

Thermal Analysis and Morphological Characterization of Thermoplastic Composites Filled with Almond Shell Flour/Montmorillonite

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The main objective of this research was to study the potential uses of almond shell flour (ASF) in the production of thermoplastic composites containing montmorillonite (MMT). Thirty, 35, and 40 wt% ASF was used, and 2.0 wt% maleic anhydride-grafted polypropylene was used as the compatibilizer. Two levels of MMT nanoclay, 2.5 and 5.0 wt%, were mixed with polypropylene (PP). The effects of MMT on the thermal properties of the blended composites were evaluated using thermogravimetric analysis (TGA), morphological characterization, scanning electron microscopy (SEM), and X-ray diffraction (XRD). The XRD data showed that the relative intercalation of the composites with 2.5 wt% MMT was higher than that of the 5.0 wt% nanoclay composites. The TGA results indicated that by increasing the MMT percentage, the degradation temperature and the thermal stability were enhanced. The MMT exhibited better dispersion in the clay layers of the polymer-matrix composites when increased from 2.5 to 5.0 wt%, and at the 5.0 wt% MMT loading, the size of MMT became larger. The total weight loss of the ASF/PP/MMT composite decreased as the filler content increased, and the thermal stability increased as the MMT content increased.

Keywords: Almond shell flour; Montmorillonite; Thermogravimetric analysis; X-ray diffraction; Scanning electron microscopy

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INTRODUCTION

Natural fibers are suitable for reinforcing plastics because of their relatively high strength, stiffness, and low density (Faruk *et al.* 2012). Lignocellulosic materials have been used as fillers in the thermoplastic industry for the replacement of conventional synthetic fibers, such as aramid and glass, because of their low density, good thermal insulation and mechanical properties, reduced tool wear, unlimited availability, low price, and problem-free disposal (Bledzki and Gassan 1999; Mishra *et al.* 2001; Belgacem and Gandini 2008; Ghasemi and Farsi 2010; Ayrilmis *et al.* 2013; Lashgari *et al.* 2013; Salmah *et al.* 2013a).

Most applications expose the materials to a wide range of temperatures, which may influence the thermal behavior. Thermal degradation of wood plastic composites (WPCs) is a crucial aspect of the application and manufacturing process of WPC products (Tabari *et al.* 2012).

Thermal analysis by thermogravimetric analysis (TGA) is common and has been particularly adapted for the study of mass variation (Bourgois *et al.* 1989; Popescu 1996; Weiland *et al.* 1998; Guo 2004). Furthermore, the measurements in TGA can be performed during rising temperature, at a static rate (isotherm) or under a temperature program. In addition, differential scanning calorimetry (DSC) and TGA have been used to characterize the thermo-chemical properties of wood-plastic nanocomposites (Tabari *et al.* 2012).

Among the inorganic layered materials, layered silicates are often included in hybrids because of their ability to intercalate and exfoliate at the nanoscale level in the thermoplastic matrix. In particular, the smectite group of clay minerals, *i.e.*, montmorillonite (MMT), has been predominantly used because of its excellent intercalation ability (Kojima 1993; Giannelis *et al.* 1999; Liu *et al.* 2003; Lee *et al.* 2005ab; Chow 2007). Nanoclay with its extremely high surface-to-volume ratio (700 to 800 m²/g) has significantly improved a variety of polymers at very low filler contents (less than 5.0 wt%), far less than those using traditional micron-scaled fillers (at greater than or equal to 20 wt%) (Khanjanzadeh *et al.* 2012). The thermal stability and flame retardancy of the thermoplastics are improved because of the formation of nanocomposites (Zabihzadeh 2005; Sahraeian *et al.* 2012).

