

# Mechanical and Thermal Properties of Glass Bead-Filled Nylon-6

Li Huang,<sup>1,2</sup> Qiang Yuan,<sup>3</sup> Wei Jiang,<sup>3</sup> Lijia An,<sup>3</sup> Shengxiang Jiang,<sup>1</sup> R. K. Y. Li<sup>4</sup>

<sup>1</sup>Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

<sup>2</sup>Enhanced Oil Recovery Laboratory, Daqing Exploration and Development Institute, Daqing 163712, China

<sup>3</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

<sup>4</sup>Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China

Received 7 August 2003; accepted 3 March 2004

DOI 10.1002/app.20822

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

**ABSTRACT:** The mechanical and thermal properties of glass bead-filled nylon-6 were studied by dynamic mechanical analysis (DMA), tensile testing, Izod impact, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) tests. DMA results showed that the incorporation of glass beads could lead to a substantial increase of the glass-transition temperature ( $T_g$ ) of the blend, indicating that there existed strong interaction between glass beads and the nylon-6 matrix. Results of further calculation revealed that the average interaction between glass beads and the nylon-6 matrix decreased with increasing glass bead content as a result of the coalescence of glass beads. This conclusion was supported by SEM observations. Impact testing revealed that the notch Izod impact strength of nylon-6/glass

bead blends substantially decreased with increasing glass bead content. Moreover, static tensile measurements implied that the Young's modulus of the nylon-6/glass bead blends increased considerably, whereas the tensile strength clearly decreased with increasing glass bead content. Finally, TGA and DSC measurements indicated that the thermal stability of the blend was obviously improved by incorporation of glass beads, whereas the melting behavior of the nylon-6 remained relatively unchanged with increasing glass bead content. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1885–1890, 2004

**Key words:** nylon; glass beads; blends; mechanical properties; thermal properties

## INTRODUCTION

Glass beads have been widely used to improve the mechanical and thermal properties of commercial polymers. In the past few decades there have been many reports of investigations related to this topic,<sup>1–22</sup> most of which have focused on polyolefin materials. For example, Liang and Li<sup>1</sup> and Yuan et al.<sup>2</sup> successfully used glass beads to strengthen polypropylene (PP) and polyethylene (PE), and found a dramatic

change in toughness with increasing glass bead content or increasing temperature. Dubnikova et al.,<sup>3</sup> the investigative groups led by Li and Liang,<sup>4–6</sup> and Stricker et al.<sup>7,8</sup> extensively studied the static and dynamic mechanical behaviors and morphology properties for polyolefin/glass bead blends. The results indicate that the rigidity and thermal stability of polyolefin can be obviously improved by incorporation of glass beads. Beside polyolefin, glass bead-filled poly(2-hydroxyethyl methacrylate),<sup>12</sup> polyester resin,<sup>13</sup> styrene-acrylonitrile random copolymer (SAN),<sup>14</sup> and so forth were also studied in terms of mechanical and thermal properties.

Compared with polyolefins, glass bead-filled nylon has been seldom studied in recent decades. Ou and Yu<sup>9</sup> investigated the effects of the interfacial adhesion on the microdamage and rheological behavior of glass beads, with or without surface agent filled nylon-6, and found that the interfacial adhesion strength significantly affected the tensile strength and rheological behavior of composites. Meddad and Fisa<sup>10</sup> studied the filler/matrix debonding in polypropylene and polyamide 6 filled with glass beads using both tensile dilatometry and an analysis of tensile stress-strain curves. It was found that, depending on the level of adhesion, either a complete or partial debonding oc-

Correspondence to: W. Jiang (wjiang@ciac.jl.cn); L. An (ljan@ciac.jl.cn).

Contract grant sponsor: National Natural Science Foundation of China (NSFC) for the General Program; contract grant numbers: 50073023 and 50373044.

Contract grant sponsor: National Natural Science Foundation of China (NSFC) for the Major Program; contract grant number: 50390090.

Contract grant sponsor: Special Pre-Funds for Major Basic Research Projects; contract grant number: 2002CCAD4000.

Contract grant sponsor: Special Funds for Major State Basic Research Projects; contract grant number: 2003CB615600.

Contract grant sponsor: The Chinese Academy of Sciences project; contract grant number: KJCXZ-SW-H07.

