

# Thermal, mechanical and morphological properties of polypropylene/clay/wood flour nanocomposites

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**Abstract.** Nanocomposites with polypropylene/clay/wood flour were prepared by melt compounding. Thermal, mechanical and morphological properties were characterized. The addition of clay, compatibilizer and wood flour considerably improved the thermal stability (i.e., decomposition and melting temperatures) of the hybrids. The tensile modulus and strength of most hybrids were highly increased with the increased loading of clay, MAPP and wood flour, compared to the hybrids without wood flour. The wide angle X-ray diffraction (WAXD) patterns showed the increased d-spacing of clay layers, indicating enhanced compatibility between PP and clay with the addition of maleated polypropylene (MAPP). The transmission electron microscopy (TEM) photomicrographs illustrated the intercalated and partially exfoliated structures of the hybrids with clay, MAPP and wood flour.

**Keywords:** nanocomposites, nanoclay, MAPP, PP, wood

## 1. Introduction

Composites can be tailored to have the desired properties by incorporating particulate fillers into a polymer matrix to suit different applications. There has been an increasing use of composites in myriad fields from the residential buildings to aeronautics industries [1]. Lignocellulosic fillers such as wood flour, rice husk, jute and sisal have numerous advantages over glass fibers including low cost, biodegradability, easiness of processing and the absence of toxic byproducts. Therefore, they have been widely used as reinforcements for thermoplastic composites [2–5]. The addition of wood flour to neat thermoplastics can greatly stiffen them, but makes them more brittle at the same time [2, 6, 7]. Compatibilizers such as maleated polyethylene (MAPE) and maleated polypropylene (MAPP)

played an important role in improving the compatibility and bonding strength between hydrophilic wood flour and hydrophobic thermoplastics [8–10]. Composites with structure and composition at the nanoscale exhibit highly improved mechanical properties and high temperature endurance [11–14]. Among the inorganic layered materials, layered silicates are often used for inclusion in the hybrids due to their ability to intercalate and exfoliate at the nanoscale in the thermoplastic matrix. In particular, the smectite group of clay minerals like montmorillonite (MMT) has been predominantly used, due to its excellent intercalation ability [15–20].

Since thermoplastics such as polyethylene (PE) and polypropylene (PP) are hydrophobic and have poor miscibility with hydrophilic layered silicates, nan-

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oclay was usually organo-chemically modified with alkylammonium groups to facilitate their interaction with thermoplastics. In addition, the miscibility between nanoclay and PE or PP can be improved by the addition of compatibilizers such as MAPE, MAPP or carboxylated PE [18, 21].

There are two concepts of intercalation and exfoliation, which can define the structures in clay-polymer hybrids. Intercalation, defined as the well-ordered and stacked multilayers that result from intercalated polymer chains within host nanoclay layers. Exfoliation refers to formation of monolayers of clay well-dispersed in a continuous polymer matrix or individually distributed in the polymer matrix. The intercalated and exfoliated hybrids exhibit improved in strength and modulus, compared with neat polymer and conventional composites [11–14, 16–18].

The enhanced properties of the composites can be achieved at a low clay loading level (e.g., less than 5.0 wt% addition of clay) [22]. At the 5 wt% clay loading, an approximately 70% increase in modulus and strength was observed for Nylon-clay systems, and both heat distortion temperature and impact strength also increased by more than 100% [23]. However, the dispersion of clay layers in most polymers is not easily accomplished due to face-to-face stacking in agglomerated tactoids and the conversion to a single platelet by complete exfoliation [24, 25].

Although some studies have been conducted on the reinforcement effect of clay in thermoplastics such as PP and PE, limited data is available on the wood flour/clay/plastic hybrids by melt compounding. With the presence of larger-size wood fibers, a synergistic combination of clay and coupling agent is often needed to achieve desired composite properties [21]. The objective of this study was to examine the effect of wood flour, clay, compatibilizer on thermal, mechanical and morphological properties of PP-based composites. Wide angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and stress-strain behavior were used to evaluate composite properties.

