

# *In Situ* Polymerization of Titanium Isopropoxide in Polycaprolactone: Properties and Characterization of the Hybrid Nanocomposites

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**ABSTRACT:** In this study, tetra isopropyl ortho titanate (TTIP) and polycaprolactone (PCL) were chosen as the ceramic precursor and the continuous phase, respectively, for the preparation of novel nanocomposites by using an *in situ* sol-gel process. In addition, acrylic acid grafted polycaprolactone (PCL-g-AA) was investigated as an alternative to PCL. The hybrids (PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub>) were characterized via Fourier transform infrared (FTIR) spectroscopy, dynamic mechanical thermal analysis (DMA), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), and Instron mechanical testing. It was found that the carboxylic acid groups of acrylic acid acted as coordination sites for the titania phase

to form chemical bonds, thus improving the properties of the acrylic acid grafted composite compared with its acrylic acid-free counterpart. The TiO<sub>2</sub> content also determined the strength of interfacial bonding between the polymer chains and the ceramic phase, as shown by changes in glass transition temperature ( $T_g$ ) with TiO<sub>2</sub> content. The maximum values of tensile strength and  $T_g$  were obtained with the PCL-g-AA/TiO<sub>2</sub> composite at 10 wt % TiO<sub>2</sub>. At TiO<sub>2</sub> contents above this, excess particles led to segregation between the organic and inorganic phases. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1749–1757, 2004

**Key words:** PCL/TiO<sub>2</sub>; PCL-g-AA/TiO<sub>2</sub>; TGA; FTIR; blends

## INTRODUCTION

It is now possible to combine polymers and ceramics via molecular-level manipulation by using a sol-gel process to create novel materials.<sup>1–12</sup> The promise of these new hybrid materials is a controllable combination of the properties of the polymer (flexibility, toughness, and easy processing) and the ceramic/glass (hardness, durability, and thermal stability). In synthesizing the organic–inorganic composite, the organic polymer is generally the dominant phase, modified by the inorganic phase.<sup>13–14</sup> Examples of organic polymers used in the sol-gel process include elastomers, glassy polymers, semicrystalline polymers, and membranes of perfluorosulfonic acid (Naflan®).<sup>15</sup> Ceramic precursors are usually organometallic compounds ( $M[OC_nH_{2n+1}]_z$ , where  $M = Si, Sn, Ti, Zr, Al$ , etc.), among which tetraethoxysilane (TEOS) is the most common.<sup>16,17</sup> Titania is seldom used. Our previous studies<sup>7</sup> and the reports of Fitzgerald<sup>18</sup> have indicated that factors such as particle size of inorganic phase, uniform distribution of inorganic phase within the organic phase, and interfacial forces between the two phases significantly affect the microstructures and

the properties of hybrid materials. Interfacial forces lead to the formation of either hydrogen bonds or covalent bonds between the two phases. Hydrogen bonds may arise from the basic group of the hydrogen acceptor in the polymer and the hydroxyl group of the intermediate species of metal alkoxides, whereas covalent bonds may result from dehydration of —OH groups in the polymer and the residual titanium-bonded isopropyl groups in the titania network.

Polycaprolactone (PCL) is one of an important group of thermoplastics and has recently received much attention because of its flexibility and biodegradability. Additionally, as with other aliphatic polyesters such as polylactide (PLA) and polyglycolide (PGA), PCL and its copolymers have commercially successful applications.<sup>19,20</sup> PCL has, however, been restricted in its application because of its low melting point, poor stability, and tendency to crack when stressed.<sup>21</sup> Extensive studies have been undertaken on graft reaction, crosslinking reaction, and blending of PCL with organic fillers in an attempt to mitigate these problems. Although Hu and Marand<sup>22</sup> have studied the *in situ* formation of PAI/TiO<sub>2</sub> composites by using a sol-gel process, and Zhang et al.<sup>23</sup> have reported some observations on the optical properties of PPV/TiO<sub>2</sub>, PCL/titania hybrids have not yet been investigated.

The purpose of this study is to characterize the thermal and mechanical properties of PCL polymer

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TABLE I  
Compositions of Various Sol-Gel Liquid Solutions for Preparation of Hybrid Materials

TiO <sub>2</sub> (wt %)	3	7	10	13	16
PCL or PCL-g-AA (g)	38.80	37.20	36.00	34.80	33.60
TTIP (g)	4.26	9.93	14.18	18.44	22.70
Isopropanol/[TTIP] <sup>a</sup>	17	17	17	17	17
Sol A					
[acetic acid]/[TTIP] <sup>a</sup>	0.01	0.01	0.01	0.01	0.01
[HCl]/[TTIP] <sup>a</sup>	0.08	0.08	0.08	0.08	0.08
[H <sub>2</sub> O]/[TTIP] <sup>a</sup>	4.0	4.0	4.0	4.0	4.0

<sup>a</sup> The mole ratio of isopropanol, acetic acid, HCl, and H<sub>2</sub>O to TTIP.

modified by titania by using a sol-gel process. In this study, the formation and dispersion of the titania network in the PCL matrix was achieved by using a new method: an *in situ* polymerization of isopropyl ortho titanate in the presence of PCL. Furthermore, PCL-g-AA was investigated as an alternative to PCL, to characterize the reaction of the carboxylic acid groups with the residual titanium-bonded isopropyl groups of the titania network. The hybrid products (PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub>) were characterized via Fourier transform infrared (FTIR) spectroscopy, dynamic mechanical thermal analysis (DMA), and X-ray diffraction (XRD). Moreover, the thermal and mechanical properties of hybrids were examined via thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), and Instron mechanical testing.