TABLE I  
Main Properties of the Glass Beads

Mean diameter ( $\mu\text{m}$ )	Density ( $\text{g}/\text{cm}^3$ )	Young's modulus ( $10^6$ psi)	Rigidity modulus ( $10^6$ psi)	Hardness (Moh)	Softening point ( $^{\circ}\text{C}$ )
4.0	2.5	10.0	4.3	6.0	704

curs in the strain range (0–8%), and the accuracy of the tensile dilatometry is not sufficient to detect the onset of debonding.

In this work, glass beads were incorporated with nylon-6 over a wide range of compositions. The purpose was to study the mechanical and thermal properties of the resulting nylon-6/glass bead blends.

## EXPERIMENTAL

### Materials

Nylon-6, produced by Heilongjiang Nylon Factory (China), had a density of  $1.14 \text{ g}/\text{cm}^3$ . Glass beads (type 6000 CP-03), treated with coupling agents, were purchased from Potters Industries (USA). The main properties are listed in Table I.

### Sample preparation

The nylon-6 blends, with different glass bead contents, were mixed with a Brabender-like apparatus at a capacity of  $55 \text{ cm}^3$  (Rheocoder XSS-300; Shanghai, China) and at  $230^{\circ}\text{C}$  for 4 min. The roller speed used for blending was 40 rpm. The temperature, mixing time, and roller speed remained unchanged for all blends. For Izod impact testing, the plaques with dimensions of  $160 \times 63 \times 3.2 \text{ mm}$  were prepared by mold pressing at  $230^{\circ}\text{C}$ , under a pressure of  $90 \text{ kg}/\text{cm}^2$ , then were naturally cooled to room temperature under a specified pressure. Izod impact specimens (dimensions:  $63 \times 12 \times 3.2 \text{ mm}$ ) were cut from the plaques. For tensile testing, the blends were molded directly into dog-bone-shaped tensile specimens [ $30 \times 15 \times 1 \text{ mm}$  gauge (length  $\times$  width  $\times$  thickness)]. Their molding pressure and temperature were the same as those mentioned previously.

### Mechanical measurements

Tensile tests were carried out on an Instron-1121 tester (United Kingdom) at a deformation rate of  $50 \text{ mm}/\text{min}$  at room temperature.

Izod impact specimens were tested by a XJU-2.75J Izod impact tester (made in Chengde, China) at room temperature ( $25^{\circ}\text{C}$ ). These specimens were sharply notched with a  $45^{\circ}$  V-shape knife. The tip radius was  $0.25 \text{ mm}$ .

The dynamic mechanical properties of the samples were studied with a Netzsch DMA 242C (Netzsch-Gerätebau GmbH, Bavaria, Germany). The test temperature range was from  $-50$  to  $100^{\circ}\text{C}$ , at a heating rate of  $3^{\circ}\text{C}/\text{min}$  and a fixed frequency of 1 Hz.

### Thermal analysis

Thermogravimetric analysis (TGA) measurements were carried out on a Perkin-Elmer 7 Series thermal analysis system (Perkin Elmer Cetus Instruments, Norwalk, CT). The TGA scans were recorded at  $10^{\circ}\text{C}/\text{min}$  under a nitrogen atmosphere from  $25$  to  $600^{\circ}\text{C}$ .

Differential scanning calorimetry (DSC) measurements for the samples with various contents of glass beads were studied on a Perkin-Elmer 7 Series thermal analysis system. The samples underwent three series of heating-cooling-heating cycles to eliminate the thermal history. Both heating and cooling scans were carried out at a rate of  $20^{\circ}\text{C}/\text{min}$ .

