

# Synthesis and Characterization of Some Polyacrylate/Montmorillonite Nanocomposites by *In Situ* Emulsion Polymerization Using Redox Initiation System

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**ABSTRACT:** Intercalated modification of Montmorillonite clay (MMT) with three different amino acids—Alanine, Leucine, and Phenylalanine—in the presence of hydrochloric acid followed by surface modification by methyl triethoxy silane coupling agent to produce double modified Montmorillonite clay which is characterized by X-ray diffraction (XRD) and Thermogravimetric analysis (TGA). The data shows an increase in *d*-spacing of modified clay as a result of cationic exchange. Double modified MMT clay was used in the preparation of Polyacrylate/clay nanocomposites by using an *in situ* redox emulsion polymerization of polyglycidylmethacrylate (PGMA) and polymethylmethacrylate (PMMA). The structure and properties

of the prepared nanocomposites were achieved by XRD, TGA, and SEM. The results show that all weight losses temperatures for the nanocomposite samples are higher than that of pure polymer in both PGMA and PMMA. It is also obvious that the increasing in the clay content plays an effective role in the increasing of thermal stability of these materials. SEM shows that the clay is more homogeneously dispersed in PMMA than in PGMA matrix. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1572–1578, 2009

**Key words:** montmorillonite; amino acid; silane coupling agent; nanocomposites; polyglycidylmethacrylate; polymethylmethacrylate

## INTRODUCTION

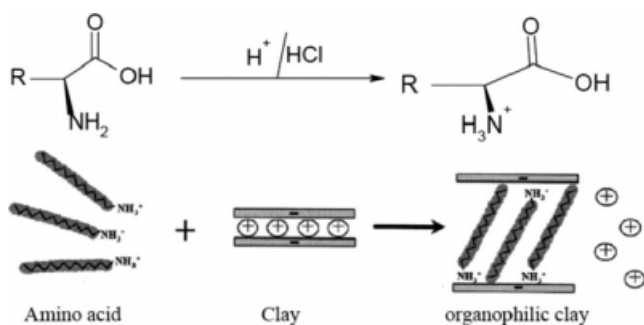
Polymer–Clay nanocomposites have attracted a great deal of attention with their improved physical and chemical properties due to the small size and large surface area of clay particles in nanoscale dimensions.<sup>1,2</sup> These materials exhibit markedly improved mechanical,<sup>3</sup> thermal,<sup>4,5</sup> optical,<sup>6</sup> and barrier properties<sup>7</sup> in comparison with a pristine polymer or microscale composites.

The polymer/clay nanocomposites have been prepared by different methods as *in situ* polymerization which was the first method used to synthesis polymer/nanocomposites based on polyamide 6.<sup>8</sup> In this technique, the organoclay is swollen in the monomer for a certain time depending on the polarity of the monomer molecules, surface treatment of organoclay, and the swelling temperature, then the reaction is initiated by addition of a curing agent in case of thermosets and by addition of a curing agent or by

increasing the temperature in case of thermoplastics.<sup>9</sup> Then the polymer formation can occur in between the clay layers. It is known, depending on the organization of the clay layers, polymer/clay nanocomposites can be classified into two types: Intercalated, where the polymer chains intercalates between the silicate layers of the clay, and Exfoliated, where the silicate layers are completely delaminated in the polymer matrix.<sup>10</sup> Exfoliated clay platelets provide better contact and distribution within the polymer matrix, and thus enhance properties of the nanocomposites more effectively.<sup>5</sup> Montmorillonite (MMT) clay is a common natural layered silicates and the suggested crystallographic structure of Montmorillonite is based on pyrophyllite consisting of two fused tetrahedral silica sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Isomorphous substitution of Si<sup>4+</sup> with Al<sup>3+</sup> in the tetrahedral lattice and of Al<sup>3+</sup> with Mg<sup>2+</sup> in the octahedral sheet cause an excess of negative charges within the Montmorillonite layers. These negative charges are counterbalanced by cations such as Ca<sup>2+</sup> and Na<sup>+</sup> situated between the layers.<sup>11</sup>

Montmorillonite clay is hydrophilic. It is very important to improve the organophilicity, so that it can

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**Figure 1** The cation-exchange process between quaternary ammonium ions and cations between the clay layers.

