titanium compound nanocomposite into the 2.5 L polycondensation reactor at general condition for direct esterification method.

Fiber Spinning and Drawing

The resins were dried in vacuum for 48 h at 120 °C before spinning. Melt spinning of PET resin was carried out with a model ABE-25 spinning machine at the take-up speed of 800 m/min. The resulted as-spun fiber was then drawn with a Barmag 3010 drawer (Barmag, Germany) set to 80 °C for the heat roller and to 150 °C for the winding roller. The mechanical properties of PET fibers were measured using an AGS-500ND materials testing machine with a gauge length of 250 mm and a tensile speed of 200 mm/min.

Characterization

The upper layer liquid distilled out with H_2O during the esterification process and BHET/titanium compound nanocomposite were characterized with a Nicolet-20SX-B Fourier Transform Infrared (FTIR) Spectrometer.

The morphology of BHET/titanium compound nanocomposite was obtained by a Scanning Electron Microscopy (JSM-5600LV, Japan).

The WAXD experiments of BHET/titanium compound nanocomposite were performed using a Rigaku model D/max-B automatic diffract meter with Cu target. The generator was operated at 40 kV and 40 mA. Samples were scanned from $2\theta = 5$ to 80°.

The thermal properties of resins were analyzed by using a Differential Scanning Calorimeter (DSC822, Mettler-Toledo Star System, Switzerland). The instrument was calibrated with an Indium standard ($T_m = 156.6\,^\circ C$, $\Delta H_f = 28.5$ J/g), and the measurement was conducted under a nitrogen atmosphere. The sample weight used in the DSC pan was kept within 6–8 mg. The samples were first heated up from room temperature to 290 °C at a rate of 10 °C/min and then maintained there for 5 min to destroy all memories of the previous thermal and mechanic histories. They were cooled down to room temperature at a rate of 10 °C/min and then heated up to 290 °C at the same rate. The crystallization temperature (T_c), the glass transition temperature (T_g) and the melt temperature (T_m) were determined from the peak of the DSC thermograms.

Results and Discussion

Esterification Process under the Existence TBOT

TBOT (0.07 mol) was introduced to the direct esterification system between PTA (3 mol) and EG (5.4 mol) by mixing TBOT with EG. The distilled liquid from condenser tube during the esterification process was collected and it is found that the liquid obviously has two layers. The chemical structure of upper liquid was characterized by FTIR and compared with butyl alcohol. As shown in Figure 1, the FTIR spectrum of the upper liquid has the absorbing peak at 3333 cm^{-1} belonging to the O–H stretching vibration, the two peaks at 2958 cm^{-1} and 2933 cm^{-1} assigned to the C–H stretching vibration, and the strong band at 1040 cm^{-1} attributed to the C–O stretching vibration of $R–CH_2–OH$. The FTIR spectrum of the upper liquid is quite similar to that of butyl alcohol except the transmittance indicating that the upper liquid is butyl alcohol from the hydrolysis of TBOT by water. The water is formed by the esterification between PTA and EG.

The volume of butyl alcohol and water distilled from esterification system was recorded at different time. As shown in Figure 2, the volume of butyl alcohol firstly increased but kept at about 13.0 mL unchanged after the liquid was discharged about 30 min, while the volume of water was kept increasing until the esterification process was finished. The total volume of butyl alcohol distilled from esterification system, about 13.0 mL, is almost amount to the theoretical value, 13.2 mL. And the total volume of water distilled from esterification system, 105 mL, is comparative to the theoretical value, 106.7 mL. These mean that the butyl alcohol from TBOT has been totally discharged from esterification system and the degree of esterification between PTA and EG can amount to 98.4%. So it can be deduced that there has no effect on the chemical structure of BHET caused by the introducing of TBOT.

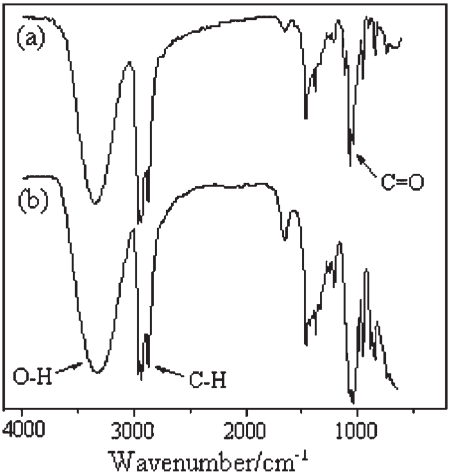

Figure 1.
FTIR spectra of butyl alcohol. (a) and the upper liquid. (b) distilled from esterification system.

