

COMPARISON OF POLYAMIDE 66/MONTMORILLONITE NANOCOMPOSITES PREPARED FROM POLYAMIDE 6 AND POLYAMIDE 66 BASED MASTER-BATCHES

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Abstract Two master-batches, polyamide 66 (PA66)/organo-montmorillonite (OMMT) and polyamide 6 (PA6)/OMMT, prepared by melt compounding with methyl methacrylate (MMA) as co-intercalation agent, have been used to prepare nearly exfoliated PA66/montmorillonite (MMT) nanocomposites. The resulting nanocomposites are compared in view of their morphology and properties. Nano-scale dispersion of OMMT is realized in both types of nanocomposites, as revealed by XRD, TEM and Molau tests. PA66/MMT nanocomposites having superior mechanical properties and heat distortion temperature (HDT) can be obtained from either PA66/OMMT or PA6/OMMT master-batch. Those from PA6/OMMT have lower tensile and flexural properties, and HDT than those from PA66/OMMT due to the presence of less stiff and less thermal resistant PA6. The crystallization behavior and crystal structure of the matrix in both types of PA66/MMT nanocomposites are also investigated by DSC and WAXD.

Keywords: Polyamide 66; Montmorillonite; Nanocomposites; Polyamide 6.

INTRODUCTION

In recent years, polymer/layered silicate nanocomposites have attracted great interest, and numerous reports have come forth in this field^[1–24]. Among them, polyamide 6/montmorillonite (PA6/MMT) nanocomposites may be the most prominent example. Similar to PA6, polyamide 66 (PA66) is also an important polyamide-type engineering plastics with extensive use in many fields. Following the early success in PA6/MMT nanocomposites^[5], considerable research has been devoted to the preparation of PA66/clay nanocomposites^[6–23]. High level of exfoliation was achieved when specially made organo-montmorillonite (OMMTs) or a co-intercalation agent such as epoxy resin or aminoundecanoic acid were used^[6–10]. When commercial OMMTs were used to prepare PA66/MMT nanocomposites, the level of exfoliation was rather limited.

In general, PA6 is considered to be easier to intercalate into OMMT layers. This has been experimentally proven by the work of Chavarria and Paul^[18]. Based on this point, Gonzalez *et al.* used PA6/commercial OMMT nanocomposite containing a high OMMT content (10 wt%) as a master-batch to prepare exfoliated PA66-based nanocomposites^[17]. However, PA6 is less stiff and less thermal resistant than PA66, it is suspected to have an opposite effect to OMMT on mechanical properties and HDT of the materials. Recently, we found that PA66/OMMT master-batch having a high level of OMMT dispersion could be prepared when methyl methacrylate (MMA) was used as a co-intercalation agent^[24]. PA66/OMMT master-batch has obvious advantages to PA6/OMMT master-batch for the preparation of PA66/MMT nanocomposites in view of the properties of the nanocomposites.

In this work, PA66/MMT nanocomposites prepared from PA6/OMMT and PA66/OMMT master-batches are compared. The dispersion of OMMT in the matrix is investigated by XRD, TEM and Molau tests. The

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Received August 8, 2007; Revised October 15, 2007; Accepted October 25, 2007

crystallization behavior and crystal structure of the matrix are characterized by DSC and WAXD. Tensile, flexural and impact tests, and heat distortion temperature (HDT) measurements are carried out to assess the mechanical properties and thermal resistance.

EXPERIMENTAL

Materials and Reagents

PA66 used in this work was Zytel 101L (Dupont) and PA6 was B3S (BASF). The OMMT was NB-901 (Huatae Group, China), it is a montmorillonite modified with tallow quaternary ammonium to increase the domain spacing of Na⁺-montmorillonite. The cation exchange capacity (CEC) of NB901 is 95 mmol/100 g, and methyl methacrylate (MMA) was of analytically grade (Yili Co, China).

