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Double *in-situ* approach for the preparation of polymer nanocomposite with multi-functionality

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Abstract: A novel one-step synthetic route, the double in-situ approach, is used to produce both TiO_2 nanoparticles and polymer (PET), and simultaneously forming a nanocomposite with multi-functionality. The method uses the release of water during esterification to hydrolyse titanium (IV) butoxide ($Ti(OBu)_4$) forming nano-TiO_2 in the polymerisation vessel. This new approach is of general significance in the preparation of polymer nanocomposites, and will lead to a new route in the synthesis of multi-functional polymer nanocomposites.

Key words: ***in-situ*** **polymerisation; nanocomposites; Polyesters; Flame retardance; fire retardant**

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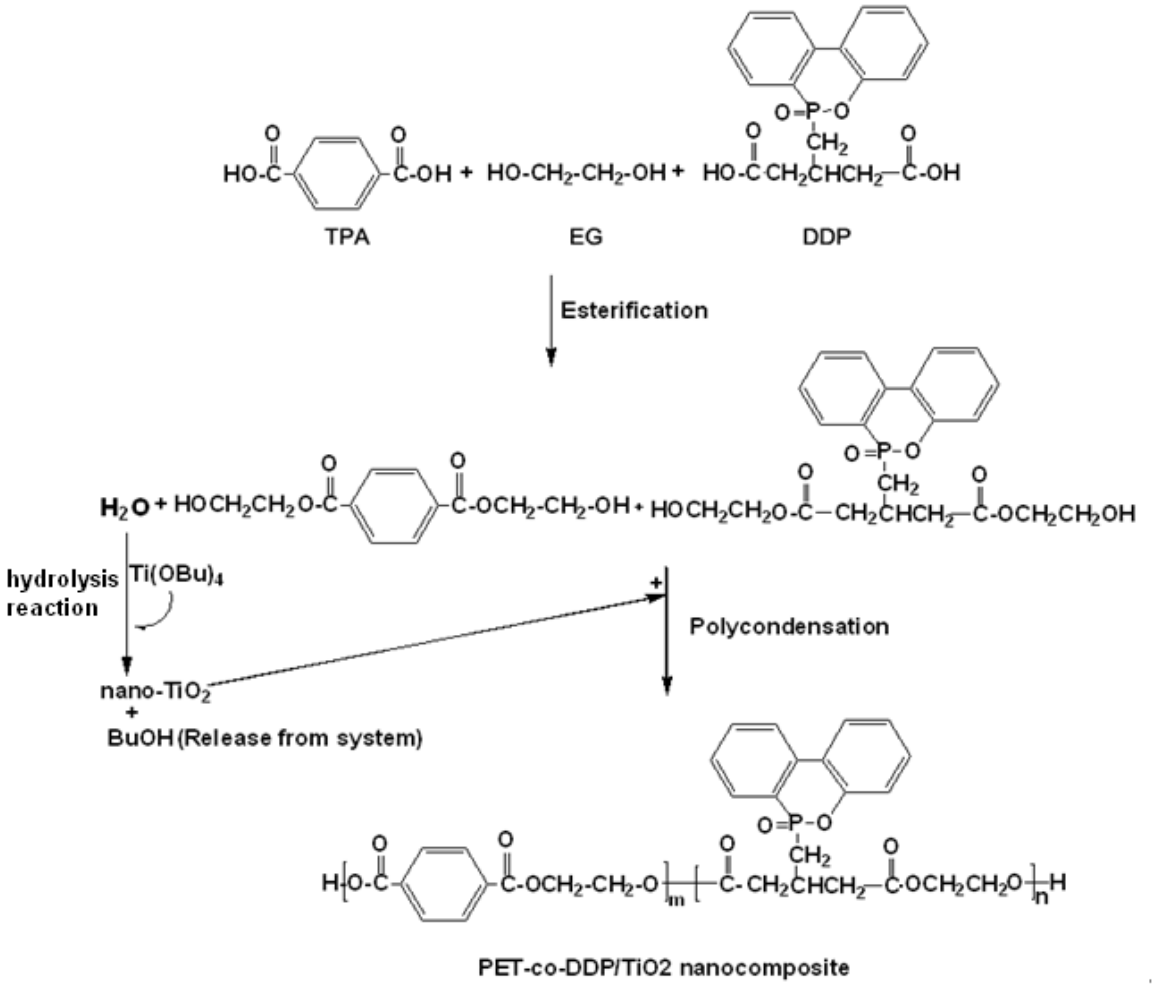
INTRODUCTION

