

SYNTHESIS AND CHARACTERIZATION OF NEW ORGANOPHILIC CLAY. PREPARATION OF POLYSTYRENE/CLAY NANOCOMPOSITE

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Abstract: The aim of this work is the synthesis of new organo-clay using montmorillonite (MMT) and 1-hexadecyl-2-[(5-methyl-isoxazol-3-yl)methylbenzimidazole] cation (**A3H⁺**). The modified montmorillonite was then used for the preparation of polystyrene/clay nanocomposites. Different methods were used for the characterization of the synthesized material.

Keywords: *composites, montmorillonite, materials, organophilic clay, polystyrene*

INTRODUCTION

Organoclay materials obtained by modifying the surface of clay minerals with organic compounds [1 – 3] have different applications in sciences and industries [4, 5]. For example they are used for water treatment, catalysis, as well as in petroleum and paper industries and plastics additives. The incorporation of nanomaterials into polymeric matrix provides significant improvements; such as an increase in mechanical and thermal properties compared with pure polymer [6 – 10].

Since the work done by Yoshiaki Fukushima of the Toyota research team [11 – 13], the use of lamellar clays as reinforcements in polymers has attracted special attention.

The preparation of nanocomposites can be done by three routes, which are solution blending, the molten state, and in situ polymerization [14 – 16].

In this study, 1-hexadecyl-2-[(5-methyl-isoxazol-3-yl)methyl]benzimidazole **A3** was synthesized and used for the intercalation of MMT as shown in Figure 1. Then we report the preparation of polystyrene-Montmorillonite nanocomposite material using melt blending technique (Figure 2). The organoclay was prepared by modification of montmorillonite (MMT) in acid medium using benzimidazole derivative and characterized with IR-FT and XRD. Therefore, we investigate the thermal properties of PS-MMT nanocomposite with TGA.



Figure 1. Intercalation of Montmorillonite

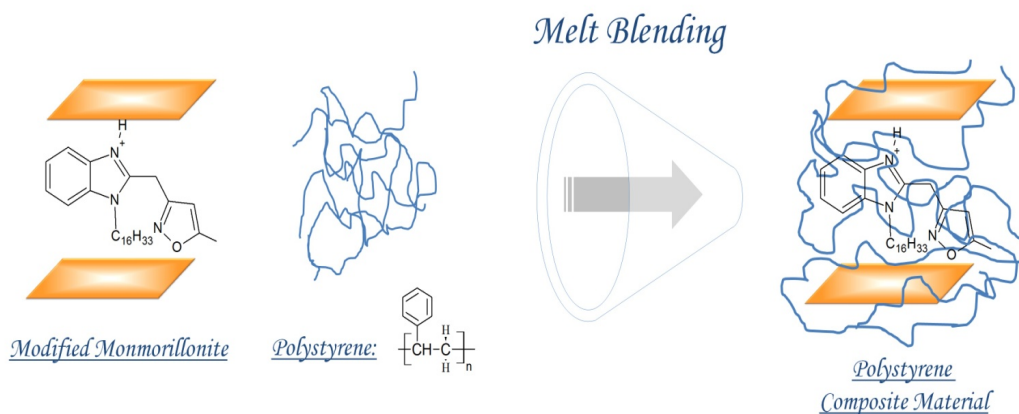


Figure 2. Preparation of polystyrene-montmorillonite nanocomposite

MATERIALS AND METHODS

Materials

Montmorillonite- Na^+ (MMT- Na^+) was purchased from Southern Clay Product Inc (USA) with $\text{CEC} = 0.96 \text{ meq} \cdot \text{g}^{-1}$ and a basal spacing of the air-dried product of spacing $d_{001} = 1.17 \text{ nm}$. Organic products were purchased from Sigma-Aldrich (Germany) and Acros (Belgium).

IR spectra were recorded on an ABB Bomem (Canada) FTLA 2000-102 FTIR instrument (ATR: SPECAC GOLDEN GATE).

NMR spectra were acquired on a Bruker Avance 300 DPX spectrometer (Bruker, Germany).

Powder X-ray diffraction (XRD) patterns were performed using a Bruker D8 Discover diffractometer equipped with $\text{CuK}\alpha$ radiation (Bruker, Germany).

