

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 TiO₂ nanoparticles and polymer (PET), and simultaneously forming a nanocomposite with multi-functionality. The method uses the release of water during esterification to hydrolyze titanium (IV) butoxide (Ti(OBu)₄) forming nano-TiO₂ in the polymerization 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.

Keywords In situ polymerization · Nanocomposites · Polyesters · Flame retardance · Fire retardant

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 and coworkers [1, 2], titanium dioxide (TiO₂) has been investigated during the last decade because of its scientific and technological importance [3]. For example, TiO₂ nanocomposites have been shown to display considerable antibacterial activity. Polymer nanocomposites have been shown to improve mechanical and flame retardant properties. The properties of TiO₂ have been studied extensively [4–10]. Generally methods of preparation of TiO₂ 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-TiO₂ 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-TiO₂ [17]. There have also been investigations of the preparation of the polymer/TiO₂ nanocomposites using the addition of nano-TiO₂ 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 (TiO₂) nanocomposites with flame retardant properties is reported. The concepts of this method are of general significance in the preparation of polymer nanocomposites.

Nano-TiO₂ has generally been prepared by the hydrolysis of titanium precursors, such as titanium (IV) butoxide

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(Ti(OBu)₄) and titanium (IV) chloride (TiCl₄). These hydrolyzes 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 (E.G) to hydrolyze the organotitanium at a controlled rate (Scheme 1). We have called this a double in situ approach, because the in situ synthesis of the nanoparticle (TiO₂) 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/TiO₂ nanocomposite to be reported. Furthermore, it is observed that the novel PET nanocomposite significantly improves the fire retardant performance of PET.

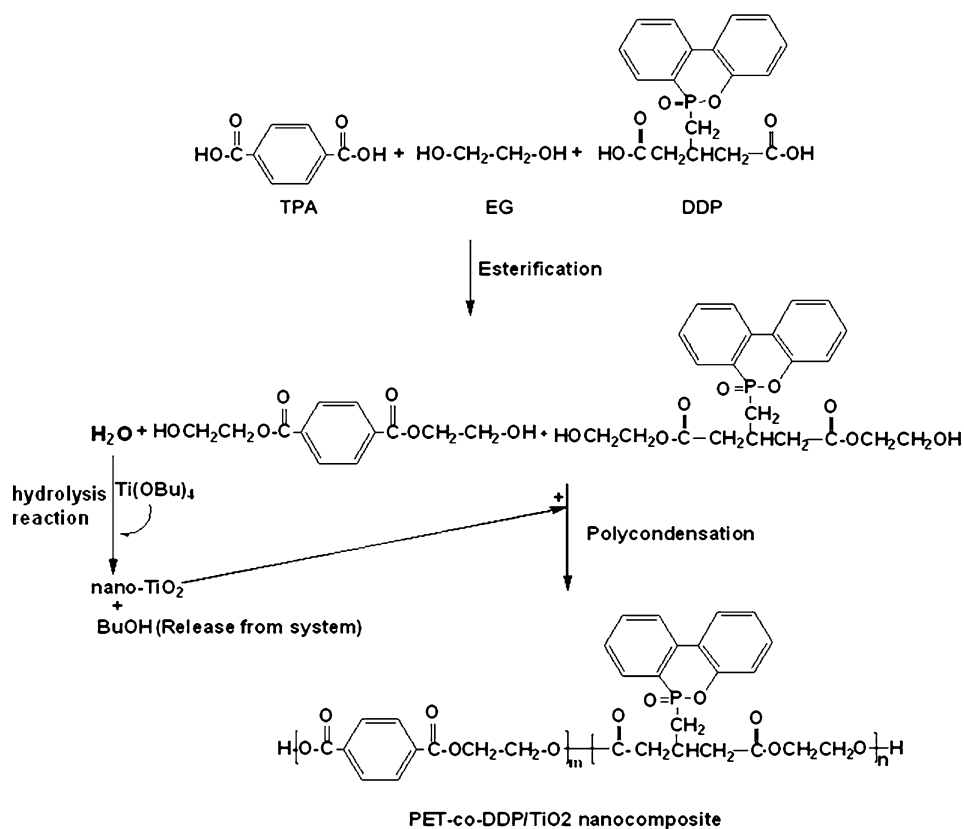
Experimental

PET-co-DDP/TiO₂ nanocomposites, containing 1% TiO₂ and 1% phosphorous, were prepared from TPA (860 g), E.G (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 240 °C under high pressure (0.4–0.5 MPa) 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 transmission electron microscope (TEM) and scanning electron microscope (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 TEM (JEM-100CX, JEOL) operated at 80 kV was used to obtain the images of the nanocomposite specimens. In addition, the PET-co-DDP/TiO₂ nanocomposite was made into films, which were broken in liquid N₂. The fresh sample face was coated with gold for SEM observation. The sample was observed under a JEOL JSM-5410 SEM with a working

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



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 $130 \times 6.5 \times 3 \text{ mm}^3$ 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 $130 \times 13 \times 3 \text{ mm}^3$ 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 and 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%.

