

Synthesis and Characterization of Recycled Isotactic Polypropylene Nanocomposites Containing Date Wood Fiber

Habib Shaban

Abstract—Nanocomposites of isotactic polypropylene (iPP) and date wood fiber were prepared after modification of the host matrix by reactive extrusion grafting of maleic anhydride. Chemical and mechanical treatment of date wood flour (WF) was conducted to obtain nanocrystalline cellulose. Layered silicates (clay) were partially intercalated with date wood fiber, and the modified layered silicate was used as filler in the PP matrix via a melt-blending process. The tensile strength of composites prepared from wood fiber modified clay was greater than that of the iPP-clay and iPP-WF composites at a 6% filler concentration, whereas deterioration of mechanical properties was observed when clay and WF were used alone for reinforcement. The dispersion of the filler in the matrix significantly decreased after clay modification with cellulose at higher concentrations, as shown by X-ray diffraction (XRD) data.

Keywords—Nanocomposites, isotactic polypropylene, date wood flour, intercalated, melt-blending.

I. INTRODUCTION

THE most important advantage of natural fibers as fillers in developing reinforced polymer composites is their eco-friendly nature, compared with traditional carbon and glass fiber-based composites. Previous results have shown that composite stiffness was sufficient, because natural fibers have high strength and stiffness [1]. However, drawbacks, such as poor filler dispersion and incompatibility with the polymer matrix, have also contributed to failures of natural fiber composites. Natural fiber composites do not attain the same strength as glass fiber composites because of incompatibility between the hydrophobic host polymer matrix and the hydrophilic natural fiber.

Date Wood flour (WF) can be used for applications like outdoor decks, railings and fences. One of the crucial properties needed by WF-based composites to be used as construction materials for load-bearing applications is effective dispersal of wood fiber. The intensity of debonding stress depends on particle size and interfacial adhesion. Interfacial interaction can be increased using various coupling agents [2]. Surface treatment of the wood by sodium hydroxide, silane, and esterification (acetylation, propionylation) is commonly used for interfacial improvement, and polymers functionalized with maleic anhydride (MA) and acrylic acid have been widely used [3].

Wood can be converted into nanodimensional particulates by sequential acid treatments to produce nanocrystals of 100–300 nm lengths and 3–5 nm diameters that can be extracted from soft wood [4].

Recently, polymers filled with nanoscale-layered silicates have shown remarkable improvements in mechanical, thermal, and physicochemical properties compared with pure polymers, even at low filler concentrations if the filler is homogenously dispersed [5]. These layered silicates have attracted attention because they are cost-effective, readily available, and have high aspect ratios, which increase energy transfer between phases. Exfoliated structures have resulted in the best mechanical properties for polymer matrices.

The use of nanosilicate layers combined with cellulose fibers for reinforcement is a new pathway for next-generation materials, [6] and there is interest in investigating synergistic effects between nanoclays and biofillers on the properties of polymer composites [7]. Thunwall et al. [8] studied the processing and properties of clay-interfaced cellulose fiber composites and concluded that treating the fiber with nanoclay improved the dispersion of fibers and the mechanical performance of the composites. Zhong et al. [9] observed that the addition of less than 5% nanoclay to the wood polyethylene matrix increased the d-spacing of the silicate layers, decreased the flexural strength by 24%, and increased the modulus by 10%. Mohanty and coworkers [10] fabricated nanocomposites from cellulose acetate powder, eco-friendly triethyl citrate plasticizer, and organically modified clay in which the tensile strength and modulus of the cellulosic plastic reinforced with organo-clay improved with decreasing plasticizer content.

This study investigated synergistic effects of reinforced cellulose micro/nanocrystals from wood and layered silicate for isotactic polypropylene (iPP) composites. iPP was selected as a matrix because it is one of the most commonly used polymers in many applications, and it addresses plastic waste problems because it is not eco-friendly. Fourier-transform infrared (FTIR) spectroscopy, mechanical analysis and X-ray diffraction (XRD) measurements were used to analyze functional group variation and the crystalline nature of the composites.

Habib Shaban is with the Department of Chemical Engineering, Kuwait University P.O. Box 5969, 13060 Safat, Kuwait (corresponding author to provide e-mail:habib.shaban@ku.edu.kw).

