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Nanocomposites of TiO_2 and Siloxane Copolymers as Environmentally Safe Flame-Retardant Materials†

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Composites of titanium dioxide (TiO_2) nanoparticles and biocatalytically synthesized dimethylsiloxane copolyamides were prepared, and their thermal and flame-retardant properties were investigated. The flammability properties such as heat release capacity and total heat release were measured from microscale cumbustion calorimetry (MCC). The thermal degradation temperatures, char yields, and the heat-release capacities of these nanocomposites were significantly improved over the pure polymers. The heat-release capacities of the siloxane copolymer nanocomposites with 20wt% of TiO_2 were found to be 167 and 129 J/g K, which is a 35% less than the pure polymers (260 and 194 J/g K, respectively). The SEM/EDAX surface-analysis studies on nanocomposite films and their char revealed that nanocrystalline-TiO_2 plays an important role in forming carbonaceous silicate char on the surface as a protective layer.

Keywords: Flame retardant, polysiloxanes, PCFC, microcalorimetry, TiO_2 nanocomposites, environmentally-safe, heat release capacity

1. Introduction

There has been tremendous interest in the area of flame-retardant (FR) materials due to their numerous applications in clothing, household furnishings, aviation, electronics, and telecommunications. Currently used flame-retardant materials are mainly based on halogens, phosphorous, nitrogen and inorganic compounds (1). Flame-retardant additives based on halogenated, aluminium trihydroxide, and antimony-based materials (2, 3) have been widely used, and more recently, nanomaterials such as carbon nanotubes (4) and nanoclays (5) have been investigated for their FR efficiency. Some of these polymers and the additives currently used are economical for FR applications. However, they have long-term ecological problems due to the release of toxic gases upon combustion, which are absorbed by living systems (1). The organic polymers such as Nomex and Kevlar have been widely used in FR textiles, but due to the processability problems for coatings, they are very expensive. Thus, research is ongoing to develop environmentally safe, economical and processable polymers and additives with efficient flame retardant properties. For example, recently Ellzey et al. reported char-forming non-halogenated polymers based on deoxybenzoin monomers for flame-retardant applications (6).

Synthesis of functional materials via biocatalytic methods using enzymes is of great importance due to advantages that include environmental compatibility, economical synthesis, and ease of processability (7, 8). We have recently shown that biocatalytically synthesized, siloxane-based, organic-inorganic hybrid polyesters and polyamides have great potential as environmentally safe FR materials (9, 10). In a copolymer (**2**, Fig. 1) crosslinked with various concentrations of hexamethylenetetramine (HMTA), the heat release capacity decreases with the increase in wt% of HMTA (11). In a crosslinked copolymer with 20 wt% of HMTA, the HR capacity drops to 90 $Jg^{-1}K^{-1}$, which is very promising and an improvement over the commercially available flame-retardant polymers such as Kevlar (292 $Jg^{-1}K^{-1}$) (12) and PEEK (180 $Jg^{-1}K^{-1}$) (12). However, the char yields and total heat release remained similar in all HMTA compositions.

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† Dedicated to the memory of Professor Sukant K. Tripathy

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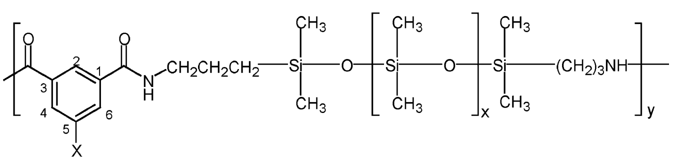


1: X = OH; **2**: X = NH$_2$

Fig. 1. Enzymatically synthesized siloxane copolyamides considered in this study.

The concept of using TiO$_2$ nanoparticles as a filler in PMMA polymer was studied previously by Laachachi et al. (13). However, this concept has not been widely used in any other FR polymers of interest. In this study, we chose nanocrystalline titanium dioxide (nc-TiO$_2$) as a potential non-toxic additive in our siloxane-based copolymers due to environmental compatability and wide use in cosmetics, sunscreens, paints, and toothpastes as well as to its high inherent thermal stability. It was anticipated that nc-TiO$_2$ could undergo a sintering process at temperatures above 400°C and form a nano-sponge structure that could enhance the thermal stability of the polymer, hinder the heat supply to the substrate, and minimize the melt drip. In this paper, we present nanocrystalline titanium dioxide as an environmentally friendly additive in our environmentally benign siloxane copolymers that improved the decomposition temperatures and flame-retardant properties. To understand the role of TiO$_2$ nanoparticles on the thermal and FR properties of our polymers, we also studied the surface analysis of the TiO$_2$-polymer nanocomposite films using scanning electron microscopy.