Polymer nanocomposites represent a new class of composite materials and have attracted considerable interest during the past few years particularly as a result of their enhanced properties i.e., fire retardation, mechanical, electrical and thermal properties. Many methods of preparing nanocomposites have been investigated, such as organic and inorganic hybridization, self-organization, *in-situ* polymerization, and so on. However, the addition of nanoparticles to the polymer matrix has been the most commonly adopted method for producing polymer nanocomposites. It is usually necessary for the nanoparticle surface to be modified in order to obtain good dispersion in the polymer. Since the pioneering work of Fujishima et al. [1,2], titanium dioxide (TiO_2) has been investigated during the last decade because of its scientific and technological importance [3]. For example, TiO_2 nanocomposites have been shown to display considerable antibacterial activity. Polymer nanocomposites have been shown to improve mechanical and flame retardant properties. The properties of TiO_2 have been studied extensively [4-10]. Generally methods of preparation of TiO_2 nanostructures involve an alkali treated hydrothermal reaction [11,12], template [13,14] and surfactant-directed methods [15]. However, the search for a one-pot synthesis of nanoscopic TiO_2 with well controlled size and shape is still a major challenge because the hydrolysis reaction is so fast [16]. One method of forming titanium complexes is by a ligand reaction to slow down the hydrolysis reaction for the preparation of nano-TiO_2 [17]. There have also been investigations of the preparation the polymer/TiO_2 nanocomposites using the addition of nano-TiO_2 particles in order to improve the mechanical properties [18]. To date there have been no reports

of a double *in-situ* approach for the preparation of functional polymer nanocomposites. In this communication, a new double *in-situ* approach for the preparation of PET/titanium dioxide (TiO_2) nanocomposites with flame retardant properties is reported. The concepts of this method are of general significance in the preparation of polymer nanocomposites.

Nano-TiO_2 has generally been prepared by the hydrolysis of titanium precursors, such as titanium (IV) butoxide ($Ti(OBu)_4$) and titanium (IV) chloride ($TiCl_4$). These hydrolyses are so fast that the nucleation and growth steps are not well separated [19]. Effective control of the hydrolysis is thus a prime difficulty. In the present approach, based on our previous work, we take advantage of the continuous generation of small quantities of water produced by an esterification reaction between terephthalic acid (TPA), 9, 10 - dihydro-10 [2,3-di(hydroxycarbonyl)propyl]-10-phosphaphenenthrene-10-oxide(DDP) and ethylene glycol (EG) to hydrolyse the organotitanium at a controlled rate (Scheme 1). We have called this a double *in-situ* approach, because the *in-situ* synthesis of the nano-particle (TiO_2) coincides with the *in-situ* polymerization, resulting in the formation of a well-dispersed polymer nanocomposite. To our knowledge, this is the first one step synthesis of a fire retarded PET/TiO_2 nanocomposite to be reported. Furthermore, it is observed that the novel PET nanocomposite significantly improves the fire retardant performance of PET.



Scheme 1 The single-step synthesis of fire retardant PET/TiO2 nanocomposite

EXPERIMENTAL

PET-co-DDP/ TiO_2 nanocomposites, containing 1% TiO_2 and 1% phosphorous, were prepared from TPA (860 g), EG (450 ml), DDP (126 mg) and $Ti(OBu)_4$ (48 ml). All the reagents were introduced to a reactor equipped with a nitrogen inlet, a condenser and a mechanical stirrer. The reactor was heated to 240ºC under high pressure (0.4-0.5MPa) and maintained for 2 h. During this stage, $Ti(OBu)_4$ was hydrolyzed by the water from the esterification reaction, simultaneously with the release of BuOH and excess water. After this stage, the pressure of the reactor was reduced to less than 100 Pa and maintained for 1.5 h. The excess water and BuOH was separated from the polymerization system, measured and

used to judge the extent of the reaction.