be compatible with organic polymers. The organophilicity of Montmorillonite clay is increased by two types of modifications as follows:

1. Interlayer galleries modification in which the MMT clay is treated with compatibilizing agents as amino acids<sup>12,13</sup> or alkyl ammonium ions,<sup>14</sup> because they can exchange easily with ions between the silicates layers, hence increasing in the distance between the clay layers results (Figure 1).
2. Surface and edges modification using silane or titanate coupling agents to generate organophilic surfaces and edges. Although quaternary ammonium salts can be adsorbed on the MMT surface, interlayer galleries modifiers are not enough for MMT surface and edges modification because this adsorption is unstable and the modification by a coupling agent on the surface and edges can form a stable covering.<sup>15</sup> The coupling agent is expected to react with the hydroxyl groups at the clay edges and surfaces (Figure 2).<sup>16,17</sup>

In this study, the structure and properties of nanocomposites prepared by *in situ* emulsion polymerization of GMA and MMA with double modified clay were investigated.

## EXPERIMENTAL

### Materials

Most of the chemicals used in this study, including alanine, leucine, phenylalanine, methanol, sodium per sulfate (SPS), sodium bisulphite, and methyl triethoxy silane were acquired from Aldrich Chemical—Germany. Sodium dodecyl sulfate (SDS), hydrochloric acid, and sodium hydroxide were obtained from Merck—Darmstadt—Germany. The monomers Glycidyl methacrylates (GMA) and Methyl methacrylate (MMA) were provided by Acros—Germany. The monomers were redistilled and stored at  $-20^{\circ}\text{C}$ .

Montmorillonite clay with cation exchange capacity (CEC) 100 meq per 100 g was supplied by Süd-Chemie—Moosburg—Germany.

## METHODS

### Intercalated modification of MMT with amino acids

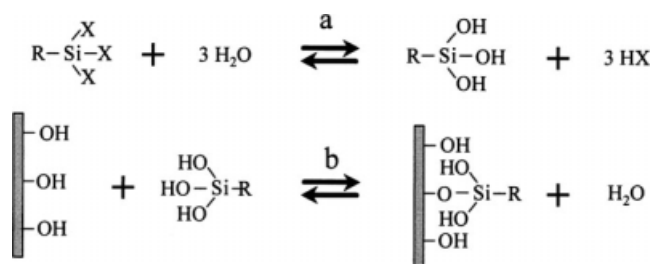
MMT (2.5 g) was dispersed into 250 mL deionized water; the mixture was stirred for 1 h and then heated to  $70^{\circ}\text{C}$  to obtain aqueous suspension of clay.<sup>18–20</sup> The desired amount of amino acid (1 and  $2\times$  concentrations of the clay based on CEC) and 2 mL of hydrochloric acid in 50 mL deionized water was added into the mixture, The pH value of the solution was adjusted to 6–8 and stirring was continued for 4 h. A white liberated precipitate was filtered and washed with deionized water. The obtained wet precipitate was dried under vacuum at  $80^{\circ}\text{C}$  for 24 h.

### Surface modification of MMT with silane coupling agent

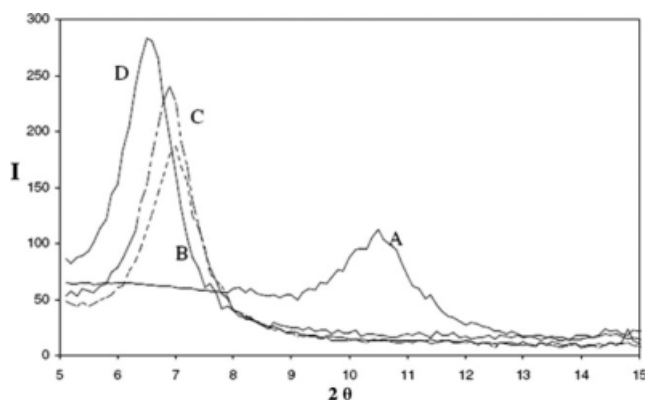
A mixture of MMT and methyl triethoxy silane (10 wt % of MMT) was added to a solution of deionized water and ethanol (10/90 volume), The pH value was adjusted to 5.5 and stirred for 2 h. The treated MMT was filtered and dried at  $80^{\circ}\text{C}$  for 24 h.

