New Toughened Polypropylene/Organophilic Montmorillonite Nanocomposites

Peiyao Li,[1,2] Guojun Song,[1,2] Lanlan Yin,[3] Li Wang,[1] Guiping Ma[2]

[1]*Institute of Polymer Materials, Qingdao University, Qingdao 266071, China*
[2]*College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China*
[3]*Haidu Institute of Qingdao Agriculture University, Laiyang 265200, China*

ABSTRACT: A new toughened polypropylene (PP)/organophilic montmorillonite (OMMT) nanocomposite was obtained by melt intercalation extrusion in a twin-screw extruder without any compatibilizer. The nanocomposites were characterized by transmission electron microscopy (TEM) observation, melt flow rate (MFR) testing, mechanical properties measurement, melting and crystallization behaviors, and thermal stability determination. TEM images revealed the existence of intercalated OMMT layers dispersed throughout the PP matrix. A clear reduction in MFR was observed as the OMMT content increased. The yield strength, elongation at yield, and initial modulus of the PP/OMMT nanocomposites increased slightly as the result of the reinforcement of the OMMT nanofiller. The ultimate value of notched impact strength of the nanocomposites was over twofold that of neat PP after incorporation with 4 wt % OMMT; meanwhile, the heat deflection temperature values showed that the thermal stability increased a little. This is a new approach for preparation for the production of a toughened PP material with a high thermal stability and rigidity. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2116–2121, 2008

Key words: nanotechnology; organoclay; poly(propylene) PP); thermal properties; toughness

INTRODUCTION

As a kind of widely used traditional plastic, polypropylene (PP) has the attractive characteristics of low cost, low weight, high heat deflection temperature (HDT) above 100°C, and extraordinary versatility in terms of properties, applications, recycling, and so on, although PP material also has the disadvantages of low tensibility, poor toughness, and so on. Traditional toughness reinforcement of PP by the addition of rubber[1,2] or elastomer[3] decreases the strength and rigidity of the materials; this especially weakens the thermal stability of the materials. In this study, we focused on a new method for enhancing the toughness of PP by adding organophilic montmorillonite (OMMT) while retaining the material's high strength, rigidity, and thermal stability.

Formerly, polymer/OMMT nanocomposites have been successfully prepared and characterized;[4–7] nevertheless, it was necessary to use a polymer containing a polar group to make the montmorillonite (MMT) disperse readily. Because PP has no a polar group to act on OMMT, which was ion-exchanged by the ordinary modifier as hexadecyl trimethyl ammonium bromide, dodecyl amine, and so on, it was difficult to disperse the OMMT particles into nanoscale. Recently, two major methods have been suggested for PP/OMMT nanocomposite preparation, one being *in situ* polymerization[8–10] and the other being melt-extrusion compounding with a PP-grafted malefic as the compatibilizer.[11–15] It was complex in the method of *in situ* polymerization to readjust the process of polymerization; by contrast, the melt intercalation method with compatibilizer was a convenient and effective processing method for nanocomposite preparation. It was supposed that without compatibilizer, the cost of the nanocomposite preparation would decrease and the processing would be simplified. In this study, we used a new type of OMMT produced and well chosen by our research center. We used X-ray diffraction (XRD) and thermogravimetric analysis (TGA) testing to characterize the optimal OMMT. The morphology of OMMT in the PP matrix was observed with transmission electron microscopy (TEM); the TEM observation confirmed the dispersion scale of OMMT layers and identified the hierarchical structure in detail. Moreover, on the basis of the testing results of the melt flow rate (MFR), mechanical properties, melting and crystallization behaviors, and thermal stability, the structure–property relationships of the PP/OMMT composites are discussed purposively. We considered the production of the new toughened PP/OMMT nanocomposite to be important for the impact strength and thermal stability of the materials.