### Morphological observations

A JXA-840 scanning electron microscope (SEM; JEOL, Tokyo, Japan) was used to study the morphologies of the fracture surfaces of impact test specimens. The specimens were cryofractured in liquid nitrogen. All

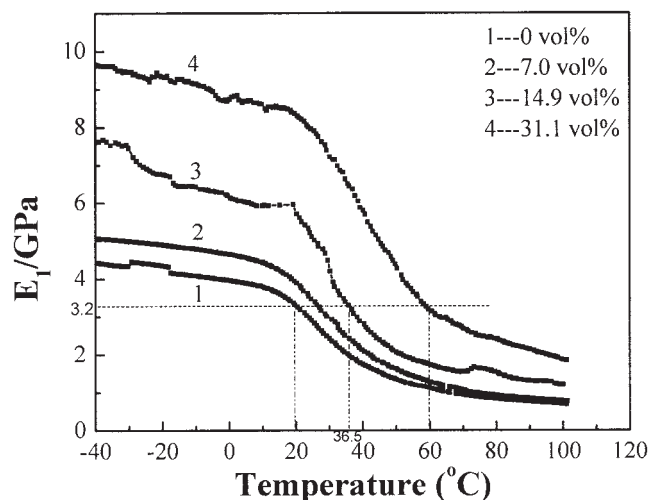


Figure 1 Storage modulus spectra for nylon-6/glass bead blends.

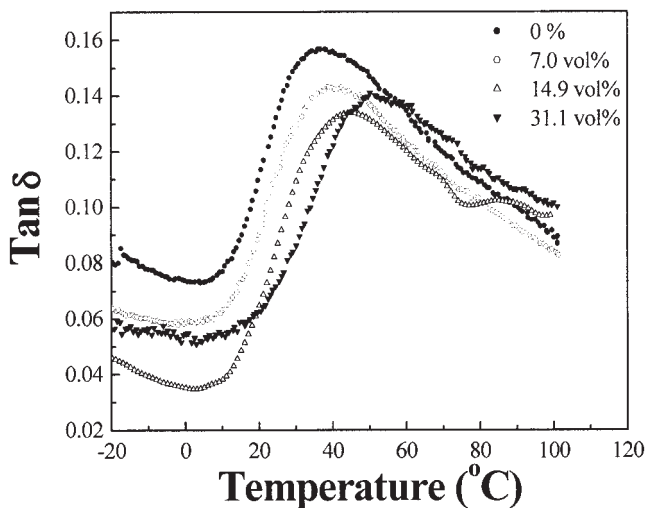


Figure 2 Loss factor,  $\tan \delta$ , versus temperature for various nylon-6/glass bead blends.

the samples were coated with a thin layer of gold before SEM observations.

RESULTS AND DISCUSSION

Figure 1 shows the variation of storage modulus ( $E'$ ) with temperature for the nylon/glass bead blends obtained from DMA measurements. The results indicate that the nylon-6 storage modulus ( $E'$ ) at 20°C is 3.2 GPa. To evaluate the heat resistance of the blends, we define the temperature at  $E' = 3.2$  GPa as  $T_{E'=3.2}$ . From Figure 1, it is observed that  $T_{E'=3.2} = 36.5^\circ\text{C}$  for the blend containing 14.9 vol % glass bead content, and  $T_{E'=3.2} = 60^\circ\text{C}$  for the blend containing 31.1 vol % glass bead content. These results imply that the heat-

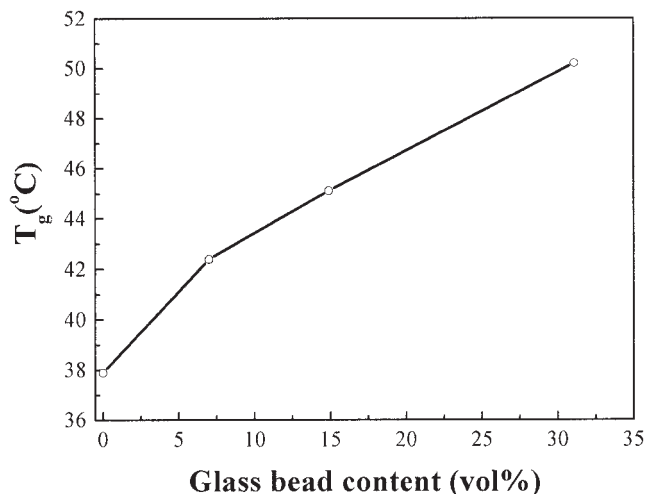


Figure 3 Variation of the glass-transition temperature with glass bead content.

TABLE II  
Values of  $\beta$  Calculated from Eq. (1) for Various Nylon-6/Glass Bead Blends

Number	Glass bead volume fraction	$\tan \delta$	$\beta$
1	0	0.157	—
2	0.07	0.143	1.27
3	0.149	0.134	0.98
4	0.311	0.141	0.33

deflection temperature of nylon-6 can be significantly improved by incorporation of glass beads.