## 2. Materials and methods

### 2.1. Materials

Polypropylene (PP 5014,  $M_w = 180\,000$  g/mol) was obtained from the Korea Petrochemical Ind. Co., Ulsan, South Korea. Neat PP was in the form of homopolymer pellets with a melt flow index of 3.2 g/10 min and a density of 0.9 g/cm<sup>3</sup>. The wood flour (Lignocel C120, particle size of 100–120 mesh per 2.54 cm<sup>2</sup>) was supplied from J. Retenmaier & Sohne Co. (Rosenberg, Germany) and manufactured from some European softwood. Maleated polypropylene (MAPP; PH-200, Honam Petrochemical Co., Daejeon, Korea) was used as a compatibilizer. The molecular weight and maleic anhydride grafting level of MAPP were 40 000 g/mol and 5%, respectively. Clay (Montmorillonite, Cloisite® 15A), chemically-modified with a quaternary ammonium salt was purchased from Southern Clay Products, Inc. (Gonzales, Texas, U.S.A.). The clay was a fine powder with a cation exchange capacity of 125 mequiv/100 g. The density and layer distance of clay were 1.6 g/cm<sup>3</sup> and 30.3 Å, respectively. The clay was dried in a vacuum oven at 90°C for 24 h prior to use. The wood flour was dried to 1–2% moisture content using an oven at a temperature of 80°C, and then stored in polyethylene bags until needed.

### 2.2. Melt compounding

The hybrids with wood flour/clay/PP were prepared with a co-rotating twin-screw extruder (Bautek Co, Uijungbu-city, Korea). The extruder had a screw diameter of 19 mm with an  $L/D$  ratio of 40. A compounding temperature of 190°C was used to prevent the thermal degradation of the wood flour. The screw speed for compounding was in the range of 100–150 rpm, depending on the processing speed through a circular nozzle. The loading levels were 0, 10, 20 and 30 phr (part based on one hundred resin) for wood flour, 0, 1, 3 and 5 phr for clay, and 3, 6 and 10 phr for MAPP. The neat PP (used as control), PP/clay and PP/clay/MAPP hybrids were compounded using a one-step method. A two-step method was used to compound wood flour with PP/clay/MAPP hybrids. In the two step process, PP/clay/MAPP hybrids were compounded and palletized first, and then wood flour was finally compounded with the pellets of PP/clay/MAPP

hybrids. The extrudate in the strand form was air-cooled and pelletized with a pelletizer (Bautek Co., Uijungbu-city, Korea). The hybrid samples were dried at 90°C for 24 h in a vacuum oven to remove the absorbed water before being injection molded at 190°C and then cooled to room temperature.

### 2.3. TGA and DSC

Thermogravimetric analysis (TGA) was used to investigate thermal decomposition behavior of hybrids with a SDT Q600 Thermogravimetric analyzer (TA Instrument Inc. New Castle, Delaware, U.S.A.). Tests were done under nitrogen at a scan rate of 10°C/min in a programmed temperature range of 30 to 600°C. A sample of 5 to 10 mg was used for each run. The weight change was recorded as a function of temperature. Derivative peak temperature ( $DT_p$ ) was taken as the maximum temperature acquired from the differentiation of the weight change as a function of time. Differential scanning calorimetry (DSC) experiments were performed with a DSC Q10 system (TA Instrument Inc. New Castle, Delaware, U.S.A.). Each sample was heated and cooled at a scanning rate of 10°C/min under nitrogen atmosphere in order to prevent oxidation. A test sample of 5 to 10 mg was placed in an aluminum capsule and heated from 30 to 200°C for each run. The melting temperature ( $T_m$ ), enthalpy ( $\Delta H_m$ ), crystallization temperature ( $T_c$ ), crystalline enthalpy ( $-\Delta H_m$ ) and crystallinity ( $X_c$ ) were determined after the melt-crystallization process.

### 2.4. Tensile properties

The tensile strength test for hybrids was performed according to ASTM D638 using an Universal Testing Machine (Zwick Testing Machine Ltd., Leominster, United Kingdom). Test specimens were molded in a size of 3.18 mm (width), 63.66 mm (length) and 3.00 mm (thickness) with a gauge length of 12.5 mm. Tensile strength and modulus were determined the testing machine with an extensometer at a crosshead speed of 10 mm/min. For each treatment level, five replicated specimens were tested.

### 2.5. Wide angle X-ray diffraction (WAXD)

The intercalation of the clay layers in the hybrids was investigated using a wide angle X-ray diffrac-

tometer (WAXD: Model Rigaku ATXG, Rigaku Corp., Tokyo, Japan). Measurements were performed using a nickel-filtered Cu-K $\alpha_1$  radiation source under a voltage of 50 kV and a current of 300 mA. The WAXD scans were obtained in the reflection mode using an incident X-ray wavelength of 31.5 Å at a scan rate of 0.01 degree/min from a  $2\theta$  range of 2 to 10°. The interlayer distance of clay in the hybrids was calculated by Bragg's law ( $d = n\lambda/2\sin\theta$ ) from the (001) plane diffraction peak in the WAXD pattern with  $d$  as the distance between the atomic layers in a crystal,  $\lambda$  as the wavelength of the incident X-ray beam, and  $n$  an integer.