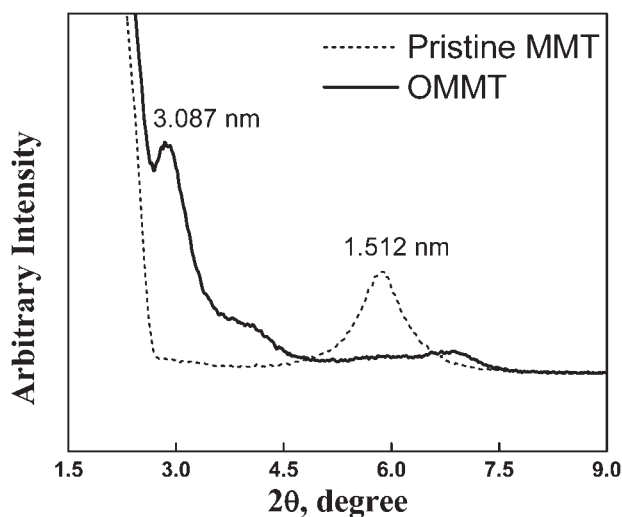WILEY
InterScience®
DISCOVER SOMETHING GREAT

Figure 1 XRD patterns of pristine MMT and OMMT.

EXPERIMENTAL

Materials

The PP (T30S) used in this study was a commercial product supplied by the Qilu Petrochemical Co., Ltd. (Zibo, Shandong, China). The MFR (at 230°C and 2.16-kg loads) and density of PP were 3.20 g/10 min and 0.91 g/cm^3, respectively. OMMT (FMO01-F) was produced by our research center, the Institute of Polymer Materials.

Preparation of OMMT

MMT was wetted with water and then purified by sedimentation and washing. The fined MMT (50 g) was dispersed into 1000 mL of distilled water at 55°C under vigorous stirring. A mixture of 85 g of ditetradecyl methyl amine and 10 mL of 98% concentrated sulfuric acid was prepared at 60°C and then added to the MMT dispersion. The reaction was maintained for 5 h. The sediment was collected by filtration, washed with water, and then dried *in vacuo*; next, it was ground and sieved.

Preparation of the nanocomposites

The PP pellets, OMMT, and antioxidant metered independently in the required proportions were placed into the homomixer. After they were mixed homogeneously, a twin-screw extruder (corotative screws, *D* (diameter) = 35.0 mm, *L/D* (length/diameter) = 32/1) was used to extrude the composites; the barrel temperature distribution was 180–200°C from the feeder to extrusion head, and the screw speed was 80 rpm. The obtained strands were grained and vigorously dried at 80°C in an oven. The dry pellets were putted into the injection machine to inject

standard samples, and the temperature range from the barrel to the spray nozzle was 180–200°C.

Characterization

XRD experiments were performed for the pristine MMT and the OMMT with a D/max-RB diffractometer (Rigaku, Tokyo, Japan), which had an X-ray generator of 12 kW, a graphite monochromator, and Cu Kα radiation (wavelength = 0.154 nm) and was operated at 40 lV and 100 mA. The samples were scanned at a speed of 5°/min under diffraction angles (2θ) in range 1–30°.

TGA was performed on a TGA/STDA851^e instrument produced from Mettler–Toledo Co. (Shanghai, China) with platinum pan with about 7 mg of material as the probe. The samples were heated at 10°C/min in a nitrogen atmosphere under a flow rate of 50 mL/min.

Samples were thin-sectioned with an ultramicrotome. Sections were collected on a copper grid and examined with a transmission electron microscope (JEM-1200EX) produced from Jeol Co. (Tokyo, Japan) running at an accelerating voltage of 60 kV.

MFR was measured according to the standard ISO1133-1997. The testing temperature was 230°C, and the loading weight used was 2.16 kg, respectively.

