Polymer Nanocomposite of Mg-Al Hydrotalcite-Type Anionic Clay Modified with Organosulfate

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The Mg-Al hydrotalcite (HT) was modified with organosulfate, sodium dodecylsulfate (SDS) by an anion exchange reaction. The modifier content and the interlayer distance of organo-modified HT (MHT) were examined. The modifier content and d-spacing in HT layers increased up to 45% of AEC and 38.0 Å. Incorporation of the modifier in HT layers at pH 7 was easier than at pH 11, due to the higher concentration of anions in HT layers at pH 11 than at pH 7. Polystyrene(PS) and poly(methyl methacrylate)(PMMA) nanocomposites with the MHT were prepared by solution and melt blending, and *in situ* polymerization; an intercalation and partially exfoliation were obtained together with thin packets of HT layers. The partially exfoliated PMMA/MHT nanocomposites were obtained even at the 5 wt% MHT loading. The nanocomposites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). The mechanical properties of nanocomposites were also investigated.

KEY WORDS: Mg-Al hydrotalcite / Organosulfate / Nanocomposite / PMMA / PS /

Polymer/layered inorganic nanocomposites (PLN) have attracted great interest in the field of material chemistry because of their novel mechanical, thermal, and optical properties,[1–8] which are mainly attributed to the high degree of dispersion of layered inorganic compounds in the polymer matrix. A mass fraction of a few percent of reinforcing agent that is properly distributed in the polymer matrix creates significantly more surface area for polymer-filler interactions than do conventional composites.[9] Among PLNs, exfoliated PLN materials usually have a molecular dispersion of high aspect ratio inorganic layers in polymer nanocomposites.[10]

Silicate clays such as montmorillonite, hectorite, and magadiite are the most common fillers used for the preparation of nanocomposites; they have a layered structure with 1 nm thickness and extremely high aspect ratios (*e.g.* 50–1000).[11] Lately, a new emerging class of nanocomposites, based on anionic hydrotalcite (HT)-like clays, has been investigated.

Anionic clays can be considered the opposite of silicate clays; positively charged sheets are stacked one on top of the other and intercalated by exchangeable anions and water molecules.[12] HTs are positively charged due to the isomorphous substitution of bivalent cations by trivalent ones. The layers are intercalated with anions in order to balance the residual charge. One of the most important properties of the HT-type material is its high anionic exchange capacity related to its lamellar structure that allows the exchange of its original anions with those present in an aqueous solution.

It is well known that HT-type compound belongs to the large class of natural and synthetic HT. HT have the general formula, $[M_{1-x}M(III)_x(OH)_2]^{x+}A_{x/z}^{z-}\cdot mH_2O$, where M is a metal cation and A is an exchangeable anion. Typically LDH anion exchange capacities vary in the range of 200–470

mequiv/100 g and are higher than the corresponding cation exchange capacity of silicate clays like sodium montmorillonite (exchange capacity = 80–145 mequiv/100 g).[1,13]

The electrostatic stacking forces between layers and intercalated anions increase with the exchange capacity; this is unfavorable for the exfoliation process.[14,15] Usually only intercalated structures with low d-spacings are obtained, as found for poly(styrene sulfonate), poly(vinyl sulfonate), poly(acrylic acid), poly(ethylene oxide), and dioctyl sulphosuccinate HT nanocomposites.[16,17]

Hsueh *et al.* have claimed complete exfoliation in a polyimide of an aminobenzoate modified HT by *in situ* polymerization.[18] Furthermore, the thermal stability was enhanced as dynamic and isothermal thermogravimetric data was revealed. Similar results have been reported for HT/epoxy, HT/acrylate, and HT/methacrylate nanocomposites by *in situ* polymerization.[19,20] Very recently, exfoliated nanocomposites of polyamide-6 were prepared by melt processing with 4-dodecylbenzenesulfate–modified HT.[21]

The current study examined the modification of the commercial HT for the preparation of polymer nanocomposites based on thermoplastics such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). An organophilic HT was prepared by an ion exchange reaction with sodium dodecylsulfate (SDS) as the modifier. The SDS content and d-spacing of the modified HT (MHT) was determined by EA and XRD, respectively. The structure of MHT was examined by FT-IR. Polymer/MHT nanocomposites were obtained through various methods including solution and melt blending and *in situ* polymerization. The nanoscale dispersion of MHT layers in the PS or PMMA matrix was characterized by XRD and TEM. The mechanical properties of nanocomposites were also investigated.

