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Effect of Chemical Foaming Agent in Enhancing Dispersion of Montmorillonite in Polypropylene Nanocomposite

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Abstract: Homogenous dispersion of the nano particles in the polymer matrix is a key factor in order to achieve enhanced properties of the polymer nanocomposites. Dispersion or exfoliation of nano clay is difficult in the matrix during melt mixing. In this study, dispersion of nano montmorillonite (MMT) in polypropylene (PP) was done by using chemical foaming agent during melt mixing process. Chemical foaming agent (CFA) added (1 %wt.) PP/MMT nanocomposites were prepared on twin screw extruder. Then, injection molding was done to the granulated nanocomposites in order to obtain tensile test samples. Thermal test and morphological investigations were done. Tensile test was applied to observe the difference in mechanical strength of the nanocomposites depending on the presence of the foaming agent during melt mixing process. The results have shown that, dispersion of MMT enhanced in the matrix due to addition of chemical foaming agent. This brought improved tensile strength about 19% for the PP/MMT nanocomposites within same concentrations of nano filler.

Keywords: Nano montmorillonite, polypropylene, melt mixing, dispersion, mechanical strength.

1. INTRODUCTION

Polymer nano clay composites have wide application area in different fields such as aerospace, automobile, construction, petroleum, biomedical and wastewater treatment. These composites are promising materials due to their superior properties, such as enhanced density and strength, flame retardancy, mechanical, thermal, optoelectronic and magnetic properties [1-5]. However, it has been know that providing homogenous dispersion of the nano clays in the matrix is the main challenge to overcome. It is difficult or almost impossible to fully disperse nano clays in the matrix during melt mixing process. There have been several studies about enhancing the distribution of the nano clay in the polymer matrix by usage of compatibilizers and dispersants [6-10]. Furthermore, it should be noted that the dispersion ability of the nano clay can change according to the polarity, non-polarity of the polymer. Polypropylene, has wide application area in industrial applications, is one of the most difficult matrix materials for dispersing the nano clays. The researchers have focused on the dispersion and exfoliation of nano clay particles in PP matrix by different ways. Lopez-Quintanilla *et al*. [11] investigated the effects of different compatibilizer as glycidyl methacrylate (GMA), acrylic acid (AA) and maleic anhydride (MA), with different types of nanoclays. PP-g-GMA and PP-g-MA gave higher results in mechanical strength of the nanocomposites than the others. Garcia-Lopez *et al*. [9] investigated the effect of two different nanoclays and two different compatibilizer such as diethyl maleate and maleic anhydride on the mechanical and morphological properties of PP / MMT nanocomposites. Tjong *et al*. [12] prepared polypropylene / organic modified MMT nanocomposites with maleic anhydride modified styrene-ethylene-butylene-styrene (SEBS-g-MA) by melt mixing processing method.

It has been seen that researchers have used various compatibilizers and dispersants in order to achieve homogeneous distribution and exfoliation of the nano clay in the polymer matrix. Usage of physical foaming agent has been experienced in the production of polymer clay nanocomposites and in this study, chemical foaming agent was used in melt mixing process as a dispersant in order to enhance the distribution of the montmorillonite and to improve the mechanical properties of the PP/MMT nanocomposites.

2. EXPERIMENTAL STUDY

2.1. Materials and Method

Polypropylene (56M10-Sabic) was with melt flow index value of 6 g/10 min and 0,90 g/cm^3. Organo silane modified montmorillonite in size of ~ avg. 30µm was purchased from Sigma Aldrich to be dispersed into nano scale by melt mixing process. The foaming agent was an endothermic chemical foaming agent (CFA) was supplied from Clariant with a trade name of Hydrocerol.

Melt mixing of the PP and MMT was done on a laboratory-type twin screw extruder (Rondol, England, L/D:10) within foaming agent concentration of 1% in

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Table 1: Melt Mixing Concentrations of PP/MMT Nanocomposites

Material	PP (%wt.)	MMT (%wt.)	CFA (%wt.)
Neat PP	100	0	0
PP-1MMT	99	1	0
PP-1MMT-CFA	99	1	1
PP-3MMT	97	3	0
PP-3MMT-CFA	97	3	1
PP-5MMT	95	5	0
PP-5MMT-CFA	95	5	1

order to disperse the MMT particles in the matrix from micro level to nano level. The concentrations of MMT was 1%; 3%; 5% (wt). Melt mixing process without chemical foaming agent was also applied as given in Table **1** in order to observe the effect of foaming agent on dispersion effectively. The operation temperature on the extruder was set from 90 to 200 °C and the screw speed was constant as 120 rpm. The extrudate filaments were pelletized for plastic injection molding. All materials were dried about 8 hours before extrusion for decreasing the moisture level to prevent thermal degradation. A 40-ton injection molding machine was used to obtain tensile test samples. The nozzle temperature was set to 220 °C, the injection pressure was constant as 90 bar, the holding pressure was set to 60 bar and mold temperature was 20 °C.