The thermal behavior of the nanocomposite was studied by differential scanning calorimetry (DSC), with a DSC822^e instrument produced from Mettler–Toledo. The sample weight was 7 mg; it was heated to 230°C and held at this temperature for 5 min to cancel previous thermal history. Then, the sample was cooled at a nominal rate of 10°C/min to room temperature and was then heated to 230°C, again at the 10°C/min rate. The sample was heated or cooled in a nitrogen atmosphere under a flow rate of 50 mL/min.
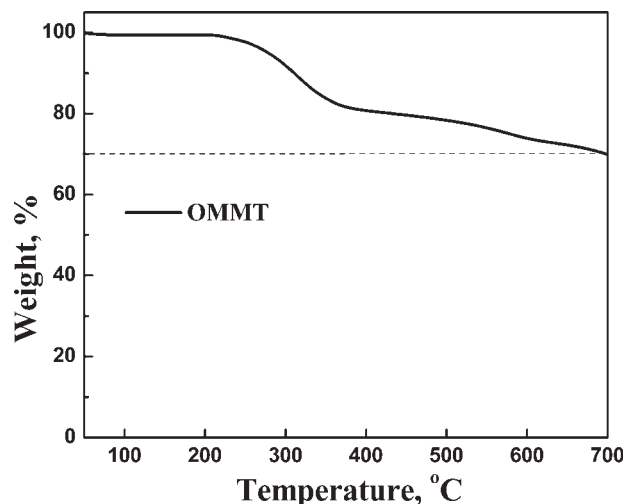

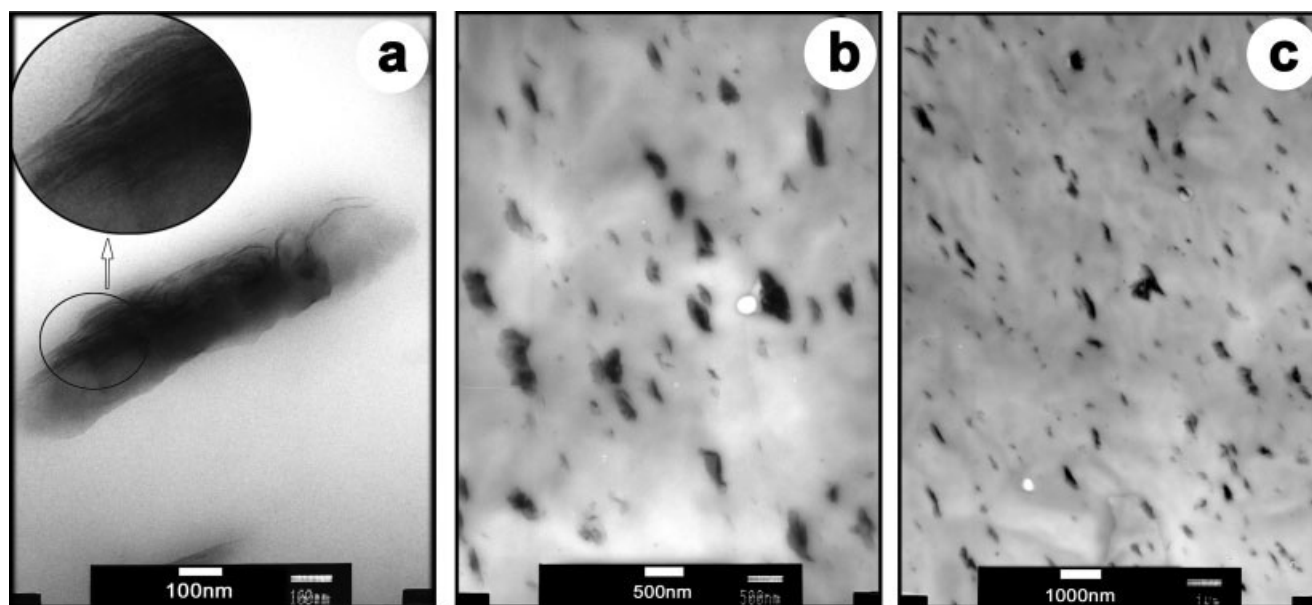**Figure 2** TGA thermograms of OMMT.

Figure 3 TEM images of the PP/OMMT nanocomposite (4.0 wt % OMMT): (a) 60,000, (b) 10,000, and (c) 5000×.