### 2.6. Transmission electron microscopy (TEM)

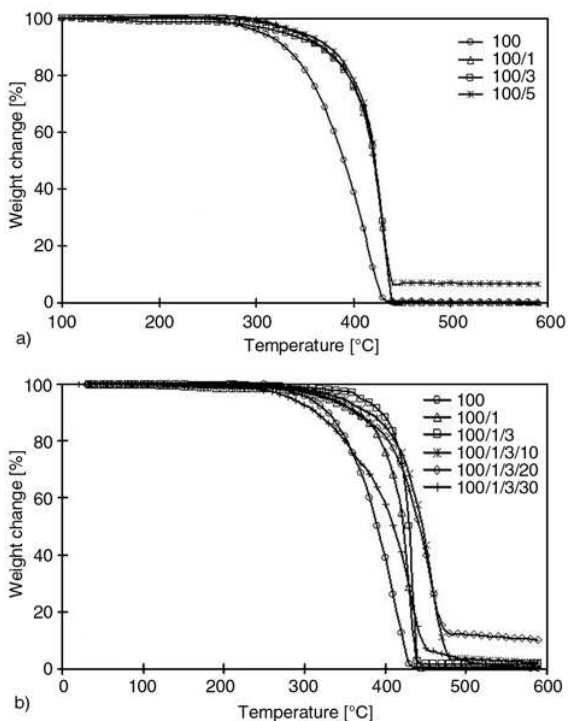
The morphology of the hybrids was imaged using a Phillips CM 30 transmission microscope (TEM: FEI Company, Hillsboro, OR, U.S.A.) with an acceleration voltage of 200 kV. Ultra-thin sections of 70–90 nm were cut from injection molded bars perpendicular to the flow direction under cryogenic conditions using a Nova CM-20 ultramicrotome and then placed on 300 mesh grids.

## 3. Results and discussion

### 3.1. Thermal properties

#### 3.1.1. TGA results

TGA curves of PP/clay hybrids are shown in Figure 1a. With the addition of clay (1 to 5 phr), a 67°C increase in decomposition temperature compared to neat PP was observed at the 50% weight loss level. The increase in decomposition temperature is attributed to the hindered diffusion (i.e., barrier effect) of volatile decomposition products caused by the dispersed clay particles in the PP matrix [26]. The derivative peak temperature ( $DT_p$ ) of neat PP was 403.7°C, while the hybrids with clay (1 to 5 phr) showed an increase in the derivative peak temperatures in the range of 17 to 32°C. Figure 1b shows the TGA thermographs of the hybrids with and without compatibilizer. The addition of compatibilizer (3 phr) to the hybrids increased the decomposition temperature by about 20°C compared to that of hybrids without compatibilizer. This increase was probably due to the physico-chemical adsorption of the volatile prod-

