

## Synthesis of Magnesium Hydroxide Nanofiller and Its Use for Improving Thermal Properties of New Poly(ether-amide)

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**ABSTRACT:** A new poly(ether-amide; PEA) as a source of polymeric matrix, containing flexible ether group in the main chain was synthesized by direct polycondensation reaction of 1,2-(4-carboxy phenoxy)ethane with 4,4-diaminodiphenyl ether in a medium consisting of *N*-methyl-2-pyrrolidone, triphenyl phosphite, calcium chloride, and pyridine. The resulting PEA was characterized by gel permeation chromatography (GPC), <sup>1</sup>H NMR and FT-IR spectroscopy. Magnesium Hydroxide (MH) nanostructure was synthesized by the reaction of magnesium sulfate and sodium hydroxide by sonochemical method. The MH particle was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Then Mg(OH)<sub>2</sub> nanostructure was added to poly(ether-amide) matrix and resulting nanocomposites were characterized by XRD, SEM, and Thermogravimetry Analysis (TGA). Thermal decomposition of the PEA shifted towards higher temperature in the presence of the magnesium hydroxide nanoparticles. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** nanofiller; nanocomposite; poly(ether-amide); magnesium hydroxide

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### INTRODUCTION

The concept of incorporation of inorganic fillers into polymer matrixes is an effective method to integrate new functions inside polymeric matrices.<sup>1</sup> Polymer nanocomposites containing inorganic nanoparticles and layered structures have attracted much attention for the past decade. Nanocomposites have been demonstrated with many polymers of different polarities including polyamide,<sup>2,3</sup> polystyrene, polycaprolactone,<sup>4</sup> poly(methyl methacrylate), and others.<sup>5,6</sup>

Polyamides possess excellent properties in terms of good thermal stability, mechanical properties, high glass temperature, and chemical resistance to solvents. Because of their high performance and superb properties, aromatic polyamides<sup>7–9</sup> and their composites<sup>10</sup> are widely used for defense and aerospace applications. The aliphatic analogs of these polymers are generally referred to as nylons used in many daily life applications. There is another class of glassy copolymer obtained from condensation of aromatic diacids and aliphatic diamines. These are often known as glass-clear nylons with exceptional properties such as good transparency, rigidity, thermal resistance, hardness, etc., and have many industrial applications. Some of their applications, however, require further property enhancement and the desired improvements can be obtained through incorporation of inorganic nanofillers.<sup>11,12</sup> It has been recognized that the

incorporation of aryl-ether linkages generally imparts an enhanced solubility, processability, and toughness of the polymers without substantial diminution of thermal properties. Such flexibility in these polymers leads to their excellent solubility in polar, aprotic solvents such as NMP, DMF, DMAc, and DMSO. It was demonstrated that aramids containing ether linkage as well as asymmetrical groups are significantly more flexible and more soluble than conventional aramids.<sup>13–18</sup>

Many polymers like polyamide must be processed at higher temperature which hinders the utilization of this compound. It is exactly in these cases that the use of magnesium hydroxide (MH) becomes attractive, owing to its higher temperature of decomposition (approximately 330°C). The main applications of MH are in polymers such as polypropylene and nylon, which should be processed at high temperatures, and in elastomeric cable coatings, which require high temperatures for rapid processing. Mg(OH)<sub>2</sub>-filled polymers are promising materials due to the low price of the hydroxide and good mechanical properties. Compared to MgO, the hydroxide is beneficial as a flame retardant due to the decomposition into H<sub>2</sub>O and MgO at higher temperature. Numerous investigations on Mg(OH)<sub>2</sub> and its properties as flame-retardant inorganic filler material were carried out, because it does not evolve toxic, gaseous, or corrosive substances during decomposition. Mg(OH)<sub>2</sub> can be

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obtained in a crystalline form if synthesized properly. As compared with MgO nanoparticles, it is not moisture sensitive and thus easier to store.<sup>19–25</sup>

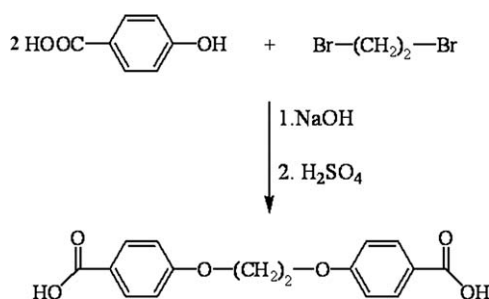
Nanocrystalline Mg(OH)<sub>2</sub>-powders can be synthesized using different pathways, for example under solvothermal conditions,<sup>26</sup> in a hydrothermal reaction using different precursors and solvents as reactants,<sup>27</sup> or via sol-gel technique.<sup>28</sup>