Characterization of the dispersion of the nanofiller within a nanocomposite is confirmed by TEM and SEM. TEM images of the nanocomposite specimens were taken at room temperature. The TEM grids were mounted in a liquid nitrogen cooled sample holder. Ultrathin sectioning (50–70 nm) was performed by ultramicrotomy at low temperature using a Reichert Ultracut E low temperature sectioning system. A transmission electron microscope (JEM-100CX, JEOL) operated at 80kV was used to obtain the images of the nanocomposite specimens. In addition, the PET-co-DDP/TiO_2 nanocomposite was made into films which were broken in liquid N_2. The fresh sample face was coated with gold for SEM observation. The sample was observed under a JEOL JSM-5410 scanning electron microscope with a working voltage of 20 kV. The limiting oxygen index (LOI) values were measured on a JF-3 oxygen index apparatus (Jiangning, China) with sheet dimensions of 130×6.5×3 mm^3 according to ASTM D2863-97. Vertical burning tests (UL-94) were conducted on a vertical burning test instrument (CZF-2-type) (Jiangning, China) with sheet dimensions of 130×13×3 mm^3 according to ASTM D3801.

RESULTS AND DISCUSSION

As the reaction proceeded, the collected liquid separated to show two clear layers: the upper is BuOH confirmed by comparison of its refractive index against standard BuOH; the lower layer is water. The presence of the two layers indicates that the hydrolysis reaction has occurred as predicted, while the quantities of water and BuOH indicate the extent of each reaction. The theoretical yields are 191 ml of water and 52 ml of BuOH. The actual volume

of water removed was 184 ml and of BuOH was 50 ml. Thus the extent of the reaction was more than 96%.

TEM images of the nanocomposite specimens were taken at room temperature. The results are shown in fig.1 and fig.2, respectively.

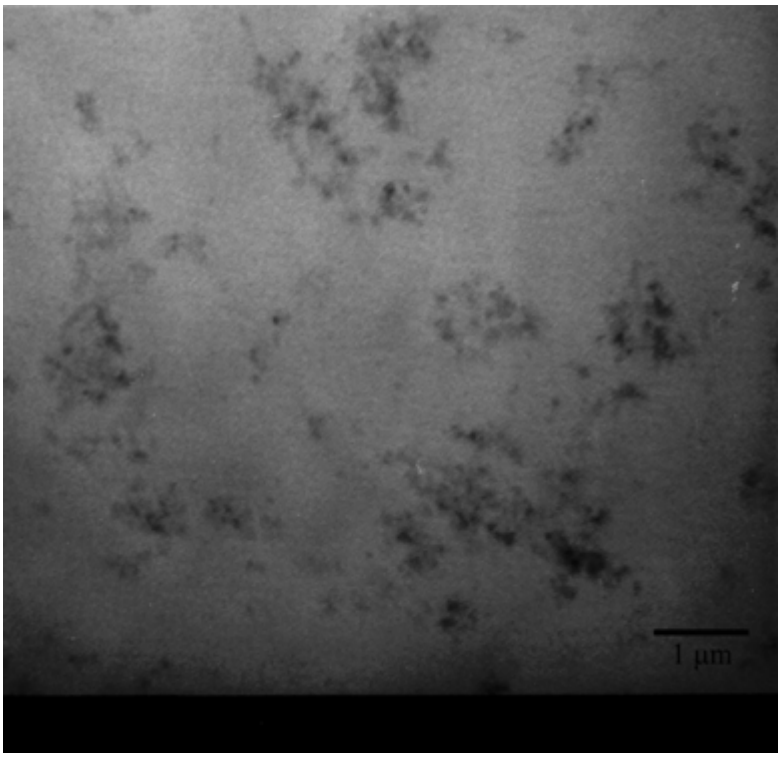


Fig. 1 TEM images for the nanocomposite

a) b)