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Polymer
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EXPERIMENTAL

Materials

The hydrotalcite (HT) of $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ used was a commercial product (Doobon Co., Korea) with an anion exchange capacity (AEC) of 5.6 mequiv/g. For the modifier, sodium dodecylsulfate (SDS) was purchased from Sigma-Aldrich. The styrene (99%, Kanto Chem. Co., Japan) and methyl methacrylate (99.5%, Junsei Chem. Co., Japan) were washed with 5% aqueous sodium hydroxide, dried over calcium hydride, and distilled under reduced pressure. PS (G144, Dongbu Hannong Chemcal, Korea) and PMMA (EF830, LG MMA, Korea) were used with the commercial products.

Modification and Synthesis of Hydrotalcite

The commercial hydrotalcite (CHT) was dispersed in distilled water at room temperature in order to minimize CO_3^{2-} in the solution. A solution of organic modifier (SDS) was added to the dispersion of CHT while being vigorously stirred. Then H_2SO_4 was added until pH 1 was reached to form a transparent solution, and was stirred continuously for 2 h. The modified HT (MHT) was prepared by the co-precipitation method at a constant pH (pH 7 or pH 11).[22]

Mg-Al hydrotalcite was synthesized by the slightly modified method of Valim *et al.*;[22] a solution was prepared by dissolving $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 6H_2O$ in 70 mL of water with a total Mg + Al concentration of 1.5 mol/L (a ratio [Mg]/[Al] of 2). This solution was added drop-wise to the solution of SDS, and a NaOH solution was added until pH = 11 was reached. The slurry was then aged for 18 h at 70 °C. The product was filtered and washed with distilled water and dried in a vacuum oven at room temperature.

Preparation of Polymer/MHT Nanocomposite

The polymer/MHT nanocomposite was prepared by *in situ* polymerization and solution and melt blending. For *in situ* polymerization, monomer (18.0 g) and MHT (0.9 g) were added to an ampule. The ampule was deoxygenated by three-thaw-pump cycles, and stirred for 4 h. 1 mol % of AIBN was added into the monomer/MHT mixture, and placed in an oil bath at 70 °C for 12 h. The polymerization product was poured into methanol, and the precipitate was filtered and dried. The PS and PMMA was dissolved in toluene and acetone, respectively, and 5 wt % MHT was added while being vigorously stirred. After homogenization, the mixture was poured into methanol, and the precipitate was filtered and dried in a vacuum oven at room temperature. For the melt blend method, the MHT (5 wt %) was dispersed in PS or PMMA using a twin-screw, co-rotating microcompounder (MiniLab Haake Rheomex CTW5). The residence time in the extruder was held constant for 1 min at 220 °C.

Characterization

The modifier content in MHT was estimated from the S

content as measured with an elemental analyzer (EA 1108, Fisions Instruments) and a thermogravimetric analyzer (TGA-50H, Shimadzu). The *d*-spacing of the HT gallery in MHT, synthesized HT (SHT), and polymer nanocomposite was measured with X-ray diffractometer (XRD, X'pert, Philips), CuKα X-ray radiation, curved crystal graphite monochromator, at 45 kV and 100 mA. The diffraction patterns were collected between 1° and 12° 2θ at a scanning rate of 1°/min. Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50H thermoanalyzer. The measurement error of the temperature was ±3 °C. The samples were run twice under nitrogen at a scan rate of 10 °C/min. The morphology was investigated using a transmission electron microscope (TEM, H-7600, Hitachi, Japan) operated at 50 kV under low-dose conditions. The TEM samples were ultramicrotomed at −10 °C using a diamond knife on a Leica Ultracut microtome to produce 80 nm thick sections.