Tensile stress and tensile modulus were measured according to the standard ISO1184-1983 with an electronic tensile tester. Notched impact strength was measured according to the ISO179-1982 standard method with standard notched specimens. All measurements were made with 10 samples, the values were averaged, and the reported results were from room temperature tests.

Standard samples prepared on the basis of the standard ISO75-1:2003 were tested for HDT with an HDT tester with a load of 0.45 MPa.

RESULTS AND DISCUSSION

Characterization of OMMT

The OMMT was prepared with a well-chosen organic modifier. As a result, the surface of the OMMT had organic characteristics. The hydrophobic organic modifier could facilitate the intercalation of a hydrophobic polymer into MMT by reducing the surface energy.

XRD and TGA tests were used to characterize OMMT. Figure 1 shows the XRD patterns of pristine MMT and OMMT. The interlayer space was determined from the diffraction peak position in the XRD with Bragg's equation. The interlayer spaces of pristine MMT and OMMT were 1.51 and 3.09 nm, respectively. This suggested the successful preparation of OMMT. It was also observed that at about 4.2 and 7.0°, there were low peaks in Figure 1; we think they were caused by the others compounds in the modifier, which contained several compounds with similar structures. Figure 2 shows the TGA thermo-

gram of OMMT. TGA curves taken from the OMMT after it was subjected to a temperature of 700°C resulted in 70 wt % ash content. Therefore, the total weight loss of 30 wt % could be attributed to the decomposition of the organic modifier that intercalated into the MMT galleries.

Microscopy analysis of the nanocomposites

Observation of TEM was used to reveal the type of the prepared nanocomposites. TEM images were screened at high and low magnifications to observe the dispersion state of OMMT in the matrix; they are presented in Figure 3. In the images, the light-color place was the PP matrix, and the dark lines or particles were the single layer or multilayer of the OMMT layers. The submicroscopic structure in detail of the nanocomposites is presented in Figure 3(a) at a 100-nm graduation scale. The photograph clearly shows the lamellar structure of OMMT intercalated by the PP macromolecular chain; the lines of the layers are well marked in the magnified circle zone. Furthermore, the interface of the OMMT and the PP matrix was indistinct, which suggests that the OMMT and PP matrix had good compatibility. Figure 3(b,c) shows the dispersion of OMMT in the nanocomposite at low magnification at 500- and 1000-nm scales, respectively; the OMMT multilayers were dispersed homogeneously and had orientated characters. According to the TEM observation, it was confirmed that the uniformly dispersed intercalated PP/OMMT nanocomposite was prepared.
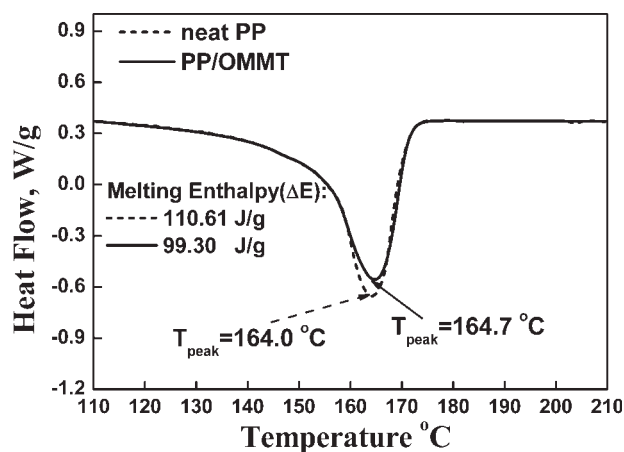
Figure 4 DSC curves of neat PP and the PP/OMMT (4.0 wt %) nanocomposite.

