CHAPTER 6

THERMAL PROPERTIES OF PMMA/MONTMORILLONITE CLAY NANOCOMPOSITE

6.1 Introduction

Knowledge of thermal properties and thermal degradation kinetics of polymer aids in the selection of a candidate for engineering applications such as in computers, heat engines of automobiles, construction materials of buildings, and in the pharmaceutical fields. Wear and tear can be minimized when a suitable polymer is chosen to draw heat away from friction-heated parts and also minimize the thermal degradation of the polymer. Polymer nanocomposites such as Poly (methyl methacrylate)/Montmorillonite (PMMA/MMT) have been found to be useful in enhancing the thermal stability of polymers. In this work the effectiveness of magnetic stirring and ultrasonic mixing is compared in determining the more stable process of synthesizing PMMA/MMT nanocomposite for industrial and medical applications. The principle used in polymer/clay nanocomposites is to separate not only clay aggregates but also individual silicate layers in a polymer. By using this, the excellent properties of the individual clay layers can function effectively, while the number of reinforcing components also increases dramatically because each clay particle contains hundreds or thousands of layers. As a consequence, a wide range of engineering properties can be significantly improved with a low level of filler loading, typically less than 5 weight %. At such a loading level, polymer such as nylon-6 shows an increase in Young's modulus of 103 %, in tensile strength of 459%, and in heat distortion temperature of 146%. Other improved physical properties include fire retardancy [1], barrier resistance [2], and ion conductivity [3].

6.2 Experimental

Polymerization of Methyl methacrylate (MMA) was carried out by keeping the experimental solution in a flat-bottom glass beaker of capacity 500 ml immersed in a Transonic Digital Ultrasonic water bath (Model Elma T490DH,

Germany). The ultrasonic water bath, which is a rectangular metallic tub filled with water to three-fourth of its total capacity gives out ultrasonic waves of fixed frequency 35kHz at a constant power 100 W/cm^2. The MMA (E-Merck, India) solution of strength 0.1M was mixed with a solution of peroxodisulphate (E-Merck, India) of strength 0.02M in a 500 mL glass beaker. MMA of 400 mL volume was mixed with 100 mL of aqueous peroxodisulphate.

Ultrasound was passed for a period of 300 minutes continuously at a constant temperature of 30^{0}C. The passage of ultrasound was stopped at the end of the 300th minute. The reaction vessel was taken out from the ultrasonic bath and 100ml of sulphuric acid (E-Merck, India) of strength 2N was slowly and gently added to the reaction mixture along the inner walls of the glass vessel and the contents were allowed to settle down. After an interval of 24 hours, a thick mass of PMMA was found to be settled at the bottom of the glass beaker. The contents of the beaker were filtered and wet powder of PMMA was obtained. This was air dried under atmospheric conditions and then kept in a hot oven at 50^{0}C for 60 minutes to eliminate water content. Thus fine powder of PMMA was obtained for further studies. MMT (K-10) was used as such without further purification supplied by Aldrich Chemical Company; Inc.

PMMA/MMT nanocomposites were synthesized by two different processes viz., magnetic stirring and ultrasonic mixing maintaining the reaction time constant in both the cases. In the magnetic stirring method PMMA was dissolved in toluene (E-Merck, India) and then MMT was added and the contents were magnetically stirred for a period of 6 hours. After the reaction was completed doubly deionized water was used to precipitate the PMMA/MMT hybrids. In the ultrasonic mixing method PMMA was dissolved in toluene (E-Merck, India) and the MMT was added to it and the contents were mixed ultrasonically using Ultrasonic water bath (Model Elma T490DH) for a period of 6 hours. After the reaction was completed doubly deionized water was used to precipitate the

PMMA/MMT hybrids. Then the products were air dried and characterized using XRD, FTIR and TG and DTA.