### Double modification of MMT with amino acid and silane coupling agent

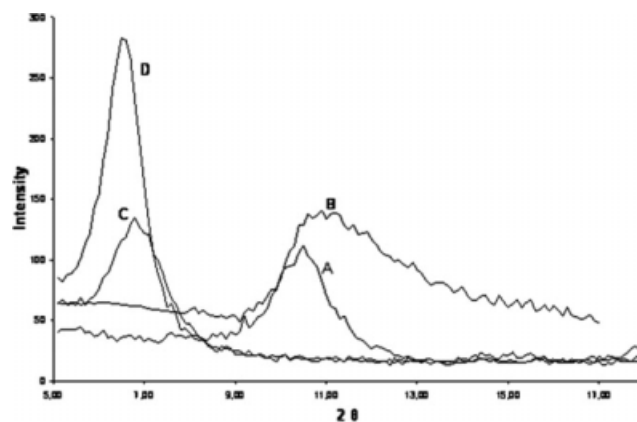
A silane coupling agent solution with MMT was prepared as described above in the surface modification. A separated solution of amino acid and 2 mL of hydrochloric acid in 50 mL deionized water was added to the solution. The mixture was then stirred for 3 h at  $70^{\circ}\text{C}$ . The white precipitate was obtained by filtration and dried under vacuum at  $80^{\circ}\text{C}$  for 24 h.



**Figure 2** (a) The hydrolysis of silane to produce a silanol group. (b) The possible reaction of a silanol group with a hydroxyl group present on the clay surface.



**Figure 3** XRD patterns of (A) pure MMT and treated with (B) alanine, (C) phenyl alanine, and (D) leucine amino acids.



**Figure 4** XRD patterns of (A) pure MMT, (B) silane surface MMT, (C) double modified MMT, and (D) leucine MMT.

### Preparation of nanocomposites by *in situ* emulsion polymerization

In 250-mL round flask, monomer, 50 mL water, 0.2 g KOH, 0.5 g emulsifier sodium dodecyl sulfate (SDS), and double modified clay were added and stirred for 30 min at room temperature, and then, the mixture was heated to 80°C. Then the initiator (SPS/SBS) is added to the mixture and stirring was continued for 5 h. After cooling, the product was precipitated in methanol. The precipitated nanocomposites hybrid was filtered, washed with methanol, and finally dried under vacuum for 24 h at 60°C. The different composite mixtures were prepared following the same procedure with different acrylate monomer and with different clay/monomer weight percent.

### Characterization

X-ray diffraction (XRD) measurements were performed using a Philips powder—Diffractogram PW

**TABLE I**  
XRD Data Obtained for Pure and Modified MMT Clay

Sample	Modifier conc.	2θ	$d_{001}$ (nm)
Pure MMT	—	10,5	7,74
Silane surface MMT	10% Weight of MMT	10,9	7,50
Alanine-MMT	1×	7,4	11,01
	2×	7,0	11,55
Leucine-MMT	1×	6,6	12,36
	2×	6,5	12,59
Phenylalanine-MMT	1×	7,1	11,38
	2×	6,9	11,75
Double modified MMT	10% weight of MMT and 2× leucine conc.	6,8	11,94

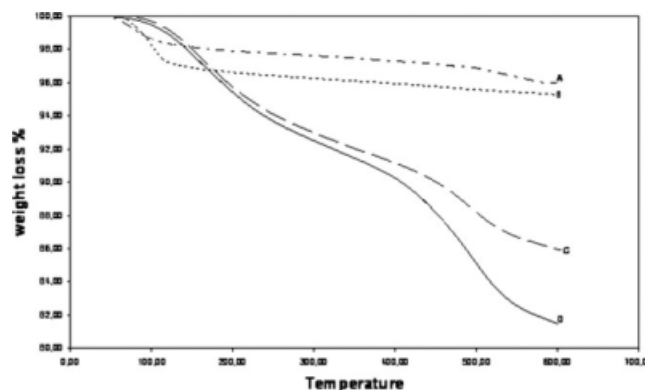
1050 with ADM software and with Ni-filtered Cu K radiation. The accelerating voltage was 40 KV, and the current was 30 mA.

Thermogravimetric analysis (TGA) was determined on TGA 7 thermogravimetric analyzer (Perkin-Elmer instrument) under a nitrogen flow at heating rate 10°C min<sup>-1</sup>. The morphology and fracture surface of the composites were examined by Scanning electron microscope (SEM) analysis using Zeiss, DSM 962 microscope.