Figure 2 shows the variation of the loss factor  $\tan \delta$  with temperature obtained from DMA measurements. It is found that the peak shifts to higher temperature with increasing glass bead content, indicating that the addition of glass bead into nylon-6 causes an increase in the glass-transition temperature ( $T_g$ ) of the blends.

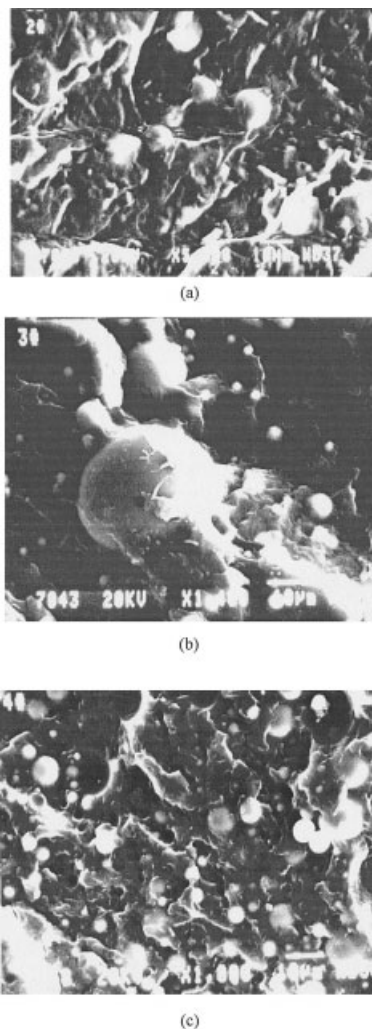


Figure 4 SEM microphotographs showing the cryofractured surface for various nylon-6/glass bead blends. Glass bead content: (a) 7 vol %; (b) 14.9 vol %; (c) 31.1 vol %.

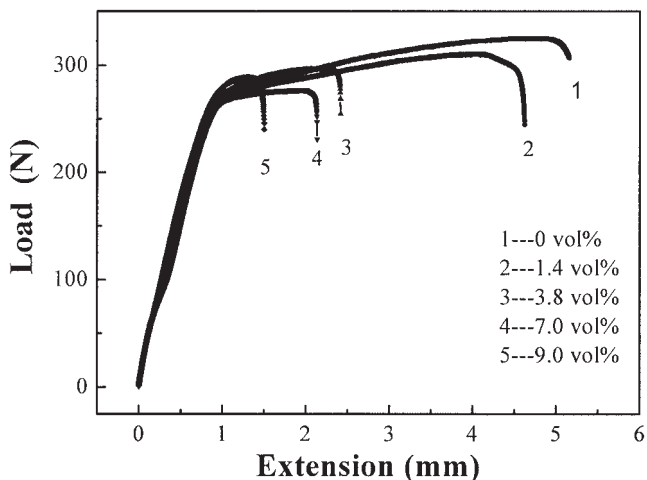


Figure 5 Load-displacement curves for various nylon-6/glass bead blends.

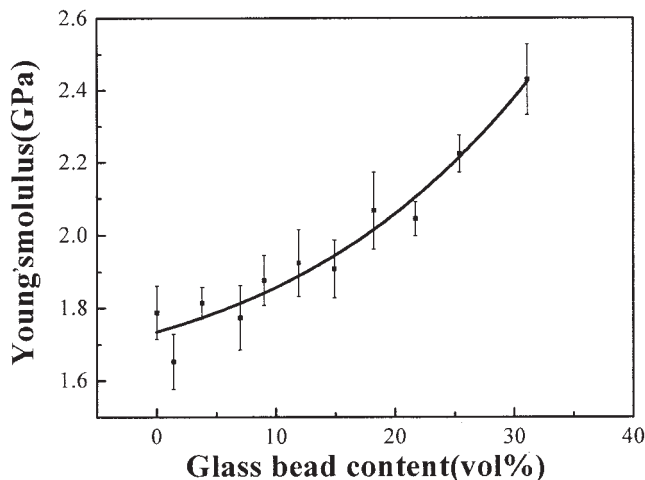


Figure 7 Variation of Young's modulus with glass bead content for various nylon-6/glass bead blends.