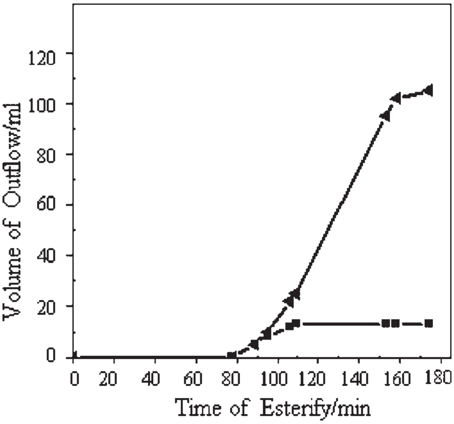

Figure 2.
Dependence of discharging on esterification time; ▲ - = water, ■ = butyl alcohol.

Structure of BHET/Titanium Compound Nanocomposite

The structure of the products of esterification between PTA and EG under the existence of different amount of TBOT has been characterized by SEM, WAXD and FTIR as shown in Figure 3, Figure 4 and Figure 5. TBOT has been assumed to be totally transferred to TiO_2, therefore the products prepared at different amount of TBOT have been represented by 0.3%, 0.5% and 1%. As shown in Figure 3, compared to the SEM micrograph of pure BHET, a new phase with slice-like morphology is homogeneously dispersed in the BHET matrix in those SEM micrographs of the products prepared at different amount of TBOT. Its thickness can amount to 100 nm as shown in Figure 3(b).

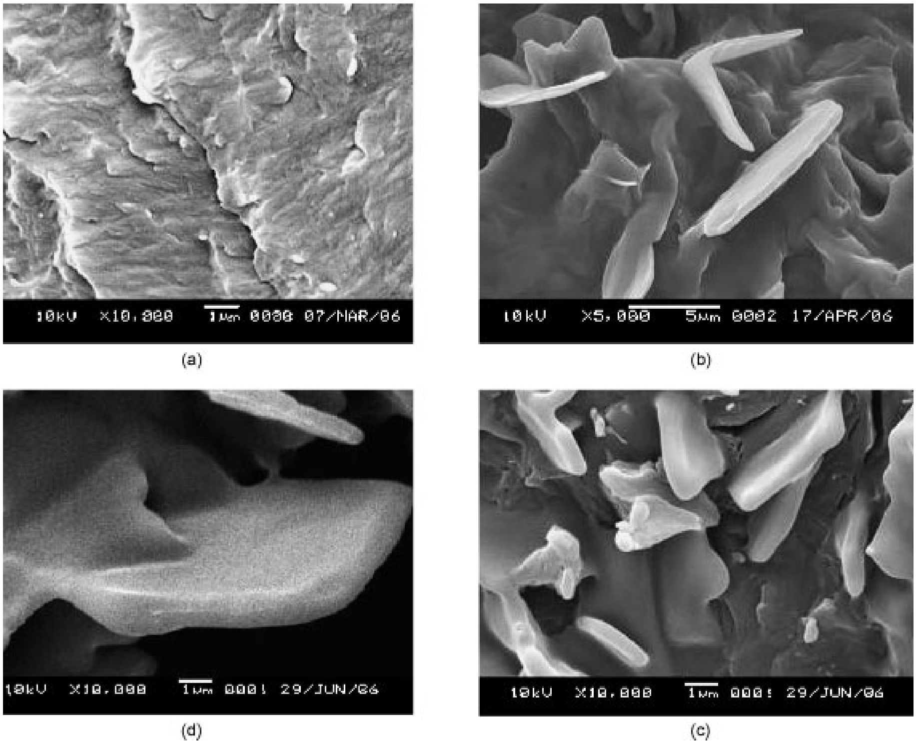

Figure 3.
SEM images of BHET and the products prepared at different amount TBOT((a) Pure BHET, (b)BHET/Titanium compound nanocomposite, 0.3%, (c)BHET/Titanium compound nanocomposite, 0.5%, (d)BHET/Titanium compound nanocomposite,1.0%).