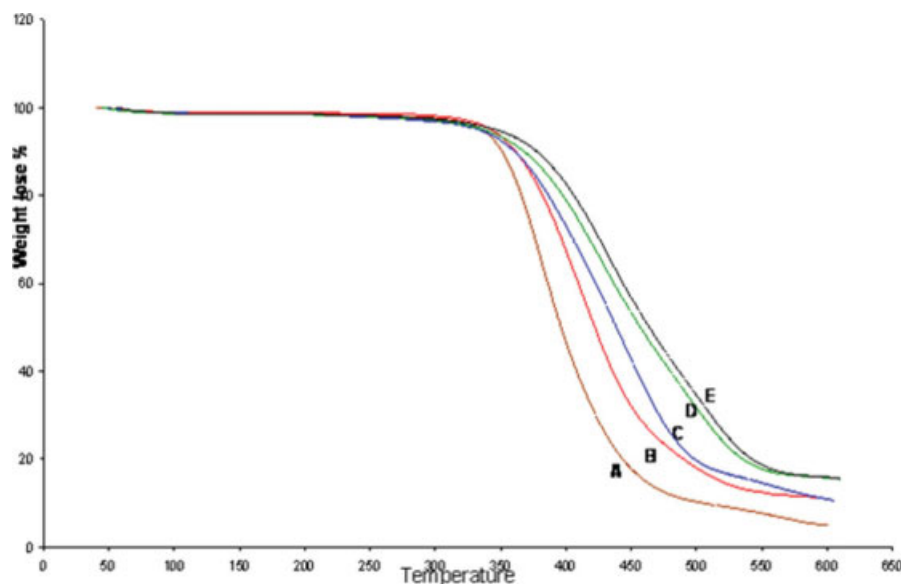
## RESULTS AND DISCUSSION

### Modification of montmorillonite clay

Three different amino acids result in different intercalation effects and structures. Figure 3 displays XRD patterns of the pure MMT clay and intercalating agent-treated MMT clays depends on amino acid concentration 2× based on MMT clay CEC, Alanine-



**Figure 5** TGA thermograms of (A) silane surface MMT, (B) pure MMT, (C) double modified MMT, and (D) leucine-MMT.



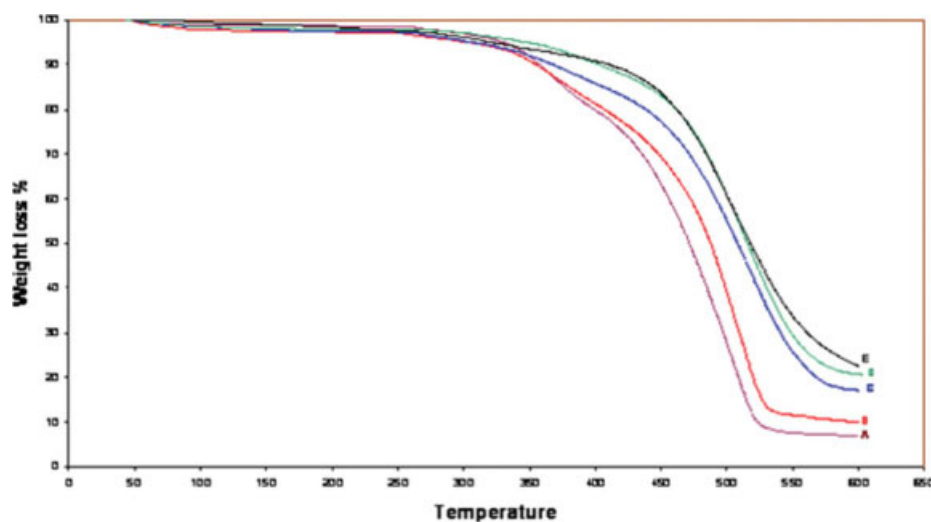
**Figure 6** TGA thermograms of (A) pure PGMA, (B) 2%, (C) 6%, (D) 10%, and (E) 20% wt % MMT in PGMA-MMT nanocomposites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

MMT, Leucine-MMT, and Phenylalanine-MMT. The basal spacing ( $d_{001}$ ) values of these samples are calculated from the peak position using Bragg's equation as follows:

$$n\lambda = 2d \sin \theta$$

Each sample has one peak at  $2\theta = 10.5^\circ$ ,  $7.0^\circ$ ,  $6.5^\circ$ , and  $6.9^\circ$ , respectively. The data for  $d$ -spacing are listed in Table I which shows that the diffraction peaks of all modified MMT clay samples are shifted to smaller angles compared with the pure MMT.