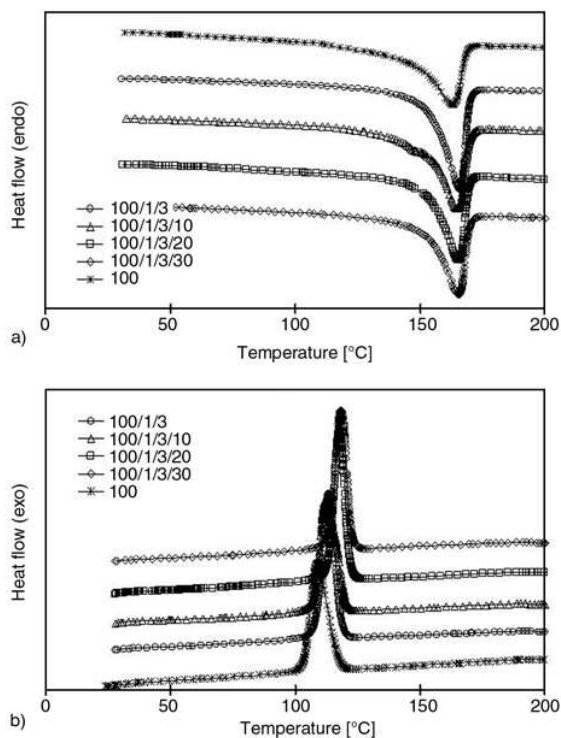


**Figure 1.** TGA thermographs of (a) PP/clay hybrids, and (b) PP/clay/MAPP/wood flour hybrids

ucts on the clay [27], which indicates that the dispersion of clay was improved by the addition of compatibilizer in polymer. The TGA thermographs of the hybrids with wood flour/clay/compatibilizer are shown in Figure 1b. The addition of wood flour (10 and 20 phr) increased the decomposition temperature of clay/compatibilizer hybrids. At the 50% weight loss level, the addition of 10–20 phr increased the decomposition by 40°C, whereas the decomposition temperature decreased slightly at the level of 30 phr wood flour.

### 3.1.2. DSC results

Table 1 shows the DSC results of PP/clay/wood flour/compatibilizer hybrids used in this study. All hybrid systems had a higher melting temperature ( $T_m$ ), compared to neat PP. Neat PP had the lowest  $T_m$  (163.1°C), while hybrids with clay (5 phr)/MAPP (10 phr)/wood flour (20 phr) had the highest  $T_m$  (166.1°C). The increased loading level of clay and MAPP had no significant effect on the  $T_m$  of the hybrids. At 1 phr loading of clay, the  $T_m$  increased up to 2.1°C with increasing wood flour content (Figure 2a). However, at the 3 and 5 phr



**Figure 2.** DSC melting results of PP/clay/MAPP/wood flour hybrids. (a) endo heat flow; (b) exo heat flow

clay loading level, the effect of wood flour on the change of  $T_m$  was not significant (Table 1).

The enthalpy ( $\Delta H_m$ ) of caloric processes was determined at the heating rate of 10°C/min (Table 1). The  $\Delta H_m$  of neat PP at transition temperature was 81.8 J/g, but the  $\Delta H_m$  with different clay (1 to 3 phr) and MAPP (3 to 10 phr) loading levels ranged from 87.5 to 90.4 J/g, indicating an increasing thermal stability. Meanwhile, the addition of wood flour from 10 to 30 phr decreased the  $\Delta H_m$  from 11.8 to 21.0 J/g. This result indicates that wood flour absorbed more heat energy in the melting of the composites as the  $\Delta H_m$  of wood flour was much lower than that of neat PP [28].

The crystalline peak temperature ( $T_c$ ) of the hybrids is shown in Table 1. The  $T_c$  of PP was 108.7°C, and the addition of clay (1 phr) and MAPP (3 phr) increased the  $T_c$  to 111.9°C. Clay and MAPP act as a nucleating agents, which increase the crystallization temperature of PP matrix [20, 29, 30]. The addition of wood flour (10 to 30 phr) to the hybrids increased the  $T_c$  to 118.3°C (Figure 2b). The addition of wood flour (30 phr) to PP/clay/MAPP hybrids increased the  $T_c$  by up to 6.4–7.9°C com-

**Table 1.** Thermal and tensile properties of PP/clay/MAPP/wood flour hybrids

Systems	PP/Clay/MAPP/WF	Thermal properties					Tensile properties	
		$T_m$ [°C]	$\Delta H_m$ [J/g]	$T_c$ [°C]	$-\Delta H_m$ [J/g]	$X_c$ [%]	Strength [MPa]	Modulus [MPa]
S1 <sup>a</sup>	100/0/0/0	163.1	81.8	108.7	91.0	39.15	32.83 (1.1) <sup>b</sup>	441.7 (21.3) <sup>c</sup>
S2 <sup>a</sup>	100/1/3/0	165.9	90.4	111.9	92.0	42.24	36.95 (7.1)	584.7 (27.2)
S3 <sup>b</sup>	100/1/3/10	164.8	88.3	113.6	86.8	43.25	37.83 (1.4)	750.3 (45.4)
S4 <sup>b</sup>	100/1/3/20	165.4	79.0	117.8	82.6	37.82	38.22 (1.9)	830.1 (51.0)
S5 <sup>b</sup>	100/1/3/30	165.2	78.7	118.3	78.2	37.63	40.08 (9.5)	905.6 (54.9)
S6 <sup>a</sup>	100/3/6/0	166.2	87.5	110.8	88.2	42.20	38.02 (1.2)	634.9 (34.0)
S7 <sup>b</sup>	100/3/6/10	164.7	75.7	117.8	80.9	41.85	36.55 (1.9)	782.0 (19.5)
S8 <sup>b</sup>	100/3/6/20	165.5	69.7	117.0	72.4	33.36	37.34 (0.8)	836.4 (36.1)
S9 <sup>b</sup>	100/3/6/30	164.6	67.6	118.6	70.0	32.35	36.46 (1.8)	958.4 (26.6)
S10 <sup>a</sup>	100/5/10/0	165.5	89.1	111.4	88.8	42.65	41.16 (1.0)	755.5 (34.0)
S11 <sup>b</sup>	100/5/10/10	165.4	79.6	115.6	82.8	38.09	47.63 (1.4)	871.3 (31.2)
S12 <sup>b</sup>	100/5/10/20	166.1	72.2	116.4	76.8	34.53	38.51 (1.5)	867.4 (46.4)
S13 <sup>b</sup>	100/5/10/30	164.9	65.2	118.1	68.8	31.20	39.90 (1.6)	963.8 (36.9)