The crystallization temperature (T_c), enthalpy (ΔH_m), and the degree of crystallinity (X_c) of nanocomposites increase with the addition of nanoclay, which indicates that an increasing nanoclay percentage enhances the degradation temperature and thermal stability (Tabari *et al.* 2012). Zahedi *et al.* (2013) reported that walnut shell/polypropylene (PP) composites at the 3.0 wt% organo-clay content had acceptable and comparable properties to wood flour composites. In addition, the organo-clay improved the interaction by better dispersion of the silicate layers in the polymer-matrix composite.

Almond (*Prunus amygdalus* L.) shell, an agricultural residue, is the lignocellulosic material forming the thick endocarp or husk of the almond tree fruit; processing the fruit obtains the edible seeds. Since the almond shell has no important industrial value, it is normally incinerated or dumped. It is a waste material in western Iran, generated during nut processing and usually burnt (Lashgari *et al.* 2013). Previous studies (Pirayesh and Khazaeian 2012; Lashgari *et al.* 2013; García *et al.* 2014) reported that almond shell flour (ASF) could play an important role in the manufacture of filled thermoplastic composites and wood-based panels, thereby reducing the demand for wood material. For example, García *et al.* (2014) reported a decrease in thermal stability and an increase in oxygen and water vapor barrier properties of the poly(ϵ -caprolactone)-based composites with ASF from 10 wt%, 20 wt%, and 30 wt% in comparison with the composites without ASF. In another study, Lashgari *et al.* (2013) investigated the effect of MMT (0, 2.5, and 5 wt%) and ASF (30, 35, and 40 wt%) on the flexural and tensile properties, and impact strength of injection-molded PP composites. They reported that the tensile and flexural modulus of PP composites containing 5 phr nanoclay increased marginally as compared with composites made up of 2.5 phr nanoclay. However, in their study, the tensile and flexural strength of the composites produced with the nanoclay and ASF decreased by about 37.7% and 25.8%, respectively, with the addition of 2.5 phr nanoclay. Furthermore, the impact strength of the composites significantly decreased with both incorporated fillers. Pirayesh and Khazaeian (2012) reported that the amount of almond shell particles in the production of particleboard should be approximately 30 wt% to meet the standards required for the mechanical properties of particleboard.

Although the physical and mechanical properties of the thermoplastic composites filled with the ASF and montmorillonite were investigated in previous studies, the thermal stability of the composites has not been studied extensively. The objective of this study was to examine the combined effect of the ASF and montmorillonite on the thermal stability, X-ray diffraction, and morphological characterization of PP-based composites.

EXPERIMENTAL

Materials

The polymer matrix was composed of PP (Arak Petrochemical Co., Iran), with a melt flow index of 7 to 10 g/10 min and a density of 0.87 g/cm³. Montmorillonite (MMT; Cloisite 15A, Southern Clay Products Co., Gonzales, Texas, USA), a nanoclay modified with dimethyl-dehydrogenated tallow and quaternary ammonium, was used as the intercalation agent (cationic exchange capacity of 125 meq/100 g clay, density of 1.66 g/cm³, and d-spacing of d₀₀₁=31.5 nm). Maleic anhydride-grafted PP (MAPP; Priex 20070, Solvay Co., Belgium, UK) was used as a coupling agent (melt flow index of 64 g/10 min, density of 0.91 g/cm³, and a grafted maleic anhydride content of 1.0 wt%). Almond (*Prunus dulcis* Mill.) shell was used as the lignocellulosic filler. The almond shells were milled using a hammer to obtain the ASF. The ASF was sifted through a 40-mesh (0.42 mm) screen and those particles retained on a 60-mesh (0.25 mm) screen were used in the experiments.

Production of Injection-Molded Composite Specimens

Before the preparation of composite specimens, ASF was oven-dried at 65 ± 2 °C until a constant weight was obtained. Then, the PP, ASF, MAPP, and MMT were weighed and bagged according to the formulations given in Table 1. Mixing was carried out in a counter-rotating intermeshing twin-screw extruder (Model T20, Collin Lab and Pilot Solutions, GmbH, Ebersburg, Germany), with a barrel temperature ranging from 155 to 190 °C at six zones (from feeding zone to the die zone) and a screw speed of 70 rpm. The pasty compound produced was cooled to room temperature and then grinded to produce suitable granules for further processing.

