

# Thermal and Structural Characterization of Quasi-Nanometer Zirconium Carbon/Polyurethane Composites Prepared Under Roller Pressure

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Received 24 September 2004; accepted 20 April 2005

DOI 10.1002/app.22800

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this study, we use quasi-nanometer zirconium carbon (ZrC) to compose with polyurethane (PU) resin under roller pressure to study the interaction between the ZrC particle and PU molecules in the composite films, and find that the values of tensile strength, modulus, energy at break,  $T_m$  of soft-segment, and  $T_g$  of soft-segment, and weight percentage of char yield are increased, and elongation and char yield temperature are decreased with the increase of ZrC composed in PU, as this composed amounts are lower than 2.5%. The infrared spectroscopic spectra and wide angle X-ray diffraction patterns reveal that the ether

and ester groups of PU polymer can interact with ZrC to lower the interlayer distance of the crystal of PU polymer in composites. We assure that the interaction between the particles of ZrC and PU under roller pressure is in preparation process and account that the interaction between the particle and PU molecule will be an important factor to evaluate whether the particle in the composite is even and perfect. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 191–197, 2006

**Key words:** composites; glass transition; melting point; polyurethanes; thermalgravimetric analysis (TGA)

## INTRODUCTION

It is known that the mineral particles can release the far infrared ray and can be used in healthy textile materials.<sup>1</sup> Other nanometer particles such as nanometer titanium dioxide were used on the fields of antibacteria, electron conductance, anionic release, etc.<sup>2–4</sup> and these were all healthy uses. Generally, the nanometer particles were mixed uniformly in resins to form a fiber, membrane, and coated material. However, the aggregation of these nanometer grade particles made the particles could not be dispersed uniformly in the resins so as to decrease the mechanical property of the products such as fiber and film. In another case,<sup>5</sup> the sheety nanometer clay was composed with poly(vinyl alcohol) to produce the membrane that could decrease the oxygen permeability and prevent the water-soluble property.

In recent years, the nanometer clay was investigated for the surface modified with chemical compounds to improve the dispersion ability in resins.<sup>6–11</sup> It is known that the addition of clay to the polypropylene, nylon, or polyester could improve the mechanical, chemical, and oxygen permeation properties of clay-resin composite.<sup>12–17</sup> There are some other methods

that were used to prepare nanocomposites such as sol-gel process and melt mixing process.<sup>18,19</sup> Chen et al.<sup>20</sup> used organophilic clay to be added to poly-(3-hydroxybutyrate-co-3-hydroxyvalerate) chloroform solution to study the effect of nanometer clay particle on the crystalline kinetic of PHVB/clay composite and found that the organophilic clay nanometer particle could affect the crystallization temperature of the composite. Sand/clay-polyester composite was investigated<sup>21</sup> and found that the unsaturated polyester would react with clay under  $\gamma$ -irradiation to form a stable composite and improve the strength of polyester. Here, it was interesting to find that the nanometer particle of zirconium carbon could be sufficiently wetted and dispersed in polyurethane- (PU) solvent solution under the suitable roller pressure to form a good strength of the films and these were formed from this composite.

In this study, we will use quasi-nanometer zirconium carbon (ZrC) to compound with PU under the roller pressure about 1.0 kg/cm<sup>2</sup> at room temperature and then to form the films for the searching of strength and fourier transform infrared (FTIR), differential scanning calorimetry (DSC), thermalgravimetric analysis (TGA), X-ray (wide angle diffraction), and SEM analyses. Here, we are interested in the interaction between zirconium carbon particle and PU molecule affects the fine structure and thermal properties of the PU in composites and trying to confirm the effects with the earlier methods.

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**TABLE I**  
**Various Mechanical Properties of the Polyurethane and the Various Nanometer Zirconium Carbon/Polyurethane Composite Films Prepared Under Roller Pressure and Under Nonroller Pressure**

Composites	Nano Zrc (%[w/w])	Tensile strength at break (Mpa)		Elongation at break (%)		Modulus <sup>a</sup> (Mpa)	Energy at break <sup>a</sup> (J)
		Pressure	No pressure	Pressure	No pressure		
PU	0	19.43	19.43	766.68	766.68	3.69	0.36
PU/Nano ZrC	1.0	19.87	18.02	766.03	687.42	3.84	0.43
PU/Nano ZrC	2.5	20.44	13.94	765.45	589.72	4.17	0.51
PU/Nano ZrC	5.0	12.78	9.75	604.59	461.15	2.02	0.20

<sup>a</sup> These data were obtained from the samples prepared under roller pressure.