## EXPERIMENTAL

### Materials

PCL, with a molar mass of 80,000 g/mol, was supplied by Solvay (Warrington, UK). Acrylic acid (AA), supplied by Aldrich (Milwaukee, WI), was purified by recrystallization from chloroform before use. Benzoyl peroxide (BPO), used as an initiator, was purified by dissolution in chloroform and reprecipitation with methanol. The other reagents were purified by using conventional methods, while tetra isopropyl ortho titanate (TTIP-Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, >97%), obtained from Merck Chemical Corp. (Whitehouse Station, NJ), was of reagent grade and therefore not further purified. The PCL-g-AA copolymer was synthesized in the laboratory as described below.

### Sample preparation

#### Synthesis of PCL-g-AA

AA was grafted onto molten PCL under a nitrogen atmosphere at 85 ± 2°C, by using xylene as the interface agent and BPO as the initiator. Reaction time was 6 h, with a rotor speed in the mixer of 60rpm. For purification, about 4 g of product was dissolved in 200 mL of refluxing xylene at 85°C and the solution was

then extracted five times, by using 600 mL of cold acetone for each extraction. The resultant acetone-insoluble polymer was then dried overnight at 80°C and used in a titration<sup>24</sup> to measure the grafting percentage. The grafting percentage was found to be about 6.05 wt % with BPO loading and AA loading maintained at 0.3 and 10 wt %, respectively.

### PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub> hybrids

A mixture, called Sol A, was prepared by dissolving a stoichiometric amount (shown in Table I) of TTIP, H<sub>2</sub>O, HCl (as the catalyst), and acetic acid in isopropanol and then stirring it at room temperature for 30 min to obtain a homogeneous solution. A predetermined amount of PCL or PCL-g-AA (also shown in Table I) was put into a Brabender Platograph 200-nm mixer W50EHT instrument with a blade-type rotor set at 50 rpm, and at a temperature of 100–110°C. When the polymer had melted completely, the Sol A was added and the sol-gel process was allowed to proceed for 20 min. Prior to characterization, each sample was dried at 105°C in a vacuum oven for 3 days to remove residual solvents. The hybrid products were pressed into thin plates by using a hot press at 100°C and then put into a dryer for cooling, after which they were made into standard specimens for characterization.

### Characterizations of hybrids

#### FTIR analysis

By using thin film samples of the hybrid product, the grafting of AA onto PCL was investigated by using an FTIR spectrophotometer (Bio-Rad FTS-7PC type). The incorporation of the titania phase into the hybrids, to such an extent that Ti-O-Ti bonds were formed, was also verified via the FTIR analysis.

#### XRD analysis

Structural changes in the hybrids were investigated by comparison of X-ray diffraction data obtained from PCL, PCL-g-AA, and hybrids, recorded with a Rigaku

D/max 3 V X-ray diffractometer, using  $\text{CuK}\alpha$  radiation at a scanning rate of  $2^\circ/\text{min}$ .

#### Dynamic mechanical analysis

Blend compatibility was evaluated by using a TA analyzer Model 2080 to measure the dynamic mechanical properties of the blends. The tests were performed at a frequency of 1 Hz, a strain level of 0.075%, and a temperature rising from  $-120$  to  $+80^\circ\text{C}$ , with a heating rate of  $3^\circ\text{C}/\text{min}$ . The results of experiments made in the linear region of elasticity and without causing drawing effects were recognized as the static force. To specify this force, several stress-strain experiments were conducted beforehand, so that the ratio of static force to dynamic force could be kept constant during the experiments.

#### DSC analysis

The glass transition temperatures ( $T_g$ ) of samples with sizes ranging from (4–6) mg were determined by using a TA Instrument 2010 DSC system, in which the melting curves were taken between  $-30$  and  $120^\circ\text{C}$ , with a heating rate of  $10^\circ\text{C}/\text{min}$ .

#### TGA analysis

A thermogravimetry analyzer (TA Instrument 2010 TGA) was used to assess whether organic-inorganic phase interactions influenced thermal degradation of the hybrids. Samples were placed in alumina crucibles and tested with a thermal ramp over a temperature range of  $30$ – $600^\circ\text{C}$ , at a heating rate of  $20^\circ\text{C}/\text{min}$ , after which their initial decomposition temperature (IDT) was obtained.