Preparation of PA66/Montmorillonite Nanocomposites

After a preparatory mixing process, the mixture of PA resin (PA66 or PA6), OMMT and MMA were dried in a ventilated oven for 5 h at room temperature and then melt compounded using a two-screw extruder with a screw speed of 120 r/min to prepare the two master-batches. The twin-screw extruder used had a screw diameter of 34 mm and a *L/D* value of 28. The blending temperature profile was set to 250–260–260–265–265–240°C. The compositions of the two master-batches are listed in Table 1.

Table 1. Compositions of the master-batches

Master-batch	PA66	PA6	OMMT	MMA
MB66	80	0	10	10
MB6	0	80	10	10

The mixture of PA66 and master-batch MB66 or MB6 was mixed and melt compounded using the same extruder as discussed above. Nanocomposites containing 1 wt%, 3 wt% and 5 wt% of OMMT were prepared and listed in Table 2. The extrudates were injection molded into tensile bars using a ZT-630 injector (Zhenda Co, china) with a barrel temperature of 260°C for measurements of mechanical properties and HDT.

Table 2. Compositions of nanocomposites

Sample	OMMT (wt%)	PA66	MB66	MB6
MB66-1	1	90	10	0
MB66-3	3	70	30	0
MB66-5	5	50	50	0
MB6-1	1	90	0	10
MB6-3	3	70	0	30
MB6-5	5	50	0	50

Characterization

X-ray diffraction (XRD) patterns were obtained on injection-molded Izod bars except for the two samples of master-batches where films pressed at 280°C were analyzed, using a BRUKER D8-Advance diffractometer connected to a computer. The diffraction scans were collected at 1.5°–10° using a scanning speed of 1 (°)/min. Transmission electron microscopy (TEM) observations were performed on a Cambridge S250MK3 microscope using an accelerating voltage of 200 kV. For TEM examinations, ultra-thin specimens with a thickness of about 50 nm were cut from the middle section of the injection-molded bars. Cutting operations were carried out using a Reichert Ultracut S microtome under cryogenic conditions, and the film was retrieved onto copper grids. Molau tests were performed with 1 g of nanocomposite in 10 mL of formic acid. Their emulsification phenomena were observed after standing for a week.

Differential scanning calorimetry (DSC) measurements were performed under nitrogen atmosphere using a TA DSC 2910 calorimeter. After kept for 10 min at 280°C to eliminate the heat history, all samples were cooled

from 280°C to 150°C and secondly heated from 150°C to 280°C at rates of 10 K/min. Wide-angle X-ray diffraction (WAXD) scans were obtained on injection-molded Izod bars, using a BRUKER D8-Advance diffractometer connected to a computer. The diffraction scans were collected at 10°–30° using a scanning speed of 1 (°)/min.

Tensile and flexural tests were carried out with a GT-TCS 2000 machine (Gotech), according to ASTM D638 and ASTM D790, at a crosshead speed of 50 mm/min and 5 min/mm, respectively. Data from five measurements were averaged for each formulation. Izod impact tests were carried out on notched specimens using a GT-7045-I Izod impact tester (Gotech), according to ASTM D256, and data from seven measurements were averaged. The HDTs were measured on a GT-HV2000 computer HDT/Vicat tester (Gotech) following the procedure described in ASTM 648. Two specimens were used for each formulation. Prior to mechanical and HDT testing, all sample bars were dried in a vacuum oven at 110°C for 18 h.

RESULTS AND DISCUSSION

Dispersion of OMMT

Figure 1 shows the XRD patterns of the two master-batches (MB66 & MB6), the two nanocomposites having 5 wt% of OMMT prepared from MB66 and MB6 (MB66-5 & MB6-5) and the original OMMT. The original OMMT shows a broad peak centered at $2\theta = 4.3^\circ$, corresponding to a basal spacing of 2 nm as calculated from Bragg equation. MB66 shows featureless pattern, while MB6 has a tiny peak at around 1.7° , suggesting that MB66 has a higher degree of OMMT dispersion than MB6 under the current experimental conditions. Both of the nanocomposites having 5 wt% of OMMT (MB66-5 & MB6-5) show featureless patterns, indicating that high degree of dispersion (possible exfoliation) could be reached by dilution from either MB66 or MB6 master-batch.