## EXPERIMENTAL

### Materials

Quasi-nanometer grade ZrC (~500 nm) was obtained from Desunnano Co., Ltd., Taipei, Taiwan. Polyurethane (PU, 30%) solid content was obtained from Nan Pao Resins Ltd., Taipei, Taiwan.

### Methods

#### Preparation of composite films

Quasi-nanometer ZrC (1.0, 2.5, 5.0 w/w %) was mixed with PU and squeezed between rollers repeatedly under the pressure of about 1 kg/cm<sup>2</sup> for 1 h to ensure that the surfaces of the nanometer particles were wetted by solvent and contacted with PU molecules. Then, the mixed solutions were coated on the glass with the thickness of 0.3 mm, dried at 90°C for 4 h, dipped in cold water for 8 h to form the films.

#### Morphology of the composite

The dispersion of quasi-nanometer ZrC in PU resin was examined using a Joel JSM-5200 scanning electron microscopy (SEM, Jeol Ltd., Tachigawa, Japan).

#### Thermal properties

TGA was performed using a Perkin–Elmer TGA-7 (PerkinElmer Co. Ltd., Shelton, CT). All samples were carried out at a heating rate of 10°C/min and under flowing air at a flow rate of 25 mL/min. The samples (10–15 mg) were placed on the plate of platinum for each experiment.

The thermal properties of pristine PU and ZrC/PU composites were also determined using a DSC (DSC Q1000 TA Instruments Inc., New Castle, DE). All scans were carried out at a heating rate of 10°C/min and under flowing nitrogen at a flow rate of 25 mL/min. The instrument was calibrated using the pure indium. Samples weighing about 5 mg were placed in standard aluminum sample pans for each DSC experiment.

#### Wide angle X-ray diffraction

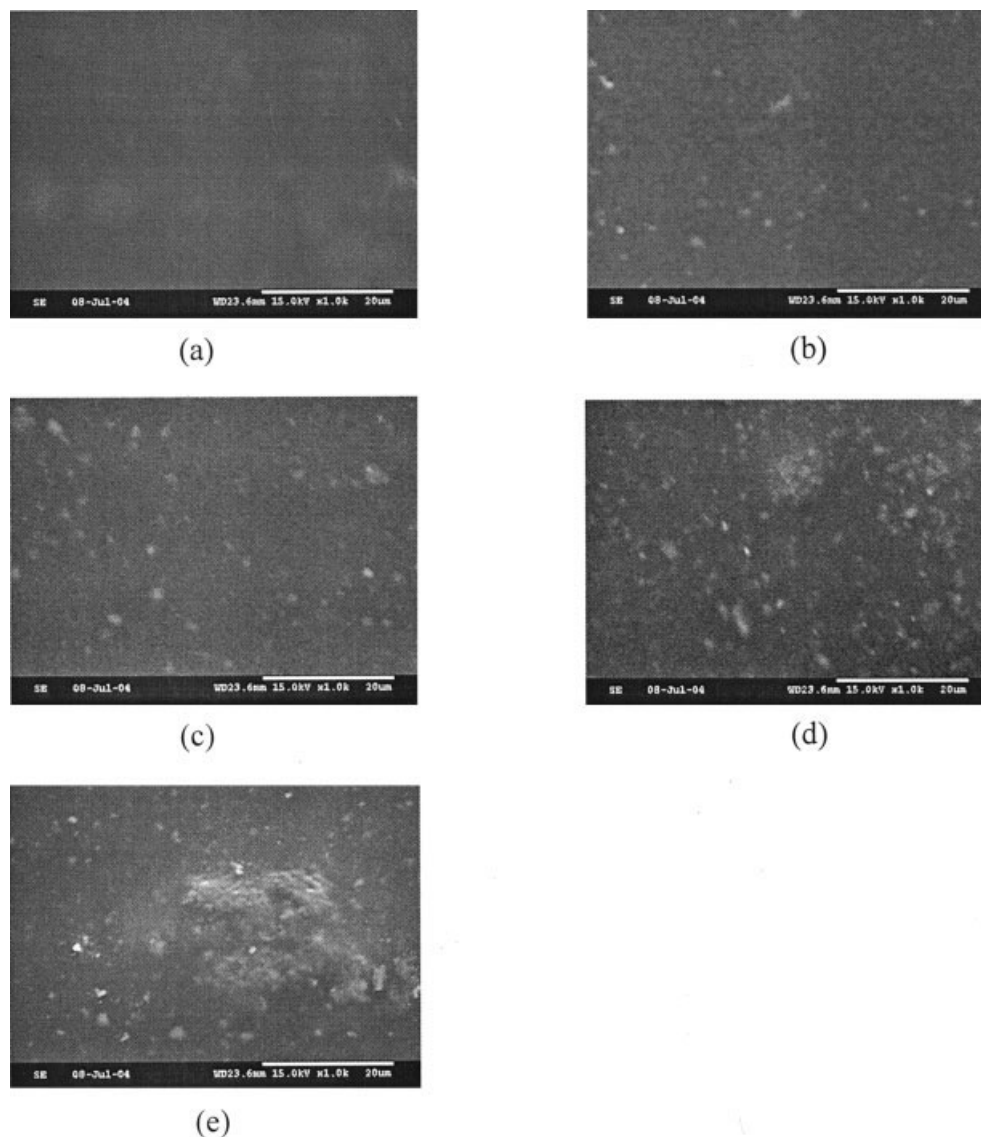
The wide angle X-ray diffraction (WAXD) was determined using a X-ray Powder Diffractometer XRD (MXP18, MAC Science, Yokohama, Japan) equipped with a Ni-filtered Cu K $\alpha$  radiation operated at 40 kV and 30 mA. Each film with 0.3 mm thickness was maintained stationary and scanned in the reflection mode from 2 to 30° at a scanning rate of 2°/min.