XRD was taken for all the samples using the wavelength 1.5418 Å by using CuK_α radiation. The samples were analyzed using NETZSCH-Geratebau Gmbh thermal analyzer for studying their TG and DTA behaviors. FTIR spectra of the samples were recorded using SHIMADZU spectrophotometer. The samples were prepared by dispersing clay sample into KBr and pressing to a pellet. The IR detection range was 4500 cm^{-1} to 450 cm^{-1} with the resolution of 4cm^{-1}.

6.3 Results and Discussion

The XRD results are shown in Figure 6.1 to 6.2b. The distances of silicate layers can be calculated by Bragg's law (n λ=2dsin θ), d = layer distance, λ= 1.5406 Å CuK_α radiation [4]. The measured d_{001}-spacing of MMT was 9.6 Å. After magnetic stirring of PMMA with MMT, the d_{001}-spacing was found to be 3.34 Å. For ultrasonic mixing of PMMA with MMT, the d_{001}–spacing was found to be 3.32 Å. An examination of XRD diffraction pattern confirmed that intercalated structure of clay coexisted in the PMMA-MMT nanocomposite.

FTIR spectra of pure PMMA, and PMMA-MMT nanocomposite for one compositions is shown in Figure 6.3 to 6.3b. The spectra reveal the presence of characteristic absorptions due to both the inorganic filler component with organic ones. It is obviously seen that there were additional absorption peaks in the composites compared to the pure PMMA and pure MMT [5]. It was clearly seen, that absorptions of these peaks increased with the increase of clay loading. The appearance of additional C=O peaks in the PMMA-MMT nanocomposite at 1730cm^{-1} confirms that the experimental nanocomposite might have increased in the bond strength, thus indicating higher stability and strength of PMMA-MMT nanocomposite
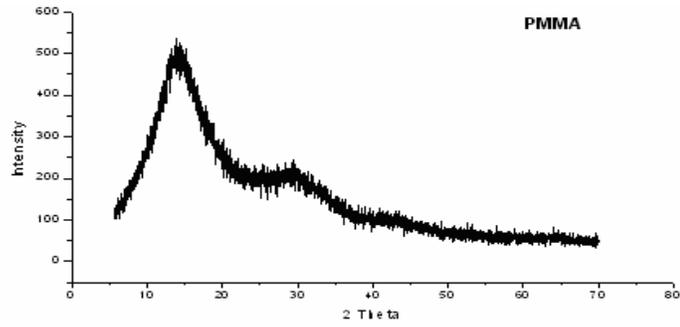
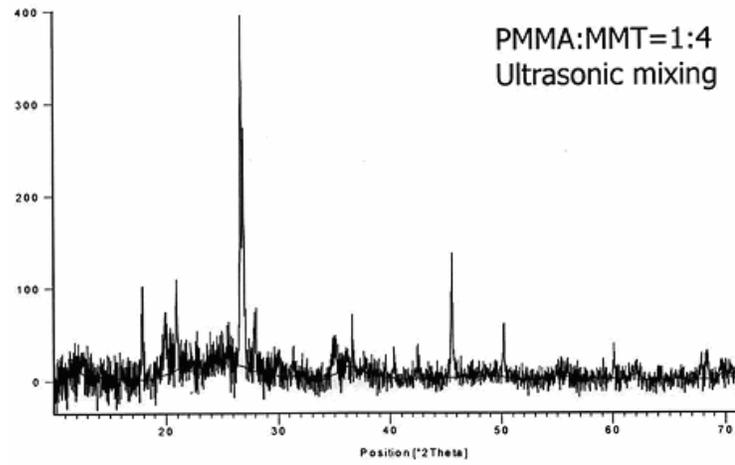**Figure 6.1 XRD Pattern ofsonochemically synthesized PMMA**