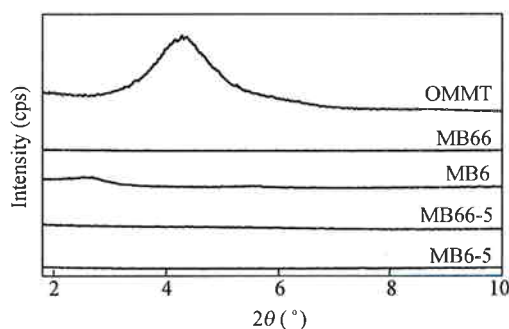


Fig. 1 XRD patterns of OMMT and PA66/MMT nanocomposites

TEM observation can provide direct evidence of OMMT dispersion. Figure 2 shows the TEM images of the two master-batches (MB66 & MB6) and the two nanocomposites having 5 wt% of OMMT prepared from MB66 and MB6 (MB66-5 & MB6-5). The dark lines represent single or stacked OMMT layers, and the white background represents PA 66-based matrix. In MB66 and MB6 (Fig. 2a & Fig. 2b), some stacks containing a few OMMT layers were observed besides the exfoliated individual layers, suggesting a mixed structure of intercalation and exfoliation. In MB66-5 and MB6-5 (Fig. 2c & Fig. 2d), most of the OMMT platelets' thicknesses are smaller than 10 nm, and a small part are around 20 nm, indicating that the nanocomposites MB66-5 and MB6-5 have a better degree of dispersion than the master-batches.

Molau tests were carried out to provide evidence about OMMT dispersion as well as interaction between OMMT and the matrix from macroscopic point of view. Since OMMT does not dissolve in formic acid, stable colloid can be obtained only when the dispersion of OMMT layers is in nano-scale, and there is sufficient interaction between OMMT layers and the polyamide matrix to stabilize dispersed OMMT layers. Figure 3 shows the results of the two master-batches (MB66 & MB6) and the two nanocomposites having 5 wt% OMMT

prepared from MB66 and MB6 (MB66-5 & MB6-5). MB66 (Fig. 3a) forms a well-distributed and stable colloid in formic acid, while some sediment was found at the bottom of the test-tube for MB6 (Fig. 3b), indicating that the dispersion of OMMT in the polyamide matrix and the interaction between OMMT layers and the matrix (which is also related to the dispersion of OMMT apart from the intrinsic properties of the corresponding components, the better the dispersion is, the stronger the interaction is) are better in MB66 than in MB6. Both the nanocomposites MB66-5 (Fig. 3c) and MB6-5 (Fig. 3d) form stable and translucent colloids, indicating good dispersion of OMMT.