#### Fourier transform infrared spectroscopy

FTIR spectroscopic measurement of films was recorded on a Perkin–Elmer FTIR Spectrum One FTIR spectrophotometer (PerkinElmer Co. Ltd., Shelton, CT), wherein 12 scans with a spectral resolution of 1 cm<sup>-1</sup> were collected during each spectroscopic measurement. Infrared spectra of the specimens were determined from the film samples with a thickness of 0.3 mm. These films used in this study were thin enough to obey the Beer-Lambert law.

## RESULTS AND DISCUSSION

Table I shows the data of tensile strength, elongation, modulus, and energy at break of composite films in which various amounts of quasi-nanometer ZrC are compounded in PU in the presence of roller pressure. The values of tensile strength, modulus, and energy at break are increased with the increase of quasi-nanometer ZrC composed in PU, but obviously decreased as the amount of ZrC reached at 5%. The elongation decreased with the increase of ZrC composed in PU, but suddenly decreased similar to that of tensile strength. However, both the tensile strength and elongation of the composite films prepared in the absence of roller pressure are decreased with the increase of ZrC composed in PU. Some investigations also showed the similar tendencies for the clay/polypropylene, nylon, or polyester composites.<sup>13,16,17</sup> The previous study<sup>21</sup> pointed out that the physical properties (especially the tensile strength) of the nanometer particle/resin composite were higher than that of resin alone. Here, we are interested in the differences be-