In this article, we describe synthesis and characterization of MH nanostructure with reaction of magnesium sulfate and NaOH by sonochemical method, and it is used as nano filler for synthesis a novel poly(ether-amide)/Mg(OH)<sub>2</sub> nanocomposites. Aromatic-aliphatic poly(ether-amide) was synthesized via direct polycondensation reaction and the neat polymer was characterized completely. The resulting nanocomposites have been characterized by XRD, SEM, and TGA analyses.

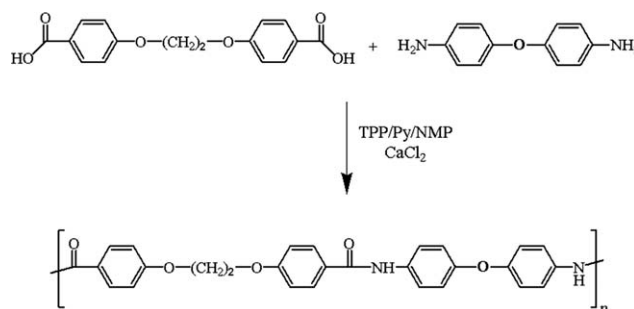
## EXPERIMENTAL

### Materials and Physical Measurements

All the chemicals were of analytical grade and were used without further purification. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu-K $\alpha$  radiation. Scanning electron microscopy images were obtained on LEO (UK) instrument. A multiwave ultrasonic generator (Bandeline, MS 72, Germany), operating at 20 KHz with a maximum power output of 75 W was used for the ultrasonic irradiation. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Weight-average (*M<sub>w</sub>*) and number-average (*M<sub>n</sub>*) molecular weights were determined by gel permeation chromatography (GPC-Apparatur von Fa. Agilent Serie1100-RI-Detektor2 Zorbax PSM Trimodal-S-DMAc+2Vol% H<sub>2</sub>O+3g/L LiCl, 0.5 mL/min, PVP-Standards). Fourier transform infrared spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid were performed by using KBr pellets. Vibration transition frequencies were reported in wave number (cm<sup>-1</sup>). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure by using a Technico Regd Trad Mark Viscometer. Thermal Gravimetric Analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N<sub>2</sub> atmosphere at rate of 10°C/min. Elemental analyses were performed by Vario EL equipment.



Scheme 1. Synthesis of diacid.



Scheme 2. Synthesis of PEA.

### Synthesis of 1,2-(4-Carboxy phenoxy)ethane

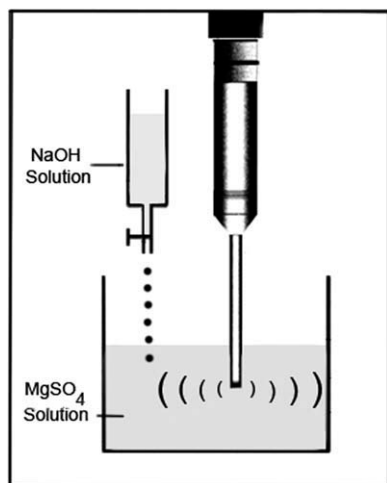
In a 250 mL round bottom flask with dropping funnel fitted with a stirring bar were placed (4.60 g, 33.3 mmol) of 4-hydroxy benzoic acid and (2.60 g, 65.0 mmol) sodium hydroxide in 14.0 mL H<sub>2</sub>O. Then 16.8 mmol 1,2-dibromo ethane was added into the reaction mixture slowly with stirring and the reaction mixture was refluxed for 3.5 h. After that, 0.66 g (16.5 mmol) NaOH was added and continued refluxing for 2 h. Then the heating was removed but the stirring was continued at room temperature for overnight (Scheme 1). After that the white precipitate was filtered and washed with 10 mL methanol, the solid was dissolved in 34 mL H<sub>2</sub>O. By adding a solution of H<sub>2</sub>SO<sub>4</sub> (6N) a white solid precipitate was obtained which was washed with cold water and filtered at room temperature until 3.36 g (67%) white product was obtained (Scheme 1). m.p.: 311–313°C, FTIR (KBr): 2500–3400 (s, br), 1680 (s, br), 1606 (s), 1514 (s), 1435 (s), 1303 (m), 1251 (m), 1167 (m), 1047 (s), 945 (m), 844 (s), 769 (m), 646 (m), 553 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, TMS)  $\delta$ : 4.41 (s, 4H), 7.06–7.08 (d, 4H), 7.88–7.91 (d, 4H), 12.64 (s, br, 2H) ppm. <sup>13</sup>C NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$ : 167.4, 162.2, 131.8, 123.3, 114.7, 66.8 ppm. Elemental analysis: calculated for C<sub>16</sub>H<sub>14</sub>O<sub>6</sub>: C, 63.57; H, 4.67; found: C, 62.29; H, 4.62.