Table 1. Raw Material Formulations Used in the Production of Thermoplastic Composites

WPC Code	ASF (wt%)	PP (wt%)	MAPP (wt%)	MMT (wt%)
WPC-control	30	70	2	0
WPC-control	35	65	2	0
WPC-control	40	60	2	0
WPC-2.5 MMT	30	70	2	2.5
WPC-2.5 MMT	35	65	2	2.5
WPC-2.5 MMT	40	60	2	2.5
WPC-5.0 MMT	30	70	2	5.0
WPC-5.0 MMT	35	65	2	5.0
WPC-5.0 MMT	40	60	2	5.0

ASF: Almond shell flour; PP: Polypropylene; MAPP = maleic anhydride-grafted polypropylene; MTT: Montmorillonite

Grinding was carried out in a laboratory mill (WGLS 200/200 Model, Wieser), and the granulated material was oven-dried at 105 °C for 4 h. Test specimens were prepared by injection molding (Model EM80, Aslanian Co., Iran) and set at 160 to 180 °C to prepare test specimens. For each molding operation, a complete set of specimens for different tests are produced. Lastly, specimens were conditioned at 23 °C and 50% relative humidity for a minimum of 40 h, in accordance with the ASTM D618 (2008) testing standard, prior to testing. The density of the composites varied from 1.00 to 1.07 g/cm³.

Thermogravimetric Analysis (TGA)

The thermal characterization of nanocomposites was carried out using a thermogravimetric analyzer. Thermogravimetric analysis was used to investigate the thermal decomposition behavior of the nanocomposites. Tests were done under a high nitrogen (99.5% nitrogen) and low oxygen (0.5% oxygen content) atmosphere, at a scan rate of 10 °C/min and a programmed temperature range of 30 °C to 600 °C. A sample of 8.0 ± 1.0 mg was used for each test. The weight change was recorded as a function of the temperature.

X-Ray Diffraction (XRD)

An X-ray diffractometer (Philips X'Pert, Netherlands), equipped with CuK α radiation, $\lambda = 1.78 \text{ \AA}$, 40 kV, 30 mA, speed: 1.2°/min, and a diffraction angle range $2\theta = 2$ to 12° was employed to perform XRD.

Morphological Characterization of Thermoplastic Composites

The small specimens with dimensions of 1 mm³ were cut from composite strips and gently oven-dried. The morphology of the composites was studied using a field-emission scanning electron microscope (FE-SEM) (S-4800, Hitachi, Japan). The specimen was fully cured in a gel time machine (Davis Instruments, USA) and then coated with carbon using a carbon coater (JEE0400, JEOL Ltd., Japan) under vacuum (3×10^{-4} Pa) for one second.

RESULTS AND DISCUSSION

Thermal Properties

The thermal properties of thermoplastic composites containing ASF/MMT with different formulations are shown in Fig. 1. When 40 wt% ASF and 5.0 wt% MMT were added to the composites, the melting temperature (T_m) and the crystallization temperature (T_c) greatly increased, whereas the crystallinity level (attributed to enthalpy of melting and crystallization) decreased.

The ASF particles are capable of acting as a nucleating agent during the nucleation stage to increase the crystallization temperature of the composites. However, ASF particles can interfere with the growth stage, decreasing in the overall crystallinity level of the composite. Adding either the plasticizer or compatibilizer did not notably influence the crystallinity level, whereas, when added together, the crystallinity decreased considerably. The lowered crystallinity level suggested that the compatibility between the ASF and MMT/PP matrix improved.