RESULTS AND DISCUSSION

The preparation method of an organo-modified hydrotalcite (MHT) appropriate to polymer/MHT nanocomposites required a considerable examination for the solution and melt blending and *in situ* polymerization. The sodium dodecylsulfate (SDS) was used as the organic modifier to achieve an organophilic HT interlayer region. SDS was preferred to other possible surfactants such as stearic acid and phosphorus based anionic surfactants,[23] due to its excellent combination of high thermal stability, high water solubility and low cost.

Characterization of MHT

The basal spacing of a homoionic organoclay depends on the content and charge density of the layered silicate. Both factors control the packing and configuration of the onium ion modifier in the constrained gallery and consequently the height of the gallery.[24,25] Organoclays are normally formed through an ion-exchange reaction of the inorganic parent clay with the desired onium ion. The partial replacement of the inorganic cations by onium ions results in the segregation of the two types of cations into separate galleries, affording either an interstratified intercalate or a mixture of organic and inorganic clay phases.

In this present study, the commercial Mg-Al hydrotalcite (CHT) was modified with SDS (1.6 g/g HT, 100% ACE) and coprecipitated at pH 7 or 11. In the presence of SDS, HT was synthesized from $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 6H_2O$ solution to obtain the synthesized HT (SHT). The structure of modified HT (MHT) produced at different pH and SHT was confirmed with FT-IR (Figure 1).

The CHT exhibited broad absorption bands at around 3500 and 1630 cm^{-1} (O-H stretching and hydroxyl groups) and 1360 cm^{-1} (CO_3^{2-} group). The SDS modifier showed absorption bands at 2800–2900 cm^{-1} (C-H stretching vibration), 1450 cm^{-1} (CH_2 bending vibration) and 1200 cm^{-1} (SO_3^{2-} group). The FT-IR spectra of MHT obtained at pH 7 (MHT-7) and pH 11 (MHT-11) were almost the same peaks as the C-H
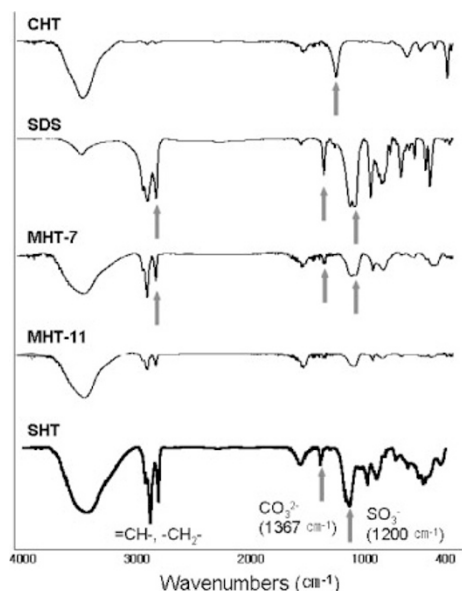
Figure 1. FT-IR spectra of commercial HT (CHT), modifier (SDS), modified HT (MHT) and synthesized HT (SHT).
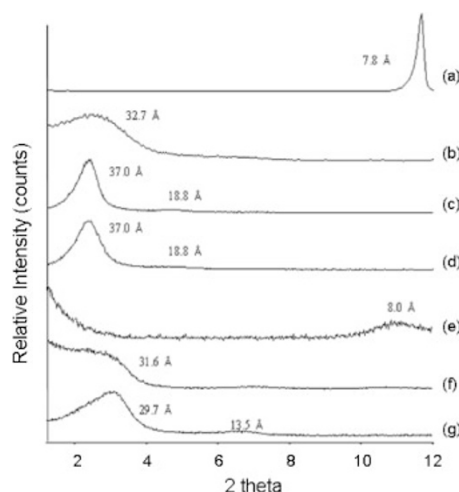
and SO_3^{2-} groups but less than the CO_3^{2-} group. The incorporation of SDS in the MHT could be confirmed by the C-H stretching vibration, CH_2 bending vibration, and SO_3^{2-} band; the absorption peak at $1360\,cm^{-1}$ of the CO_3^{2-} group had almost disappeared. It seems that the anion exchange reaction between the CO_3^{2-} anion and SO_3^{2-} group of SDS occurred in the modification procedure. In addition, it was confirmed that the structure of SHT was similar to MHT which did not appear the CO_3^{2-} group.