2. Experimental

2.1. *Materials and methods*

All the polymers were synthesized according to our reported procedure (9–11). Nanocrystalline TiO$_2$ with average particle size 25–50 nm was purchased from Degussa (Germany). Thermal decomposition temperatures and char yields were obtained under air atmosphere using a TA Instruments 2050 thermogravimetric analyzer (TGA). Flammability properties were measured using a microscale combustion calorimeter (MCC) also know as pyrolysis-combustion flow calorimeter (PCFC) (12, 14). MCC is a standardized nonflaming combustion method developed by FAA, which separately reproduces the gas phase and condensed phase processes of flaming combustion and forces them to completion in a single quantitative test using milligram sized samples and oxygen consumption calorimetry. Three replicates were prepared for each sample, and the average of all three is reported.

Polymer-TiO$_2$ nanocomposite samples for all the studies were prepared as follows. To a weighed polymer in a vial, a small amount of acetone was added to prepare a concentrated polymer solution, followed by the addition of the required amount of nanoparticle grade TiO$_2$ (5, 10, 15 and 20% by weight). The mixture was placed in a sonicator for 5 min, and the resultant paint-like slurry was dried under vacuum at 60°C overnight. For scanning electron microscopy studies, the TiO$_2$ composite was spin-coated on an ITO coated glass plate. After drying in a vacuum for 12 h, it was charred in an oven at 500°C for 2 h. The thick charred film was peeled off and both sides were characterized by a scanning electron microscope (SEM, JOEL JSM7401F) and energy dispersive X-ray spectrometry (EDAX). A thin film ($\sim$0.5–1 μm) and a thick film (5–10 μm) of polymer **2**-TiO$_2$ nanocomposite for SEM studies were prepared by spincoating a solution on a quartz glass plate

3. Results and discussion

The siloxane copolyamides considered in this study are shown in Figure 1. To study the effect of functional groups on polymer-TiO$_2$ interactions, we selected copolyamides **1** and **2** with functional groups on isophthalate moiety at C-5 position, OH and NH$_2$ respectively. It is interesting to see (Table 2) that although both polymers have similar degradation temperatures, **2** has higher inherent HR capacity compared to **1**. However, we studied copolyamide **1** with varying TiO$_2$ concentration (5–20 wt%) in detail to examine the effect of concentration of TiO$_2$ nanoparticles on thermal and flame-retardant properties in these nanocomposites. In the various composites of **1**, the optimum composition was found to be 20 wt% of TiO$_2$, and thus we used only this composition to prepare the polymer **2**-TiO$_2$ composite for all the studies.

3.1. *Thermal and flammability properties*

Thermogravimetric analysis (TGA) studies were carried out on the various TiO$_2$-polymer compositions to find out the effect of TiO$_2$ nanoparticles on the decomposition temperature of these polymers. As can be seen from Table 1, the decomposition temperature of polymer **1** is increased from 408 to 425°C by adding 20 wt% of nc-TiO$_2$. The microscale test method, TGA also demonstrates that the polymer degradation kinetics are affected positively and enhanced the thermal stability due to the inclusion of TiO$_2$ nanoparticles. Char yields from TGA improved from 14% to 28% due to TiO$_2$ (Table 1), but the effect was not statistically distinguishable from increase due to the non-volatile TiO$_2$ added. This aspect was confirmed with theoretical char yields (Table 1) calculated based on the value of the polymer with zero-TiO$_2$, times fraction of non-TiO$_2$ polymer in blend, plus the percent TiO$_2$.