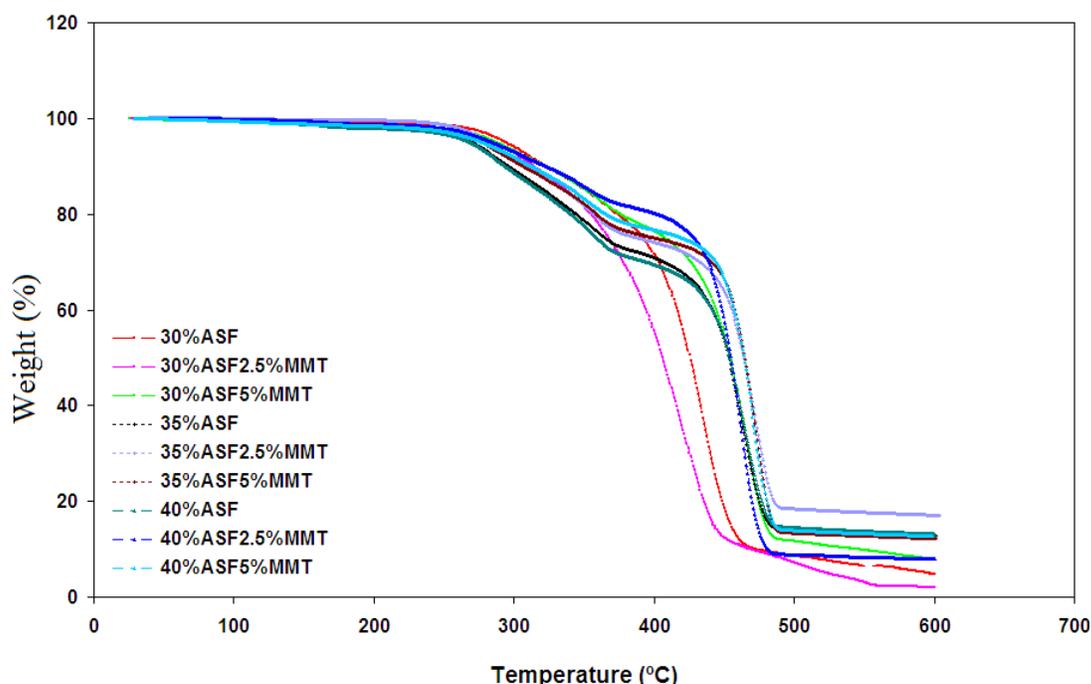


Fig. 1. Comparison of thermogravimetric analysis curves of WPCs containing almond shell flour/montmorillonite (ASF/MMT) with different formulations

The thermal stability of the 30 wt% ASF composite was studied by the TGA analysis (Fig. 1). The initial step between 50 °C and 200 °C of the DTG curve (Fig. 2) resulted from the loss of volatile compounds and water (Valdés *et al.* 2013; García *et al.* 2014). The thermal stability PP decreased with the incorporation of the ASF (Fig. 1). A similar result was found in wood filled thermoplastics. For example, Nemati *et al.* (2013) reported that increasing wood flour content deteriorated the thermal stability of thermoplastics by weight loss at a lower temperature. However, the thermal stability of the composites increased with the incorporation of the MMT. The maximum degradation temperature decreased with increasing MMT content (from 2.5 to 5.0 wt%) in comparison with the 0 wt%, and a increase in thermal stability was observed.

TGA measurements showed explicitly a stabilizing effect of modified MMT platelets on thermal degradation of PP with the ASF in the oxygen-free atmosphere. Thermal degradation of plain PP is related to the endothermic effect and occurs before the mass loss starts. In nanocomposites the endothermic effect is eliminated and thermal degradation is shifted towards higher temperatures and correlated with mass loss (Golebiewski and Galeski 2007). Selvakumar and Manoharan (2014) determined that nanoclay in PP could improve the crystallization of polymer matrix, since the crystallization temperature increased by 1.5 °C. They also reported that melting temperature (T_m) remained unaltered after the addition of nanoclay and thermal stability of the base polymer increased with nanoclay loading. A similar result was observed in this study.