Further evidence of the presence of SDS in the interlayer of MHT and SHT was investigated with XRD (Figure 2).

The reflection of CHT clearly displays a peak ($2\theta = 11.5°$) that demonstrates 7.8 Å layer spacing. The reflections of SHT and MHT shifted to lower angles and the pristine peak of CHT
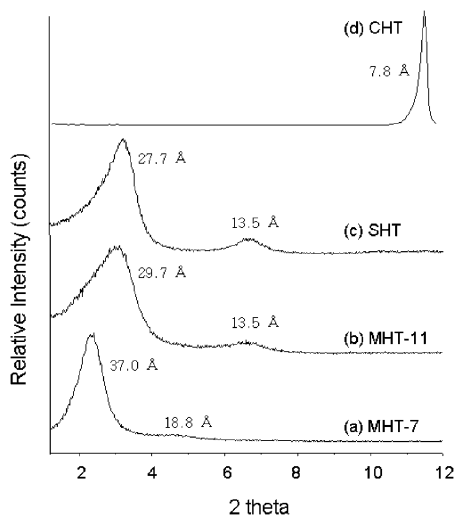
Figure 2. XRD patterns of MHT obtained at pH 7 (MHT-7) (a), pH 11 (MHT-11) (b), synthesized HT (SHT) (c) and commercial HT (CHT) (d).

($2\theta = 11.5°$) disappeared. The basal plane (001) peaks of SHT and MHT-11 appeared around $2\theta = 3.1–3.2°$. The MHT-7 peak shifted to a lower angle at $2\theta = 2.4°$, showing that the gallery distance was enlarged to 37 Å. A secondary reflection of SHT and MHT-11 appeared at $2\theta = 6.6°$ and that of MHT-7 appeared at $2\theta = 4.6°$. The fact that in all patterns the (001) reflection can be seen indicates that tactoids are present and that complete exfoliation was not achieved. The (001) peak width of the MHT-7 was smaller than that of SHT and MHT-11, indicating that the tactoids thickness of MHT-7 is larger than the others.

In order to investigate the effect of the treating amount of SDS on the modification of HT, a small portion of the MHT was dried and characterized by XRD (Figure 3).

By increasing the treating amount of SDS, the d-spacings became larger and the reflection of CHT corresponding to d-spacing of 7.8 Å disappeared completely that of the MHT obtained at pH 7. The interlayer distance of MHT gradually expanded from the original 7.8 Å to about 37.0 Å.

In the case of MHT-11, the reflections were less sensitive to the amount of SDS so that the anion exchange reaction occurred with a small amount of SDS (0.4 g/g HT) because the concentration of OH^- anion was so large at pH 11. From the above observations, it is hypothesized that the modification condition was more effective on the d-spacing of MHT.


Figure 3. XRD patterns of MHT treating with various amounts of SDS (g/g HT). MHT obtained at pH 7; (a) 0.0, (b) 0.4, (c) 0.8, (d) 1.6 MHT obtained at pH 11; (e) 0.4, (f) 0.8, (g) 1.6.

Polymer/MHT Nanocomposites

PMMA/MHT nanocomposites were prepared using three different procedures: solution, melt blending and *in situ* polymerization. The reflections of PMMA/MHT-7 and PMMA/MHT-11 series nanocomposites were examined, as shown in Figure 4.