Lyon et al. reported a detailed study on PCFC method and its efficacy to screen various plastics for their flame

Table 1. Decomposition temperatures at 10% weight loss, char yields at 700°C from TGA, heat release capacity, total heat release from PCFC at various weight percentages of TiO_2 in siloxane copolyamide, **1**

	PCFC			*TGA*		
nc-TiO_2 wt% of	*($Jg^{-1}K^1$) Theor. HRC*	*($Jg^{-1}K^1$) Exptl. HRC*	*(kJg^{-1}) Total HR*	*(°C) T_{dec}*	*Yield, Theor. Char*	*Yield^b Exptl. Char*
0	—	260.2	21.2	408	—	14.0
5	247.2	211.1	11.0	413	18.3	23.9
10	234.2	192.7	10.7	417	22.6	24.1
15	221.2	179.7	10.0	418	26.9	24.9
20	208.2	167.5	9.70	425	31.2	28.0

retardancy (15). They also described the correlation of heat release properties of several polymers and additives using the PCFC method with other flaming combustion methods like cone calorimetry and limiting oxygen index (LOI). In their study, good correlation (R = 0.9) was observed between heat release capacity and peak HRR in forced flaming combustion (16). Thus, we used PCFC as a tool to assess the flame retardancy of our polymers and nanocomposites in milligram scale. PCFC measurements on our polymer nanocomposites revealed that as the concentration of TiO_2 nanoparticles increased, the flame-retardant properties such as HR capacity and total HR decreased substantially. From Figure 2, it is clearly seen the reduction in the peak HRR and total HR (calculated from the area under the curve) of TiO_2 nanocomposite compared to the pure polymer. As shown in Figure 3, an initial large decrease of heat-release capacity from 260 to 211 J/g K is seen with 5 wt% addition of TiO_2 and a steady linear decrease was observed in subsequent additions. This graph, heat release vs. temperature curves and the theoretical heat release capacities presented in Table 1 (calculated based on the value of the polymer with zero-TiO_2, times fraction of non-TiO_2 polymer in blend) suggests that the effect of TiO_2 on the flammability properties is not due just to the mass fraction of the inert particles. Table 2 gives the FR properties of the siloxane copolymers, **1** and **2** with and without the addition of TiO_2. It is clear from Table 2 that upon addition of 20 wt% nc-TiO_2, the polymers **1** and **2** show a similar decrease (35% and 34%, respectively) in HR capacities. It is interesting to note from Table 2 that HRC values for both the nanocomposites were found to be <200 J/g K, which fall within the self-extinguishable region (UL-94, V-0) of the Lyon et al. correlation of heat release capacities from MCC and UL-94 burning test ratings of various polymers (15). Since polymer **2** has lower intrinsic HR capacity than **1**, we chose **2** for all the other studies. It is well known that in nc-TiO_2-based dye- sensitized solar cells, the light-absorbing dyes with COOH or catechol groups are covalently attached onto TiO_2 nanoparticles to harvest the sun light into electricity (17). Presumably, in the case of the copolyamides, **1** and **2**, there could be a weak hydrogen-bonding interactions between amide bonds and TiO_2 nanoparticles.

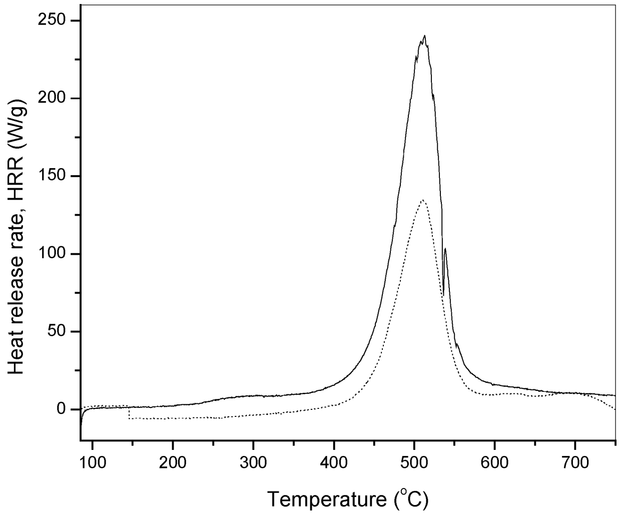


Fig. 2. Heat release rate vs. temperature curves from MCC measurements of the pure polymer **2** (solid line) and its 20 wt% TiO_2 nanocomposite (dotted line).