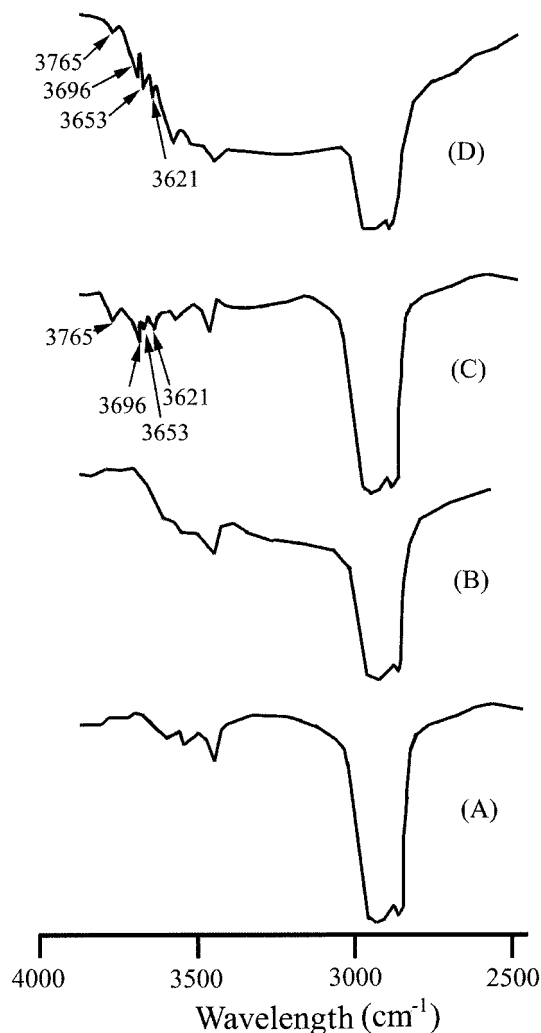
#### Mechanical testing

An Instron mechanical tester (Model Lloyd, LR5K type) was used to measure the tensile strength and elongation at break of blends, following the ASTM D638 method. The film samples were conditioned at  $50 \pm 5\%$  relative humidity for 24 h and then tested at a  $20$  mm/min crosshead speed. Each blend was tested by using five samples and the results were averaged to obtain a mean value.

## RESULTS AND DISCUSSION

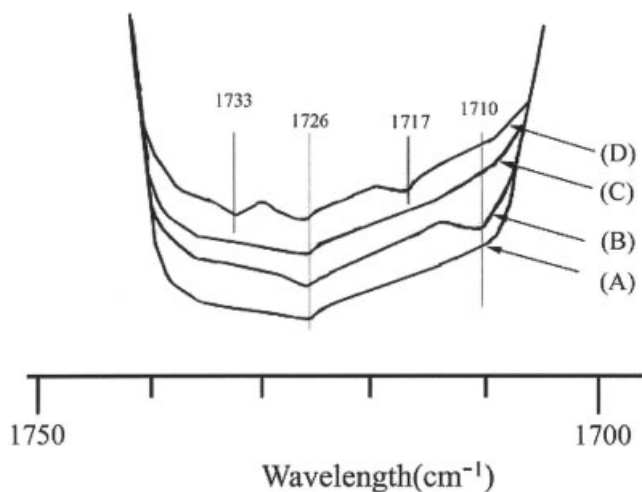
#### Infrared spectroscopy

FTIR spectroscopic analysis of PCL, PCL-g-AA, PCL/ $\text{TiO}_2$  (10 wt %), and PCL-g-AA/ $\text{TiO}_2$  (10 wt %) showed that all the characteristic peaks of PCL at  $2840$ – $2928$   $\text{cm}^{-1}$  appear in all four polymers [Fig. 1(A–D)].<sup>20,25</sup> The spectrum of PCL-g-AA [Fig. 1(B)] also



**Figure 1** FTIR spectra in the limited range of  $3000$ – $3800$   $\text{cm}^{-1}$  for (A) pure PCL, (B) PCL-g-AA, (C) PCL/ $\text{TiO}_2$  (10 wt %), and (D) PCL-g-AA/ $\text{TiO}_2$  (10 wt %).

indicates a broad O—H stretching absorbance at about  $3000$ – $3600$   $\text{cm}^{-1}$ , absent in the PCL spectrum [Fig. 1(A)]. Similar results have been reported elsewhere.<sup>20,26,27</sup> The PCL-g-AA/ $\text{TiO}_2$  hybrid also produced a broad O—H bond stretching at about  $3000$ – $3800$   $\text{cm}^{-1}$  [Fig. 1(D)]. This is due to the formation of heteroassociated hydrogen bonds between carboxylic acid groups of PCL-g-AA and the titanium-bonded isopropyl group.<sup>28</sup> In addition, acetate ligands of the PCL-g-AA/ $\text{TiO}_2$  hybrid can participate in a direct condensation reaction that yields isopropyl acetate as a byproduct along with the Ti—O—Ti condensed bridge.<sup>4,29</sup> Similarly, a condensation reaction can also occur between free acetic acid and bound isopropyl groups or free alcohol and bound acetate, and the possible combinations of ester production will ultimately create oxygen linkages between titanium atoms, as was also indicated in the work of Birnie and Bendzko.<sup>4</sup>



**Figure 2** FTIR spectra in the limited range of 1700–1750  $\text{cm}^{-1}$  for (A) pure PCL, (B) PCL-g-AA, (C) PCL/TiO<sub>2</sub> (10 wt %), and (D) PCL-g-AA/TiO<sub>2</sub> (10 wt %).

To better understand the hydrogen-bonding interaction between PCL-g-AA and TiO<sub>2</sub> in the hybrids, the FTIR spectra for PCL-g-AA [Fig. 1(B)] and PCL-g-AA/TiO<sub>2</sub> [Fig. 1(D)] in the range of 3000–3800  $\text{cm}^{-1}$  were examined more closely. There are additional stronger bands at 3621, 3653, and 3696  $\text{cm}^{-1}$  in both spectra, characteristic of tetrahedral coordinated vacancies and designated as  ${}_{4}\text{Ti}^{4+}\text{—OH}$ . A further band at 3765  $\text{cm}^{-1}$  was assigned to octahedral vacancies and designated as  ${}_{6}\text{Ti}^{3+}\text{—OH}$ . This region at 3600–3800  $\text{cm}^{-1}$  was therefore identified as being representative of non-hydrogen-bonded hydroxyl groups (labeled as isolated or free hydroxyl groups). This is in agreement with the X-ray data analysis of Kumar et al.<sup>30</sup> and will be further discussed below.