The  $T_g$  increases from 37.9 to 50.2°C with increasing glass bead content from 0 to 31.1 vol % (Fig. 3).

In general, it has been established that the shift of  $T_g$  results from the contribution of the interaction between the dispersed phase and matrix and the volume fraction of the resulting interface. To evaluate the average interaction for the nylon-6/glass bead blends, the following equation<sup>23</sup> was used in this study:

$$(\tan \delta_{\max})_c / (\tan \delta_{\max})_m = 1 - \beta V_f \quad (1)$$

where  $(\tan \delta_{\max})_c$  and  $(\tan \delta_{\max})_m$  are the maximum value of  $\tan \delta$  for the blends and matrix, respectively;  $V_f$  is the volume fraction of the filler; and  $\beta$  is a coefficient that depends on the interaction between the dispersed phase and the matrix.  $\beta > 1$  means strong

interaction. Table II lists the calculated results from eq. (1) for various blends. It is found that the value of  $\beta$  increased substantially up to 1.27 with decreasing glass bead content. The results indicate that the average interaction between the dispersed phase and the matrix becomes weaker for higher glass bead content as a result of the coalescence of glass beads. This behavior can be further studied from SEM observation. Figure 4(a)–(c) introduce SEM microphotographs showing the cryofractured surfaces for various nylon-6/glass bead blends. It is found that glass beads were embedded in nylon-6 for lower glass bead content. The results imply that there is a strong interaction between the nylon-6 matrix and glass beads. With increasing glass bead content, the coalescence of glass beads can be observed. The SEM observations are in

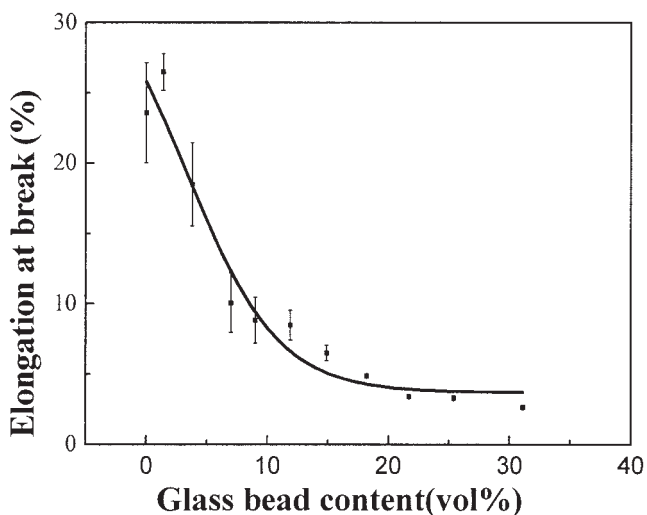


Figure 6 Variation of elongation at break with glass bead content for various nylon-6/glass bead blends.

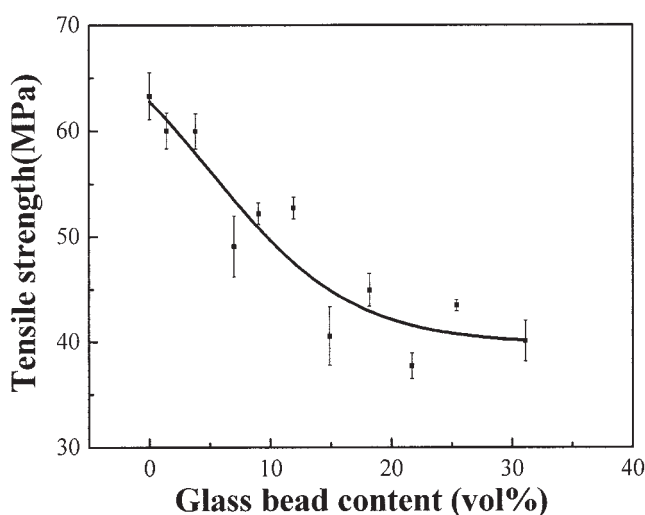


Figure 8 Variation of tensile strength with glass bead content for various nylon-6/glass bead blends.