2.2. Differential Scanning Calorimetry (DSC)

Thermal behavior of the PP/MMT composites were determined by differential scanning calorimetry (DSC8000, Perkin Elmer Diamond) under nitrogen flow at a rate of 10 °C/min from 40 to 200 °C. Two cycles were applied in order to remove the thermal history of the nanocomposites were cooled down to 20°C at a rate of 10 °C/min.

2.3. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was employed with a Perkin Elmer Spectrum 100 FTIR Spectrometer to detect the interactions between HNT and PLA. A minimum of 14 scans were signal-averaged with a resolution of 4 cm^{-1} in the wavenumber range of 650 to 4000 cm^{-1} based on an attenuated total reflectance (ATR) technique.

2.4. Scanning Electron Microscopy (SEM)

The morphologies of the fracture surfaces of the samples were investigated by scanning electron microscope (SEM) (Philips-FEI XL30 ESEM) at an acceleration voltage of 5 kV. SEM observations were performed after sputtering the samples with a thin film of gold.

2.5. Mechanical Test

Tensile test was performed by a universal testing machine (INSTRON- 5982) with 25 mm/min of test speed at room temperature according to the standard test method (ISO 527).

3. RESULTS AND DISCUSSION

3.1. FTIR

The FTIR spectra of PP, MMT and PP/MMT composites are given in Figure **1**. Among the spectra, PP shows its character by the peaks of asymmetric -CH_3 at 2970 cm^{-1}, symmetric -CH_3 at 2910 cm^{-1}, asymmetric -CH_2 at 2870 cm^{-1}, -CH_2- at 2840 cm^{-1}, -CH_2- at 1460 cm^{-1}, and -CH_3 at 1370 cm^{-1}. The organosilane modified MMT shows peaks of Si-O at 1113 cm^{-1} and at 1000 cm^{-1}, Si-O-Si peaks at 1032 and 470 cm^{-1}. As expected, the presence of CFA has not been observed in FTIR analysis due to its conversion of gas during melt mixing process. Additionally, the FTIR spectra of neat PP and PP-MMT has not shown apparent difference due to the low concentration of MMT.

3.2. DSC

The thermal behavior of PP/MMT composites are reported in Figure **2**. Cold crystallization temperature (Tcc), enthalpy of cold crystallization (ΔHcc), melting temperature (Tm), and melting enthalpy (ΔHm) and degree of crystallinity (Xc) are summarized in Table **1**. It has been seen that cold crystallization temperature increased due to the late crystallization of PP/MMT composites. The presence of MMT in the matrix

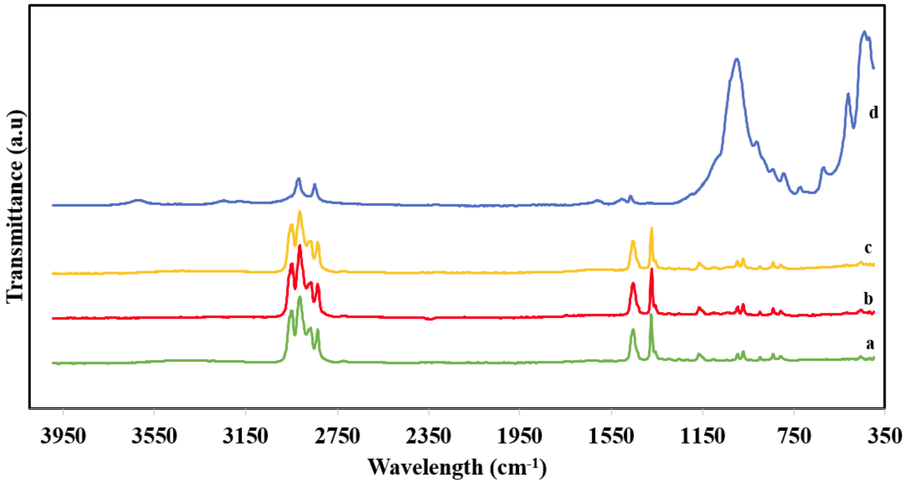


Figure 1: The FTIR spectrum of a) Neat PP, b) PP-1MMT, c) PP-1MMT-CFA, d) MMT.