The reflections of the PMMA/MHT-7 series exhibited no peaks while those of the PMMA/MHT-11 nanocomposites exhibited a broad peak at low 2 theta value, which indicates that the PMMA/MHT-7 nanocomposite was partially exfoli-
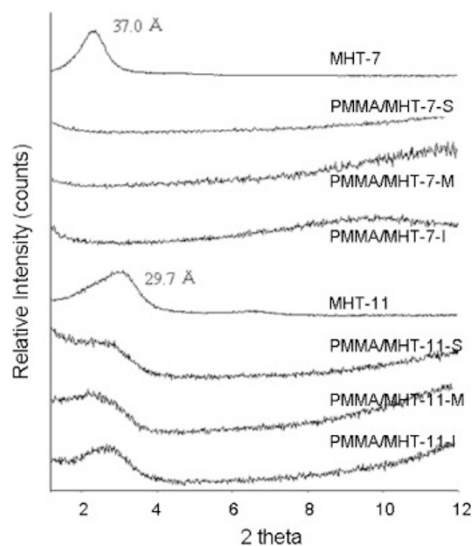
Figure 4. XRD patterns of PMMA/MHT-7 and PMMA/MHT-11 nanocomposites prepared by various methods of solution (PMMA/MHT-7-S and PMMA/MHT-11-S), melt blending (PMMA/MHT-7-M and PMMA/MHT-11-M) and *in situ* polymerization (PMMA/MHT-7-I and PMMA/MHT-11-I).
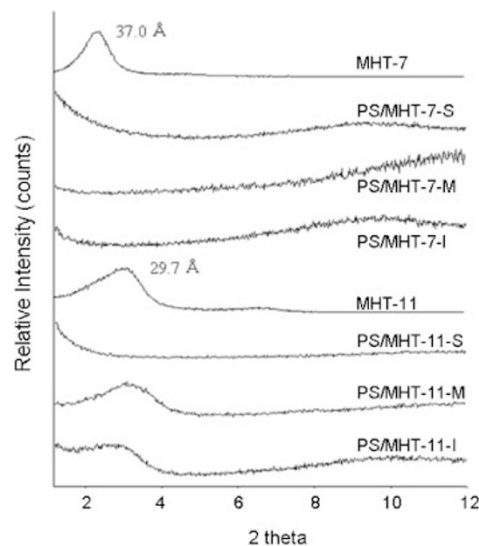
Figure 5. XRD patterns of PS/MHT-7 and PS/MHT-11 nanocomposites prepared by various methods of solution (PS/MHT-7-S and PS/MHT-11-S), melt blending (PS/MHT-7-M and PS/MHT-11-M) and *in situ* polymerization (PS/MHT-7-I and PS/MHT-11-I).

ated while the PMMA/MHT-11 series was intercalated. This observation might be understood by the larger *d*-spacing due to the higher SDS content of MHT-7 compared to that of MHT-11.

Concerning the preparation procedures, the solution blending produced the more dispersed nanocomposite than that produced by melt blending and *in situ* polymerization. With the solution blending, the partially exfoliated structures of nanocomposites were obtained for PMMA/MHT-7-S, but the (001) peaks of PMMA/MHT-11-S appeared around $2\theta = 2.1$–$3.0°$. The peak of PMMA/MHT-11-S was broader than that of PMMA/MHT-11-M and PMMA/MHT-11-I and the peak width of the PMMA/MHT-11-S was larger, indicating that the tactoids were present and intercalation occurred.

PS/MHT nanocomposites were prepared using three different procedures and the reflections of the PS/MHT-7 and PS/MHT-11 series nanocomposites were examined as shown in Figure 5.

The PS/MHT-7 series and PS/MHT-11-S had no peaks, while PS/MHT-11-M and PS/MHT-11-I gave a broad peak at low 2 theta value. The layer distance of MHT for nanocomposites obtained by solution blending was larger than that obtained by melt blending and *in situ* polymerization. Thus, the solution method for preparation of nanocomposites is more distinguishable than others.

The morphological structures of PMMA/MHT and PS/MHT nanocomposites were studied and TEM images of PS/MHT-7-S and PMMA/MHT-7-S nanocomposites are shown in Figure 6.

It can be seen that the MHT-7 layers are homogeneously dispersed in the PS and PMMA matrix. The dark entities are the face of intercalated MHT layers. The partially exfoliated MHT-7 layers combined with the SDS modifier were dispersed
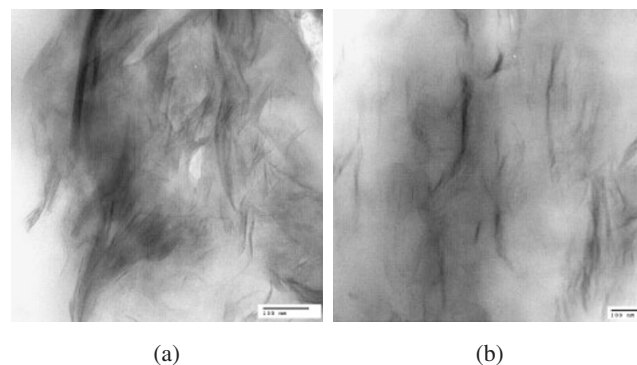
Figure 6. TEM images of (a) PS/MHT-7-S and (b) PMMA/MHT-7-S nanocomposites.