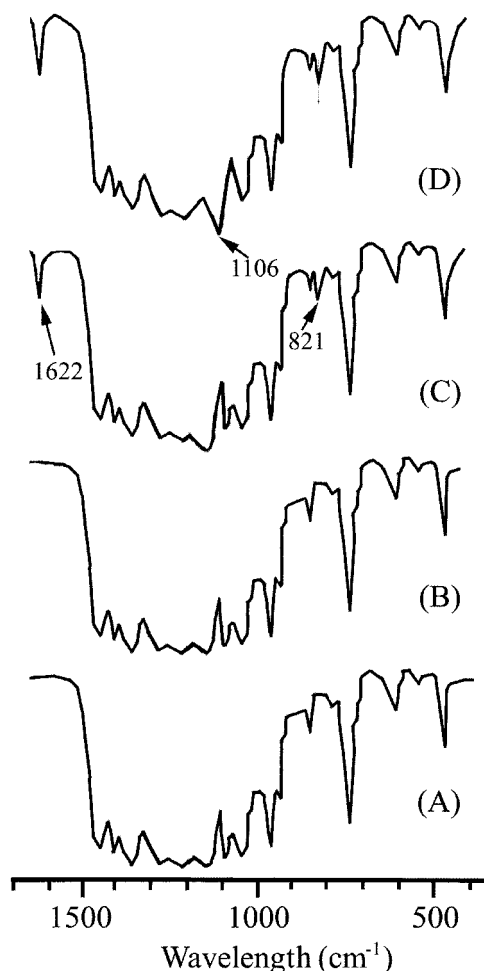
Expansion of the FTIR spectra in the limited range of 1700–1750  $\text{cm}^{-1}$  (Fig. 2) more clearly illustrates the difference between the spectra with and without AA grafted onto the polymer. The PCL spectrum [Fig. 2(A)] shows only the  $\text{—C=O}$  stretching vibration, a strong broad band at 1725–1736  $\text{cm}^{-1}$ , a result similar to that obtained by Wang et al.,<sup>31</sup> while the PCL-g-AA spectrum [Fig. 2(B)] shows an extra peak at 1710  $\text{cm}^{-1}$ , caused by the grafting of AA onto PCL. However, PCL-g-AA in the hybrid, PCL-g-AA/TiO<sub>2</sub>, loses its peak at 1710  $\text{cm}^{-1}$  and gains two new peaks at 1733 and 1717  $\text{cm}^{-1}$  [Fig. 2(D)]. This result may be due to the formation of ester groups through the reaction between carboxylic acid groups of PCL-g-AA and titanium-bonded isopropyl groups of the titania network.<sup>7,32</sup>

Furthermore, a comparison of the PCL and PCL/TiO<sub>2</sub> (10 wt %) spectra shows new peaks between 3000 and 3800  $\text{cm}^{-1}$  (Fig. 1) and at 821 and 1622  $\text{cm}^{-1}$  (Fig. 3) in the latter. The broad stretching at about 3000–3800  $\text{cm}^{-1}$  [Fig. 1(C)] is due to the hydrogen bonds of

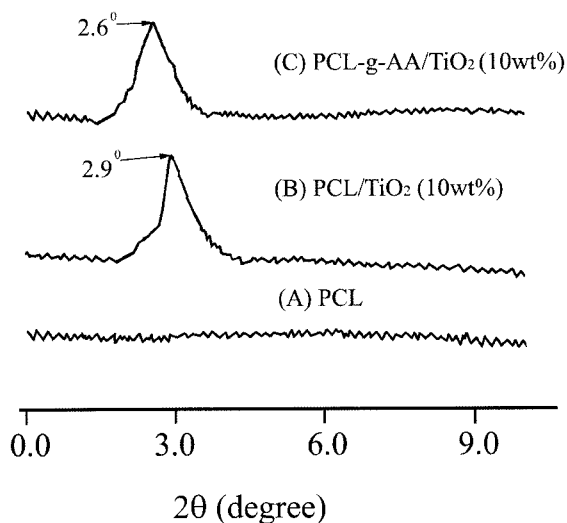
$\text{—OH}$  and indicates the existence of  $\text{Ti—OH}$ . The peaks at 821 and 1622  $\text{cm}^{-1}$  [Fig. 3(C)] were assigned to the  $\text{Ti—O}$  and  $\text{Ti—O—Ti}$  stretching modes, as they have been by Chiang and Whang<sup>33</sup> and Shao et al.<sup>34</sup> Therefore, it is proposed that the interfacial force between the PCL matrix and the titania network is mainly established by hydrogen bonds. As was true in the PCL polymer, peaks not seen in PCL-g-AA occur in the PCL-g-AA/TiO<sub>2</sub> hybrid. Figure 3(D) shows three extra peaks at 821, 1106, and 1622  $\text{cm}^{-1}$ , in the spectrum of the latter. The peak at 1106  $\text{cm}^{-1}$  indicates the  $\text{Ti—O—C}$  bond, which may be produced from the reaction between PCL-g-AA and the titanium-bonded isopropyl group.<sup>23,33,35</sup> An interesting trait associated with the titania phase in both hybrids was a peak at about 1622  $\text{cm}^{-1}$ , assigned to  $\text{Ti—O}$  bending deformation.