All of the composites showed multi-stepped degradation because of the various species present. The thermal degradation started at 220 °C and continued up to about 480°C with two successive peaks. Two main decomposition peaks are shown with arrows on the derivative TGA thermograph (Fig. 1). The first peak was about 250 to 350 °C

depending on the composite formulation (Fig. 2), which was assigned to the thermal decomposition to the cellulose and lignin while the second peak was 380 to 420 °C was assigned to the PP (Fig. 1).

The first degradation observed around 220 °C was due to the hemicelluloses, which are understood to be the most thermally sensitive components in the lignocellulosic filler, followed by cellulose/lignin and then PP. Above 450 °C, the composites showed peaks of degradation that were mostly related to the combustion of degradation products formed during the initial thermal process.

These results concerning the thermal stability of the ASF as a reinforcement material in PP matrix were in agreement with the previous studies (Essabir *et al.* 2013; Valdés *et al.* 2013; García *et al.* 2014).

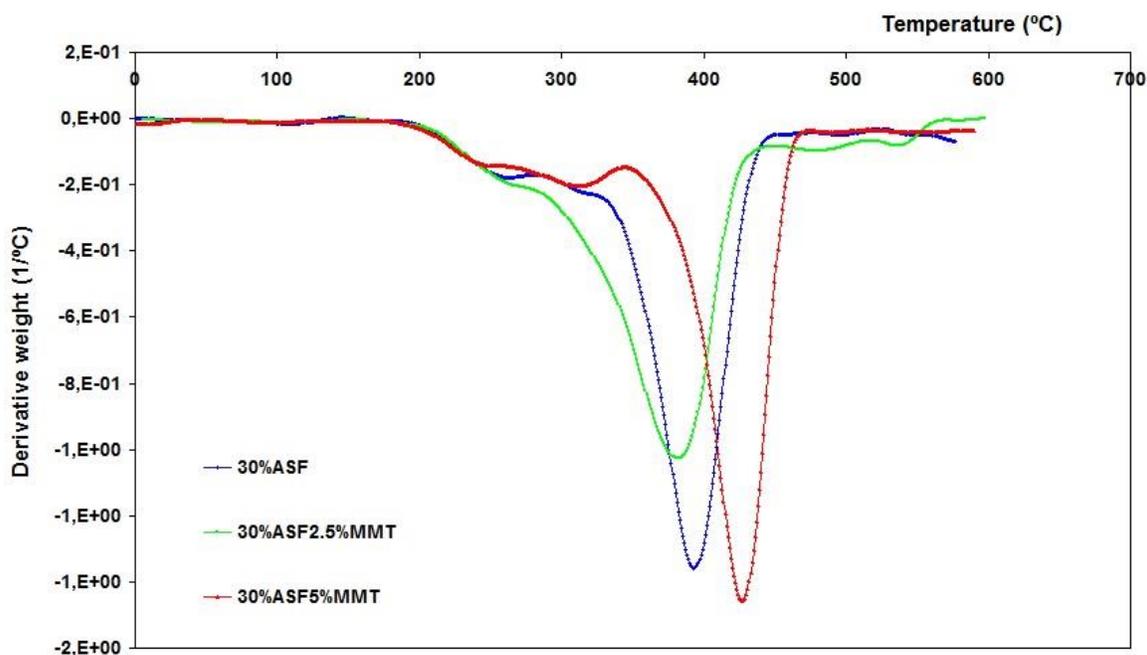


Fig. 2. Comparison of the thermogravimetric analysis of differential thermogravimetric curves of thermoplastic composites containing 30 wt% ASF with 0 wt%, 2.5 wt% or 5.0 wt% of montmorillonite

Morphological Properties

Scanning electron microscopy (SEM)

Figure 3 shows the SEM imaging of the ASF/PP composites without the addition of MMT. The SEM of the control and samples containing MTT composites showed some detachment of the ASF filler from the matrix. This indicated insufficient bonding between the PP and the ASF filler, resulting in less cellular adhesion (Salmah *et al.* 2013b; García *et al.* 2014).