This indicates that MMT clay was successfully intercalated with amino acids. The results also show that—in all modifiers—the addition of  $2\times$  concentration of amino acid based on clay CEC give increment in interlayer spacing more than in the addition of  $1\times$  concentration. The listed data in Table I concluded that the more interlayer spacing is given by using  $2\times$  concentration of Leucine amino acid based on MMT CEC. Figure 4 shows XRD curves of pure MMT, silane surface modified MMT, Leucine-MMT, and double modified MMT clays, these peaks are assigned to the  $d$ -spacing of MMT.<sup>10,18</sup> The data for



**Figure 7** TGA thermograms of (A) pure PMMA, (B) 2%, (C) 6%, (D) 10%, and (E) 20% wt % MMT in PMMA-MMT nanocomposites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

*d*-spacing of each sample is given in Table I. From the table, it can be seen, that silane surface treatment did not cause any positive significant difference in the basal spacing of pure MMT clay, and the *d*-spacing of double modified MMT clay was found to be 11.94 nm which is lower than the *d*-spacing of Leucine-MMT (12.9 nm). This is due to the effect of the silane coupling agent which coat the surface of the MMT clay and then the clay layer becomes closed for amino acid penetration between the silicate layers.<sup>10</sup>

TGA results of pure MMT, silane surface modified MMT, Leucine-MMT, and double modified MMT clays are illustrated in Figure 5. From this figure, it is clear that the thermogram of pure MMT is quite different from that of Leucine-MMT and double modified MMT clays. It is also clear that the position of double modified clay decomposition curve is between the decomposition curves of Leucine-MMT and decomposition curve of pure MMT, whereas the silane surface MMT has higher thermal characteristic than pure MMT. This result can be accepted as an indication of successful insertion of both silane coupling agent and Leucine amino acid into MMT clay.

### Structures and properties of nanocomposites

The thermal stability of pure PMMA, pure PGMA, and the prepared nanocomposites with different clay contents was determined by measuring the thermogravimetric analysis (TGA) within the temperature range 50–600°C, as shown in Figures 6, 7. In general, it is clear that all weight lose temperatures for the nanocomposites samples are higher than that of pure polymer, which can be attributed to the restriction of the motion of organic chains attached to MMT clay.<sup>19</sup> It is also obvious, that the increasing in the clay content plays an effective role in the increasing of thermal stability of these materials, which can be explained by the increasing in homogenous dispersion between the individual layers, which lead to increasing in the thermal stability. The TGA results of PGMA and PGMA-MMT are listed in Table II, which shows that the weight lose temperatures of

**TABLE II**  
TGA Data Obtained for Pure PGMA and PGMA-MMT Nanocomposites

Degradation temperature	Content of double modified clay (%)				
	0%	2%	6%	10%	20%
$T_{10}$	355	361	365	372	377
$T_{20}$	370	382	386	397	406
$T_{30}$	380	396	405	418	425
$T_{50}$	400	422	438	456	463
$T_{80}$	445	454	498	535	542