Thermogravimetric analyses (TGA) were performed on a Q500 (TA instrument, Canada).

Preparation of nanocomposite

Synthesis of 2-[(5-methyl-3-isoxazolyl)methyl]-1H-hexadecyl-Benzimidazole (A3)

The reaction between ortho phenylenediamine and dehydroacetic acid (A0) in refluxing xylene for two hours gave the expected 4-acetonylidene-1,5-benzodiazepin-2-one. Then, the action of hydroxylamine in stoichiometric amount or in excess of benzodiazepine, led to benzimidazole derivative (A2). The N-alkylation using 1-bromohexadecane was achieved at room temperature which afforded compound A3 in good yield (73 %). The synthesis is summarized in figure 3 [17 – 20].

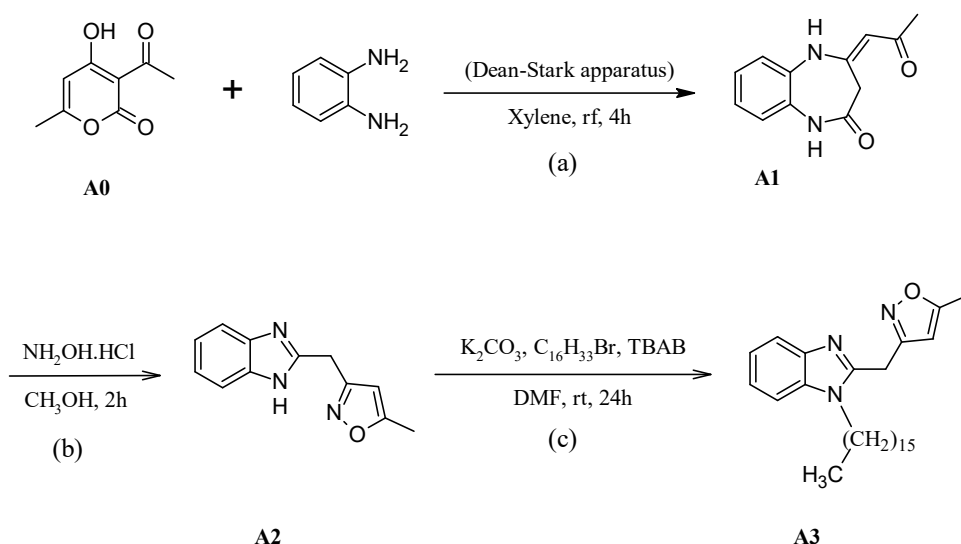


Figure 3. Synthesis of 2-[(5-methyl-3-isoxazolyl)methyl]-1H-hexadecyl-Benzimidazole

Reaction mechanism

The formation of compound A2, can be explained by the attack of hydroxylamine, via the NH_2 group on the sp^2 carbon at the position 4 of the diazepine ring.

The intermediate, thus formed, after the loss of a molecule of water, leads to spiroisoxazoline [C]. The latter undergoes a bond cleavage reaction ring of the C4-N5 bond of the diazepine ring to give the intermediate [D] which, after the loss of a molecule of water, leads to the compound **A2** as shown in Figure 4.