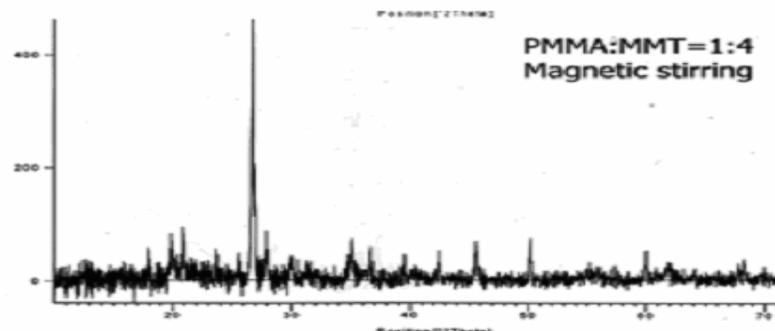**Figure 6.1a XRD Pattern of PMMA:MMT=1:4 for Ultrasonic mixing**

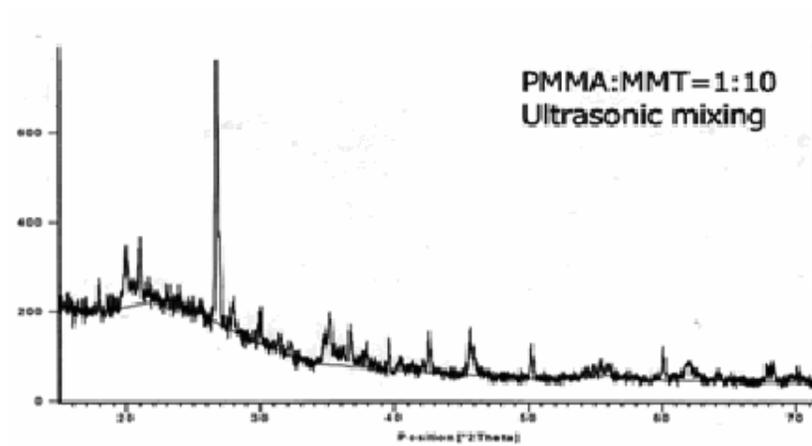**Figure 6.1b XRD Pattern of PMMA:MMT=1:4 for Magnetic stirring**

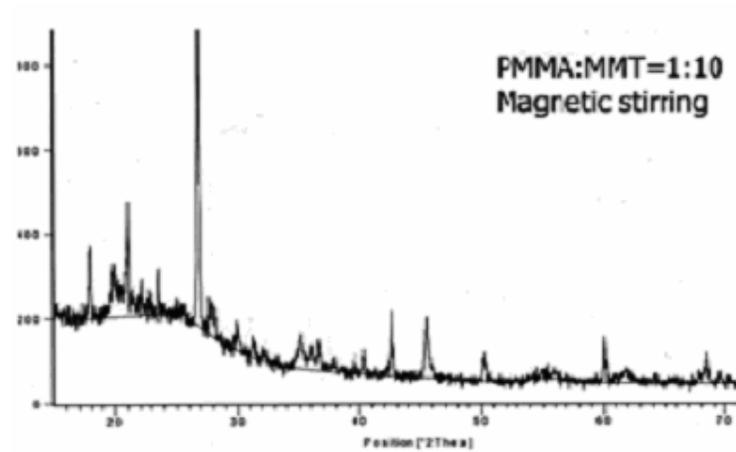**Figure 6.2 XRD Pattern of PMMA:MMT=1:10 for Ultrasonic mixing**