**TABLE III**  
TGA Data Obtained for Pure PMMA and PMMA-MMT Nanocomposites

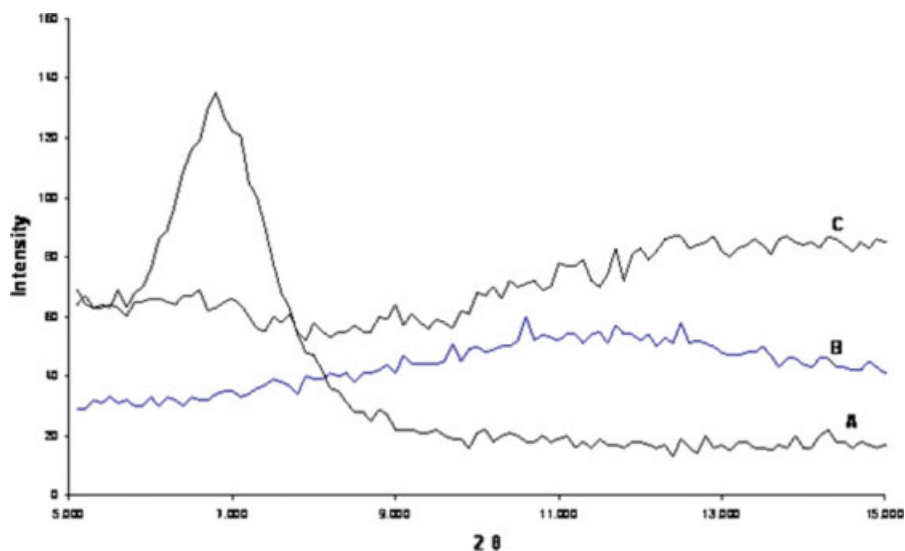
Degradation temperature	Content of double modified clay (%)				
	0%	2%	6%	10%	20%
$T_{10}$	347	360	367	402	410
$T_{20}$	399	406	438	461	461
$T_{30}$	433	448	471	485	484
$T_{50}$	471	487	508	515	518
$T_{80}$	508	519	568	–	–

nanocomposites are higher than that of pure PGMA. For example,  $T_{dc}$  (central weight lose) of PGMA-MMT is higher than that of pure PGMA (400°C), and increases by increasing the double modified clay content by 22, 38, 56, and 63°C when 2, 6, 10, and 20 wt % of double modified clay is added, respectively. Table III contains the TGA results of pure PMMA and PMMA-MMT nanocomposites and shows that  $T_{dc}$  of pure PMMA is 472°C and increased by 17, 37, 44, and 46°C when 2, 6, 10, and 20 wt % double modified clay is added, respectively. Table IV shows a comparison in the weight loss % in different temperatures between PGMA-MMT and PMMA-MMT when 6 wt % of double modified clay is added. From the table, it can be concluded that PMMA-MMT nanocomposites have more thermal resistance compared with PGMA-MMT nanocomposites when using the same weight % of clay content. PGMA-MMT nanocomposites lose the weight more rapidly and at lower temperature than PMMA-MMT nanocomposites.

X-ray diffractograms of PGMA-MMT and PMMA-MMT nanocomposites when 6 wt % of double modified clay is used are illustrated in Figure 8. It shows

**TABLE IV**  
Comparison in the Weight Loss % Between PGMA-MMT and PMMA-MMT When 6 wt % MMT is Added in Different Temperatures

Temperature	Weight loss %	
	PGMA-MMT	PMMA-MMT
300	3,16	4,64
325	4,37	6,00
350	7,47	7,94
375	14,9	10,93
400	27,00	14,20
425	41,29	17,75
450	57,4	22,97
475	71,89	31,89
500	80,36	44,91
525	83,50	60,89
550	85,46	74,30
575	87,60	81,40
600	89,16	82,88