Melting and crystallization behavior

To investigate the effect of the nanoscale layers of OMMT on the melting and crystallization behaviors, DSC experiments were done. Shown in Figure 4 are the heating curves for the neat PP and PP/OMMT nanocomposites with 4.0 wt % OMMT content. The curves show that the peak of the melt temperature increasing from 164.0 to 164.7°C only changed a little. The values of melting enthalpy decreased from 110.6 J/g of neat PP to 99.3 J/g of nanocomposite; this meant that the crystallinity of the nanocomposite was lower than that of neat PP. Figure 5 shows the DSC cooling curves of neat PP and the nanocomposite. The curves indicate that the temperatures of the maximum crystallization rates (T_{peak}'s) were similar. The starting temperature of the onset crystallization (T_S) clearly increased; this meant the crystallization behavior was initiated earlier, during the cooling
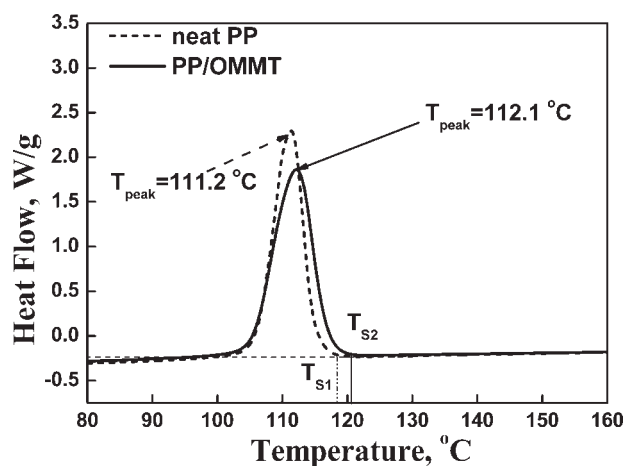

Figure 5 Crystallization behavior of neat PP and the PP/OMMT (4.0 wt %) nanocomposite. TS1, the starting temperature of the onset crystallization of the neat PP sample; TS2, the starting temperature of the onset crystallization of the PP/OMMT nanocomposites.
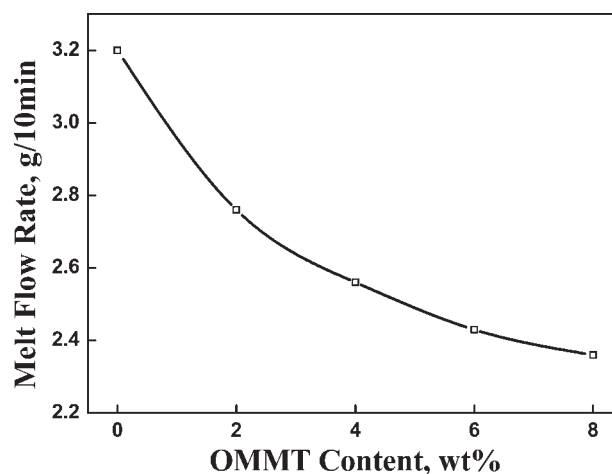

Figure 6 Effects of the OMMT loading on the MFR of the nanocomposites.

crystallization processing. The changes in the melting and crystallization behaviors were explained by the fact that the intercalated OMMT layers had heterogeneous nucleation effects on the PP macromolecular segments, which caused the crystallization behavior to occur earlier during crystallization processing; also, the heterogeneous nucleation effect of the OMMT layer resulted in some crystal defects. Thus, the crystallinity of the nanocomposite decreased.

Melt fluidity analysis

The value of MFR is a critically important index for any plastic material. Those of the nanocomposites are shown in Figure 6 with various OMMT contents. The results show that the MFR values of the nanocomposites decreased monotonously with increasing OMMT content. This was believed to be associated with the unique lamellar structure of the OMMT layers carrying the effect of steric interference and the increase of the system viscosity caused by the good compatibility of OMMT and the PP matrix, as shown in Figure 3. For the effects of the previous two factors, the importation of OMMT layers restricted the macromolecular movement and increased the melting viscosity of the nanocomposites, so the values of MFR of the nanocomposites decreased.