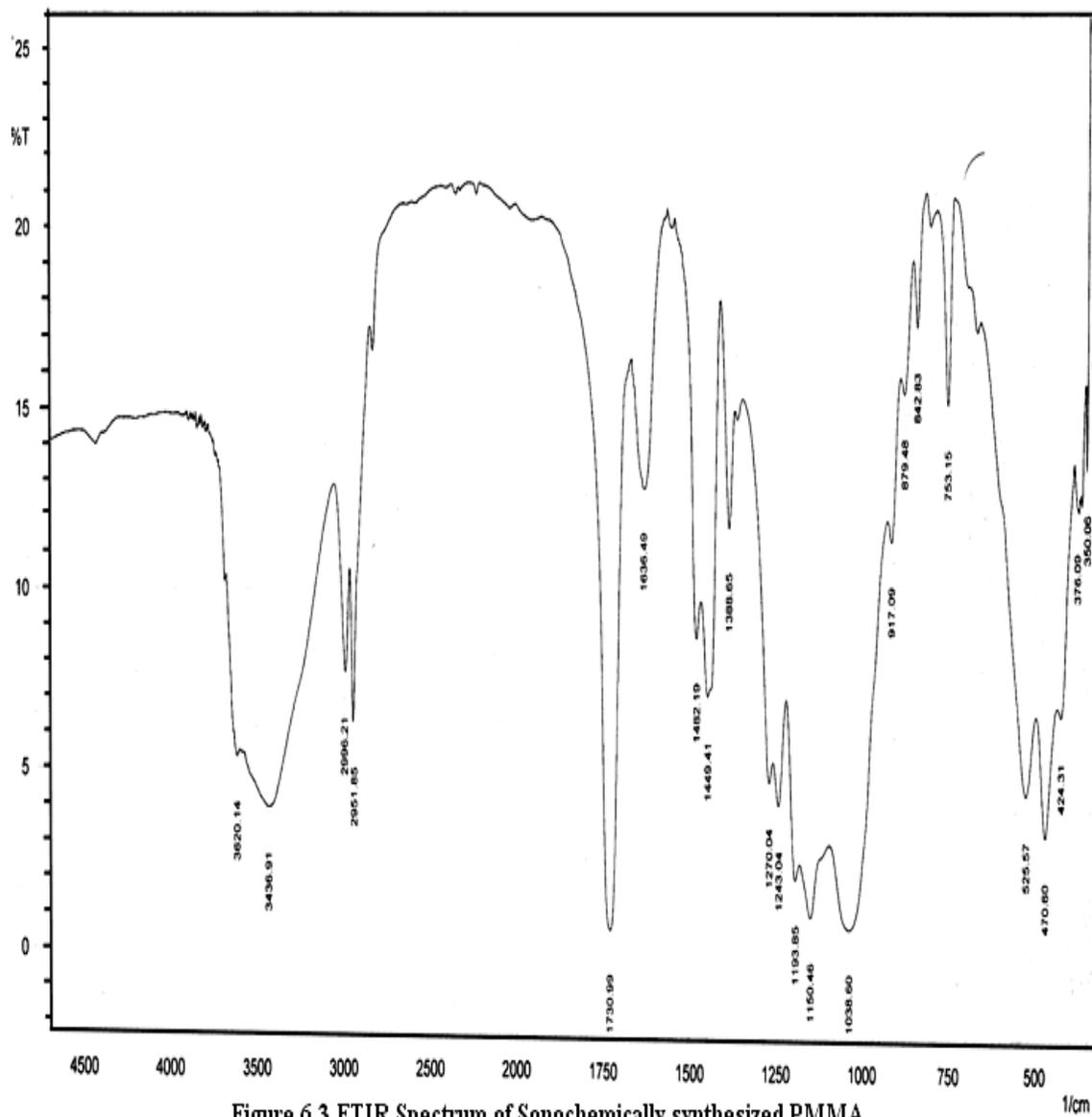**Figure 6.2b XRD pattern of PMMA:MMT=1:10 for Magnetic stirring**