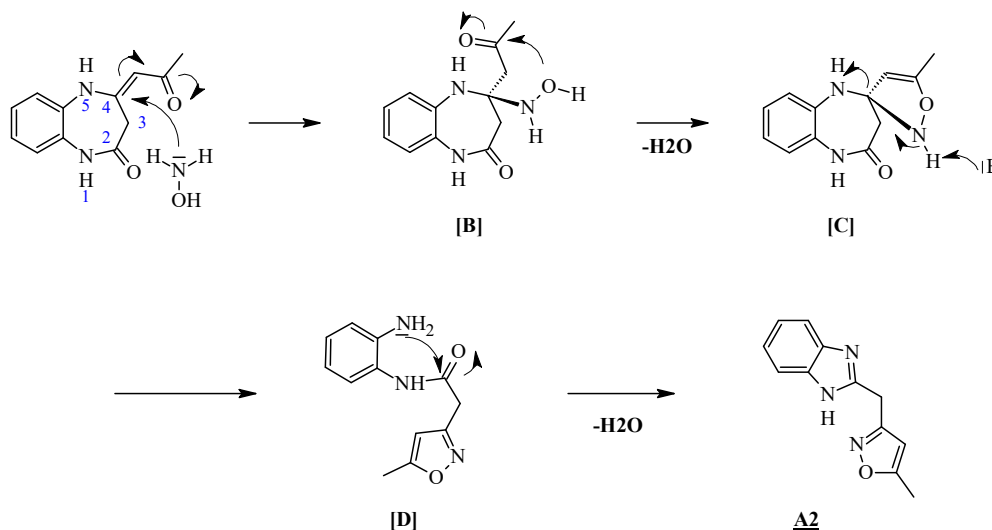


Figure 4. Synthesis Plausible mechanism for the synthesis of **A2**

General procedure for the synthesis of **A3**

- In a 100 mL flask equipped with a Dean and Stark apparatus is introduced 60 mL of xylene, 10 mmol (1.86 g) of dehydroacetic acid and 1.3 g of *o*-phenylenediamine. The mixture is heated at reflux for 4 hours. After cooling, the precipitate was filtered and washed under vacuum with xylene to give **A1** (Rdt: 70 %)
- A mixture of **A1** (2 g, 9.25 mmol) and hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$; 0.65g) in 40 mL of methanol was refluxed for 2 hours. After neutralization with NaHCO_3 , the solid formed was filtered and purified by flash column chromatography on silica gel (cyclohexane/ ethyl acetate: 9/1) to afford **A2**.
- To a solution of **A2** (1.06 g; 5 mmol) in DMF (50 mL) was added K_2CO_3 (1.39 g, 10 mmol), tetrabutylammonium bromide (0.154 g, 0.5 mmol) and hexadecyl bromide (10 mmol). The mixture was stirred at room temperature for 24 h and then it was filtered through celite. The organic phase was extracted three times with ethyl acetate, dried with magnesium sulfate, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (cyclohexane/ ethyl acetate 8 : 2).

Characterization of **A3**

The final product (**A3**) was obtained with 73 % yield. The structure of this compound was unambiguously established by ^1H (Figure 5) and ^{13}C (Figure 6) NMR and IR-TF spectrometry.

NMR DAT :

^1H NMR (300 MHz, DMSO) δ : 0.85 (t, 3H), 1.23-1.48 (m, 28H), 1.75 (m, 2H), 2.59 (s, 3H), 3.35 (s, 2H), 5.87 (s, 1H), 7.04-8.38 (m, 4H).

^{13}C NMR (75 MHz, DMSO) δ : 159.167, 150.085, 149.739, 138.399, 136.817, 122.298, 122.197, 120.335, 119.956, 100.016, 31.679, m (28.640 – 29.804), 22.431, 14.207.