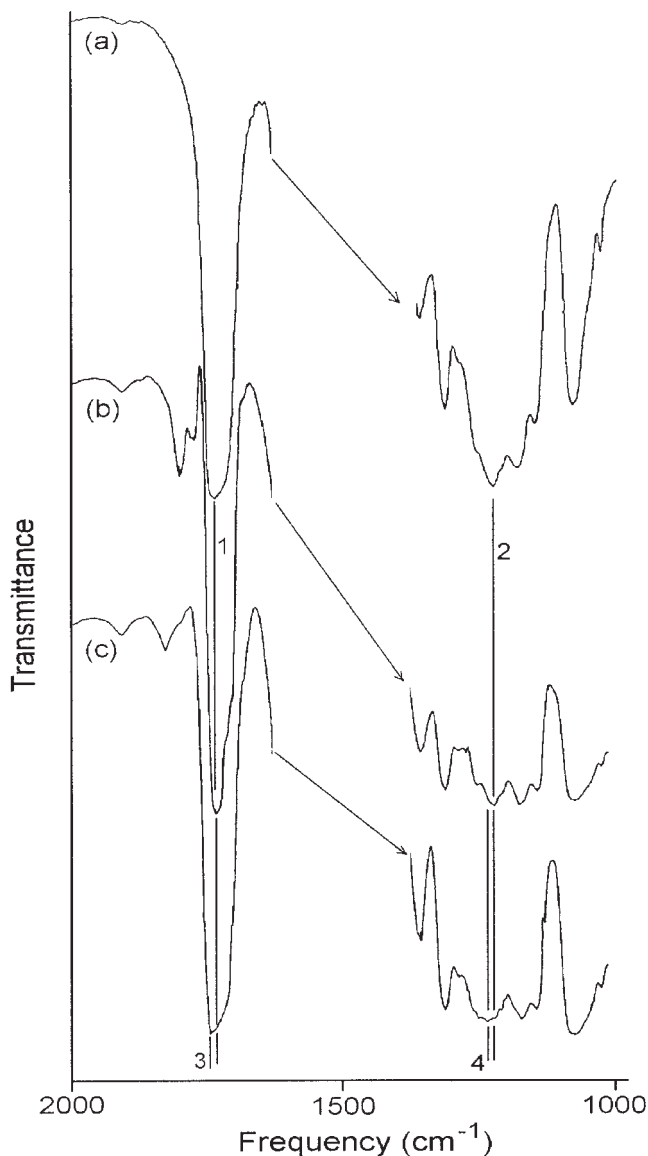


**Figure 1** SEM photographs of the films for (a) pristine PU, (b) 1% ZrC/PU composite prepared with roller pressure, (c) 2.5% ZrC/PU composite prepared with roller pressure, (d) 5% ZrC/PU composite prepared with roller pressure, and (e) 2.5% ZrC/PU composite prepared without roller pressure.

tween the composite films that were produced under roller pressure and under nonroller pressure.

First, to understand whether the quasi-nanometer ZrC particles were fully dispersed in PU resin, the films of the various ZrC/PU composites prepared in the presence of roller pressure were examined using SEM shown in Figure 1(a–d) for pristine PU, 1% ZrC/PU composite, 2.5% ZrC/PU composite, and 5% ZrC/PU composite, respectively. These figures show that the quasi-nanometer ZrC particles were dispersed in the PU resin fully except 5% ZrC/PU composite, in which some aggregations are found but not significantly. On the other hand, the quasi-nanometer ZrC particles (2.5% of PU) are aggregated significantly in the PU resin film prepared in the absence of roller pressure shown in Figure 1(e). The even dispersion of ZrC particles in PU resin prepared

under roller pressure may come from the interaction between the particle and resin. The interaction between the particle and PU molecule is an important factor for the composite. The higher values of tensile strength, modulus, and energy at break of the lower weight percentage (<2.5 wt %) of quasi-nanometer ZrC composed in Zr/PU composites adumbrate that the interaction between ZrC particle and PU molecule in the composite film prepared under roller pressure is possible, whereas the interaction between the particle and PU molecule in the composite film prepared in the absence of roller pressure is not possible. Additionally, the sudden decreasing of mechanical properties as the quasi-nanometer ZrC carbon particles composed in ZrC/PU composites was reached at about 5% shown in Table I may be caused by the too close together of those particles (the



**Figure 2** FTIR spectra of the films of (a) pristine PU alone, (b) full mixture of PU and 2.5% of ZrC without roller pressure, and (c) full mixture of PU and 2.5% of ZrC with roller pressure. (1) 1731, (2) 1223, (3) 1743, (4) 1234  $\text{cm}^{-1}$ .