### Synthesis of Poly(ether-amide)

In a 25 mL round-bottom flask which was fitted with a stirring bar were placed 4,4'-diamino diphenyl ether (0.128 g, 0.64 mmol), diacid (0.64 mmol), calcium chloride (0.20 g, 1.80 mmol), triphenyl phosphite (1.68 mL, 6.00 mmol), pyridine (0.36 mL), and *N*-methyl-2-pyrrolidone (1.6 mL). The reaction mixture was heated under reflux on an oil bath at 60°C for 1 h, then 90°C for 2 h, and 120°C for 8 h. Then the reaction mixture was poured into 50 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with hot methanol and dried at 60°C for 12 h under vacuum to leave 0.28 g (94%) of brown solid PEA. The inherent viscosity of this soluble PEA is 0.69 dL/g (Scheme 2).

### Synthesis of MH Nanostructures

MgSO<sub>4</sub> (0.5 g) was dissolved in 100 mL of distilled water. Subsequently, under ultrasonic waves (30 min, 75 W) 20 mL of NaOH solution 0.1M was slowly added to this solution. A white precipitate was obtained which confirmed the synthesis of MH. Then, the precipitate was centrifuged and washed with distilled water (Scheme 3).



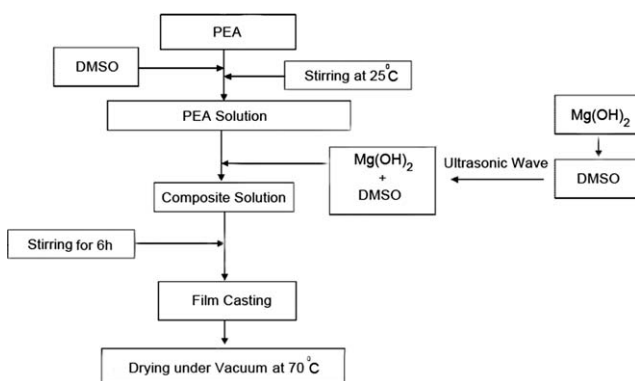
Scheme 3. Experimental setup used for the sonochemical reactions.

### Preparation of PEA/Mg(OH)<sub>2</sub> Nanocomposite

The nanocomposites were prepared as following method (Scheme 4). First, PEA was dissolved in 3 mL of DMSO and MH nanostructures were dispersed in 2 mL of DMSO using ultrasonic waves (40 W) for 20 min. After that, the solution containing nanostructures was added to the polymer solution slowly and was mixed for another 5 h. The reaction mixture was agitated to high speed stirring at 70°C for 1 h and then at 25°C for 24 h for uniform dispersion of clay platelets in the polyamide matrix. Various compositions ranging from 0 to 20 wt % of MH were prepared by mixing various amounts of Mg(OH)<sub>2</sub> to the polymer solution. Thin composite films of uniform thickness were obtained by pouring the hybrid solutions into Petri dishes followed by solvent evaporation at high temperature. These films were further dried at 80°C under reduced pressure to a constant weight.

## RESULTS AND DISCUSSION

1,2-(4-Carboxy phenoxy)ethane diacid was prepared from the reaction of 4-hydroxy benzoic acid with 1,2-dibromo ethane in presence of NaOH solution. The chemical structure and purity of the diacid was proved with elemental analysis,



Scheme 4. Preparation of Mg(OH)<sub>2</sub> nanocomposite.