Figure 4(a) and Figure 4(b) show the WAXD patterns of pure BHET and the products prepared at different amount of TBOT. Compared with the pattern of pure BHET, those of the products show a series of new diffraction peaks between 2-$\Theta = 6.9^\circ$ and 10.2°, and their intensity increases with the titanium content. These diffraction peaks with lower 2-Θ may attribute to slice-like morphology of the products.

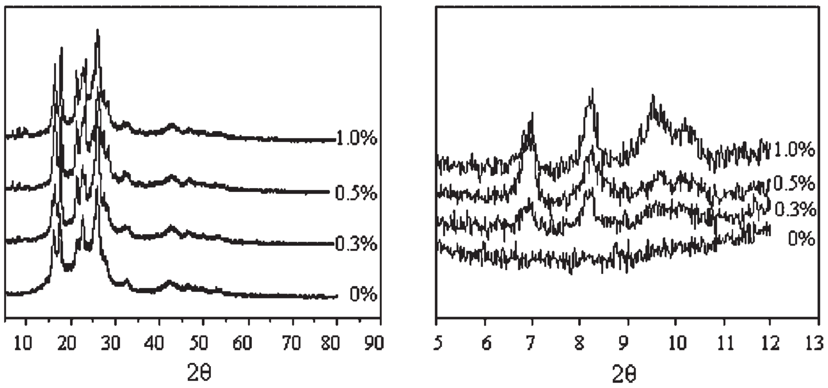

Figure 4.
XRD patterns of BHET with various TiO_2 contents.

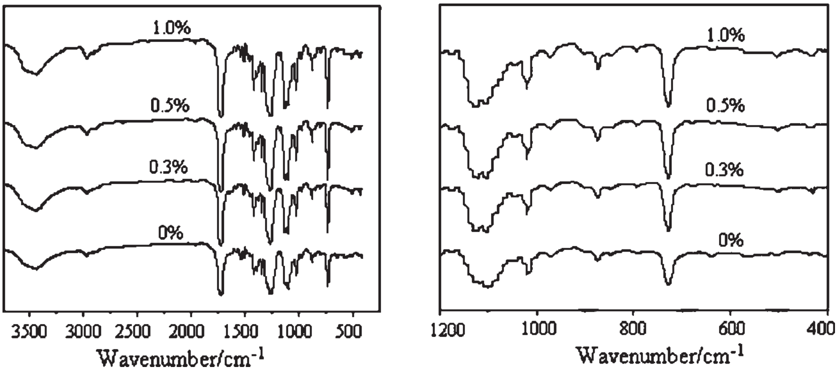

Figure 5.
FTIR spectra of BHET with various titanium contents.

Figure 5(a) and Figure 5(b) show the FTIR spectra of pure BHET and the products prepared at different amount of TBOT. In the FTIR spectra of the products, there occur the peaks among 500 cm^{-1} and 600 cm^{-1} belonging to Ti–O, and the new peak at 1100 cm^{-1} attributed to Ti–O–C. Except these peaks there has been no difference between the FTIR spectrum of pure BHET and the products prepared at different amount of TBOT. It indicates that titanium compound with a special chemical structure and slice-like morphology is formed via an in situ sol-gel process and the product is the composite of BHET and the titanium compound.

Catalysis of BHET/Titanium Nanocomposite

The BHET/titanium compound nanocomposite was used as the catalyst for synthesis of PET. Its catalyst activity at different concentration and physicochemical properties of resulted PET resin were shown in Table 1. It can be seen that the condensation polymerization period decreases with increasing the concentration of the catalyst at the same high vacuum condition. The condensation polymerization period was just 80 min as the dosage of catalysts was 16.5 ppm. The transparency (L value) of PET increases while the yellowness coefficient (b value) decreases with decreasing

Table 1.
The catalyst activity of BHET/titanium nanocomposite and the physicochemical properties of resulted PET.