### X-ray diffraction

The titania surface layers were modified by dispersing titania uniformly into the organic modifier, PCL or



**Figure 3** FTIR spectra in the limited range of 500–1700  $\text{cm}^{-1}$  for (A) pure PCL, (B) PCL-g-AA, (C) PCL/TiO<sub>2</sub> (10 wt %), and (D) PCL-g-AA/TiO<sub>2</sub> (10 wt %).



**Figure 4** X-ray diffraction spectra in the limited range of 0–10° for (A) pure PCL, (B) PCL/TiO<sub>2</sub> (10 wt %), and (C) PCL-g-AA/TiO<sub>2</sub> (10 wt %).

PCL-g-AA. To investigate the effect of the modifier on the morphology of the nanocomposite, PCL and PCL-g-AA with different TiO<sub>2</sub> network chain lengths were analyzed by using X-ray diffraction. The spectra are shown in Figure 4.

Using Bragg's equation, the interlayer distance of the hybrid can be determined as

$$d = \frac{n\lambda}{2 \sin \theta}$$

where  $d$  is the interplanar distance of diffraction faces,  $\theta$  is the diffraction position, and  $\lambda$  is the wavelength of incident X-rays.

Basal peak reflections were not observed for either hybrid [Fig. 4(B, C)], demonstrating that TiO<sub>2</sub> in both systems exfoliates and disperses homogeneously. However, a weak peak is visible in the PCL/TiO<sub>2</sub> spectrum at  $2\theta = 2.9^\circ$ , and in the PCL-g-AA/TiO<sub>2</sub> spectrum at  $2\theta = 2.6^\circ$ . Note that there is also a weak peak at about the same angle of the modified titanate investigated by Hu and Marand.<sup>22</sup> Furthermore, the position of angles in the X-ray patterns shows clearly that interlayer spacing is greater for PCL-g-AA/TiO<sub>2</sub>. This greater spacing is indicative of a more successful modification, something also suggested by Wang et al.<sup>36</sup> in their study of a maleated PE/clay nanocomposite.

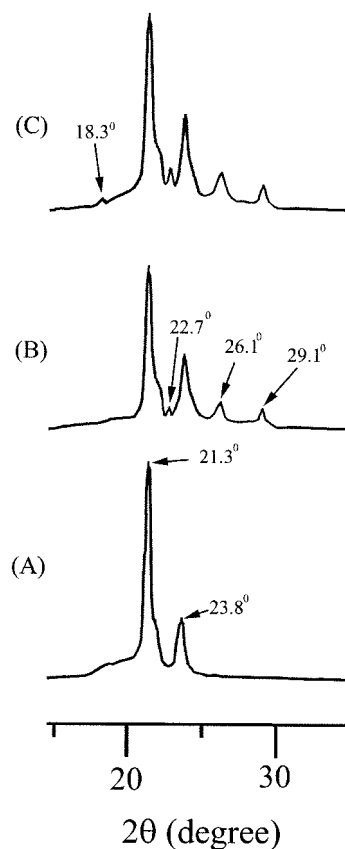
To further investigate the crystalline structures of PCL, PCL/TiO<sub>2</sub>, and PCL-g-AA/TiO<sub>2</sub>, the X-ray diffraction patterns at 15–35° ( $2\theta$ ) were examined. The spectrum obtained for unmodified PCL [Fig. 5(A)] is similar to that obtained by Wu (i.e., ref. <sup>20</sup>), two peaks at about 23.8 and 21.3°. A comparison of this spectrum with that for PCL-g-AA/TiO<sub>2</sub> [Fig. 5(C)] reveals new

peaks in the latter, at  $2\theta = 18.3^\circ$ ,  $22.7^\circ$ ,  $26.1^\circ$ , and  $29.1^\circ$ . The new peak at  $18.3^\circ$ , which may be due to the formation of an ester carbonyl functional group as described in the discussion of FTIR analysis, was also reported by Shogren et al.<sup>37</sup> Also, one can refer the appearance of the new peaks at  $2\theta = 26.1^\circ$  and  $29.1^\circ$  to the generation of a titanium-bonded isopropyl functional group in the anatase and rutile phase,<sup>30</sup> and the appearance of the new peak at  $2\theta = 22.7^\circ$  to the generation of a titania functional group in the Ti<sub>2</sub>O<sub>3</sub> phase.