II. EXPERIMENTAL

A. Materials

Recycled iPP was purchased from a local chemical industry in Sabhan, Kuwait. It had an MFI of 1.7 g/10 min and a density of 0.91 g/cm³. Date wood fiber was purchased from a local company in Kuwait. The particle size of the date WF was 100 µm. Other chemicals were purchased from Sigma-Aldrich Chemical Company U.K., and they were used after drying and purification. Closite Na⁺ was the nanoclay used in this study and was purchased from Southern Clay, Gonzales, Texas, U.S.A.

B. Preparation of Composites

Maleic anhydride grafted PP (PP-g-MA), used as a compatibilizer, was prepared as follows. At first, 6% MA (w/w of PP), 0.10% dicumyl peroxide and iPP were dry-mixed and poured into a hopper with a single-screw extruder. Then, different temperature zones were set on the extruder from 145 to 180°C. The strands of MA-g-PP were converted into pellets using a pelletizer. These pellets were used as a compatibilizer for PP at a constant concentration of 6%, referred to as C-PP. Date wood flour was soaked in 0.5% alkali solution for 10 days and boiled for 2 hours at 80°C with a 2% NaOH solution, followed by washing with deionized water. Hydrolysis by 65% H₂SO₄ was conducted at 60°C for 30 minutes followed by centrifugation, sonication and neutralization. The resulting suspension of cellulose crystals contained a mixture of nano and micro-crystals referred as crystalline cellulose.

TABLE I
COMPOSITIONS OF SAMPLE

Nano-datewood-clay (NWC) % wt/wt	Date-wood-fiber (WF)	Nanoclay (Closite Na ⁺)	Isotactic polypropylene (iPP)	Sample code
6	0	0	94	NWC6
12	0	0	90	NWC12
0	6	0	94	WF6
0	12	0	90	WF12
0	0	6	94	CL6
0	0	12	90	CL12

The silicate layer (closite Na⁺) was dissolved in water for 3 days to produce a greenish yellow gel-like colloid solution. The water-dispersed crystalline cellulose was added to the colloid solution of clay at 12:88 (clay:cellulose) ratio. The mixture was stirred for 24 h at room temperature, followed by heating for 1 h at 100°C. The suspension was sonicated for 35 min at a 40% power output. This nanowood clay (NWC) was filled in the PP matrix at different loadings using the single-screw extruder. The temperature of the mixing zone was maintained at 185°C with a screw speed of 250 rpm. The extruded strand was cooled in a water bath and pelletized using a pelletizer. Extruded pellets were oven-dried at 85°C for 48 h and stored in sealed polyethylene bags to minimize moisture. The PP matrix was reinforced with clay and date WF under similar conditions at 6 and 12 filler concentrations. The dry pellets were molded for mechanical property measurements by injection molding using a Thermo-Haake

minijet injection molding machine. The composites of treated WF and layered silicates were prepared for comparison. The different compositions of the samples synthesized in this work are shown in Table I.

C. Characterization Techniques

Fourier-transform infrared spectroscopy (FTIR) spectra of the samples were recorded using a FTIR, Thermo, Nicolet IS 10. The incident beam angle was 45°.

D.X-Ray Diffraction (XRD)

XRD patterns of the samples were obtained using a Rigaku (Japan) diffractometer with Cu-Kα radiation at 50 kV and a scan rate of 1°/min. The d-spacing was calculated using Bragg's equation with λ at 0.154 nm.

E. Mechanical Properties

The tensile test for the composites was performed according to ASTM D638 using a Tinius Olsen UTM machine. Sample specimens were molded using a Thermo Minijet injection molding machine (557-2286). The cylinder temperature of the machine was 190°C, and the mold temperature was 50°C. For each sample, five replicates were tested, and the results represent the average of five values. Tensile deformation was determined using an extensometer at a crosshead speed of 10 mm/min.

III. RESULTS AND DISCUSSION

A. FTIR Spectroscopy

The date wood flour was pulverized semi-crystalline date wood containing amorphous and highly crystalline regions. It comprised of hemicellulose, lignin, and cellulose. FTIR spectroscopy indicated that cementing material like lignin was removed through various treatments (Fig. 1). Alkaline treatment eliminated lignin, as confirmed by the reduction in the peaks at 1140, 1222, and 1510 cm⁻¹ assigned to aromatic skeletal vibrations. This treatment caused degradation of aromatic structures, as indicated by diminished peak intensity from 1530 to 1550 cm⁻¹[11]. The peak observed at approximately 1735 cm⁻¹ was attributed to C=O vibrations and indicated the partial washout of hemicelluloses [12]. XRD graphs in Fig. 2 show three main peaks approximately at 22, 16, and 34° that correspond to the 200, 023, or 004 and 110 planes, respectively [13], [14]. The relative sharpness of XRD peaks for treated flour was attributed to the high crystalline content. This may have been due to decomposition of the amorphous zone during acid digestion, resulting in highly crystalline regions [15]. The composites showed a slight decrease in the hydroxyl region of the FTIR spectra, which was identical for all NWCs, regardless of filler content. The MA groups, present in the host polymer, decreased the hydroxyl region [16] due to association between negative oxygen atoms in the carboxylic groups and hydrogen in the filler. Esterification may have occurred between functionalities of cellulose and the maleated portion of the matrix, as indicated by the appearance of peaks at 1722–1746 cm⁻¹ [13] in the solution-blended composites in the presence of