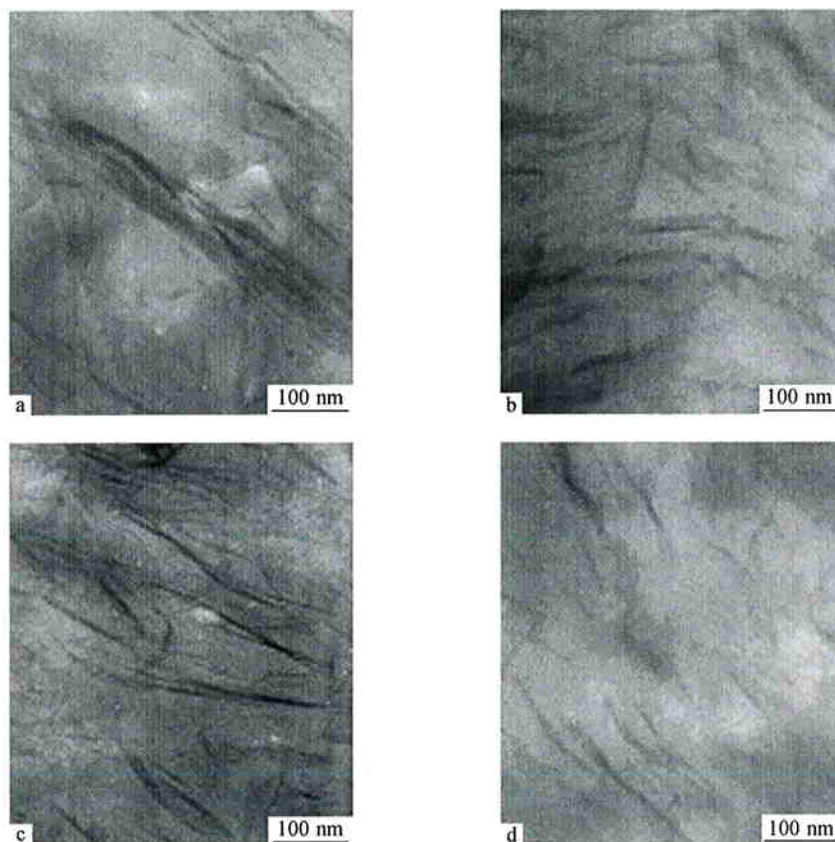


Fig. 2 Photomicrographs of PA66/MMT nanocomposites: (a) MB66, (b) MB6, (c) MB66-5 and (d) MB6-5

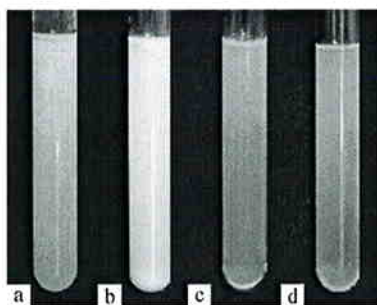


Fig. 3 Photographs of Molau tests: (a) MB66, (b) MB6, (c) MB66-5 and (d) MB6-5

Crystallization Behavior and Crystal Structure

Figures 4a and 4b show DSC cooling scans and the second heating scans of neat PA66, PA66/PA6 blend and the two nanocomposites having 5 wt% OMMT (MB66-5 & MB6-5) at a heating rate of 10 K/min. Two melt

peaks at 252.3°C (T_{m1}) and 261.1°C (T_{m2}) were observed for neat PA66. A decrease (1.1°C) in T_{m2} is observed after incorporation of OMMT (MB66-5) most probably due to the presence of PMMA, which is resulted from polymerization of the co-intercalation agent MMA. For PA66/PA6 (50/45, the same proportion as in MB6-5) blend, the two melt peaks of PA66 decrease to 248.0°C (T_{m1}) and 257.2°C (T_{m2}) due to the presence of PA6, and the melt peak of PA6 is observed at 212.5°C. The appearance of both melting temperatures of PA66 and PA6 is in agreement with the published work^[25]. However, only the two melt peaks of PA66 are observed for nanocomposite MB6-5. The absence of the melt peak of PA6 suggests that PA6 is almost amorphous in the nanocomposite MB6-5, indicating that the crystallization of PA6 is hindered by the presence of OMMT. This is in agreement with the work of Gonzalez *et al.*^[13]. A decrease in both T_{m1} (3.0°C) and T_{m2} (6.0°C) of PA66 is observed for MB6-5 as compared to PA66/PA6 blend due to the presence of PMMA.

The crystallization temperature (T_c) of PA66 also decreases for MB66-5 (1.7°C) as compared to that of neat PA66, and for MB6-5 (6.0°C) as compared to PA66/PA6 blend. The decreasing extent for MB6-5 is much bigger than that in the work of Gonzalez *et al.*^[17] mentioned above due to presumably the presence of PMMA. In some work found in the literature concerning PA66/OMMT nanocomposites^[8, 11], a significant increase (1–10°C) in T_c was reported, which was attributed to the increase of crystallization rate by OMMT and the hetero phase nucleation effect of OMMT. In the current work, the decrease in T_c of PA66 is most probably due to the presence of both PMMA and PA6.