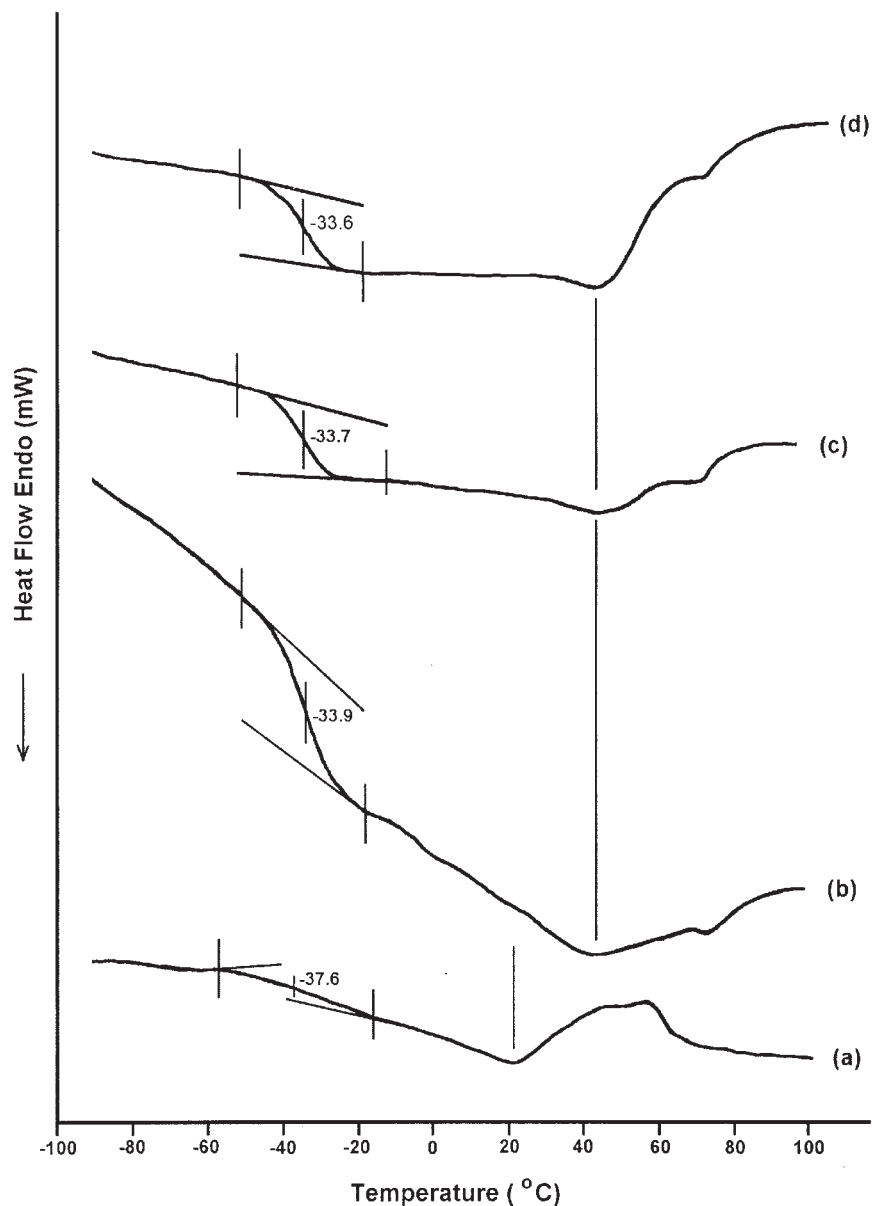
upper position in Fig. 1(d)) in the composite resins that may decrease the adhesive property between PU polymers. If this observation is true, the interaction between the particle and PU molecule will be an important factor for the formation of composite.

To confirm the interaction between nanometer zirconium carbon particle and PU molecule, the FTIR spectra of the films of (a) pristine PU, (b) full mixture of PU and 2.5% of ZrC prepared without roller pressure, and (c) full mixture of PU and 2.5% of ZrC prepared with roller pressure are shown in Figure 2(a–c), separately. The interesting and important absorbing bands are the ether group at 1223  $\text{cm}^{-1}$  and ester group at 1731  $\text{cm}^{-1}$  [Fig. 2(a)]. The film obtained from full mixture of PU and 2.5%

of ZrC that is prepared without roller pressure has the similar absorbing bands of ether and ester groups. However, the absorbing bands of ether and ester groups for the film obtained from full mixture of PU and 2.5% of ZrC that is prepared with roller pressure significantly shift to 1234 and 1743  $\text{cm}^{-1}$  separately. These results strongly suggest the interaction between quasi-nanometer ZrC particle and PU molecule and it is believed that the bond is coordinative bonding between the ether/ester groups of PU and the cationic ion of zirconium, and the ether group is containing in soft-segment and ester group is nearing the hard-segment. These results clearly reveal the interaction between ZrC particle and PU molecule in the presence of roller pressure is existed, but not existed in the absence of roller pressure. Meanwhile, the dispersion of ZrC particle will be evenly in the PU resin in the presence of roller pressure to form higher physical properties of composite films. To further assure the interaction between the ZrC particle and PU in the presence of roller pressure, the following thermal and crystalline properties are researched.

If the bonding between the ether/ester groups of PU and the cationic ion of zirconium is existence under roller pressure process, the thermal properties of the ZrC/PU will differ from those of pristine PU. Figure 3(a–d) shows the DSC thermograms of the films of pristine PU, 1% ZrC/PU composite, 2.5% ZrC/PU composite, and 5% ZrC/PU composite, respectively, and reveal that there is an obvious endothermic peak before 100°C for all cases. The endothermic peaks, that are believed to be the melting points of soft-segment, for the pristine PU, 1.0% ZrC/PU composite, 2.5% ZrC/PU composite, and 5% ZrC/PU composite are 21.3, 43.2, 43.4, and 43.5°C, respectively (Table II). These data for the composites are significantly higher than that for pristine PU and are only slightly increased with the increasing amounts of ZrC particle composed in the composites. The values obtained from the aslope regions of the initial endothermism in Figure 3 and those listed in Table II are the glass transition temperatures of soft-segment for ZrC/PU composites, and are also slightly increased with the increasing amounts of ZrC particle composed in the composites. These results are believed to be caused by the composition of quasi-nanometer ZrC and again affirm the interaction between the ether/ester groups of PU and the cationic ion of zirconium discussed in the earlier section of IR spectra in the presence of roller pressure.