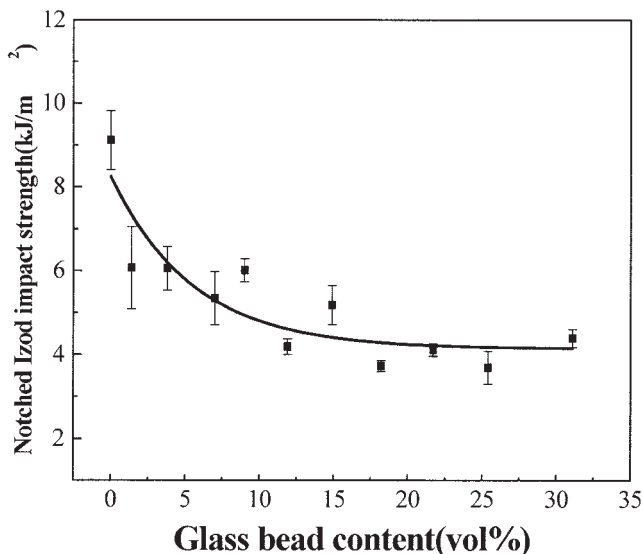


Figure 9 Variation of notched Izod impact strength with glass bead content for various nylon-6/glass bead blends.

agreement with the previous discussion on the  $\beta$ -values.

Figure 5 is the plot of load force versus displacement for various nylon-6/glass bead blends. It is found that the extension of the nylon-6 obviously decreases by the introduction of glass beads. As a result, the elongation at break of the blend decreases considerably with increasing glass bead content (Fig. 6). Moreover, tensile testing results show that the Young's modulus of the blend increases continuously with increasing glass bead content (Fig. 7), whereas the tensile strength correspondingly decreases with increasing glass bead content (Fig. 8).

Figure 9 shows the notch Izod impact strength versus glass bead content for the nylon-6/glass bead blends at room temperature. The results show that the impact strength reduces sharply with increasing glass bead content up to 11.9 vol %, after which it decreases slowly.

Figure 10 shows the DSC results for various nylon-6/glass bead contents. The melting temperature of the nylon-6 used in this study is 221.7°C. Moreover, the results reveal that introduction of glass beads has less effect on the melting temperature of the nylon-6.

Finally, the thermogravimetric behavior from TGA testing is shown in Figure 11. The results indicate that the decomposition temperature of the blend clearly increases with increasing glass bead content.

CONCLUSION

The mechanical and thermal behaviors of glass bead-filled nylon-6 were studied by DMA, tensile testing, Izod impact, TGA, and DSC tests. DMA test results showed that the incorporation of glass beads could

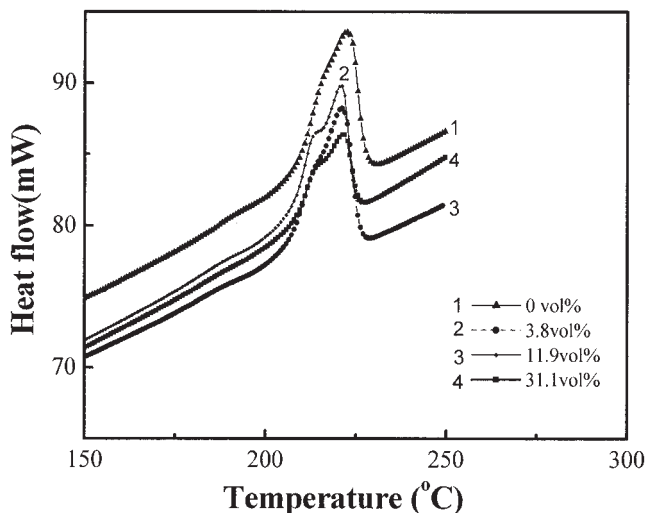


Figure 10 DSC results for various nylon-6 blends.

lead to a substantial increase of the glass-transition temperature ( $T_g$ ) of the blend, indicating that there is strong interaction between glass beads and the nylon-6 matrix. Further calculation results revealed that the average interaction between glass beads and the nylon-6 matrix decreased with increasing glass bead content as a result of the coalescence of glass beads. This conclusion was in substantial agreement with the SEM observation. Static tensile measurements showed that the Young's modulus of the blend increased considerably with increasing glass bead content, whereas the tensile strength clearly decreased with increasing glass bead content. Impact testing showed that the notch Izod impact strength of the nylon-6/glass bead blend significantly decreased with increasing glass bead content. TGA and DSC measurements suggested that the thermal stability of the blend was obviously improved by incorporation of glass beads, whereas