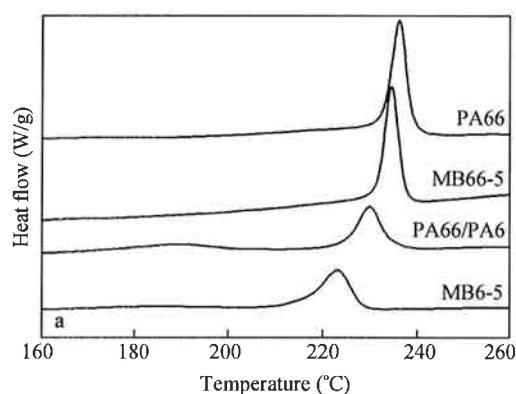


Fig. 4a DSC cooling scans of PA66, PA66/PA6 blend and PA66/MMT nanocomposites

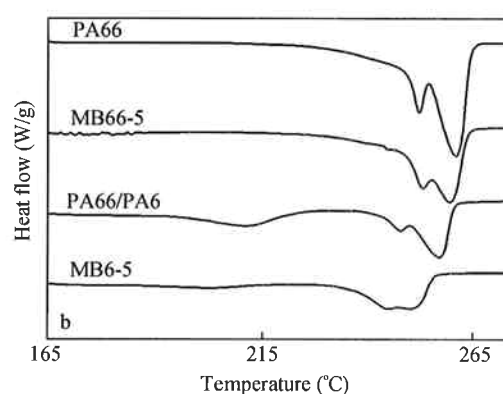


Fig. 4b DSC heating scans of PA66, PA66/PA6 blend and PA66/MMT nanocomposites

As shown in Table 3, the crystallization enthalpy (ΔH_c) is almost unchanged with the incorporation of OMMT (MB66-5), indicating that the degree of crystallinity of the matrix does not change by the presence of OMMT. The presence of PA6 in the nanocomposite (MB6-5) lowers the degree of crystallinity of the matrix significantly, but does not change significantly the degree of crystallinity of PA66.

Table 3. Crystallization and melting parameters of PA66, PA66/PA6 blend and PA66/MMT nanocomposites

Sample	T_{m1} (°C)	T_{m2} (°C)	T_c (°C)	ΔH_c (J/g)	$\Delta H_{c,PA66}$ (J/g)*
PA66	252.3	261.1	236.2	53.5	53.5
MB66-5	252.2	260.0	234.5	52.6	55.4
PA66/PA6	248.0	257.2	229.9	28.0 (PA66) + 6.9 (PA6)	53.2
MB6-5	245.0	251.2	223.1	29.7	59.4

* $\Delta H_{c,PA66} = \Delta H_c / \text{PA66 content}$

The crystal structure of PA66, MB66-5 and MB6-5 was investigated by WAXD. Polyamides have various polymorphic crystalline structures. The most important phases for PA66 are triclinic α -form and γ -form and for

PA6 monoclinic α -form and pseudohexagonal γ -form^[9]. In Fig. 5, only two α -crystalline peaks at 20.3° and 23° , which are coded as α_1 and α_2 respectively, are observed for all the three samples. Since PA6 is almost amorphous as revealed by DSC, α_1 and α_2 can be identified as α -form crystals of PA66^[13]. Kang *et al.* observed the appearance of γ -form crystal at $2\theta = 21.8^\circ$ after incorporation of OMMT into PA66 and attributed the phenomenon to heterogeneous nucleation effect of OMMT^[11]. As discussed above on DSC data, in the current work, the crystallization of PA66 is hindered due to the presence of other components (PMMA and PA6). Therefore, it seems understandable that no γ -form crystal presents. It is noted that the relative intensities of α_1 and α_2 change significantly when OMMT is present in PA66 (sample MB66-5) and when PA6 is involved (MB6-5). This indicates that the arrangement of molecules in α -form crystals is affected by the presence of OMMT and PA6.