Figure 4(a–c) shows the patterns of DSC (from 120 to 260°C) for pristine PU, 1.0% nanometer zirconium carbon/PU composite, and 2.5% nanometer zirconium carbon/PU composite, respectively, prepared under roller pressure and reveal a significantly higher melting temperature for the hard-segment of PU in the quasi-nanometer ZrC/PU composites. However, the values of melting temperature of



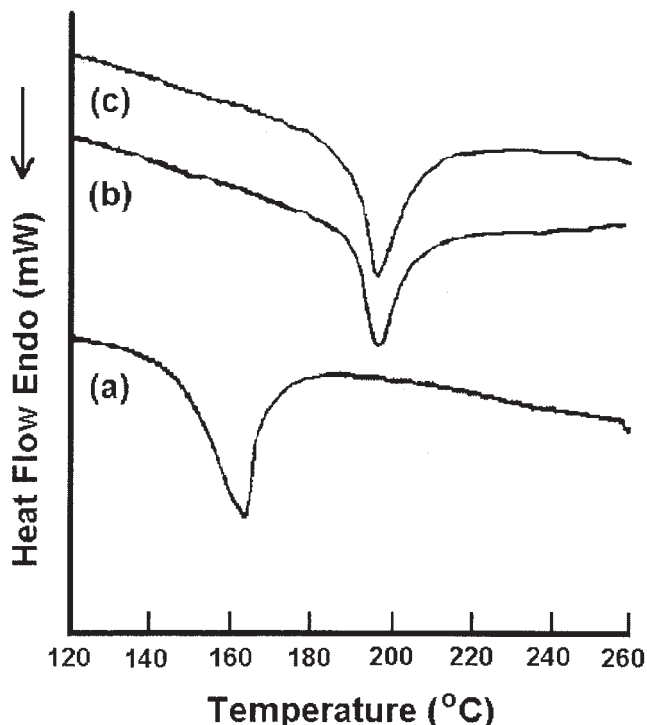
**Figure 3** DSC thermograms (from  $-100$  to  $100^{\circ}\text{C}$ ) of the films for (a) pristine PU, (b) 1% ZrC/PU, (c) 2.5% ZrC/PU, and (d) 5% ZrC/PU prepared under roller pressure.

hard-segment are almost the same with each other for the 1.0% nanometer zirconium carbon/PU composite and 2.5% nanometer zirconium carbon/PU

composite. This phenomenon may be caused by the crystalline structures for the various quasi-nanometer ZrC/PU composites are similar each other.

**TABLE II**  
The Data of Char Yield at  $800^{\circ}\text{C}$  and Char Yield Temperatures of the Polyurethane and the Various Nanometer Zirconium Carbon/Polyurethane Composite Films

Composites	Nano Zrc (%[w/w])	$T_g$ (soft-segment) ( $^{\circ}\text{C}$ )	$T_m$ (soft-segment) ( $^{\circ}\text{C}$ )	$T_m$ (hard-segment) ( $^{\circ}\text{C}$ )
PU	0	-37.6	21.3	163.5
PU/Nano ZrC	1.0	-33.9	43.2	196.3
PU/Nano ZrC	2.5	-33.7	43.4	196.4
PU/Nano ZrC	5.0	-33.6	43.5	—



**Figure 4** DSC thermograms (from 120 to 260°C) of the films for (a) pristine PU, (b) 1.0% ZrC/PU, and (c) 2.5% ZrC/PU prepared under roller pressure.

However, the interaction between the ZrC particle and PU molecule is again confirmed.

From the melting temperatures of hard-segment and soft-segment obtained from Figures 3 and 4, we account that the crystalline structures for the ZrC/PU composites prepared under roller pressure are different from that for pristine PU. Figure 5(a–c) reveal the patterns of WAXD for pristine PU, 2.5% ZrC/PU composite, and 5% ZrC/PU composite, respectively, and show that the main  $2\theta$  angles at about  $6^\circ$  and  $19^\circ$  for the film of pristine PU are increased significantly as the quasi-nanometer ZrC is composed in PU resin in the presence roller pressure. However, the difference between the composites is not so significant, that is the  $2\theta$  angles for 5% ZrC/PU are only slightly larger than that for 2.5% ZrC/PU. From the Bragg's equation, we realized that the interlayer distance in the crystalline region of PU resin is larger than those of Zr/PU composites so as to have lower melting temperature (Table II).