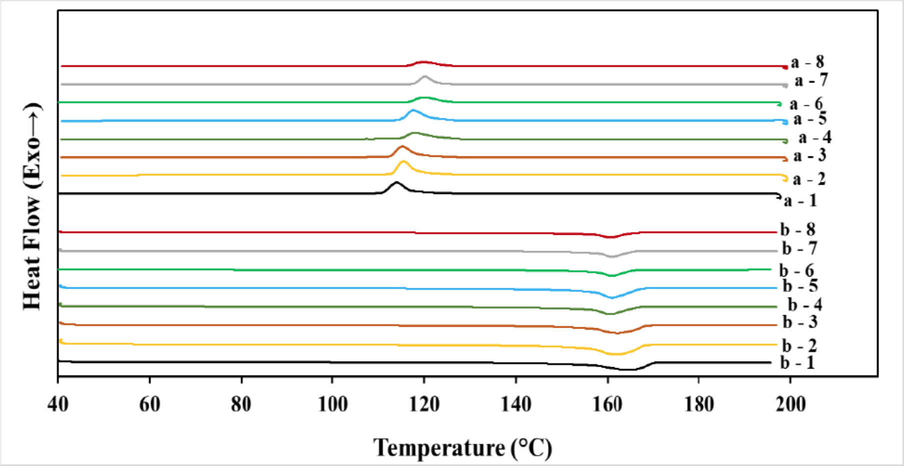


Figure 2: DSC thermograms of a) cooling b) heating (1) Neat PP; (2) Neat PP-1CFA; (3) PP-1MMT; (4) PP-1MMT-1CFA; (5) PP-3MMT; (6) PP-3MMT-1CFA; (7) PP-5MMT; (8) PP-5MMT-1CFA.

hindered the molecular mobility of the chains and this decreased the degree of crystallization of PP/MMT composites when the results were compared with that of neat PP. However, under the same concentrations of MMT, PP-1MMT and PP-1MMT-CFA, degree of crystallization increased from 43% to 45%. The similar trend was observed for PP-3MMT and PP-3MMT-CFA; for PP-5MMT and PP-5MMT-CFA. The presence of CFA during melt mixing process enhanced the dispersion of the MMT particles, consequently, fine dispersed nano particles behaved as nucleating agent.

3.3. Morphology

The fracture surfaces of PP/MMT nanocomposites are given in Figure **3-5**. Figures **3a**, **4a**, **5a** show the morphology the polymer nanocomposites obtained without usage of foaming agent. It could be clearly observed that the absence of foaming agent during melt mixing process resulted in agglomerations, almost bigger than 2 μm as shown in red circles. On the other hand, the presence of foaming agent enhanced the distribution of the MMT particles seriously in 1% MMT and 3%MMT (Figures **3b-4b**) and it was seen that MMT particles could be dispersed to nano size level. The CFA in the melt extrusion decomposes with increasing temperature and the gases formed form gas cells within the matrix, which form a biaxial stretch around the cell walls. The biaxial stress generated during cell growth by the interface binding between the polymer and the nanoparticles is transferred from the polymer matrix to the nanoparticles. This transferred stress contributes to the shear stress generated by the extrusion, resulting in a more efficient force for dispersing the nanoparticles into the agglomerate. Thus, the presence of the foaming agent in the polymer matrix increased the dispersion of the nanoparticles

Table 2: DSC Results of PP/MMT Nanocomposites

Material	T_{cc} (^{0}C)	ΔH_{cc} (J/g)	Crystallinity (%)	T_m (^{0}C)
Neat PP	114.0	96.7	46,3	164.0
PP - 1 MMT	115.2	89.3	43,2	162.3
PP - 1 MMT – CFA	118.1	93.6	45,7	160.6
PP - 3 MMT	117.6	82.0	40,4	160.9
PP - 3 MMT - CFA	120.0	89.3	44,5	160.8
PP - 5 MMT	120.0	73.0	36,7	160.9
PP - 5 MMT – CFA	120.1	81.8	41,6	160.5