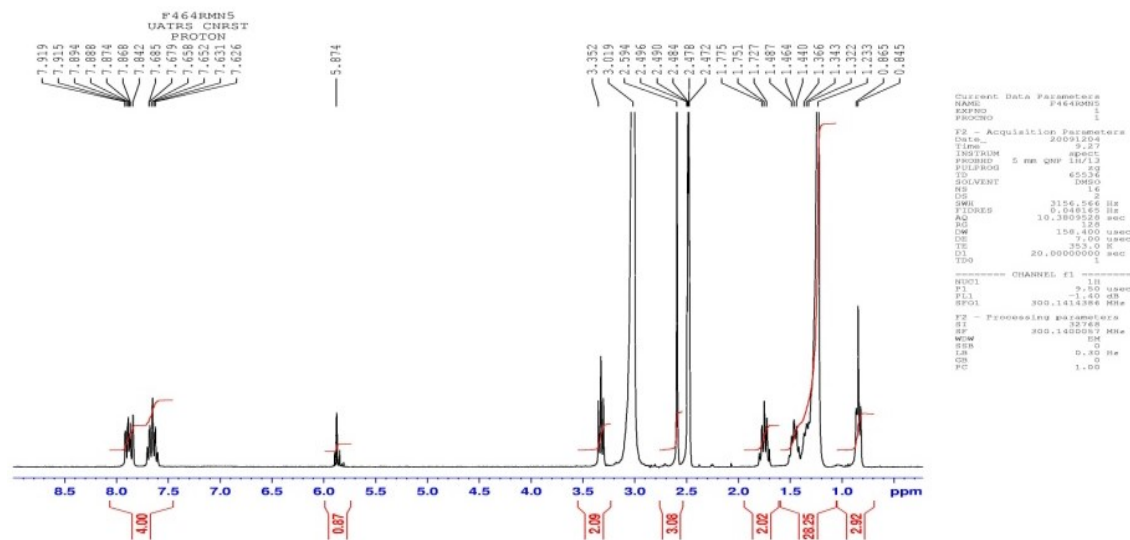


Figure 5. ^1H NMR of A3

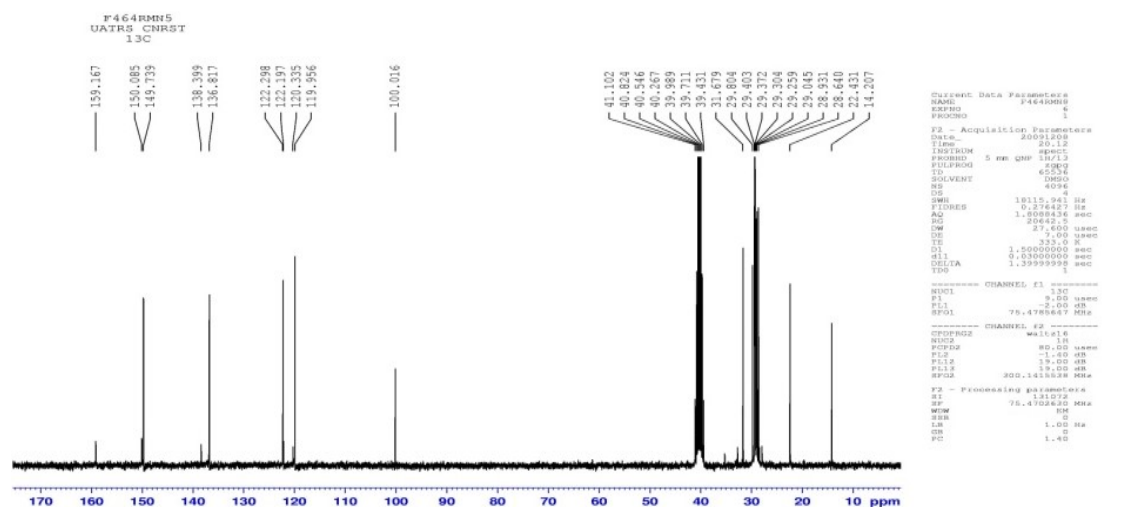


Figure 6. ^{13}C NMR of A3

Preparation of organoclay

Montmorillonite (0.5 g, CEC 110 meq/100 g, Southern Clay) was dispersed in 50 mL of distilled water at 80 °C. Benzimidazole derivative A3 was first protonated by addition of 5 mL of HCl (2N) solution into 0.36 g (8 mmol) of A3, previously dissolved in 50 mL of distilled water under stirring (Figure 7). The solution was then poured into the hot clay/water suspension and stirred vigorously for 2 h at 80 °C. A white solid was isolated by filtration and washed in soxhlet for 2 h with ethanol/water solution [21, 22].

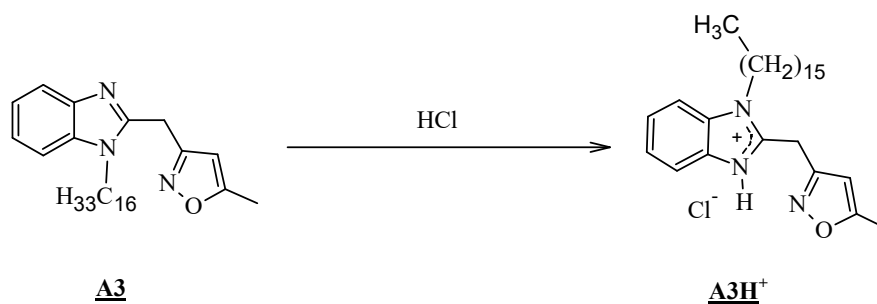


Figure 7. Formation of benzimidazolium salt in acid medium

Preparation of polystyrene-MMT nanocomposite

Nanocomposite of polystyrene/organophilic montmorillonite was prepared by melt blending [23, 24] using a co-rotating twin-screw extruder (Thermo Scientific HAAKE PolyLab). The nanocomposites were prepared from a batch containing maleated polystyrene and 1 wt % of modified montmorillonite clay (MMT-A3H⁺). The preparation was achieved at 200 °C for 14 min (Figure 8).