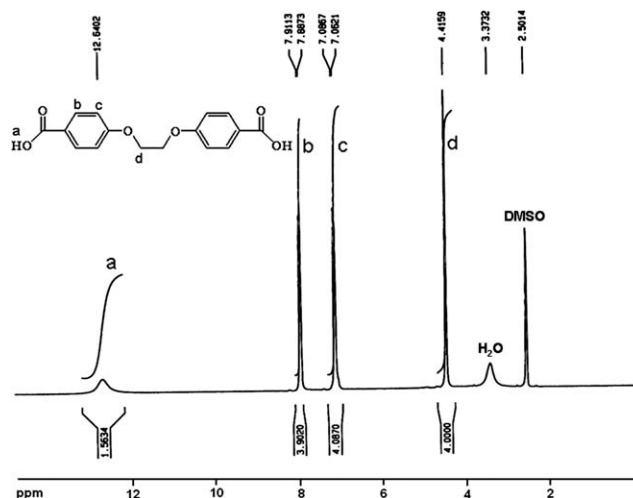


Figure 1. <sup>1</sup>H NMR spectrum of diacid.

<sup>1</sup>H NMR, and FTIR spectroscopy. The measured results in elemental analyses of the diacid closely corresponded to the calculated ones, demonstrating that the expected compound was obtained. The FTIR spectrum of the compound showed a broad peak between 2500 and 3400 cm<sup>-1</sup>, which was assigned to the COOH groups. The <sup>1</sup>H NMR spectrum showed a broad singlet peak at 12.64 ppm, which was assigned to the H(a) protons of the COOH groups. Two doublet peaks are noticed to be appeared between 7.06–7.08 ppm and 7.88–7.91 ppm, which were assigned to the protons of the phenyl ring. Furthermore, the singlet peaks at 4.41 was assigned to the aliphatic protons of the methylene groups (Figure 1).

Figure 2 displays <sup>13</sup>C NMR spectrum of dicarboxylic acid, that this spectrum shows six different signals for carbon atoms. Carbon atoms for acidic carbonyl group appeared in 167.4 ppm and related to Aromatic carbon atoms appeared in the range of

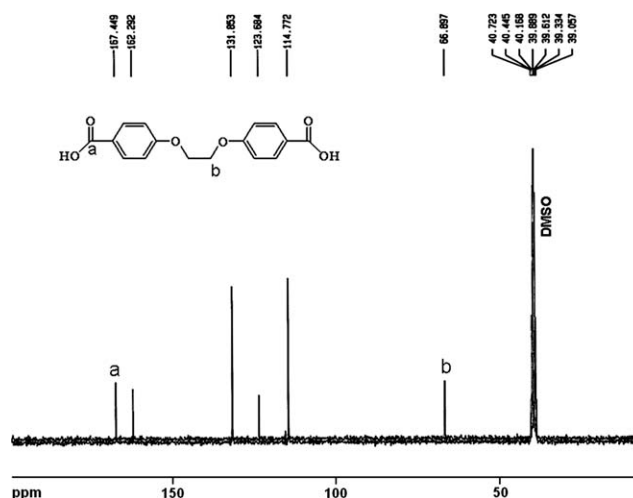


Figure 2. <sup>13</sup>C NMR spectrum of diacid.

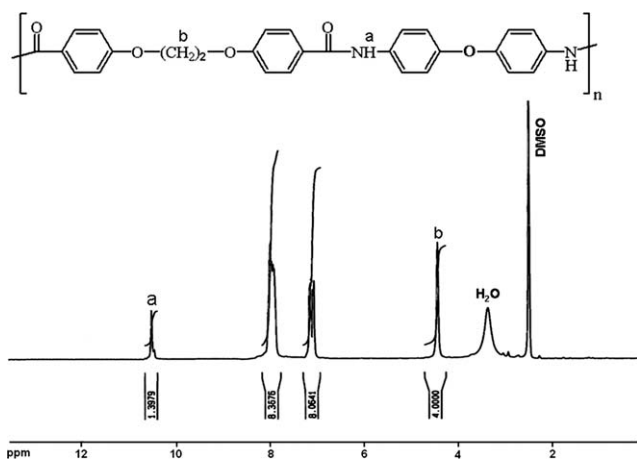


Figure 3.  $^1\text{H}$  NMR spectrum of PEA.

114–162 ppm. These peaks in  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra along with elemental analyses data confirmed the proposal structure of the diacid.

$^1\text{H}$  NMR spectrum of PEA shows peaks that confirm its chemical structure (Figure 3). The aromatic protons related to the polymer appeared in the region of 7.05–7.99 ppm and the peak in the region of 10.51 ppm is assigned for N–H of amide groups in the main chain of polymer. Decaying peak related to carboxylic acid protons and appearing peaks related to amide groups and aromatic protons of diamine in the polymer chain confirmed the proposed structure of PEA.