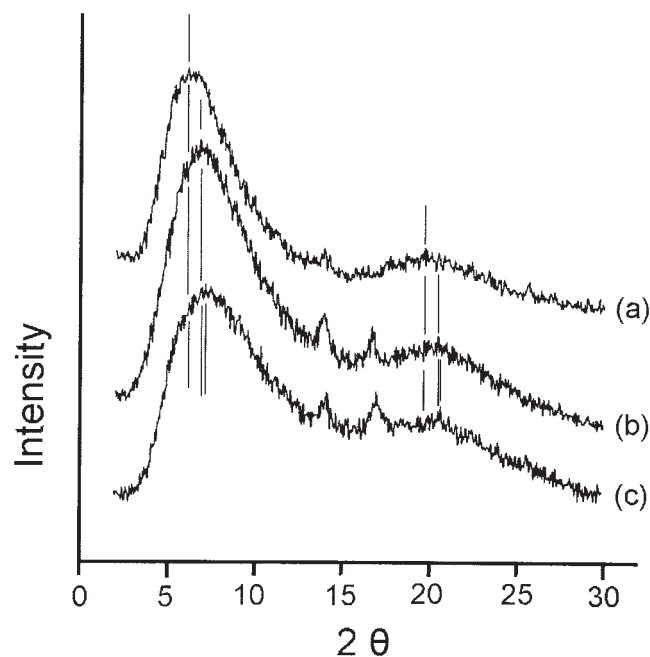
These patterns of TGA for the various composite films shown in Figure 6 reveal that the amounts of char yield for composites are obviously higher than that for pristine PU and are increased with the increasing amounts of quasi-nanometer ZrC composed in composites, however the char yield temperatures show inversely. The amounts of char yield listed in Table III show an interested phenomenon that these values are not in agreement with the amounts of quasi-nanometer ZrC composed in the composites. In

fact, the weight percentages of char yield for Zr/PU composites are significantly higher than those of quasi-nanometer ZrC used in composites. Additionally, the temperatures of weight loss at 10% ( $T_{d0.1}$ ) listed in Table III obtained from Figure 6 for the composite films are lower than that for pristine PU and these temperatures for the various composites are similar. These phenomena can only be caused by the composition of quasi-nanometer ZrC and can further affirm that the quasi-nanometer ZrC can interact with PU molecules under roller pressure and significantly affect the thermal properties of the composites and promote the formation of char and the degradation of PU polymer for the composites at the lower temperatures.

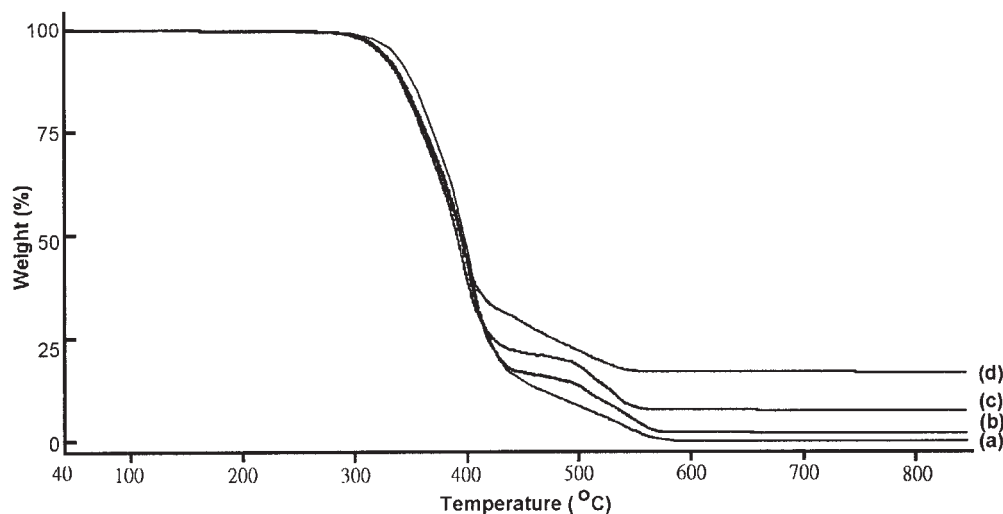
From these discussions, we can assure that the interaction between ZrC particle and PU under roller pressure is in preparation process. At the same time, the interaction between the particle and PU molecule will be an important factor to evaluate whether the particle in the composite is even and perfect.

## CONCLUSIONS

We prepared composite films of PU with ZrC in the presence of roller pressure to study the interaction between the ZrC particle and PU molecules. The physical properties such as tensile strength, modulus, and energy at break have maximum values as the amount of ZrC reached at 2.5%; however, the values of elongation are decreased with the increase of ZrC composed in PU matrix. IR spectra of ether and ester groups for the films



**Figure 5** Patterns of WAXD of the films for (a) pristine PU, (b) 1.0% ZrC/PU, and (c) 2.5% ZrC/PU prepared under roller pressure.