<sup>a</sup> and <sup>b</sup> the hybrid systems made using a one-step and two-step compounding method, respectively

<sup>c</sup> mean and standard deviation based on five samples. MAPP = maleated polypropylene, WF = wood flour

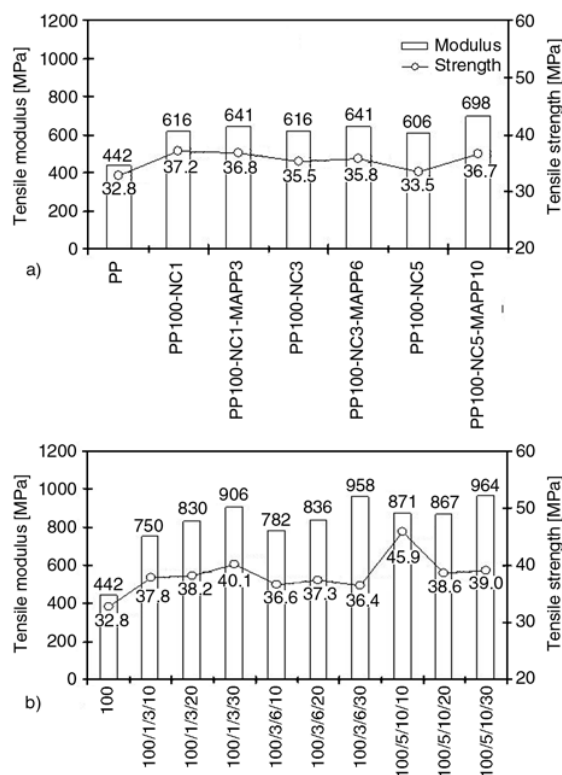
$T_m$  = melting point;  $\Delta H_m$  = enthalpy;  $T_c$  = crystalline temperature;  $-\Delta H_m$  = crystalline enthalpy;  $X_c$  = crystallinity

pared to the hybrids without wood flour. This result indicates that the nucleating effect of clay was further strengthened by the addition of wood flour (Table 1).

The crystalline enthalpy ( $-\Delta H_m$ ) of neat PP was 90.95 J/g. As clay, MAPP and wood flour were added, the  $-\Delta H_m$  decreased (Table 1). Since the addition of clay and wood flour interfered with crystallization, it is assumed that the decrease of  $-\Delta H_m$  was closely related to the decrease of crystal size itself. However, crystallization occurs because the clay and wood flour played a role of nucleating agent. As shown in Table 1, the crystallinity ( $X_c$ ) of PP was 39.15%. With the addition of clay and MAPP into neat PP, the  $X_c$  increased. As clay loading increased, the  $X_c$  of hybrids decreased gradually. The addition of wood flour (10 phr) had no significant effect on the  $X_c$ , while the higher loading of wood flour (20–30 phr) greatly reduced the  $X_c$ . This indicates that the  $X_c$  is generally affected by the dispersion, the loading level, the surface chemistry of fillers and the viscosity of hybrids [31].