catalyst. Esterification has also been reported in the melted state, which was facilitated by reaction with activated cellulose containing large amounts of free hydroxyl groups on the surface [17]. In this study, there was no detectable peak in the ester region. Most of the hydroxyl groups were confined between platelets of layered silicate and reduced the possibility of reactions with carbonyl groups of MA-grafted polymer chains.

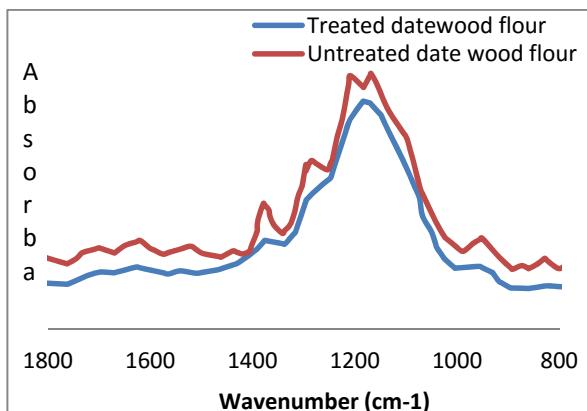


Fig. 1 FTIR spectra of treated and untreated date wood flour

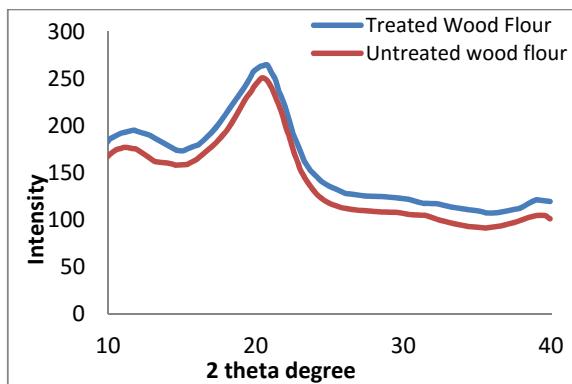


Fig. 2 XRD patterns of untreated and treated date wood flour

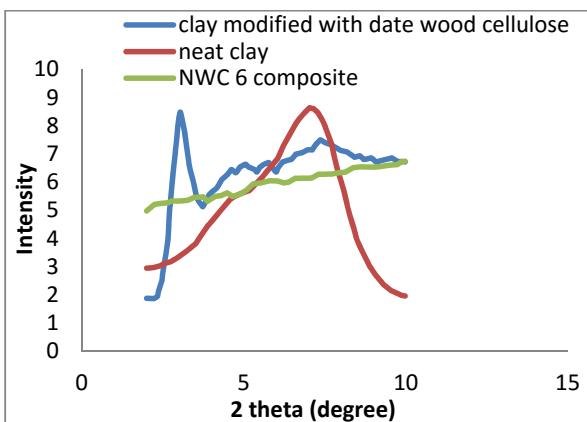


Fig. 3 XRD patterns of modified clay, neat clay and NWC 6 composites

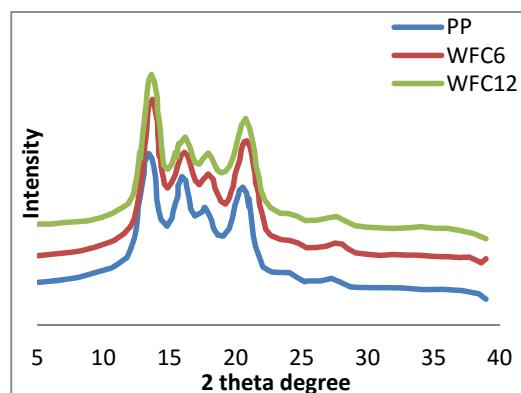


Fig. 4 XRD patterns of PP, WFC6 and WFC 12

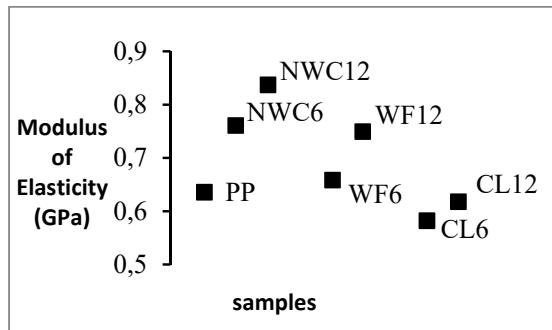


Fig. 5 Modulus of elasticity of different date wood flour composites

B. XRD Analysis

The crystalline status of the host polymer in composites defines the mechanical properties. Thus, the crystalline nature and other material properties can be tailored in the resulting hybrid. The properties of nanocomposites are often related to their structures and to the orientation of their particles. Cellulose is a highly crystalline material that forms through degradation of amorphous regions, and XRD data in

Figs. 2-4 suggested the presence of cellulose-I, which likely did not change during processing.

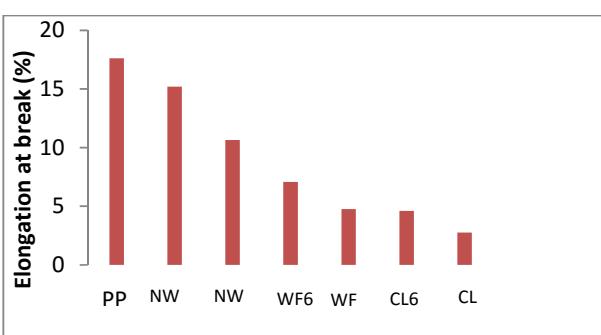


Fig. 6 Elongation at break for different date wood flour composites

The neat clay had a characteristic peak at 7.2° that corresponds to the 2.3 nm interlayer spacing. After mixing with crystalline WF, the peak shifted toward lower angles,