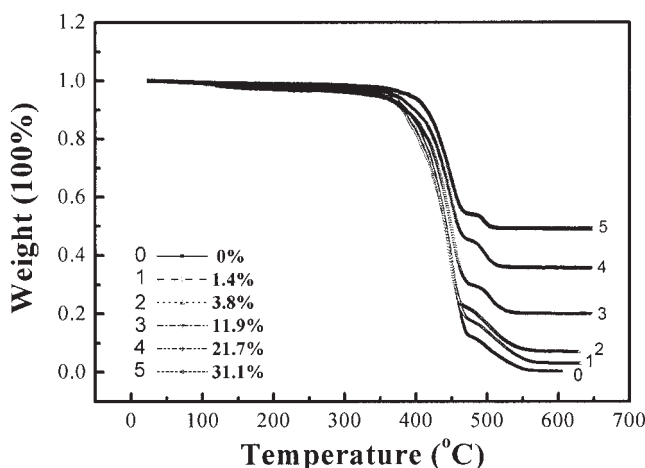


Figure 11 Weight loss versus temperature for nylon-6 and nylon-6/glass bead blends.

the melting behavior of the nylon-6 remained relatively unchanged with increasing glass bead content.

## References

1. Liang, J. Z.; Li, R. K. Y. *Polymer* 1999, 40, 3191.
2. Yuan, Q.; Jiang, W.; Zhang, H. X.; Yin, J. H.; An, L. J.; Li, R. K. Y. *J Polym Sci Part B: Polym Phys* 2001, 39, 1855.
3. Dubnikova, I. L.; Berezina, S. M.; Antonov, A. V. *J Appl Polym Sci* 2002, 9, 1911.
4. Li, R. K. Y.; Liang, J. Z.; Tjong, S. C. *J Mater Process Tech* 1998, 79, 59.
5. Liang, J. Z.; Li, R. K. Y.; Tjong, S. C. *Polymer Test* 2001, 19, 213.
6. Liang, J. Z.; Li, R. K. Y.; Tjong, S. C. *Polymer Test* 1997, 16, 529.
7. Stricker, F.; Bruch, M.; Mulhaupt, R. *Polymer* 1997, 38, 5347.
8. Stricker, F.; Maier, R. D.; Bruch, M.; Thmann, R.; Mulhaupt, R. *Polymer* 1999, 40, 2077.
9. Ou, Y. C.; Yu, Z. *Polym Int* 1995, 37, 113.
10. Meddad, A.; Fisa, B. *J Appl Polym Sci* 1997, 4, 653.
11. Perrier, G.; Bergeret, A. *J Polym Sci Part B: Polym Phys* 1997, 35, 1349.
12. Kolařík, J.; Janáček, J.; Nicolais, L. *J Appl Polym Sci* 1976, 20, 841.
13. Leidner, J.; Woodhams, R. T. *J Appl Polym Sci* 1974, 18, 1639.
14. Narkis, M.; Nicolais, L. *J Appl Polym Sci* 1971, 15, 469.
15. Droste, D. H.; Dibenedetto, A. T. *J Appl Polym Sci* 1969, 13, 2149.
16. Friedrich, C.; Scheuchenpflug, W.; Neuhäusler, S.; Rösch, J. *J Appl Polym Sci* 1995, 57, 499.
17. Peng, J.; Wei, G. H.; Zhang, Y. D. *J Appl Polym Sci* 2003, 88, 2478.
18. Bai, S. L.; Chen, J. K.; Huang, Z. P.; Liu, Z. D. *Polym Int* 2001, 50, 222.
19. Tjong, S. C.; Xu, S. A. *J Appl Polym Sci* 2001, 81, 3231.
20. Fedors, R. F.; Landel, R. F. *J Polym Sci Polym Phys Ed* 1975, 13, 579.
21. Liang, J. Z.; Li, R. K. Y. *J Appl Polym Sci* 1999, 73, 1451.
22. Dekkers, K. E. J.; Heikens, D. *J Appl Polym Sci* 1983, 28, 3809.
23. Ashida, M.; Noguchi, T. *J Appl Polym Sci* 1985, 30, 1011.