Mechanical property analysis

Figures 7 and 8 show that the values of the mechanical property measurement of the nanocomposites evidently increased with increasing OMMT content and that the values possessed a maximum value at an OMMT content loading of 4.0 wt %. The ultimate yield strength, elongation at yield, and initial modulus of the nanocomposites increased from 31.67 to 33.85 MPa, from 10.41 to 11.53%, and from 661.52 to
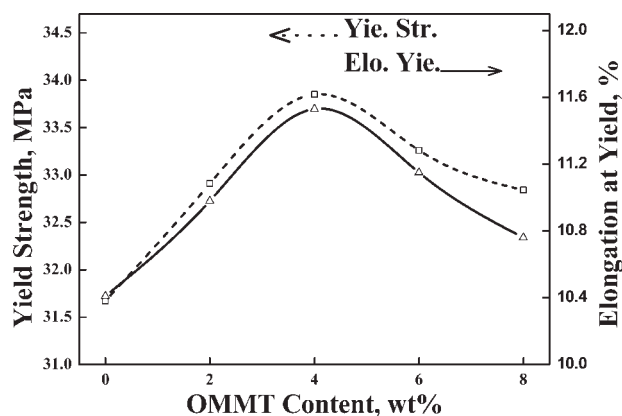
Figure 7 Effects of the OMMT loading on the yield strength and elongation at yield of the nanocomposites.

699.56 MPa, respectively. All of the increases were small; by contrast, the ultimate value of the notched impact strength shown in Figure 8 remarkably went up to 10.30 kJ/m^2, which was double of the value of neat PP (5.08 kJ/m^2). This was a great development in the polymer/OMMT nanocomposites, with the tensile strength, rigidity, and impact strength enhancing together. The enhancement of the impact strength was considered to be associated with the lamellar structure of the OMMT layers with the intercalation of the PP macromolecular chain, which is clearly shown in Figure 3(a). According to the theory of craze absorption for compounded composites, when the nanocomposites samples were struck, the areas of the intercalated lamella structures respond first, and the split of the lamellar structure absorbs extra impact energy, so the impact strength of the nanocomposites improved greatly.

Above the critical 4.0 wt % OMMT loadings corresponding to the previous strengths, the decrease in the strengths of the nanocomposites was mainly due to the agglomeration of OMMT particles.[16,17] As the
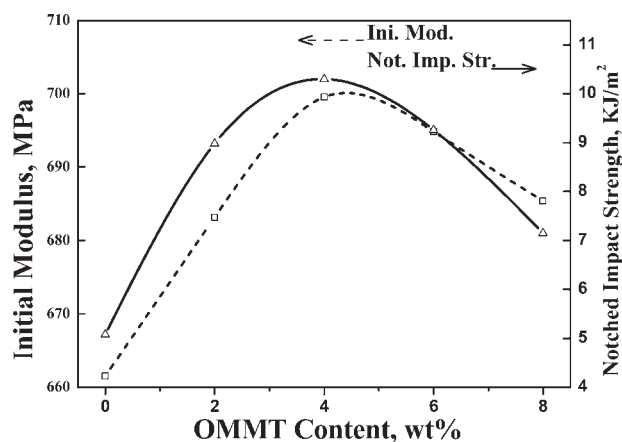

Figure 8 Effects of OMMT loading on the initial modulus and notched impact strength of the nanocomposites.
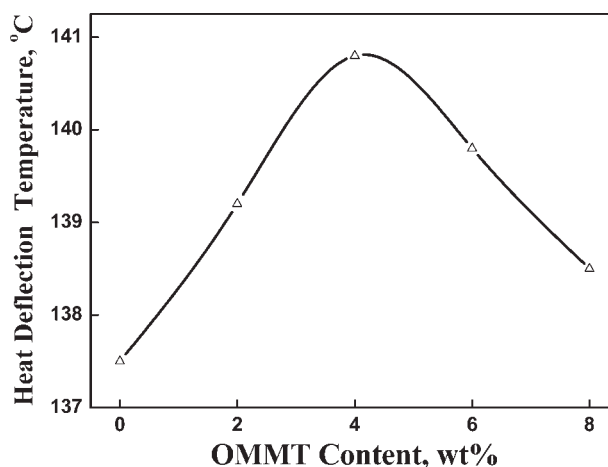
Figure 9 Effect of the OMMT loading on the HDT of the nanocomposites.