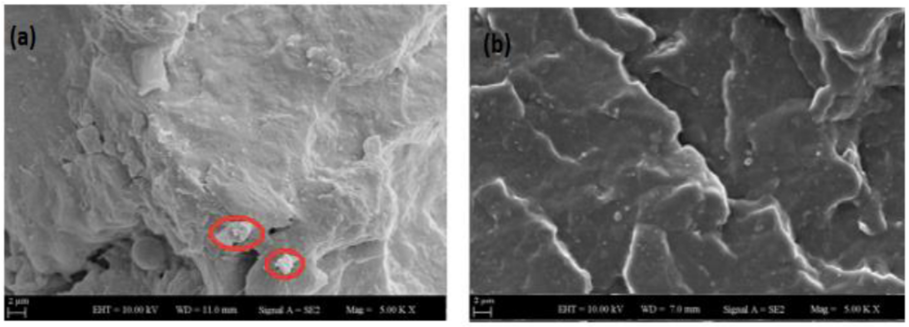


Figure 3: SEM images of fracture surfaces of (**a**) PP-1MMT, (**b**) PP-1MMT CFA.

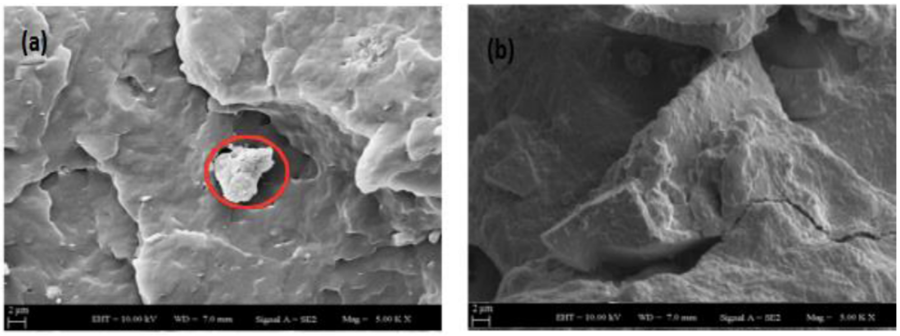


Figure 4: SEM images of fracture surfaces of (**a**) PP-3MMT, (**b**) PP-3MMT-CFA.

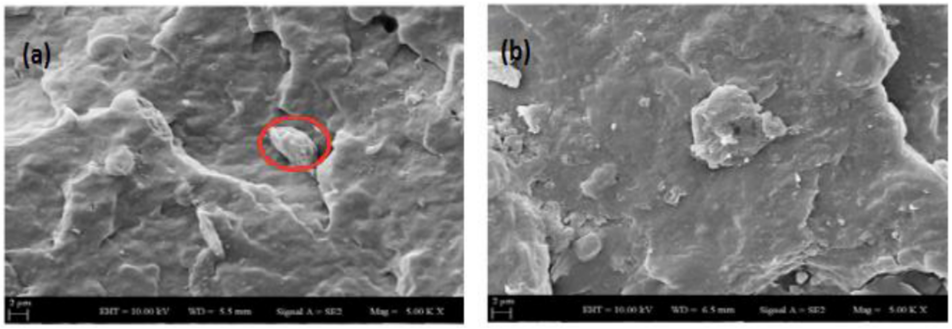
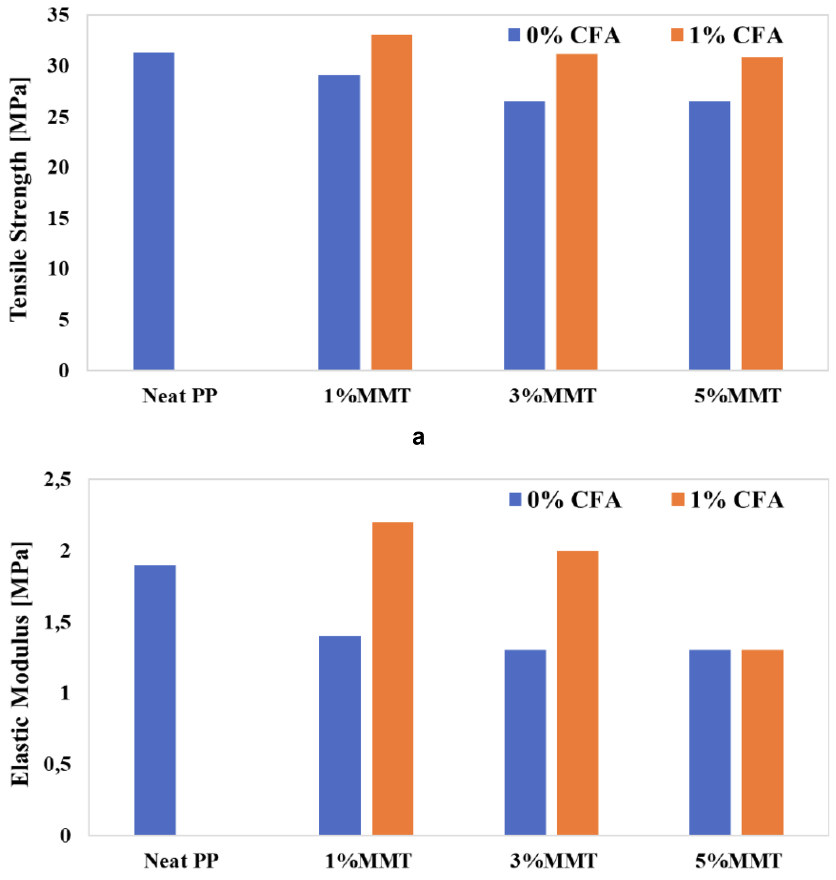