in a disorderly manner in the PMMA matrix. The reflections in Figure 4 also appear in the MHT-7 layers in the nanocomposites, which were partially exfoliated as mentioned above.[11] Thus, it is possible that SDS was used to expand the HT layers and to obtain partially exfoliated nanocomposites. The schematic diagrams for the formation mechanism of the PMMA/MHT and PS/MHT nanocomposites are shown in Figure 7.

Two different structures are possible; monolayered and bilayered intercalation. The similar formation mechanism of the partially exfoliated PMMA/clay nanocomposites has been reported in the literature.[26,27]

The effect of the procedure methods on the tensile strength can be measured, the results are shown in Table I.

PMMA/MHT nanocomposites showed a improvement of tensile strength with respect to those of the PMMA, at which the tensile strength increased by 20%. However, the tensile strength of PS/MHT nanocomposites dramatically decreased with the incorporation of MHT. The enhancements are strictly related to the processing methods; the tensile strength of
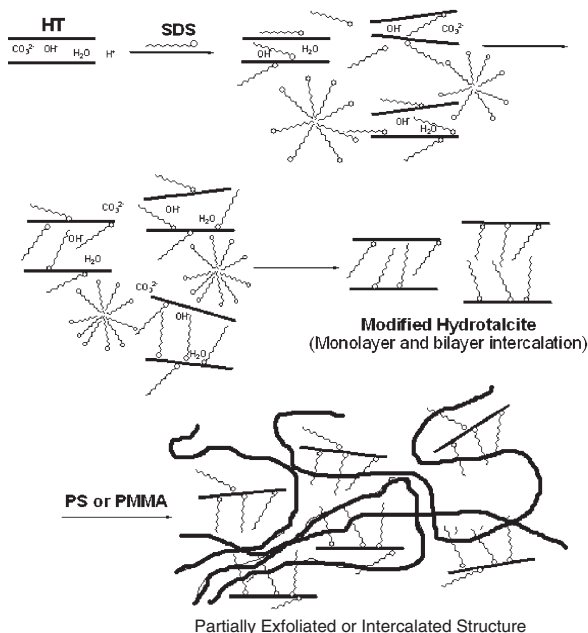
Figure 7. Schematic diagrams of formation procedure of exfoliated polymer/MHT nanocomposites.

Table I. Effect of the Procedure Methods on Tensile Strength of PMMA/MHT and PS/MHT Nanocomposites

Samples	Tensile Strength (kg·f/mm^2)
PMMA	1.84
PMMA/MHT-7S	2.21
PMMA/MHT-7M	1.98
PMMA/MHT-7I	1.92
PS	3.05
PS/MHT-7S	2.05
PS/MHT-7M	1.98
PS/MHT-7I	1.32

Figure 8. TGA differential curves of neat PMMA and PMMA/MHT-7 nanocomposites with different procedures; solution (PMMA/MHT-7-S), melt blending (PMMA/MHT-7-M) and *in situ* polymerization (PMMA/MHT-7-I) methods.

Figure 9. TGA differential curves of neat PS and PS/MHT-7 nanocomposites with different procedures; solution (PS/MHT-7-S), melt blending (PS/MHT-7-M) and *in situ* polymerization (PS/MHT-7-I) methods.

nanocomposites produced by solution blending was slightly higher than that prepared with others.

The TGA differential curves of neat PMMA and PMMA/MHT-7 nanocomposites are shown in Figure 8.

The degradation temperature of the PMMA/MHT-7 nanocomposites was higher than that of neat PMMA. The first step of weight loss for the PMMA/MHT-7-I occurred at about 250 °C due to the evaporation of polymerization medium and the low molecular weight of PMMA. The second step of weight loss took place in the temperature range of 300–450 °C due to the thermal decomposition of PMMA chains. The thermal decomposition rate temperature of PMMA/MHT-7-S was slightly higher than that of neat PMMA.