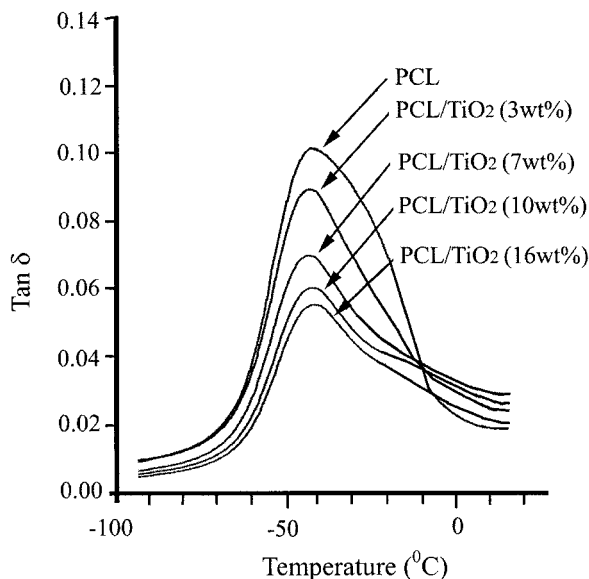
## Dynamic mechanical analysis

### Nonbonded PCL-titania hybrid materials

Variations in the loss tangent ( $\tan \delta$ ) with temperature for pure PCL and PCL hybrid materials (those materials with no chemical bonding between the polymer and the titania) are shown in Figure 6 and Table II. Results (in Fig. 6) show that the  $\tan \delta$  increased sharply at a particular temperature, with the onset of segmental motion. Moreover, the temperatures at which peaks occurred in the hybrids increased with titania content and were slightly higher than that in



**Figure 5** X-ray diffraction spectra in the limited range of 15–35° for (A) pure PCL, (B) PCL/TiO<sub>2</sub> (10 wt %), and (C) PCL-g-AA/TiO<sub>2</sub> (10 wt %).

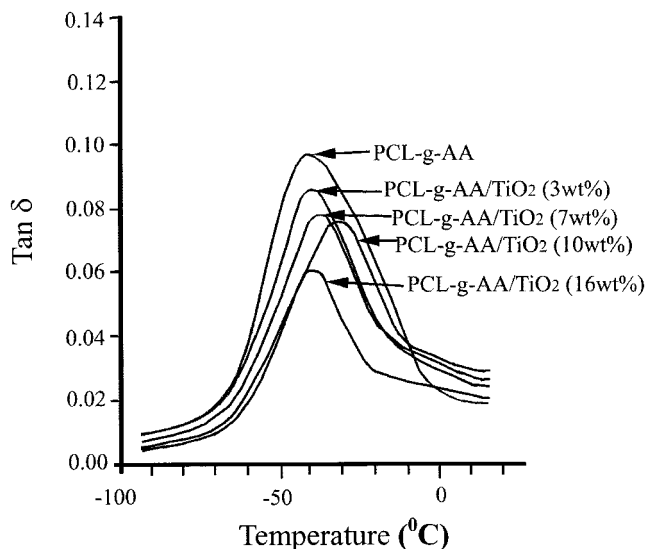


**Figure 6** Variation in the loss tangent ( $\tan \delta$ ) with temperature for PCL/TiO<sub>2</sub> composites.

pure PCL (Table II). Titania shifted the temperature at which peaks occurred upward because its inorganic network hindered segmental motions of the polymer chains. There was a small shoulder at higher temperatures, suggestive of a physical interaction between the inorganic phase and parts of the polymer matrix. Additionally, the peaks generally broadened and decreased in intensity with increasing titania content (Fig. 6).

#### Bonded PCL-g-AA-titania hybrid materials

Variations in the  $\tan \delta$  with temperature for PCL-g-AA and PCL-g-AA/TiO<sub>2</sub> (those materials in which there was chemical bonding between the polymer and the titania) are shown in Figure 7 and Table II. With titania, the single sharp peak of PCL-g-AA again split into a peak and a broad shoulder, and the small peak of PCL-g-AA shifted to higher temperatures as TiO<sub>2</sub> content increased up to 10 wt %. However, at TiO<sub>2</sub> content above 10 wt %, the temperature at which the



**Figure 7** Variation in the loss tangent ( $\tan \delta$ ) with temperature for PCL-g-AA/TiO<sub>2</sub> composites.

peak occurred decreased again. Although a feature of both systems, the shifts in  $\tan \delta$  to higher temperatures in the chemically bonded system were far larger, suggesting increased adhesion between the polymer and the titania in this system. The most efficient bonding was seen in PCL-g-AA/TiO<sub>2</sub> with 10 wt % titania, in which  $\tan \delta$  was shifted up to a maximum temperature that was much higher than in other hybrids.<sup>38</sup> This increased bonding efficiency with AA implies that the more chain ends available for chemical bonding, the better, and that bonding of the PCL-g-AA chains with the titania is the origin of the considerable shifts in the  $T_g$ ,  $\beta$  values. The subsequent decrease in temperature at which the peak occurred with titania contents above 10 wt % may have been due to excess titania particles, causing separation of the organic and inorganic phases and lowering their compatibility. It is concluded, therefore, that the maximum interfacial interactions occurred at approximately 10 wt % titania.

#### Thermal stability of hybrids (DSC and TGA tests)

It is well known that the thermal stability of organic/inorganic hybrids depends on the interaction between the polymer chains and the inorganic network, and the consequent uniform distribution of the latter in the former.<sup>39,40</sup> The thermal properties of hybrids with various titania contents were obtained via DSC and TGA tests, and the results are given in Table III. The glass transition temperature ( $T_g$ ) of the hybrid composites is associated with a cooperative motion of long-chain segments, which may be hindered by the titania network.<sup>7</sup> Therefore, as expected, both PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub> recorded higher glass tran-

**TABLE II**  
Glass Transition Temperature of PCL/TiO<sub>2</sub>  
and PCL-g-AA/TiO<sub>2</sub> Hybrids

TiO <sub>2</sub> (wt %)	PCL/TiO <sub>2</sub>	PCL-g-AA/TiO <sub>2</sub>
	$T_{g,\beta}$ (°C)	$T_{g,\beta}$ (°C)
0	-43.3	-40.3
3	-42.7	-38.8
7	-41.2	-36.2
10	-40.7	-30.9
13	-40.5	-36.9
16	-40.3	-39.2