Figure 5: SEM images of fracture surfaces of (**a**) PP-5MMT, (**b**) PP-5MMT-CFA.

[13-14]. However, when the nano filler concentration was higher than 3%, several agglomeration have been observed (Figures **5a-b**).

3.4. Tensile Properties

The tensile test results of the prepared composites are given in Figure **6** and Table **3**. It has been seen that



a

b

Figure 6: Comparison of **a**) tensile strength, **b**) elastic modulus of PP/MMT nanocomposites with CFA and without CFA.

Table 3: Tensile Properties of PP/ MMT Nanocomposites

	Tensile Strength (MPa)	Yield Strength (MPa)	Elastic Modulus (MPa)
Neat PP	31,3	22,1	1,9
PP – 1MMT	29,1	18,3	1,4
PP – 1MMT – CFA	33,1	20,5	2,2
PP – 3MMT	26,5	16,3	1,3
PP – 3MMT – CFA	31,2	18,6	2,0
PP – 5MMT	26,5	16,3	1,3
PP – 5MMT – CFA	30,9	18,2	1,9

during the melt extrusion, the increase in MMT concentration resulted in lower tensile strength and elastic modulus when the foaming agent was not added. This result can be explained by the inadequate dispersion of MMT particles in the absence of foaming agent which would behave as a dispersant. Consequently, the relatively higher MMT concentrations caused agglomeration in the PP matrix and leaded to apparent reductions in mechanical strength (Figure **6**). In order to enhance the mechanical strength of the composites, it is very important to increase the interface area by dispersing the nanoparticles. In this regard, dispersion of the nano particles has been improved by the usage of foaming agent during melt mixing. As a result, for polypropylene composites within the same concentrations of MMT, improved mechanical strength values were obtained as follows: tensile strength was increased from 29 MPa (without CFA) to 33 MPa (with CFA) for 1% of MMT addition; and from 26 MPa (without CFA) to 31 MPa (with CFA) for 3% of MMT addition. Similar trend was observed for 5% concentration as given in Table **3**.

4. CONCLUSION

This study includes an alternative method for dispersion of nano montmorillonite in polypropylene matrix. In this regard, chemical foaming agent was used during melt mixing process. The results have shown that usage of CFA during melt mixing process enhanced the distribution of MMT. Consequently, nano composites prepared by the addition of CFA within 1% and 3% concentrations of MMT, gave 16- 19% of increment in tensile strength and apparent improvement in elastic modulus when the results were compared with that of absence of CFA. However, over 3% of MMT, the presence of CFA was not effective enough for distribution of the MMT. Consequently, possible agglomerations have been observed but still the size of the agglomerates were smaller. Finally, it could be concluded that in production of polymer nano clay nanocomposites by melt mixing process, usage of chemical foaming agent could be an alternative and promising method in low concentrations of nano filler. For future works, different types and amounts of chemical foaming agents could be experienced to enhance the dispersion of the nano fillers.

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