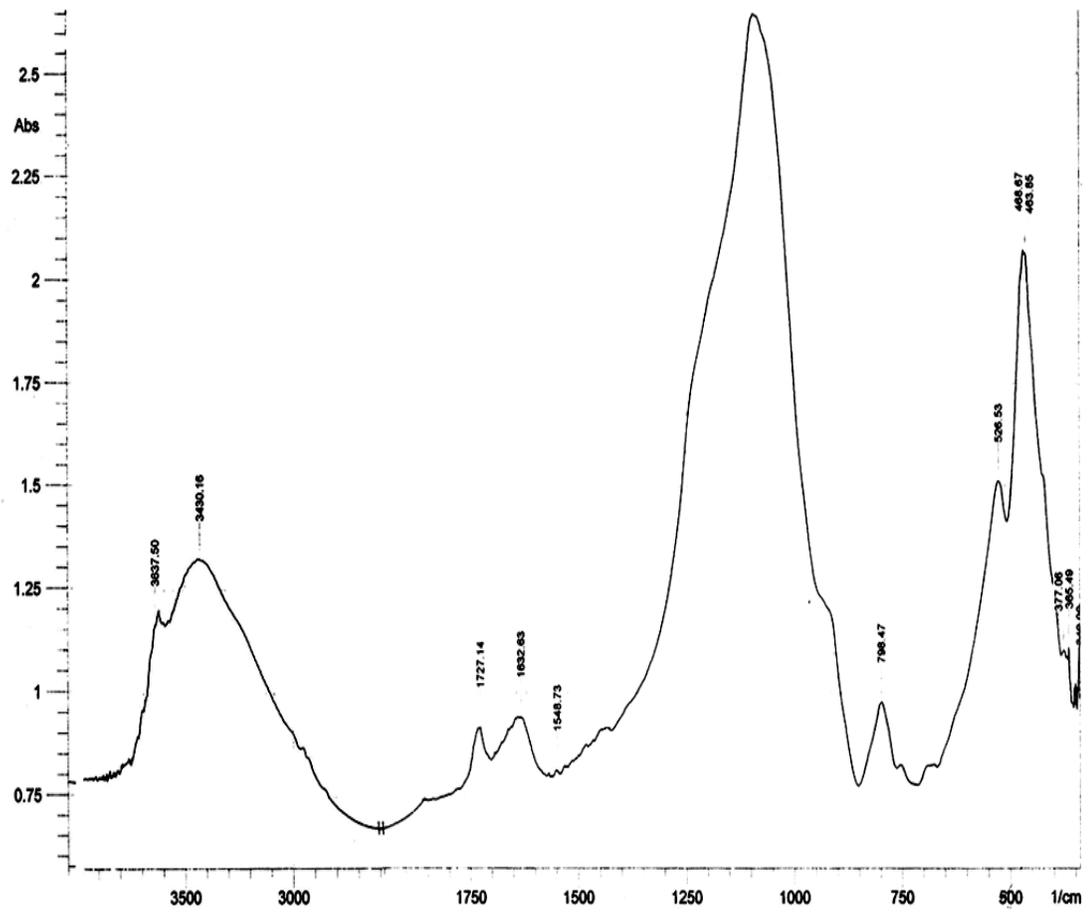Figure 6.3 FTIR Spectrum of Sonochemically synthesized PMMA