Transmission electron microscope images of the nanocomposite specimens were taken at room temperature. The results are shown in Figs. 1 and 2, respectively.

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.

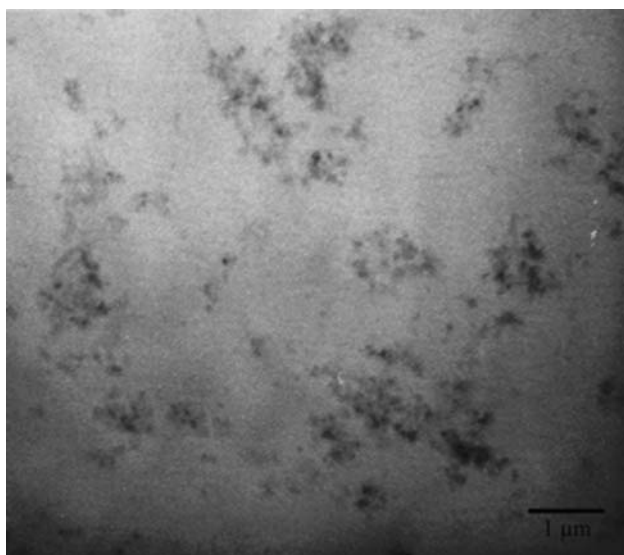


Fig. 1 TEM images for the nanocomposite

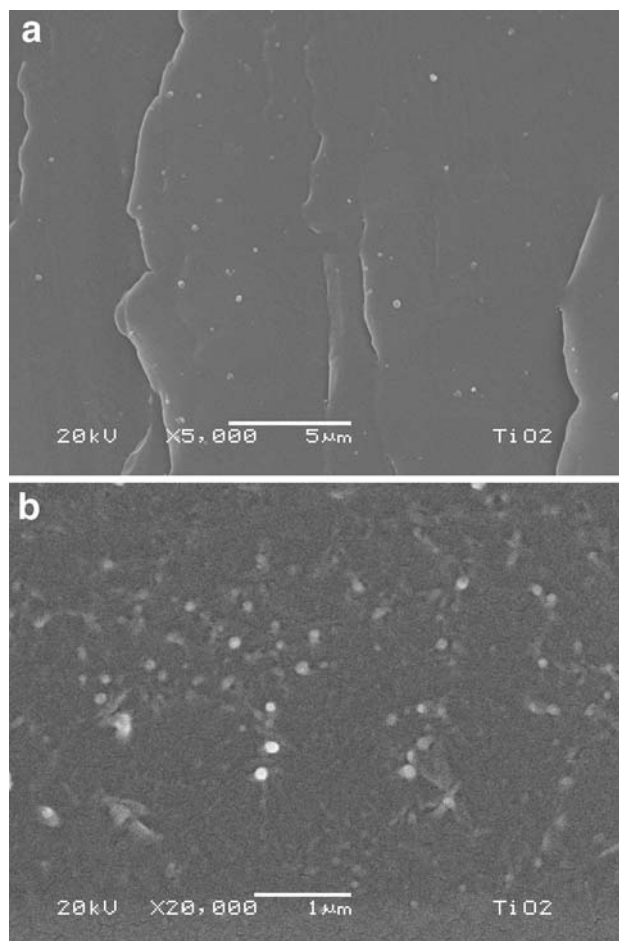


Fig. 2 SEM images for the nanocomposite: **a** $\times 5,000$ and **b** $\times 20,000$

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 to 30.8–32.6 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

Table 1 The LOI values and UL-94 test results

Sample	P (wt%)	TiO_2 (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

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 analysis studies (unpublished work) also show that the PET-co-DDP/TiO₂ nanocomposite is more thermally stable than either PET or PET-co-DDP. The multifunctional properties TiO₂ nanoparticles provide hope that the PET-co-DDP/TiO₂ nanocomposite will have other exploitable properties besides fire retardancy. Further work is required to confirm this.