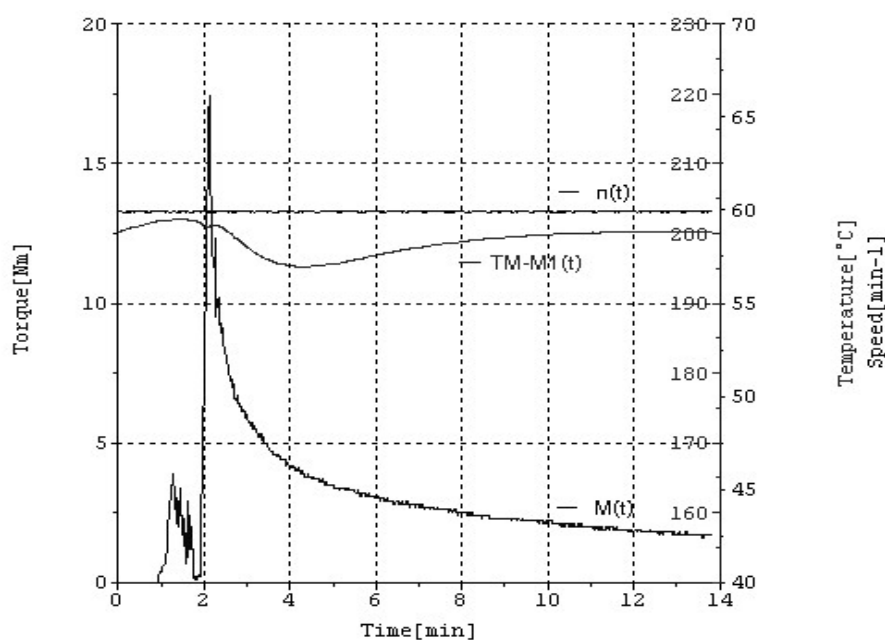


Figure 8. Conditions of the mixture of polystyrene and modified clay

RESULTS AND DISCUSSION

The obtained materials were characterized by different techniques (XRD, FT-IR and TGA). The results have established the intercalation of organic molecules in the interlayer space of montmorillonite clay. The spacing of the clay layers varies depending on the size of the molecule introduced. The d-spacing was enhanced reaching, 17.31 Å.

FT-IR analysis

In the FT-IR spectra of the MMT A3 (Figure 9), the bands in 3628 cm^{-1} is due to OH stretching mode of Si-OH of montmorillonite, at 2853 cm^{-1} and 2928 cm^{-1} are attributed to the asymmetric and symmetric vibration of methylene groups of the aliphatic chain. 1464 cm^{-1} is attributed to the aliphatic C-C bonds of the long chain.