The SEM imaging verified the interaction of ASF with the polymer, as well as the effectiveness of MMT in improving the interaction. The micrograph of MMT-treated composites showed that ASF was better dispersed in the matrix (Fig. 3). The MMT content of the composition matrix indicated that the presence of MMT resulted in less detachment and agglomeration of the ASF/PP matrix and showed complete fiber/matrix impregnation, which indicated the miscibility between the MMT and the ASF/PP matrix.

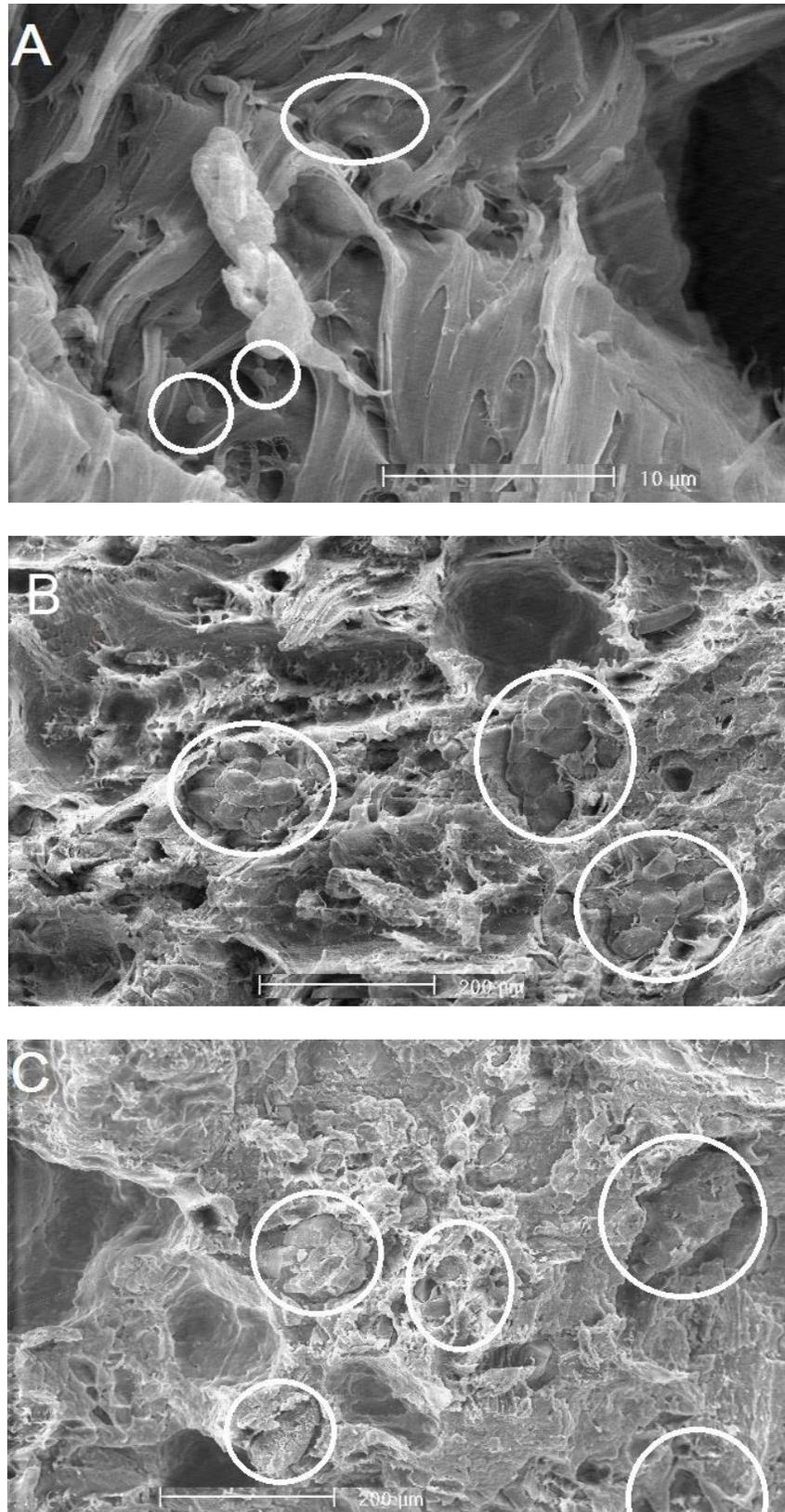


Fig. 3. Scanning electron micrographs of the wood polymer composites: A) 30 wt% almond shell flower (ASF) and 70 wt% PP; B) 35 wt% ASF and 65 wt% PP; C) 40 wt% ASF and 60 wt% PP. Circles refer to ASF agglomerates