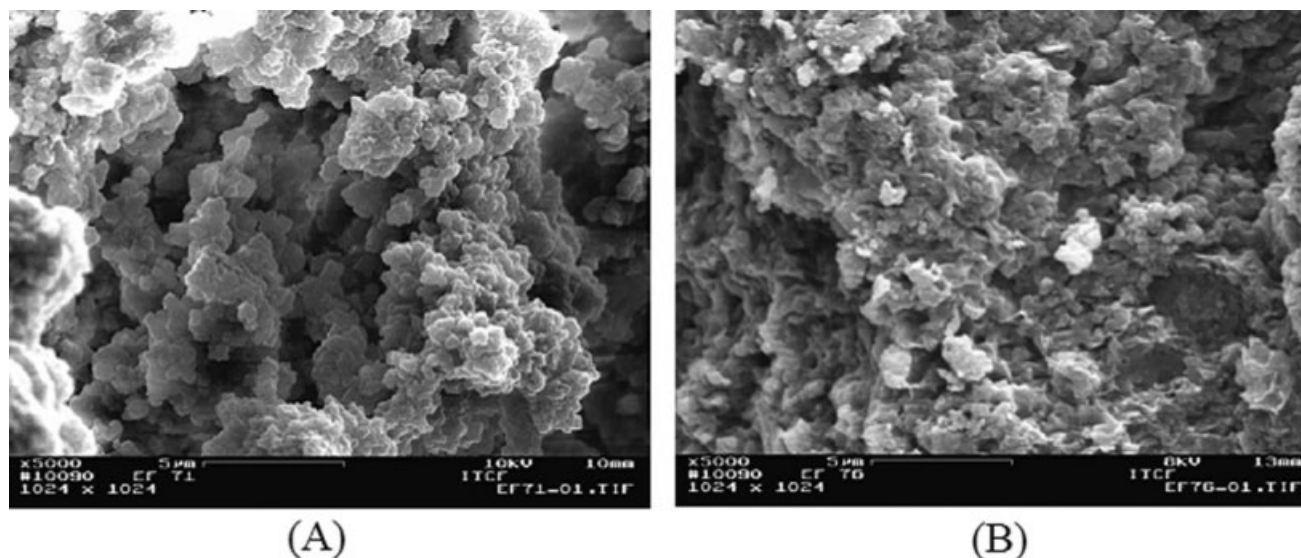


**Figure 8** XRD patterns of (A) double modified MMT, (B) PGMA-MMT nanocomposites, and (C) PMMA-MMT nanocomposites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

that there is no noticeable organoclay peak reflection appearing in the diffraction pattern for both PGMA-MMT and PMMA-MMT nanocomposites. This means that the silica layers were completely delaminated and led to production of exfoliated nanocomposites<sup>20</sup> with both PGMA and PMMA.

The examination of the surface of prepared samples was investigated by SEM. The SEM images indicate that the PGMA and PMMA are homogeneously intercalated in the interlayer of MMT clay to produce clay/polymer nanocomposites. Figure 9 shows SEM of pure PGMA and PGMA-MMT nanocomposites where small aggregates of around 5  $\mu\text{m}$  in size together with few large aggregates are

observed in the PGMA-MMT image, the presence of these aggregates indicate the poorly dispersed of MMT clay particles in the polymer matrix. On the other hand, Figure 10 shows SEM of pure MMA and PMMA-MMT nanocomposites where MMT particles did not appear at micro level where the absence of MMT particles indicates that the agglomerate did not reveal the inorganic domain. The particle size of MMT is not visible because it is well adherent to the polymer. This indicates that the mineral domains are submicron and homogeneously dispersion of MMT clay particles in the polymer matrix and also indicates that the PMMA was intercalated in the interlayer of MMT clay in a homogenous matter.<sup>21</sup>



**Figure 9** SEM images of (A) pure PGMA and (B) PGMA-MMT.

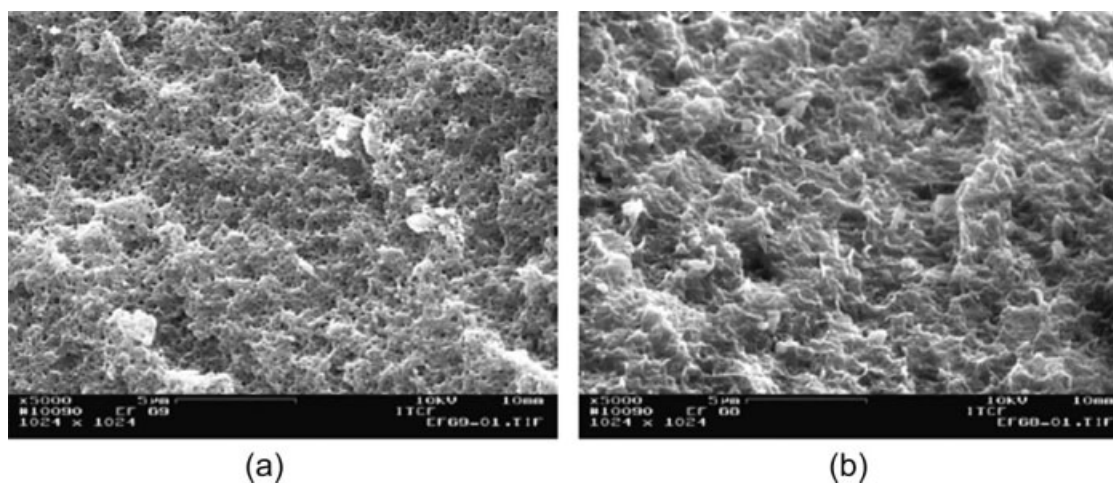


Figure 10 SEM images of (A) pure PMMA and (B) PMMA-MMT.