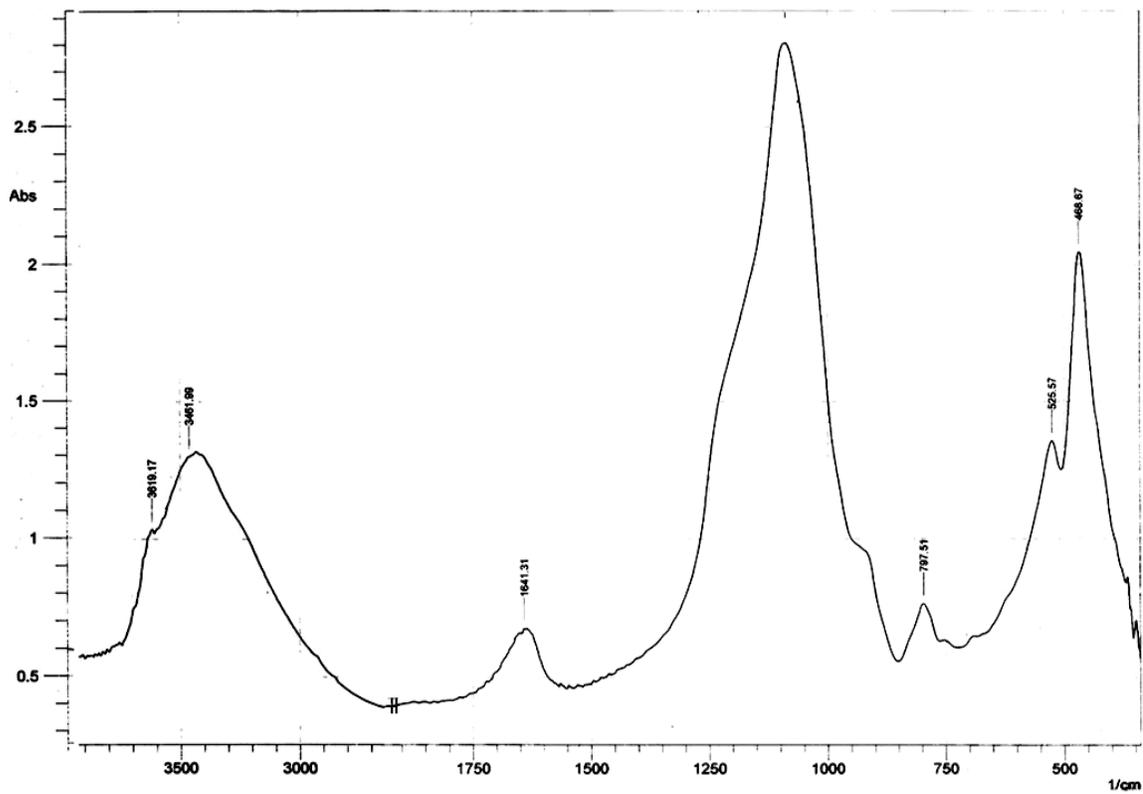**Figure 6.3a:** FTIR Spectrum of PMMA: MMT=1:4 for Ultrasonic Mixing

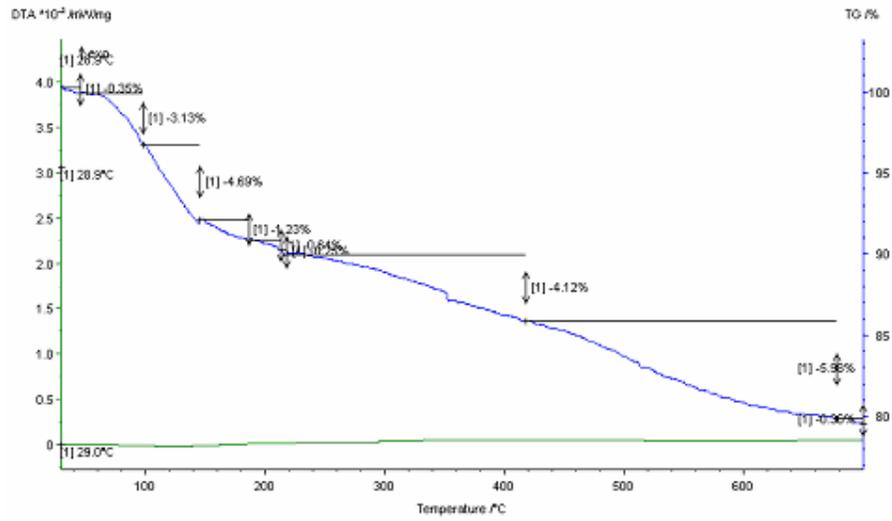**Figure 6.3b:** FTIR Spectrum of PMMA: MMT=1:4 for Magnetic Stirring