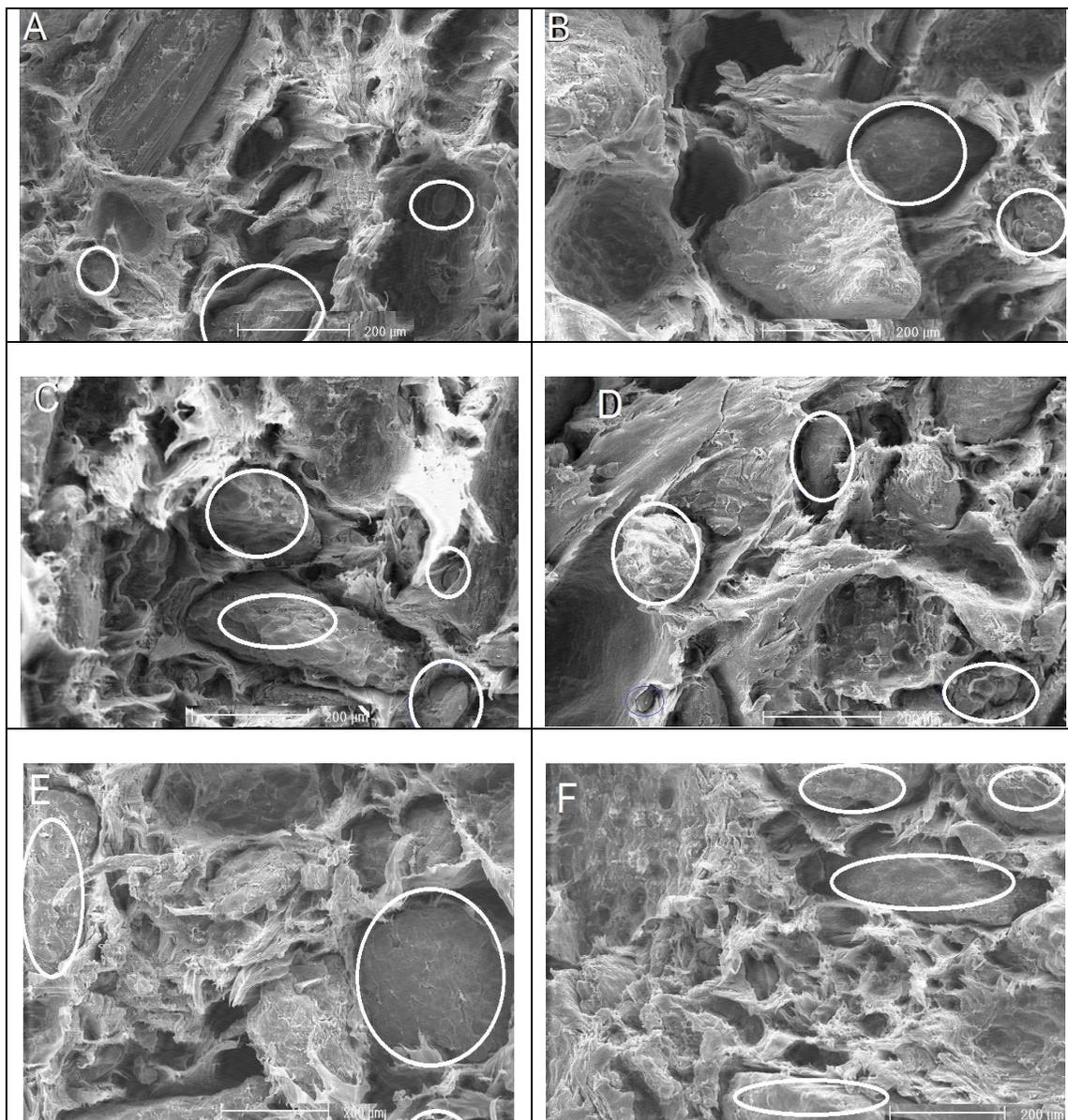


Fig. 4. Scanning electron micrograph of the wood polymer composites (ASF/PP/MMT): A) 30 wt% almond shell flour (ASF) and 2.5 wt% nanoclay; B) 30 wt% ASF and 5.0 wt% nanoclay; C) 35 wt% ASF and 2.5 wt% nanoclay; D) 35 wt% ASF and 5.0 wt% nanoclay; E) 40 wt% ASF and 2.5 wt% nanoclay; F) 40 wt% ASF and 5.0 wt% nanoclay

The dispersion of the nanoclay layers in the composites was observed at the 2.5 wt% and 5.0 wt% MMT loadings (Fig. 4). The MMT exhibited better dispersion of the clay layers in the polymer-matrix composite at the 5.0 wt% loading (Zhao *et al.* 2006; Deka and Maji 2010; Zahedi *et al.* 2013). Zahedi *et al.* (2015) found better dispersion of silicate layers in WPCs at the 3.0 wt% loading of MMT.

X-ray diffraction (XRD)

The XRD patterns of pure MMT and nanocomposites, with different percentages of nanoclay, are shown in Table 2. The pure MMT showed a characteristic intense peak at $2\theta = 3.84^\circ$. The composite specimens with 2.5 wt% and 5.0 wt% nanoclay showed a