indicating increased intergallery distance. The new peak was located at 3.2° and was sharper than the original, indicating that the stacking order was destroyed and platelets moved apart, but maintained order [18]. The samples filled with 6% clay modified with cellulose did not show a peak in this region, indicating better dispersion of silicate layers inside the matrix. The reflection peak collected for NWC6 and NWC12 did not show any variation in position, supporting the conclusion that a higher percentage of cellulose-modified clay (NWC 12) inside the matrix did not cause further separation of tactoids.

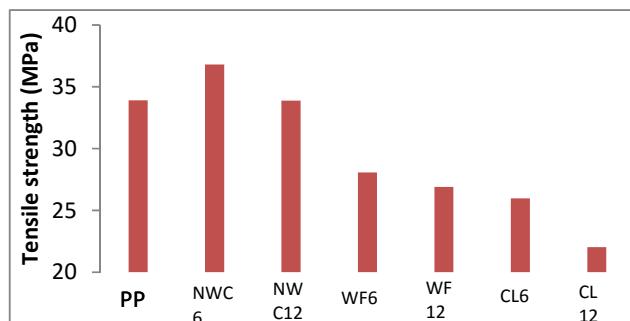


Fig. 7 Tensile strength of different date wood flour composites

C. Mechanical Properties

Mechanical property measurements are shown in Figs. 5-7. They depended on the amount of filler inside the polymer matrix. The stiffness of the composites increased linearly with increasing filler content in the matrix for certain composites. There may have been orientation effects in which reinforcing phases oriented toward the direction of the load and increased the stiffness. The tensile strength of CLs (Table I) decreased drastically and it was attributed to the lack of interaction between the host matrix and the filler. The reduction in CLs mechanical properties was greater than that of WFs, which was attributed to the presence of increased attraction through electrostatic bonding between MA-grafted polymer chains and hydroxyl groups in WF. The strength was markedly higher in NWC6 than in other samples.

It was assumed that interfacial adhesion in these samples was similar to WF6 and WF12, and the only difference was the existence of silicate layers in the matrix. Because silicate layers were not compatible with the host matrix due to highly hydrophobic nature of polymer, the extent of dispersion of the fillers in the matrix must have been responsible for the higher strength in NWC6.