The TGA differential curves of neat PS and PS/MHT nanocomposites prepared with different procedures were measured, as shown in Figure 9.

Thermal decomposition of neat PS occurred in the range of 350–450 °C. The degradation temperature of the PS/MHT nanocomposites was higher than that of neat PS. The thermal stability of PS/MHT-7-S was higher than that of others and the therm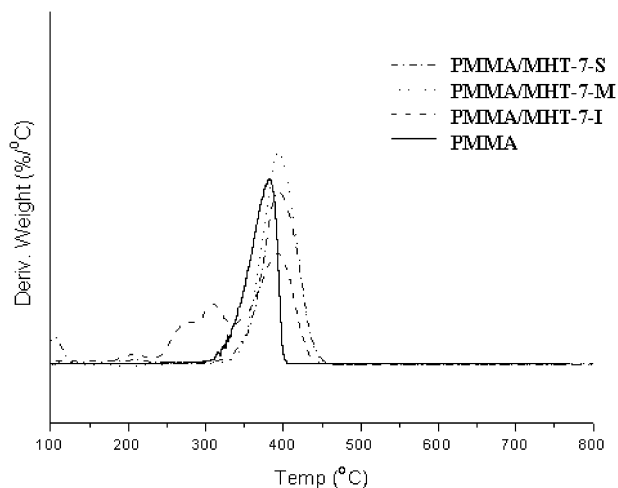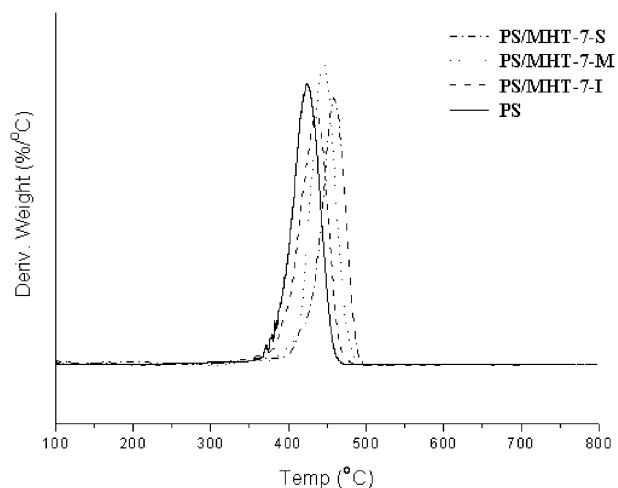al decomposition of PS/MHT-7-S occurred at above 400 °C. The maximum thermal decomposition rate temperature of neat PS and PS/MHT-7-S was determined as 423 and 458 °C, respectively. The thermal decomposition rate temperature of PS/MHT-7-S was 35 °C higher than that of neat PS. Such thermal behavior could be caused by changing the relative extents of partially exfoliated MHT layers in the nanocomposites. This beneficial effect could be understood due to the hindered effect of MHT layers caused by the diffusion of oxygen and volatile products throughout the composite materials.

CONCLUSIONS

The commercial Mg-Al based hydrotalcite (HT) was modified with sodium dodecylsulfate (SDS) for polymer nanocomposites. The SDS content and *d*-spacing in HT layers

increased up to 45% of AEC and 38.0 Å, respectively. Complete anion exchange reaction occurred between CO_3 in HT and SDS. Incorporation of SDS in HT layers at pH 7 was easier than at pH 11, because the concentration of anion (OH^-) in HT layer at pH 11 was higher than that at pH 7.

A partially exfoliated polymethylmethacrylate (PMMA) and intercalated polystyrene (PS)/MHT nanocomposites have been prepared *via* solution, melt blending and *in situ* polymerization in the presence of sodium dodecylsulfate as a modifier. The partially exfoliated PMMA/MHT nanocomposites were obtained even at the 5 wt % MHT loading, and the tensile strength was improved with respect to pristine PMMA. The decomposition temperature of PS/MHT was 35 °C higher than that of neat PS.

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