TABLE III  
Thermal Properties of PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub> Hybrids

TiO <sub>2</sub> (wt %)	PCL/TiO <sub>2</sub>			PCL-g-AA/TiO <sub>2</sub>		
	IDT (°C)	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	IDT (°C)	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)
0	333	-59.6	62.5	329	-58.3	61.3
3	335	-58.2	62.0	347	-55.6	60.3
7	339	-56.5	61.6	356	-52.7	58.9
10	343	-55.7	60.9	366	-45.2	57.3
13	345	-56.1	60.7	370	-53.8	59.3
16	337	-57.3	60.5	373	-56.7	59.5

sition temperatures than pure PCL (Table III). It was also found that the enhancement in  $T_g$  for PCL-g-AA/TiO<sub>2</sub> hybrids was more significant than that for PCL/TiO<sub>2</sub> hybrids. This is because the titania phase was able to form chemical bonds on coordination sites provided by the carboxylic acid groups of PCL-g-AA/TiO<sub>2</sub>. These bonds are stronger than the hydrogen bonds in PCL/TiO<sub>2</sub> and therefore more able to hinder the motion of the polymer chains.

Table III shows, however, how the enhancement effect of titania on the  $T_g$  was not high for either PCL/TiO<sub>2</sub> or PCL-g-AA/TiO<sub>2</sub>, and that a maximum value of  $T_g$  occurred at 10 wt % of TiO<sub>2</sub>. The low increment of  $T_g$  in the PCL-g-AA/TiO<sub>2</sub> hybrid might have been due to the low grafting percentage (about 6.05 wt %) of the PCL-g-AA copolymer because the increment of  $T_g$  is dependent on the number of functional groups in the copolymer matrix able to react with the residual titanium-bonded isopropyl groups in the titania network.<sup>41</sup> With titania content above 10 wt %, excess titania particles were dispersed physically in the polymer matrix. Such excess particles might have caused separation of the organic and inorganic phases and lowered their compatibility, causing the  $T_g$  of both hybrids to drop from its maximum value. Table III also shows how the melt temperature ( $T_m$ ) decreased with increasing TiO<sub>2</sub> content for PCL/TiO<sub>2</sub>, whereas for PCL-g-AA/TiO<sub>2</sub>, the lowest  $T_m$  occurred at 10 wt % TiO<sub>2</sub>. Notably,  $T_m$  values for all PCL-g-AA/TiO<sub>2</sub> hybrids were lower than their PCL/TiO<sub>2</sub> equivalents. This lower melt viscosity of PCL-g-AA/TiO<sub>2</sub> makes it a more easily processed blend.

Both PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub> hybrids raised the IDT value (Table III). Moreover, despite PCL-g-AA having a lower IDT value than PCL, the PCL-g-AA/TiO<sub>2</sub> hybrids produced IDT values higher than those of the equivalent PCL/TiO<sub>2</sub>. This outcome is a result of the difference in interfacial forces in the two hybrids: the weaker hydrogen bonds of PCL/TiO<sub>2</sub> compared with the stronger coordination sites associated with the carboxylic acid groups of AA and the —OH of the titanium-bonded isopropyl group. Table III also shows that the increment of IDT for both hybrids was not significant with titania content above 10 wt %. This

was because of the occurrence of phase separation in the hybrids.

Thermal properties of pure PCL, PCL/TiO<sub>2</sub>, and PCL-g-AA/TiO<sub>2</sub>, obtained via DSC, are given in Figure 8. The fusion heat ( $\Delta H_f$ ) of pure PCL was 72.5 J/g. The value of this parameter increased with the crystal formation while it decreased as the TiO<sub>2</sub> content increased. The decrease in crystallization was probably caused by increased difficulty in arranging the polymer chain because of TiO<sub>2</sub> prohibiting movement of the polymer segments. Another potential cause is the hydrophilic character of TiO<sub>2</sub>, which would lead to poor adhesion with the hydrophobic PCL. Nam et al.<sup>42</sup> studied the properties of a clay nanocomposite and its blends with polypropylene and reported a similar phenomena. Figure 8 also shows that  $\Delta H_f$  decreased with increasing TiO<sub>2</sub> content for both PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub>. Additionally,  $\Delta H_f$  was about 2–10 J/g higher with PCL-g-AA in the composite in place of PCL. Higher  $\Delta H_f$  is caused by the formation of the ester carbonyl functional group from the reaction between the —OH group of TiO<sub>2</sub> and the —COOH group of PCL-g-AA. In particular, the ester carbonyl group will confer higher mobility for the molten poly-