Furthermore, as soon as the loading increased, aggregation also increased, decreasing the elongation of the composites, as shown in Fig. 6. Only NWC6 was similar to the neat matrix. When the content of particles in the composites increased, they touched each other and generated large bundles that could not carry a sufficient external load and fell apart. In addition, the stress transfer from one phase to another became difficult and produced a product with poor mechanical properties. Previous studies showed that strong interaction by chemical bonding between hydroxyl groups in cellulose and the

functionalized host matrix increased with increasing functionality, resulting in increased polymer strength [19]. This was not detected in this study because of a limited number of hydroxyl groups in the cellulose-modified clay; hydroxyl groups were not available for chemical bonding with anhydride due to bonding with layered silicates. Thus, modified layered silicates were responsible for higher dispersion and competitive strength in composites with smaller amounts of functionalized polymer. Furthermore, larger amounts of MA are not advisable in composites during melt blending due to the possibility of matrix degradation [20].

IV. CONCLUSIONS

This study developed fillers with synergistic properties between microcrystalline cellulose and clay. Agglomeration increased with increasing filler concentration, due to better interaction between clay and cellulose that promoted random accumulation of silicate tactoids. Dispersion was better at lower concentrations, attributed to the availability of a greater amount of functional groups from MA-grafted polymer chains in these samples. Because the mechanical properties improved at lower filler loadings, uniform dispersion of fillers was considered more important than the filler concentration in the host matrix. In conclusion, microcrystalline cellulose-modified clay may be useful for improving the mechanical properties of composites at certain filler concentrations and preventing phase separation that results in poor performance.

ACKNOWLEDGMENT

The authors would like to thank the research administration of Kuwait University for granting funds from project EC 01/13 to carry out this work.

REFERENCES

- [1] Mohanty, A. K.; Misra, M.; Drzal, L. T. *J. Polym Environ* 2000, 10, 19.
- [2] Danya di, L.; Janecska T.; Szabo, Z.; Nagy, G.; Moczo , J.; Pukanszky, B. *Compos Sci Technol* 2007, 67, 2838.
- [3] Samir, M. A. S. A.; Alloin, F.; Dufresne, A.; *Biomacromolecules* 2005, 6, 612.
- [4] Candanedo, S. B.; Roman, M.; Gray, D. G. *Biomacromolecules* 2005, 6, 1048.
- [5] Pandey, J. K.; Lee, J. W.; Chu, W. S.; Saini, D. R.; Mohanty, A. K.; Mishra, M.; Lan, T.; Ahn, S. H. *Nanocomposites of Polyolefins for Packaging Applications*, Chapter 4. In the book on *Polymer Nanocomposites for Packaging Application*; Nalwa, H. S., Mohanty, A. K., Eds.; American Scientific Publishers: Valencia, CA, 2010.
- [6] Gao, F. *Mater Today* 2004, 7, 50.
- [7] Hetzer, M.; Kee, D. D. *Chem Eng Res Design* 2008, 86, 1083.
- [8] Thunwall, M.; Boldizar, A.; Rigidahl, M.; Banke, K.; Lindstrom, T.; Tufvesson, H.; Hogman, S. *J Appl Polym Sci* 2008, 10, 918.
- [9] Zhong, Y.; Poloso, T.; Hetzer, M.; Kee, D. D. *Polym Eng Sci* 2007, 47, 803.
- [10] Park, H.; Misra, M.; Drzal, L. T.; Mohanty, A. K. *Biomacromolecules* 2004, 5, 2281.
- [11] Cave, I. D.; Hutt, L. *Wood Sci Technol* 1968, 2, 268.
- [12] Taiz, L.; *Ann Rev Plant Physiol* 1984, 35, 385.
- [13] Helbert, W.; Sugiyama, J.; Ishihara, M.; Yamanaka, S. *J Biotechnol* 1997, 57, 29.
- [14] Tserki, V.; Matzinos, P.; Kokkou, S.; Panayiotou, C. *Compos Part A* 36: 965 2005.
- [15] Wang, N.; Ding, E.; Cheng, R. *Polymer* 2007, 48, 3486.

- [16] Freudenberg, U.; Zschoche, S.; Simon, F.; Janke, A.; Schmidt, K.; Behrens, S. H.; Auweter, H.; Werner, C. *Biomacromolecules* 2005, 6, 1628.
- [17] Bledzki, A. K.; Gassan, J. *Prog Polym Sci* 1999, 24, 221.
- [18] Pandey, J. K. PhD Thesis, University of Pune, 2007.
- [19] Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
- [20] Pandey, J. K.; Reddy, R. K.; Kumar, A. P.; Singh, R. P. *Polym Degrad Stab* 2005, 88, 234.