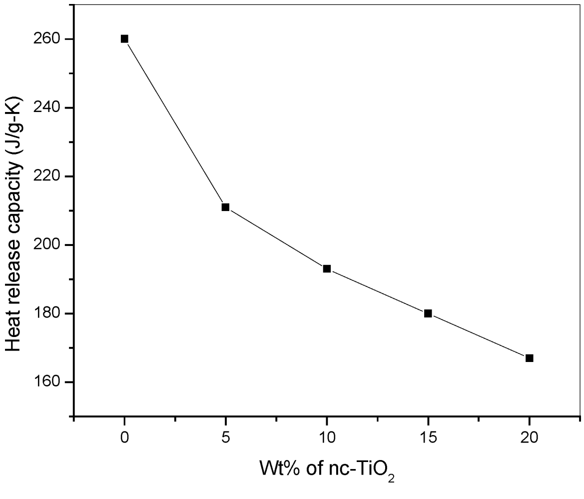


Fig. 3. Heat release capacity vs. wt% of TiO_2 in siloxane copolyamide, **1**.

Table 2. Comparison of heat release capacities, total heat releases and char yields of siloxane copolyamides with and without nc-TiO_2.

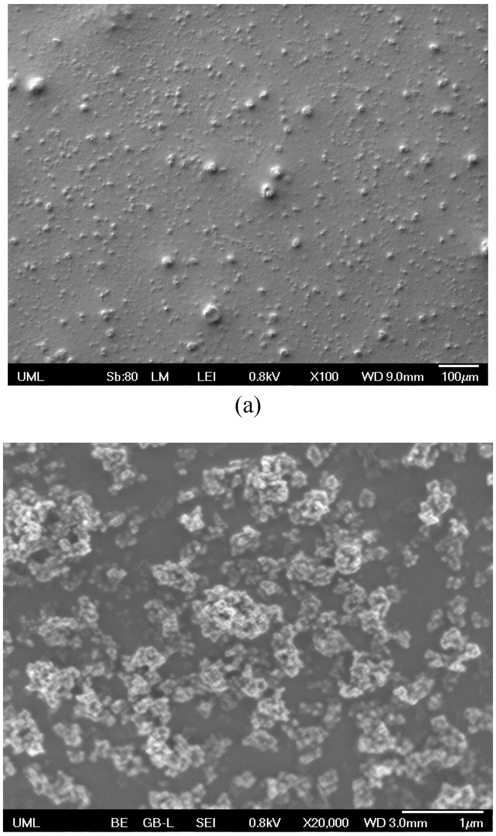
	PCFC		*TGA*	
Polymer	*HRC ($Jg^{-1}K^{1}$)*	*Total HR (kJg^{-1})*	T^{a}_{dec} *(°C)*	*Char Yield*^{b}
1	260.2	21.1	408	14.0
$+TiO_2^c$	167.5	9.7	425	31.2
2	194.0	15.8	407	15.0
$+TiO_2^c$	128.9	8.8	426	33.7

^{a}at 10% wt loss; ^{b}at 700°C; ^{c}20 wt% of TiO_2.

3.2. *Surface Analysis of Nanocomposites*

To further investigate the role of TiO_2 nanoparticles in thermal and FR properties of our polymers, we carried out surface analysis by SEM. Figures 4(a–b) show the SEM images of polymer-TiO_2 composite thin film on ITO substrate before and after heating at 500°C for an hour, respectively. The surface coverage by TiO_2 nanoparticles is clearly seen after burning the nanocomposite in Figure 4(b). However, for studying the nature of the char by SEM/EDAX, we prepared a thick film of the same composition. Figures 5(a) and (b) show the SEM images of the bottom surface and top surfaces of the char obtained after heating the thick film at 500°C for an hour. We analyzed the polymer char without TiO_2 and both sides of the TiO_2 nanocomposite char by EDAX for their elemental compositions.