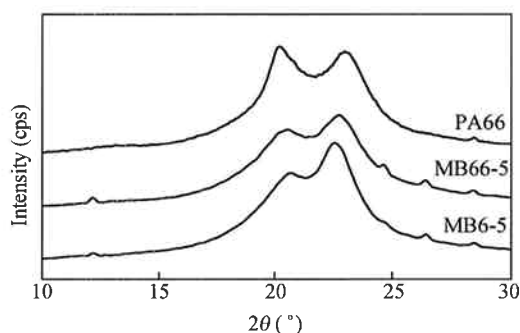


Fig. 5 WAXD patterns of PA66 and PA66/MMT nanocomposites

Mechanical Properties and HDT

To compare the effect of composition on the properties of the nanocomposites, the mechanical properties and HDT of the nanocomposites having different OMMT contents and prepared from either MB66 or MB6 are measured and summarized in Figs. 6a–6e.

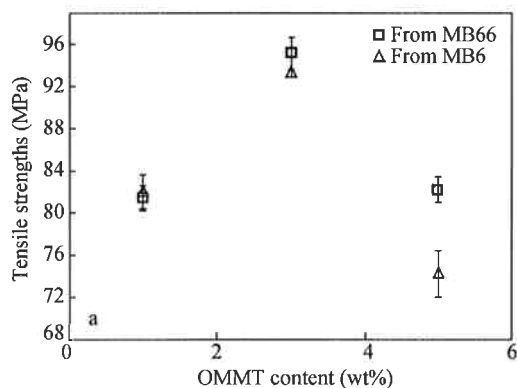


Fig. 6a Effect of OMMT content on tensile strength of PA66/MMT nanocomposites

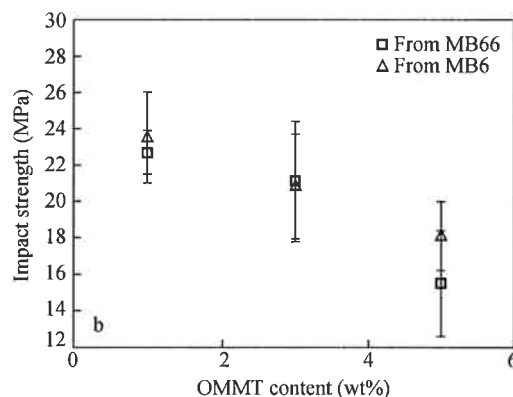


Fig. 6b Effect of OMMT content on impact strength of PA66/MMT nanocomposites

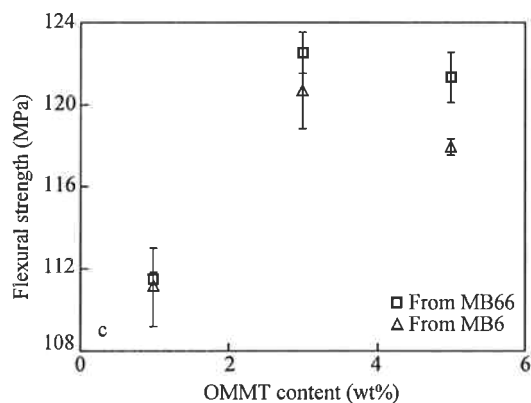


Fig. 6c Effect of OMMT content on flexural strength of PA66/MMT nanocomposites

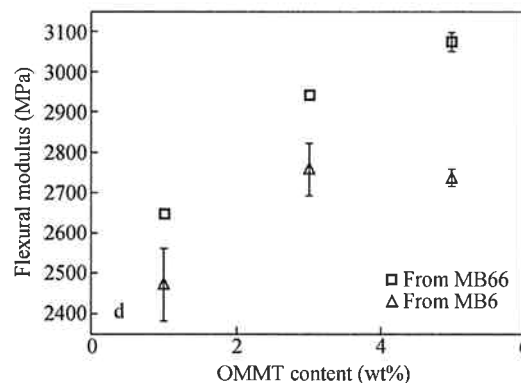


Fig. 6d Effect of OMMT content on flexural modulus of PA66/MMT nanocomposites

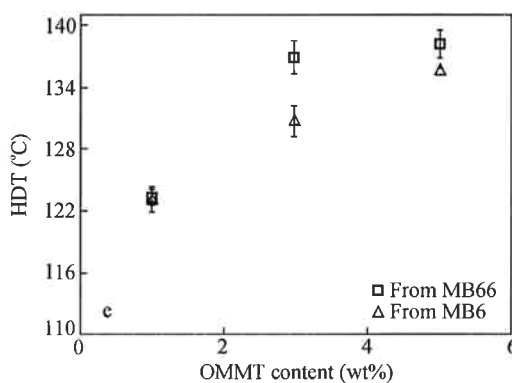


Fig. 6e Effect of OMMT content on HDT of PA66/MMT nanocomposites

The tensile strength (Fig. 6a) of both types of nanocomposites increases significantly with the addition of 1 wt% and 3 wt% OMMT. An increase of 30% is observed for both types of nanocomposites at 3 wt% OMMT content. Further increase in OMMT content (5 wt%) leads to a decrease in tensile strength. Bigger decreasing extent is observed in MB6 series due to presumably the decrease in crystallinity of the matrix as observed by DSC measurements. It is noted that all the nanocomposites prepared in this work show brittle fracture in tensile tests when measured at dry state. The elongation at break is less than 5% for all the nanocomposites.

The impact strength (Fig. 6b) decreases sharply with the increase of OMMT content due to incorporation of rigid OMMT, which is similar to other related work^[8, 11-13]. The impact strength at 5 wt% for MB6 series is bigger than for MB66 series, probably due to the presence of large amount of PA6 which is tougher than PA66.