Conclusions

A novel one-step synthetic route, the double in situ approach, has resulted in both TiO₂ 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 nanoparticle. Based on the observation of SEM and TEM images, TiO₂ 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/TiO₂ 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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References

1. A. Fujishima, K. Honda, *Nature* **37**, 238 (1972)
2. R. Wang, K. Hashimoto, A. Fujishima, *Nature* **388**, 431 (1997). doi:[10.1038/41233](https://doi.org/10.1038/41233)
3. S.J. Bu, Z.G. Jin, X.X. Liu, L.R. Yang, Z.J. Cheng, *J. Eur. Ceram. Soc.* **25**, 673 (2005)
4. R. Asahi, T. Morikawa, T. Ohwaki, A. Aoki, Y. Taga, *Science* **293**, 269 (2001). doi:[10.1126/science.1061051](https://doi.org/10.1126/science.1061051)
5. T. Umabayashi, T. Yamaki, H. Itoh, K. Asai, *Appl. Phys. Lett.* **81**, 454 (2002). doi:[10.1063/1.1493647](https://doi.org/10.1063/1.1493647)
6. T. Sano, N. Negishi, K. Koike, K. Takeuchi, S. Matsuzawa, *J. Mater. Chem.* **14**, 380 (2004). doi:[10.1039/b311444a](https://doi.org/10.1039/b311444a)
7. X.Q. Li, L. Zhang, J. Mu, J.L. Qiu, *Nanoscale Res. Lett.* **3**, 169 (2008). doi:[10.1007/s11671-008-9132-6](https://doi.org/10.1007/s11671-008-9132-6)
8. H. Tokudome, M. Miyauchi, *Chem. Lett.* **33**, 1180 (2004)
9. P.K. Thomas, S.K. Satpathy, Æ.I. Manna, K.K. Chakraborty, G.B. Nando, *Nanoscale Res. Lett.* **2**, 397 (2007). doi:[10.1007/s11671-007-9074-4](https://doi.org/10.1007/s11671-007-9074-4)
10. L. Manna, E.C. Scher, L.S. Li, *J. Am. Chem. Soc.* **124**, 7136 (2002). doi:[10.1021/ja025946i](https://doi.org/10.1021/ja025946i)
11. Y. Zhu, H. Li, Y. Koltypin, Y.R. Hacoben, A. Gedanken, *Chem. Commun.*, 2616 (2001)
12. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Adv. Mater.* **11**(15), 1307 (1999). doi:[10.1002/\(SICI\)1521-4095\(199910\)11:15<1307::AID-ADMA1307>3.0.CO;2-H](https://doi.org/10.1002/(SICI)1521-4095(199910)11:15<1307::AID-ADMA1307>3.0.CO;2-H)
13. Z.Y. Zhong, Y. Yin, B. Gates, Y. Xia, *Adv. Mater.* **12**, 206 (2000). doi:[10.1002/\(SICI\)1521-4095\(200002\)12:3<206::AID-ADMA206>3.0.CO;2-5](https://doi.org/10.1002/(SICI)1521-4095(200002)12:3<206::AID-ADMA206>3.0.CO;2-5)
14. P. Hoyer, *Langmuir* **12**, 1411 (1996). doi:[10.1021/la9507803](https://doi.org/10.1021/la9507803)
15. K. Kanic, T. Sugimoto, *Chem. Commun.*, 1584 (2004)
16. Z.Y. Zhong, T.P. Ang, J.Z. Luo, H.C. Gan, A. Gedanken, *Chem. Mater.* **17**, 6814 (2005). doi:[10.1021/cm051695b](https://doi.org/10.1021/cm051695b)
17. P.D. Cozzoli, A. Kornowshi, H. Weller, *J. Am. Chem. Soc.* **125**, 14539 (2003). doi:[10.1021/ja036505h](https://doi.org/10.1021/ja036505h)
18. B.D. Yang, K.H. Yoon, K.W. Chung, *Mater. Chem. Phys.* **83**, 334 (2004). doi:[10.1016/j.matchemphys.2003.10.003](https://doi.org/10.1016/j.matchemphys.2003.10.003)
19. X. Jiang, T. Herricks, Y. Xia, *Adv. Mater.* **15**(12), 1205 (2003). doi:[10.1002/adma.200305105](https://doi.org/10.1002/adma.200305105)