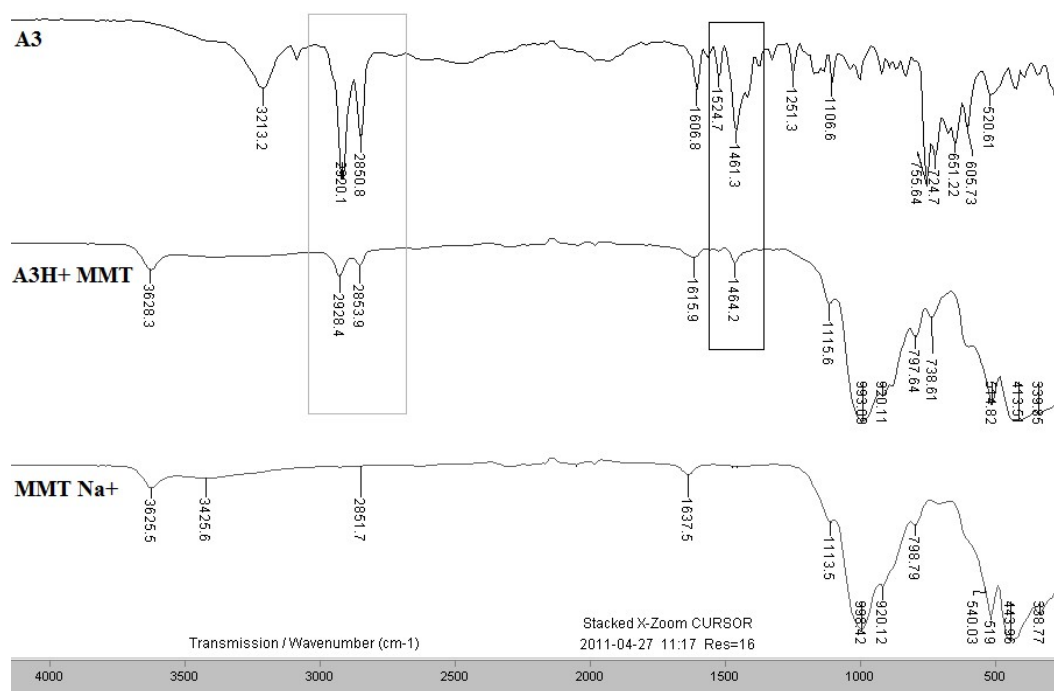


Figure 9. Comparison of FTIR of A3, MMT and modified MMT

X-Ray Diffraction analysis

The basal spacing (d_{001}) from XRD measurement is calculated at peak positions according to Bragg's law: $d = \lambda/2\sin\theta$. Figures 10 and 11 shows the XRD patterns of MMT-NA^+ and MMT-A3H^+ . The interlayer spacing is 11.7 \AA and 17.3 \AA respectively.