The flexural strengths (Fig. 6c) of both MB66 and MB6 series follow the same trend as a function of OMMT content. With a small OMMT content (1 wt%), no change in flexural strength is observed. When the OMMT content is increased to 3 wt%, the flexural strength increases significantly for both MB66 (10%) and MB6 (8%) series. With further addition of OMMT (5 wt%), the flexural strength drops. Similar to the case of tensile strength, the decreasing extent for MB6 series is bigger than for MB66 series due to presumably the decrease in crystallinity of the matrix.

The flexural modulus (Fig. 6d) of MB66 series increases with increasing OMMT content. An 18% increase is observed with 5 wt% OMMT. This seems reasonable, since addition of a rigid inorganic filler always brings an increase in modulus. The flexural modulus of MB6 series is a bit complicated. It should be a combined effect of the stiff OMMT and the less stiff PA6. With 3 wt% and 5 wt% OMMT, an increase in flexural modulus is

observed, but the values are much smaller than those in MB66 series due to the presence of large amount of less stiff PA6.

HDT (Fig. 6e) is an important property to evaluate engineering plastics. The HDTs of both MB66 and MB6 series are all enhanced with the increase of OMMT content. Those of MB6 series at 3 wt% and 5 wt% OMMT contents are considerably smaller than those of MB66 series due to the presence of large amount of PA6 which is less thermal resistant than PA66.

CONCLUSIONS

Nearly exfoliated PA66/MMT nanocomposites can be successfully prepared via melt compounding by dilution from either PA66/OMMT or PA6/OMMT master-batch. The crystalline melting point and crystallinity of the matrix of the PA66/MMT nanocomposites prepared from PA6/OMMT master-batch are lower than those from PA66/OMMT master-batch. Only α form crystals were observed in all the nanocomposites prepared in this work. Both types of nanocomposites have better mechanical properties and HDT than neat PA66. The nanocomposites prepared from PA6/OMMT master-batch have lower tensile and flexural properties and HDT than those prepared from PA66/OMMT master-batch due to incorporation of PA6, which is less stiff and less thermal resistant than PA66.

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