Physicochemical properties	Catalyst		
	BHET/titanium nanocomposite		
Dosage of catalyst (1)/10-6	16.5	33	50
Polymerization period (2)/min	80	70	66
L(3)	73.99	72.04	71.94
b(3)	8.82	11.26	16.12
a(3)	−1.84	−2.51	−3.63
DEG/%	4.30	3.87	3.61
Carboxyl content/mol · kg−1	6.4	21.4	17.9
Relative viscosity/dl · g−1	0.638	0.630	0.647
Tg/°C	72.51	74.56	74.5
Tm/°C	241.47	242.97	243.25

[*] (1) The dosage of catalyst is the corresponding dosage of TiO2 content in composites.

[b] (2) The condensation polymerization period at high vacuum is from the time when the vacuum degree in reaction kettle is lower than 50 Pa to the time when the reaction is over.

[b] (3) The value of L, a and b can describe the hue of PET resin, L represents the brightness measure and the luminousity at range from 0 to 100 (100 = white;0 = black),a is a measure of red tones and it varies from −a to +a(−a = green, +a = red), and b is a measure of yellow tones and it varies from -b to +b (−b = blue,+b = yellow).

Table 2.
Spinnability of the resulted PET resin.

Screw temperature/°C	Pump delivery/g · min^{-1}	Spinpack pressure/MPa	Screw presure/MPa	Screw speed/rpm	Winding ability	Drawing ability
285–297	30	48–51	58–59	41	good	good

the dosage of catalysts. When the dosage of catalysts is 16.5 ppm, the value of b of PET is 8.82, which is almost up to the first quality of PET resin for fiber making. Carboxyl content is relatively low, indicating the relatively narrow molecular weight distribution of the resulted PET. The value of T_g was not affected markedly, but the melting temperature (T_m) decreases with increasing the dosage of catalyst in feed.

The resulted PET resin has the same good physicochemical properties in the condition from little content reactor. The BHET/titanium compound nanocomposite possesses catalysis in comparison with the common titanic catalysts for polyester polycondensation.

The spinnability of the resulted PET resin synthesized at 16.5 ppm of the catalyst has been examined at a model ABE-25 spinning machine. As shown in Table 2, the spinnpack pressure keeps stable at 48–51 MPa and winding ability is good as well as drawing ability when chest temperature is 305 °C and the pump delivery is 35.6 g · ml^{-1}. The tensile strength of resulted PET fiber gradually increases with draw ratio and it can amount to 3.78 cN/dtex when the draw ratio is 4 (see Figure 6). These indicate that the resulted PET resins have good spinnability.

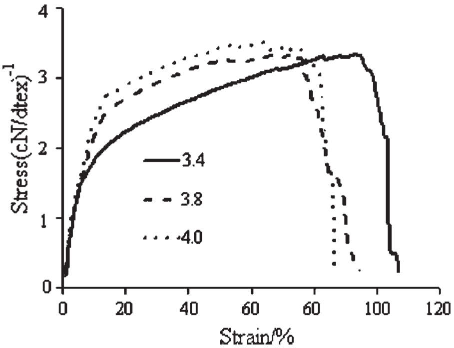

Figure 6.
Stress-strain curves of resulted PET fiber with different drawing ratio.

Conclusion

The bis(2-hydroxyethyl)terephthalate (BHET)/titanium compound nanocomposite can be synthesized by esterification between PTA and EG at the existence of tetrabutylorthotitanate (TBOT). The TBOT is hydrolyzed by H_2O produced during the esterification of pure terephthalic acid (PTA) and ethylene glycol (EG), and the butylalcohol from the hydrolysis of TBOT is almost distilled out with H_2O and there has no effect on the chemical structure of BHET caused by the introducing of TBOT. A kind of novel titanium compound is manufactured during the esterification under the existence of TBOT, which show slice-like morphology from SEM micrographs and special XRD pattern with new diffraction peaks between $2\text{-}\Theta = 6.9°$ and $10.2°$. The BHET/titanium compound nanocomposite possesses catalysis in comparison with the common titanic catalysts for polyester polycondensation. The resulted PET resins have good spinnability and the tensile strength of resulted PET fiber can amount to 3.78 cN/dtex when the draw ratio is 4.

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