## CONCLUSIONS

### Modification of MMT clay

1. MMT clay with interlayer spacing 7.74 nm and CEC 100 meq per 100 g was successfully modified with different amino acids in the presence of hydrochloric acid. Alanine-MMT, Leucine-MMT, and Phenylalanine-MMT display the biggest interlayer spacing of 11.1, 12.36, and 11.75 nm, respectively, when using 1 $\times$  concentration of amino acid based on clay CEC and 11.55, 12.59, and 11.94 nm, respectively, when using 2 $\times$  concentration of amino acid based on clay CEC.
2. Surface modifier phenyl triethoxy silane coupling agent was used to modify the surface and edges of the MMT clay where the interlayer spacing of MMT clay after double modification by 2 $\times$  concentration of Leucine amino acid and Methyl triethoxy silane was 11.94 nm.

### Preparation and characterization of nanocomposites

1. Nanocomposites were successfully prepared by *in situ* Emulsion Polymerization of GMA and MMA monomers using redox initiation system.
2. XRD investigation showed that exfoliated structures were formed during the preparation of P<sub>g</sub>ma-MMA and P<sub>m</sub>ma-MMT.
3. SEM shows that MMT clay is poorly dispersed in polymer matrix in case of PGMA while it is homogenously dispersed in polymer matrix in case of PMMA.
4. TGA results show that all weight loses temperature for the nanocomposites samples are higher than that of pure polymer in both PGMA and

PMMA. And it is also obvious that the increasing in the clay content plays an effective role in the increasing of thermal stability of these materials.

### References

1. Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
2. Alexander, M.; Dubois, P. *Mater Sci Eng* 2000, 28, 1.
3. Zilg, C.; Thomson, R.; Mulhaupt, R.; Finter, J. *Adv Mater* 1999, 11, 49.
4. Su, S.; Wilkie, C. A. *J Polym Sci Part A: Polym Chem* 2003, 41, 1124.
5. Yui, D.; Fu, H.; Chang, Y.; Kuo, S.; Huang, J.; Chang, F. *J Polym Sci Part B: Polym Phys* 2007, 45, 1781.
6. Petrella, A.; Tamborra, M.; Curri, M.; Cosma, L. P.; Striccoli, M.; Cozzoli, P. D.; Agostiano, A. *J Phys Chem* 2005, 109, 1554.
7. Xin, T.; Haicha, Z.; Tao, T.; Zhiliu, F.; Baotong, H. *J Polym Sci Part A: Polym Chem* 2002, 40, 1706.
8. Okoda, A.; Kawasumi, M.; Usuki, A.; Kojima, Y.; Kurauchi, T.; Kamigaito, O. *Mater Res Soc Symp Proc* 1990, 171, 45.
9. Messersmith, P. B.; Giannelis, E. P. *J Appl Polym Sci A: Polym Chem* 1995, 33, 1047.
10. Sinan, S.; Mine, M.; Nihan, N.; Turgut, N. *Polym Int* 2006, 55, 216.
11. Peter, C.; Zhen, W.; Thomas, P. *Appl Clay Sci* 1999, 15, 11.
12. Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1174.
13. Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
14. Wang, Z.; Pinnavaia, T. *J Chem Mater* 1998, 10, 1820.
15. Klapayta, Z.; Fujita, T.; Lyi, N. *Appl Clay Sci* 2001, 19, 5.
16. Krysztafkiewicz, A.; Werner, R.; Lipska, L. K.; Jesionowski, T. *Colloids Surf A* 2001, 182, 65.
17. Alkadas, N.; Kapadi, U. R.; Hundiwale, D. G. *J Appl Polym Sci* 2004, 93, 1299.
18. Qian, X.; Liao, M.; Zhang, W. *Polym Int* 2007, 56, 399.
19. Ding, Y.; Guo, C.; Dong, J.; Wang, Z. *J Appl Polym Sci* 2006, 102, 4313.
20. Shim, J. H.; Kim, E. S.; Joo, J. H.; Yoon, J. S. *J Appl Polym Sci* 2006, 102, 4983.
21. Akelah, A.; Rehab, A.; Agag, T.; Betiha, M. *J Appl Polym Sci* 2007, 103, 373.