PEA exhibited number-average molecular weights ( $M_n$ ) and weight-average molecular weights ( $M_w$ )  $2.1 \times 10^4$  and  $4.6 \times 10^4$  respectively, as measured by GPC, relative to poly(vinylpyridin); PVP) standards.

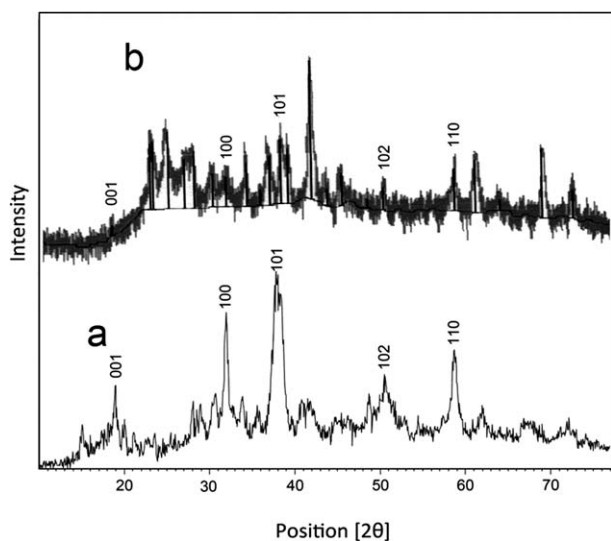


Figure 4. XRD patterns of (a) as synthesized  $\text{Mg}(\text{OH})_2$  and (b) PEA/10%  $\text{Mg}(\text{OH})_2$  nanocomposite.

### XRD Characterization

The XRD patterns of as synthesized  $\text{Mg}(\text{OH})_2$  nanostructures and PEA/ $\text{Mg}(\text{OH})_2$  nanocomposite 10% are shown in Figure 4. Figure 4(a) shows the XRD pattern of MH was indexed as a pure hexagonal phase which is very close to the values in the literature (JCPDS No 44-1482, Space group P-3m1). In Figure 4(b) XRD pattern of PEA/ $\text{Mg}(\text{OH})_2$  nanocomposite is shown that peaks of  $\text{Mg}(\text{OH})_2$  in XRD pattern of nanocomposite confirmed existence of MH in polymer matrix nanocomposite.

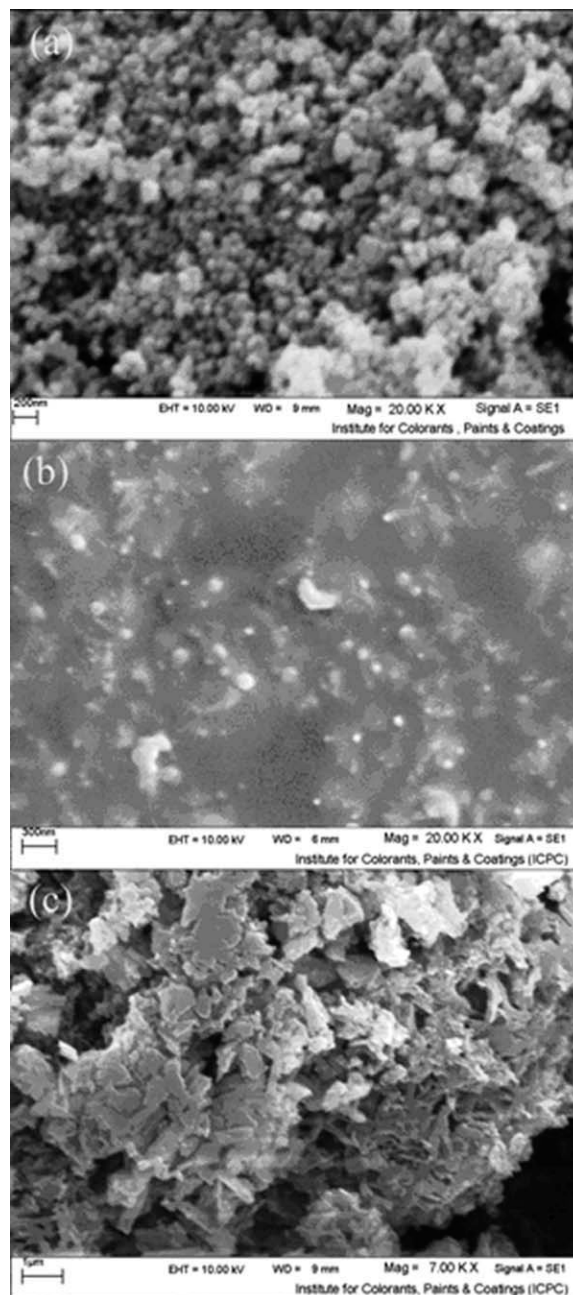
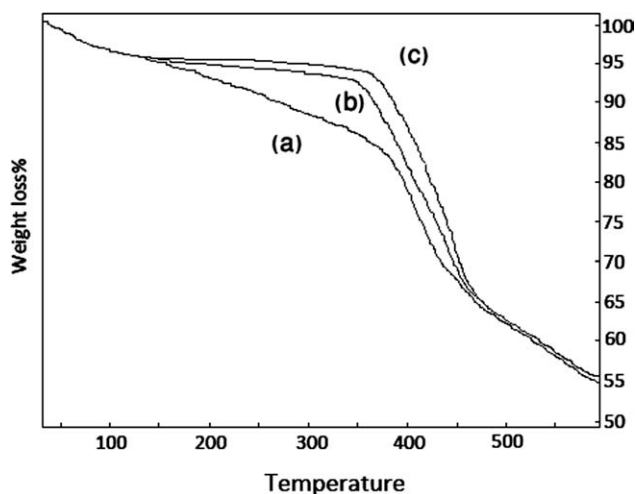