loadings of OMMT was up to 6.0 and 8.0 wt %, the dispersion of OMMT in the PP matrix was not homogeneous, so poor dispersion of OMMT initiated some OMMT agglomerates, and the agglomerates decreased the mechanical properties.[18]

Thermal properties

HDT is a critical thermal stability index for plastic material in practical applications. PP as a conventional plastic has the advantage of a high HDT with wide use. The values of HDT measurement are shown in Figure 9. The results demonstrate that the HDT of the nanocomposites increased slightly and also possessed a maximum value at 4.0 wt % OMMT loading. Over the critical 4.0 wt % OMMT loading, the HDT of the nanocomposites began to decrease but still overtopped that of neat PP. The
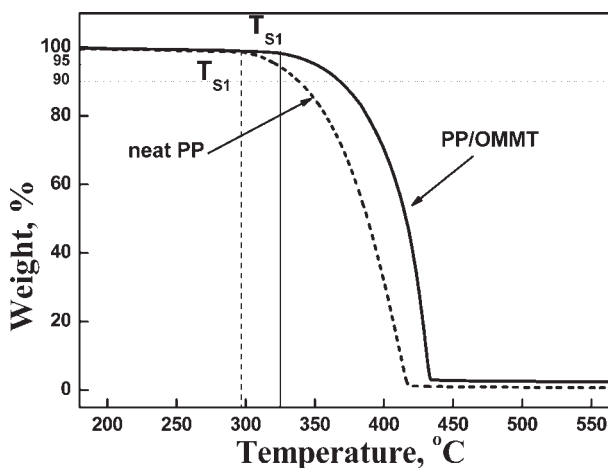

Figure 10 Thermogravimetric curves of neat PP and the PP/OMMT (4.0 wt %) nanocomposite. TS1 (above), the temperature of the starting point of deposition for the PP/OMMT nanocomposites; TS1 (below), the temperature of the starting point of deposition for the neat PP sample.
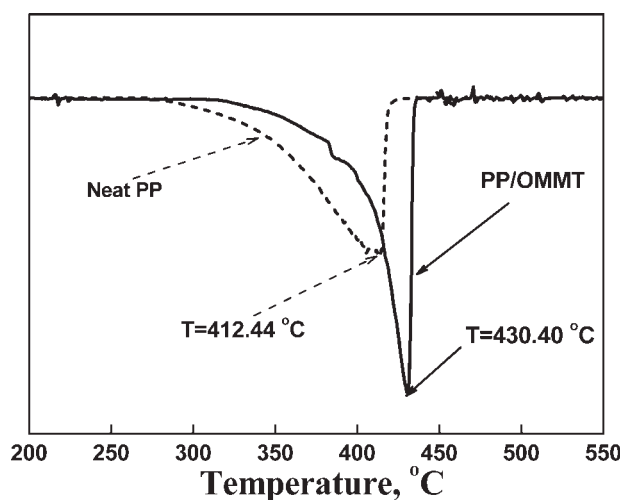
Figure 11 Differential curves of the TGA curves shown in Figure 10. T was the T_{max}, they were the temperature of the maximum deposition rate.

increase in HDT was considered due to the incorporation of rigid OMMT layers. Associated with the previous mechanical property measurements, especially the impact strength, the results show that the PP was greatly toughened and that the thermal stability concerning the HDT increased a little but did not decrease.