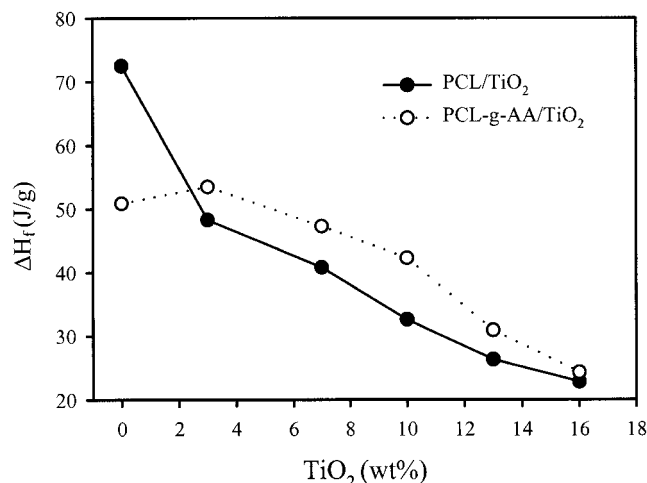
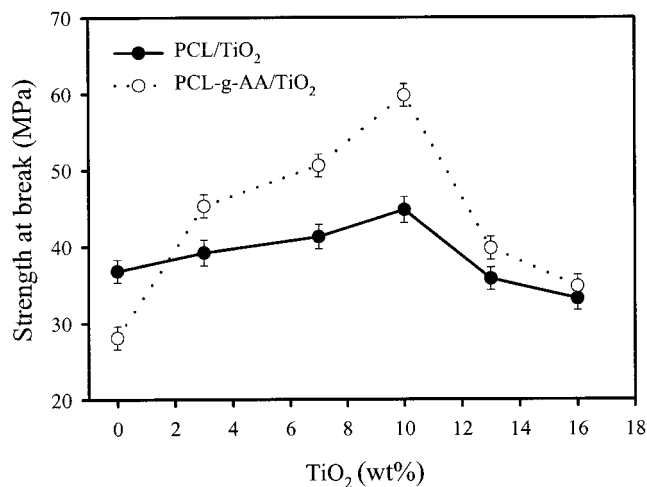


Figure 8 Fusion heat versus TiO<sub>2</sub> content for PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub> composites.



**Figure 9** Tensile strength at break versus TiO<sub>2</sub> content for PCL/TiO<sub>2</sub> and PCL-g-AA/TiO<sub>2</sub> composites.

mer segments; hence, the melt viscosity of PCL-g-AA/TiO<sub>2</sub> is lower.

### Tensile strength of hybrids

As for thermal stability, 10 wt % TiO<sub>2</sub> provided the most favorable outcome in both hybrids for tensile strength, with maximum values at this titania content (Fig. 9). For PCL/TiO<sub>2</sub> hybrids, the effect of titania content on the tensile strength is somewhat insignificant because the interfacial force between the PCL matrix and the titania network is only one of relatively weak hydrogen bonds. The PCL-g-AA/TiO<sub>2</sub> hybrid exhibited much better tensile strength than the equivalent PCL/TiO<sub>2</sub>, even though PCL-g-AA had a lower tensile strength than pure PCL. The enhancement in tensile strength was attributed to the presence of the titania network and the consequent formation of chemical bonds, perhaps the Ti—O—Ti bond, through the dehydration of carboxylic acid groups in PCL-g-AA with the residual titanium-bonded isopropyl group in the titania network. However, the tensile strength of the PCL-g-AA/TiO<sub>2</sub> hybrid decreased markedly with titania content above 10 wt %. This, similar to the deterioration in other properties above 10 wt % titania, is due to separation between the organic and inorganic phases. For PCL-g-AA/TiO<sub>2</sub>, the highest  $T_g$  at 10 wt % titania, gave an attractive strength at break of 60 MPa and signaled a significant improvement in interaction between the phases, compared with PCL/TiO<sub>2</sub>.

### CONCLUSION

Organic–inorganic hybrid materials were prepared via an *in situ* polymerization of TTIP in PCL or PCL-g-AA. FTIR spectra verified that the AA had been

grafted onto the PCL copolymer, that there were titanium bonded isopropyl functional groups in the titania network, and that Ti—O—C bonds were formed in the PCL-g-AA/TiO<sub>2</sub> hybrid. The Ti—O—C bonds may be produced through dehydration of carboxylic acid groups in the PCL-g-AA matrix with residual titanium-bonded isopropyl groups in the titania network. Additionally, as a result of the FTIR analysis, it was found that Ti atom coordination around TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub> units is predominant. This was in agreement with structural interpretation of the spectra. TGA tests showed that the PCL-g-AA/TiO<sub>2</sub> hybrids produced higher values of initial decomposition temperature than the equivalent PCL/TiO<sub>2</sub>. Meanwhile, maximum tensile strength and glass transition temperature values occurred at about 10 wt % TiO<sub>2</sub> for PCL-g-AA/TiO<sub>2</sub> hybrids. Above this 10 wt %, it is proposed that excess titania particles may cause separation between the organic and inorganic phases, so reducing compatibility between the titania network and PCL-g-AA. Compared with the pure polymer, PCL/TiO<sub>2</sub> showed only a small change in  $T_g$ , consistent with the relatively poor bonding between the organic and inorganic phase. However, with the PCL-g-AA chains chemically endlinked into the inorganic network, the shifts in  $T_g$  were much larger, because of the interfacial forces of PCL-g-AA/TiO<sub>2</sub> associated with the Ti—O—C and heteroassociated hydrogen bonds. The PCL/TiO<sub>2</sub>, on the other hand, only has weaker hydrogen bonds. The PCL-g-AA/TiO<sub>2</sub> hybrid is a significant improvement over PCL/TiO<sub>2</sub> as far as its thermal and mechanical properties are concerned, not least the enhancement in  $T_g$ . Such properties could be useful in a variety of high-temperature applications.

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