Figure 5. SEM images of (a) as synthesized  $\text{Mg}(\text{OH})_2$  nanostructures, (b) PEA/10%  $\text{Mg}(\text{OH})_2$ , and (c) PEA/20%  $\text{Mg}(\text{OH})_2$ .





**Figure 6.** TGA curves of (a) pure PEA polymer, (b) PEA/10% Mg(OH)<sub>2</sub>, and (c) PEA/20% Mg(OH)<sub>2</sub>.

### Scanning Electron Microscopy

SEM images of Mg(OH)<sub>2</sub> nanostructures shows thickness of the individual nanostructures is 20–60 nm (Figure 5). SEM image of PEA/Mg(OH)<sub>2</sub> nanocomposite in 10% concentration of MH [Figure 5(b)] shows that Mg(OH)<sub>2</sub> nanoparticles were dispersed in PEA matrix regularly but SEM image of nanocomposite in 20% concentration of MH shows that Mg(OH)<sub>2</sub> was agglomerated in PEA matrix [Figure 5(c)].

### Thermal Properties

Thermogravimetric analysis was performed on aromatic–aliphatic poly(ether-amide)/Mg(OH)<sub>2</sub> nanocomposites under inert atmosphere. Thermograms of the composites are described in Figure 6. Thermal decomposition temperatures of the nanocomposites were found in the range of 350–450°C. Char yields of the nanocomposites and the polymer are found to be more than 55% at 600°C. However, the pure poly(ether-amide) shows initial weight loss between 100 and 200°C, which may be due to the removal of moisture and some volatiles. The residual weight loss in TGA is roughly proportional but does not correspond to the inorganic ratio introduced into the samples due to the loss of combined water from the nanofiller at high temperature. So, it is evident from these measurements that nanocomposites are thermally stable compared to the pure polyamide. The thermal decomposition temperature of the nanocomposites shifted towards higher value in the presence of the MH nanostructures because MH releases water at about 330°C with an endothermic conversion.<sup>29</sup> The main mechanism of Mg(OH)<sub>2</sub> is heat absorption and dilution of the flame with water vapors. Also, MgO is a highly refractory powder that provide heat insulation by reflecting heat when collect on a surface.

### CONCLUSION

In this study, new polyamide/Mg(OH)<sub>2</sub> nanocomposites containing ether moieties was successfully prepared by a solution technique. Poly(ether-amide) as a source of polymer was syn-

thesized from polycondensation reaction of 1,2-(4-carboxy phenoxy)ethane with 4,4-diaminodiphenyl ether in a medium consisting of NMP, TPP, calcium chloride, and pyridine. Ether and methylene flexible units were prepared to improve the solubility and flexibility of the final polyamides. MH was synthesized successfully in nanoscale in the presence of ultrasonic waves. The uniform small sizes of Mg(OH)<sub>2</sub> nanostructured was used as filler in polymer matrix. This study showed that the synthesized nanocomposites have better thermal properties than the pure polymer. From the SEM and XRD investigations, the Mg(OH)<sub>2</sub> nanoparticles homogeneously dispersed in the PEA matrix in nanocomposite 10%. The release of water and heat absorption of Mg(OH)<sub>2</sub> make it as an interesting filler for synthesis of nanocomposites with good thermal stability.

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