peak shift to a lower diffraction angle (2θ) than pure MMT to 2.92° and 2.94° , respectively. In addition, the relative interaction (%) of nanocomposites with 2.5 wt% MMT was higher than the composited with 5.0 wt% MMT. These results indicated an increase in the interlayer spacing between silicate layers and an intercalation of polymer chains between the clay layers (Table 2). The reduction in peak intensity was attributed to the low concentration of clay in the samples (Deka and Maji 2010; Khanjanzadeh *et al.* 2012; Zahedi *et al.* 2013).

Table 2. X-Ray Diffraction Summary

MMT (wt%)	Pure MMT (wt%)	MMT (2.5 wt%)	MMT (5.0 wt%)
2θ ($^\circ$)	3.84	2.92	2.94
d -Spacing (nm)	3.15	3.49	3.48
Relative intercalation (%)	-	10.79	10.48

MMT: montmorillonite

CONCLUSIONS

1. The total weight loss of ASF/PP/MMT composites decreased as the filler content increased, and the thermal stability increased with increasing MMT contents.
2. By XRD analysis, the composites with 2.5 wt% and 5.0 wt% nanoclay exhibited peak shifts to lower diffraction angles (2θ) than pure MMT, and the relative intercalation of the composites with 2.5 wt% MMT was higher than the composites with 5.0 wt% MMT.
3. The thermal stability of ASF/PP/MMT nanocomposites was improved by the addition of MMT.

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