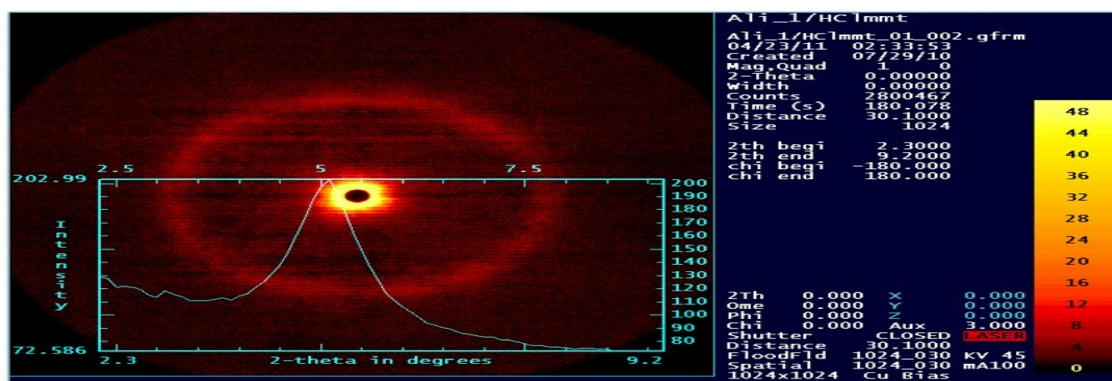


Figure 10. XRD curves of modified MMT

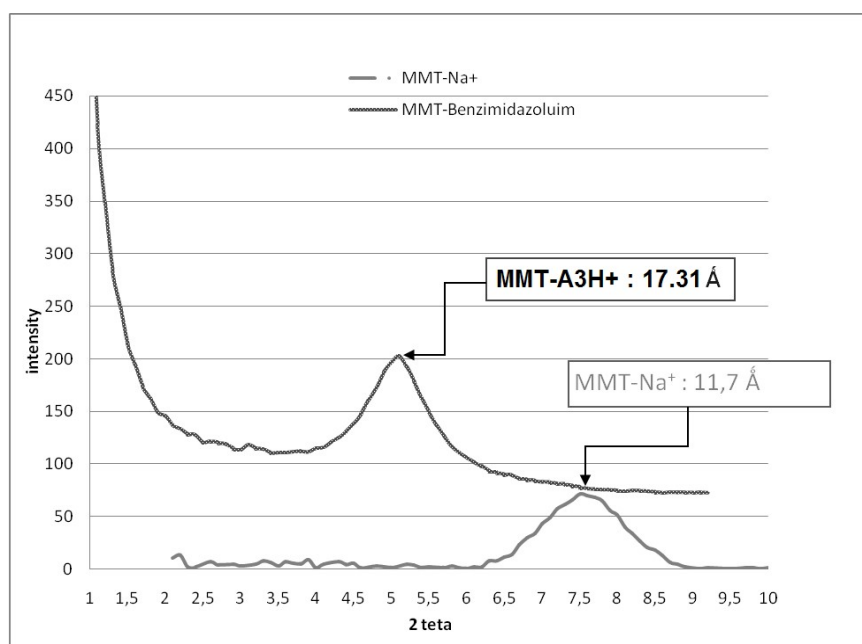


Figure 11. Comparison of the X-ray diffraction (XRD) patterns of MMT-NA⁺ and intercalated montmorillonite

Thermal properties of the composite

As shown in Figure 12. Thermogravimetry analysis showed that the degradation temperatures of the nanocomposites were higher than that of polystyrene. Thus, 95 % of the mass loss of polystyrene was observed at 295 °C. However, for polystyrene-MMT composite, 95 % of the mass losses were observed at 354 °C.

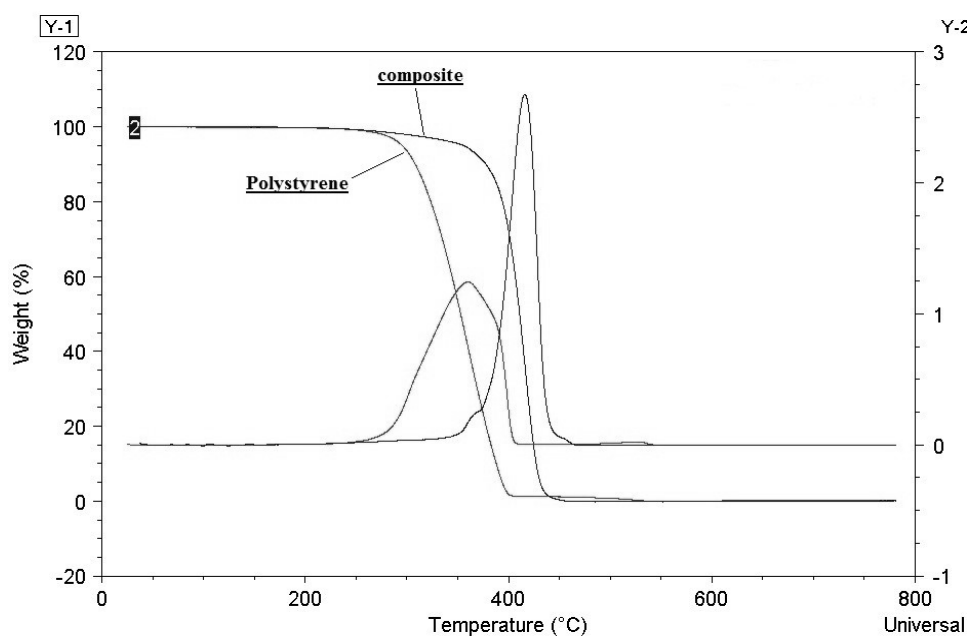


Figure 12. TGA of polystyrene and polystyrene-MMT composite

CONCLUSION

In conclusion, our results reveal that montmorillonite (MMT) suitably modified by benzimidazolium salt can be dispersed into polystyrene (PS) matrix to prepare stable PS-MMT nanocomposite.

The presence of benzimidazolium salt molecules in the interlayer spacings of MMT was confirmed by the occurrence of peaks at around 2928-2853 cm⁻¹ and 1464 cm⁻¹. However the XRD results confirm that the characteristic peak (d001) of MMT-Na⁺ was shifted to lower angles which corresponds to an increase in d001 of about 5.61 Å.

Polystyrene/clay nanocomposite has been prepared by melt blending and the thermogravimetric analysis showed that the degradation temperature of nanocomposite with organo-modified nanoclay increased by 60 °C, compared to neat polystyrene.

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