**Figure 6** Patterns of TGA of the films for (a) pristine PU, (b) 1.0% ZrC/PU, and (c) 2.5% ZrC/PU, and (d) 5% ZrC/PU prepared under roller pressure.

obtained from ZrC/PU composite films prepared under roller pressure shift about  $11\text{--}12\text{ cm}^{-1}$  as compared with those for pristine PU. These values of  $T_m$  of soft-segment and  $T_g$  of soft-segment for the PU matrix of composites both are significantly higher than that for pristine PU and slightly increased with the increasing amounts of zirconium carbon particle composed in the composites. The values of  $T_m$  of hard-segment for PU matrix of ZrC/PU composites are also significantly higher than that for pristine PU but similar each other. The interlay distance in the crystalline region of PU resin is larger than those of PU matrix in Zr/PU composites that were confirmed with WAXD patterns. The weight percentages of char yield for Zr/PU composites are obviously higher than that for pristine PU and are increased with the increasing amount of ZrC composed in composites. However, the char yield temperatures and the temperatures of weight loss at 10% for the composites are lower than those for pristine PU and the formers are decreased

with the increasing amount of ZrC composed in composites. The ZrC particles can interact with PU polymers in the presence of roller pressure, and will change the thermal properties and fine structure of the composite films and improve the mechanical properties, as the weight percentages of nanometer ZrC particle composed are lower than 2.5%.

## References

- Jung, Y. K. U.S. Pat. 6,108,581 (2000).
- Kim, Y. G. Eur. Pat. 1,390,083 (2002).
- Cho, J. E.; Kim, E. Y. Eur. Pat. 1,355,866 (2003).
- Toru, T. Jpn. Pat. 2003112381 (2003).
- Yeh, J. M.; Yu, M. Y.; Liou, S. J. *J Appl Polym Sci* 2003, 89, 3632.
- Lee, D. C.; Jang, L. W. *J Appl Polym Sci* 1998, 68, 1997.
- Chen, G.; Yao, K.; Zhao, J. *J Appl Polym Sci* 1999, 73, 425.
- Takeuchi, H.; Cohen, C. *Macromolecules* 1999, 32, 6792.
- Lin, J. J.; Cheng, I. J.; Wang, R.; Lee, R. J. *Macromolecules* 2001, 34, 8832.
- Kornmann, X.; Lindberg, H. *Polymer* 2001, 42, 1303.
- Zheng, H.; Zhang, Y.; Peng, Z.; Zhang, Y. *J Appl Polym Sci* 2004, 92, 638.
- Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kuracshi, T.; Kamigaito, O. *J Mater Res* 1993, 5, 1179.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kuracshi, T.; Kamigaito O. *J Appl Polym Sci* 1993, 49, 1259.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kuracshi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
- Ogata, N.; Kawakage, S.; Ogihara, T. *J Appl Polym Sci* 1997, 66, 573.
- Laval, T. U.S. Pat. 5,876,812 (1999).
- Ke, Y. C.; Long, C. F.; Qi, Z. N. *J Appl Polym Sci* 1999, 71, 1139.
- Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. *Macromolecules* 1995, 28, 8080.
- Gonsalves, K. E.; Chen, X. H. *Polym Mater Sci Eng* 1995, 73, 285.
- Chen, G. X.; Hao, G. J.; Guo, T. Y.; Song, M. D.; Zhang, B. H. *J Appl Polym Sci* 2004, 93, 655.
- Ismail, M. R.; Ali, M. A. M.; El-Milligy, A. A.; Afifi, M. S. *J Appl Polym Sci* 1999, 72, 1031.

**TABLE III**

The Values of  $T_g$  (Soft-Segment),  $T_m$  (Soft-Segment), and  $T_m$  Polyurethane and the Various Nanometer Zirconium Composite Films, Respectively

Composites	Nano ZrC (%[w/w])	Char yield (%[w/w]) <sup>a</sup>	Char yield temperature (°C) <sup>b</sup>	$T_{d0.1}$ (°C) <sup>c</sup>
PU	0	0	575	341
PU/Nano ZrC	1.0	1.7	566	322
PU/Nano ZrC	2.5	7.2	552	320
PU/Nano ZrC	5.0	16.8	539	322

<sup>a</sup> Char yields were obtained at 800°C.

<sup>b</sup> The temperatures that char were beginning to yield.

<sup>c</sup> The temperatures that had 10% weight loss.