TGA was used to characterize the degradation and thermal stability of the polymers. Figure 10 shows the TGA curves for neat PP and the PP/OMMT nanocomposite with 4.0 wt % OMMT content. The data of differential calculus of the TGA curves are shown in Figure 11; these were used to determine the temperature of the maximum deposition rate (T_{max}). The initial thermal stability (T_i) was characterized by the temperatures tabulated in Table I at the starting point (T_S) and 5% ($T_{i\text{-}5 \text{ wt } \%}$) and 10 wt % ($T_{i\text{-}10 \text{ wt } \%}$) weight loss. As shown in Table I, the T_i and T_{max} of the PP/OMMT nanocomposites increased remarkably relative to those of neat PP. The results demonstrate that the degradation of the nanocomposites took place at higher temperatures than that of neat PP in the presence of OMMT. This behavior could be explained by the presence of the barrier effect of OMMT lamellar layers, which limited the emission of the produced degradation gases

and the transmission of heat; therefore, these resulted in the improvement of the thermal stability of the nanocomposite materials.[19]

CONCLUSIONS

This study was devoted to the investigation of toughened PP/OMMT nanocomposites with good tensile strength, rigidity, and thermal stability. The following conclusions could be drawn:

- The intercalated PP/OMMT nanocomposite was successfully prepared with a uniform dispersion of OMMT layers.
- The notched impact strength of the intercalated nanocomposite was over twofold that of neat PP with a high tensile strength, rigidity, and thermal stability at the 4.0 wt % OMMT content. This is a great development in toughened PP materials, with the retention of high thermal stability, and it will provide a new ideas for nanocomposite research.

References

1. Fond, C.; Lobbrecht, A.; Schirrer, R. Int J Fract 1996, 77, 141.
2. Zebarjad, S. M.; Bagheri, R.; Reihani, S. M. S.; Lazzeri, A. J Appl Polym Sci 2003, 90, 3767.
3. Bai, S.-L.; Christian, G.; Hiver, J.-M.; Mathieu, C. Polymer 2005, 46, 6437.
4. Ou, C. F.; Ho, M. T.; Lin, J. R. J Polym Res 2003, 10, 127.
5. Zong, R. W.; Hu, Y.; Wang, S. F.; Song, L. Polym Degrad Stab 2004, 83, 423.
6. Takashi, K.; Richard, H.; Zhang, X.; Briber, R. M.; Cipriano, B. H.; Raghavan, S. R.; Awad, W. H.; Shields, J. R. Polymer 2004, 45, 881.
7. Serge, B.; Jeffrey, W. G.; Charles, A. W. Polym Degrad Stab 2004, 84, 483.
8. Sun, T.; Garces, J. M. Adv Mater 2002, 14, 128.
9. He, A. H.; Wang, L. M.; Li, J. X.; Dong, J. Y.; Han, C. C. Polymer 2006, 47, 1767.
10. Kaempfer, D.; Thomann, R.; Mülhaupt, R. Polymer 2002, 43, 2909.
11. Pham, H. N.; Pralaly, M.; Okamoto, M. Polymer 2001, 42, 9633.
12. Gianelli, W.; Ferrara, G.; Camino, G. Polymer 2005, 46, 7037.
13. Lertwimolnun, W.; Vergnes, B. Polymer 2005, 46, 3462.
14. Wang, Y.; Chen, F.-B.; Li, Y.-C. Compos B 2004, 35, 111.
15. Tang, Y.; Lewin, M. Polym Degrad Stab 2007, 92, 53.
16. Chang, J.-H.; Yeong, U.-A. J Polym Sci Part B: Polym Phys 2002, 40, 674.
17. Chang, J.-H.; Yeong, U.-A.; Cho, D.; Giannelis, E. P. Polymer 2003, 44, 3718.
18. Masenelli, V. K.; Reynaud, E.; Vigier, G.; Varlet, J. J Polym Sci Part B: Polym Phys 2002, 40, 278.
19. Duquesne, S.; Jama, C.; Brasa, M. L.; Delobel, R.; Recourt, P.; Gloaguen, J. M. Compos Sci Technol 2003, 63, 1141.

TABLE I
Weight-Loss Temperatures of Neat PP and the PP/ OMMT Nanocomposite (4.0 wt %)

Sample	T_S (°C)	$T_{i\text{-}5 \text{ wt } \%}$ (°C)	$T_{i\text{-}10 \text{ wt } \%}$ (°C)	T_{max} (°C)
Neat PP	296.70	323.02	338.65	412.44
PP/OMMT nanocomposite	325.12	353.88	370.16	430.40