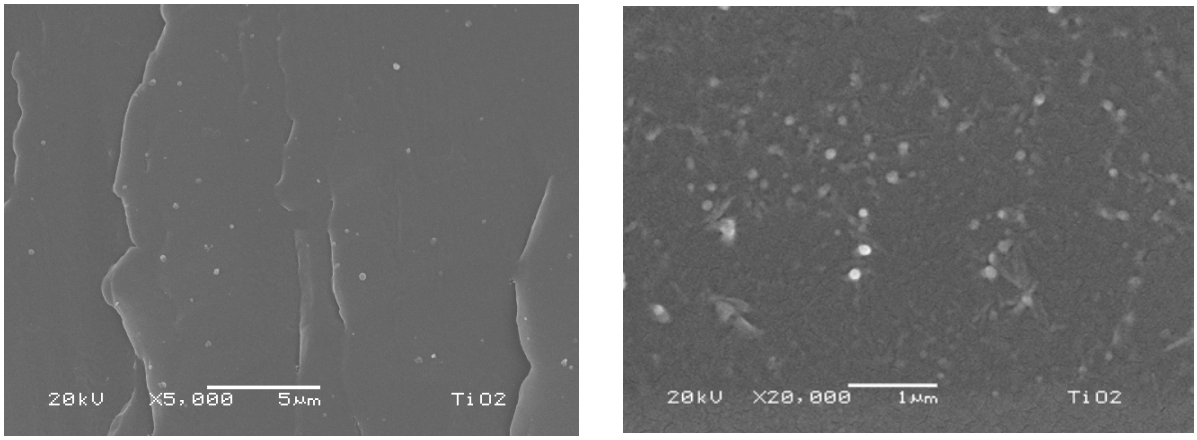


Fig. 2 SEM images for the nanocomposite (a) ×5000; (b) ×20000

From the SEM images in fig. 2, it can be observed that the TiO_2 nanoparticles form as spheres which are uniformly dispersed in the polymer matrix. This is also observed by TEM (Fig. 1). The particle diameters are mainly under 100 nm. These observations are in accordance with polymer/TiO_2 nanocomposite produced by the addition of nano-TiO_2 particles to the polymer matrix [18]. Thus our novel one-step synthesis route produces a typical PET/TiO_2 nanocomposite.

The fire retardant properties of this PET/TiO_2 nanocomposite have been characterized by LOI and UL-94. The results of these tests are shown in table 1 and compared with those of PET and PET-co-DDP. It can be observed that the fire retardant performance of the nanocomposite is an improvement, compared to the polymer and copolymer. The LOI values have risen from 21.2 and 30.8 to 32.6 on forming the nanocomposite. More significantly the UL-94 rating, based on a vertical upward flame spread test, has been improved from V-2 to V-0, although the total nanoparticle content is only 1%. Essentially, this is a consequence of the increase in melt viscosity near the burning temperature reducing the tendency to drip. A V-2 classification shows limited flame spread but the presence of flaming drips, while V-0 shows self-extinguishing behaviour without burning drips. While the increase in melt viscosity is to be expected on incorporation of well dispersed nanofiller, this stabilization of the polymer matrix allows the surface temperature to increase more rapidly increasing the ease of ignition. Since the LOI measures ease of extinction, which essentially depends on the same physical phenomena as ignition, the results suggest that there has been a simultaneous improvement in both the dripping and ignition resistance. Thus the nanocomposite formulation has the potential to improve the burning behaviour of fire retardant PET.

Thermogravimetric (TG) analysis studies (unpublished work) also show that the PET-co-DDP/TiO_2 nanocomposite is more thermally stable than either PET or PET-co-DDP. The multifunctional properties TiO_2 nanoparticles provide hope that the PET-co-DDP/TiO_2 nanocomposite will have other exploitable properties besides fire retardancy. Further work is required to confirm this.

Sample	P wt%	TiO2 wt%	LOI	UL-94
PET	0	0	21.2	----
PET-co-DDP	1	0	30.8	V-2
PET-co-DDP/TiO_2 nanocomposite	1	1	32.6	V-0

Table 1 The LOI values and UL-94 test results

CONCLUSIONS:

A novel one-step synthetic route, the double in-situ approach, has resulted in both TiO_2 nanoparticles and polymer (PET), leaving the nano-titania dispersed in the polymer as a nanocomposite. This was achieved by the release of water during the esterification reaction, forming polyester, which hydrolyzed the titanium (IV) butoxide forming nano-titania. Normally, this rapid reaction results in larger titania particles, but in this case it was inhibited by the polymer which formed around each nonoparticle. Based on the observation of SEM and TEM images, TiO_2 nanoparticles form as spheres which are uniformly dispersed in the polymer matrix, the diameters are mainly under 100 nm. In comparison with fire retarded properties of PET and PET-co-DDP, the performance of the nanocomposite formed by the double *in situ* approach resulted in a significant improvement: LOI value 32.6, UL-94 rating V-0. It is most notable that UL-94 rating, which uses a vertical upward flame spread test, has been improved from V-2 (PET-co-DDP) to V-0 (PET-co-DDP/TiO_2 nanocomposite), although the total nanoparticle content is only 1%. Essentially, this is a consequence of the increase in melt

viscosity near the burning temperature reducing the tendency to drip. This novel approach overcomes two of the barriers to polymer nanocomposite formation – synthesis and agglomeration-prevention of nanoparticles, and ensuring nanodispersion within the polymer. This work is of significance to the preparation of polymer nanocomposites involving condensation polymerization, such as polyesters.

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