Figure 7.4a TG an DTG curve of PMMA:MMT=1:4 for Ultrasonic mixing
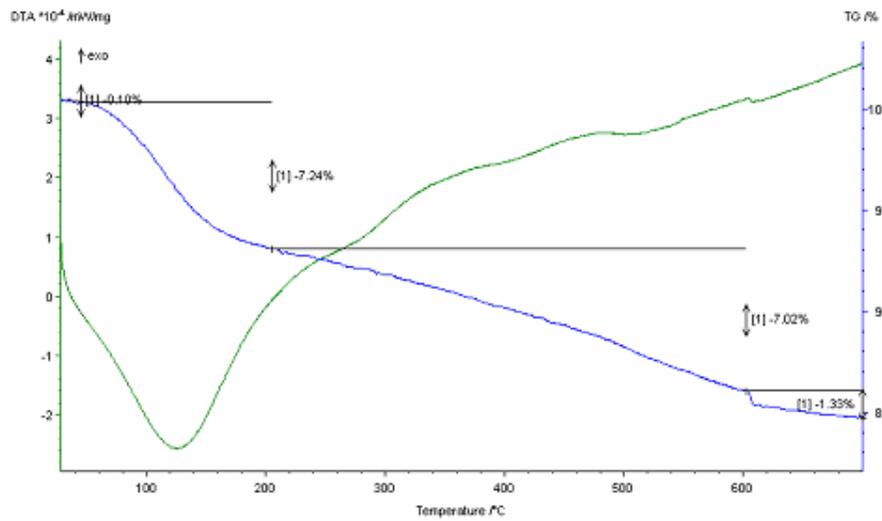

Figure 6.4b Tg an DTG curve of PMMA:MMT=1:4 for Magnetic stirring

The thermogravimetric analysis (TG) is the most powerful tool used to determine the thermal behavior of materials. Figure 6.4a, 6.4b are the overlay of TG and differential thermogravimetric analysis (DTG) curves of PMMA-MMT nanocomposites prepared by magnetic stirring and ultrasonic mixing for extreme minimum loading conditions of the clay. It shows that the thermal stability of the nanocomposite prepared by ultrasonic mixing with low filler composition was increased by a factor of 30% than that of the nanocomposite prepared by magnetic stirring with the same filler composition. The experimental data reveals that both linear and crosslinking PMMA intercalated into MMT layers have a 50-100^{0}C higher decomposition temperatures depending upon the amount of filler [6].

In the TG curve of PMMA-MMT nanocomposite prepared by ultrasonic mixing with low filler (~2 wt%) there was an exothermic peak at a temperature of 476.9^{0}C compared to the exothermic peak at 460^{0}C for the PMMA-MMT nanocomposite prepared by magnetic stirring for the same filler (~2 wt%). This indicated the increase in the melting temperature of the nanocomposite prepared by ultrasonic mixing.

6.4 Conclusion

The structural investigations of the present study confirm that the products are intercalated with PMMA chain molecules oriented parallel to the direction of lamellar layers where separation was consequently more enlarged than in the polymer-free clay. It has been satisfactorily explained the polymer clay nanocomposite prepared by ultrasonic mixing with low filler composition was thermally more stable than that of the nanocomposite prepared by magnetic stirring for the same filler composition. When the clay fills the PMMA matrix, glass transition temperature of MMT filled PMMA shows an increase compared to pure PMMA.

References

[1.] J.W. Gilman, *Appl. Clay Sci*, **15(1-2)**, 31 (1999)

[2.] G. Gorrasi, *Polymer*, **44(8)**, 2271 (2003)

[3.] R. A. Vaia, *Adv. Mater.*, **7**, 154 (1995)

[4.] Duangporn Saramas, David C. Martin and Rathanawan Magaraphan, *Rev. Adv. Mater. Sci*, **5**, 199 (2003)

[5.] Jyh Ming Hwu, George J. Jiang, Wei Xie, Wei Ping Pan, *J. App. Poly. Sci.,* **83**, 1702 (2002)

[6.] A. Blumstein, *J. Polym. Sci. A*, **3**, 2665, (1965).