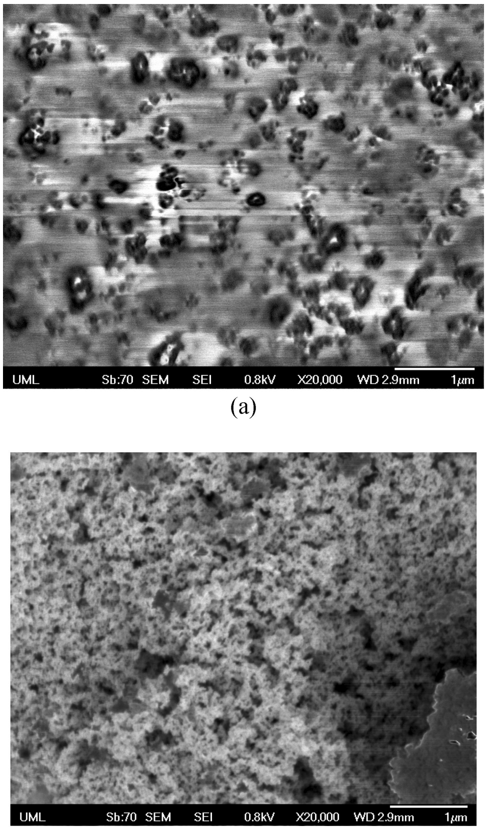
It is interesting to see from EDAX analysis (Table 3) that, in the nanocomposite char, the bottom white surface (char-B) is rich in titanium while the top black surface (char-T) contains mostly silicon and enhanced carbon compared to pure polymer char. This difference indicates the migration of cyclic siloxanes to the surface upon combustion in the presence of nc-TiO_2 nanoparticles and formation of carbonaceous silicate char which is colored. We believe that nc-TiO_2, which is an efficient catalyst in many reactions and polymerizations, is probably playing a vital role in catalyzing the protective thick char formation. In the case of pure polymer, the char formed is very thin and brittle due to the less C and Ti content compared to nanocomposite char. This silicon-rich char with carbon on the top surface



(a)

(b)

Fig. 4. Scanning electron microscopy images of thin film of polymer **2**– 20 wt% TiO_2 nanocomposite (a) before (b) after heating at 500°C for an hour.



(a)

(b)

Fig. 5. Scanning electron microscopy images of char of a thick film of Polymer **2**– 20 wt% TiO_2 nanocomposite after heating at 500°C for an hour: (a) back surface (char-B), (b) top surface (char-T).

Table 3. Relative elemental composition in atomic % from SEM/EDAX analysis of the pure polymer and chars (poly char, nanocomposite chars, char-B and char-T; see text for details).

Material	*C*	*O*	*Si*	*Ti*
Poly Char (0% TiO_2)	26.9	58.9	14.1	0.0
Char-B (20% TiO_2)	13.8	57.7	9.2	19.3
Char-T (20%TiO_2)	39.4	43.2	15.7	1.7

and titanium oxide on the bottom surface in nanocomposite could act as a heat shield and slow the conduction of heat that drives pyrolysis and combustible-gas generation, thus lowering the heat-release capacity. The sintering of TiO_2 nanoparticles at high temperatures may also be a possible explanation for the lower HR capacities of these composites. It may be anticipated that due to the mesoporous nature of the nanoparticle and silicate char, the melt drip of the substrate material should be minimized, which would be an added advantage. We added TiO_2 up to 20 wt%, and further addition of TiO_2 did not improve the properties significantly.

4. Conclusions

Nanocrystalline TiO_2 has been explored as a green additive in environmentally friendly siloxane-based copolymers. We found that addition of TiO_2 in these polymers not only enhances their thermal stability but also improves their flame-retardant properties substantially with respect to the dilution of polymer by the nonvolatile additive. The siloxane copolymer-TiO_2 nanocomposite, **2** showed heat release capacity of 129 J/g K, which is significantly lower than commercially available flame-retardant polymers such as Kevlar and PEEK. Char formed on the surface mostly contains Si, C, and O, which suggests the formation of a carbonaceous silicate char. The significant improvement in flammability properties is most likely due to the important role of TiO_2, which affects the thermal degradation kinetics and hinders heat transfer to the combustable gases upon char formation. This study suggests that nc-TiO_2 is an environmentally safe additive in our environmentally safe FR polymers. We are currently exploring the incorporation of TiO_2 nanoparticles in various other polymers.

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