### 3.2. Mechanical properties

The tensile properties of wood flour/clay hybrids manufactured by the one-step and two-step compounding methods are summarized in Table 1. The tensile strength and modulus of neat PP (S1) were, respectively, 32.8 and 441.7 MPa. Figure 3a shows



**Figure 3.** Tensile properties of (a) PP/clay/MAPP hybrids; (b) PP/clay/MAPP/wood flour hybrids

the effect of clay and compatibilizer contents on the tensile properties of hybrids made by the one-step compounding method. The addition of clay (1, 3 and 5 phr) to PP increased the tensile modulus to 37.1 to 39.4% and increased the tensile strength to



9.1 to 13.4%, compared with those of neat PP. However, the loading level of clay to neat PP showed no effect on the tensile modulus of hybrids. The addition of clay (1, 3 and 5 phr) and MAPP (3, 6 and 10 phr) for systems S2, S6 and S10 increased the tensile modulus and strength, compared with the hybrids with only clay. For example, the tensile modulus of the hybrid with 5 phr clay and 10 phr MAPP increased by 15.2% and the tensile strength increased by 9.6%, compared with the hybrids without MAPP. From these results, the high tensile strength is seen to be an intercalation phenomenon of clay layers by MAPP. On the other hand, the increased tensile modulus is attributed to the increased stiffness and brittleness of hybrid composites by the addition of clay.

Figure 3b shows the influence of clay, compatibilizer and wood flour contents on the tensile modulus of the hybrids made by the two-step compounding method. At the loading level of 1% clay, the tensile modulus of hybrids increased as wood flour content increased. As wood flour loading increased to 10, 20 and 30 phr, the tensile modulus increased 21.8, 34.7 and 47.1%, respectively, compared to the system S2. The tensile modulus of most hybrids was highly increased with the increased loading of clay, MAPP and wood flour, compared to the hybrids (S2, S6 and S10). The maximum tensile modulus (964 MPa) was obtained from system S13. This value is 38.1% higher than that of system S10. From these results, it is assumed that the increased modulus is highly related to the increased brittleness and stiffness of the hybrids, due to the addition of wood flour.

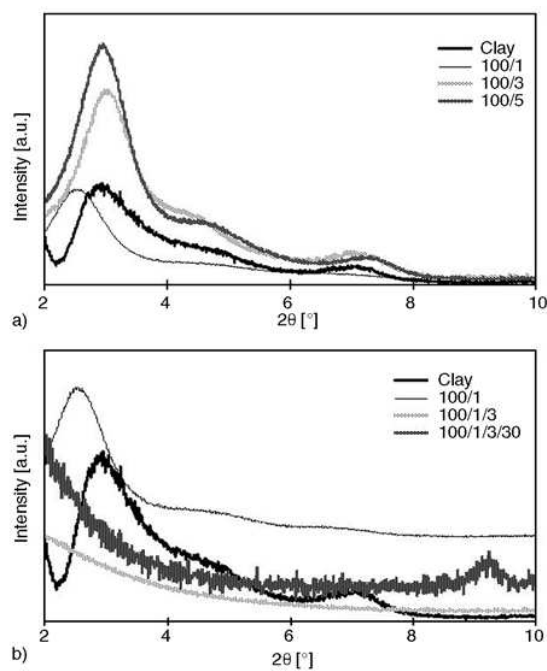
The influence of clay, compatibilizer and wood flour contents on the tensile strength of the hybrids is shown in Figure 3b. At the loading of 1 phr clay, the tensile strength of hybrids increased as wood flour content increased. As wood flour loading increased to 10, 20 and 30 phr, the tensile strength increased 2.7, 3.8 and 9.0%, respectively, compared to system S2. On the other hand, the tensile strengths of hybrids at a clay loading level of 3 phr were lower than those at 1 phr clay. At 3 phr clay, the tensile strengths of the clay/MAPP hybrid composites with 10, 20 and 30 phr wood flour were increased by 2.2, 4.2 and 1.7%, respectively, compared to system S6. In other words, the tensile strengths leveled-off as the wood flour loading increased. At 5 phr clay loading, the tensile

strength of hybrids decreased as wood flour content increased. The maximum tensile strength (45.9 MPa) was obtained at the wood flour loading of 10 phr (system S11). The tensile strengths of clay/MAPP hybrid composites with 20 and 30 phr wood flour were increased by 5.2 and 6.3%, compared to those of system S10. These results indicate that the increase in tensile strength with the increase of wood flour at low levels of clay is related to the improved bonding strength between wood flour and neat PP compared to the intermolecular bonding of neat PP [2, 8]. It is assumed that the decrease in tensile strength with increasing wood flour at higher clay levels is highly related to the increased viscosity of the hybrids rather than the bonding strength.

### 3.3. Morphology from WAXD and TEM

#### 3.3.1. WAXD results

The WAXD of clay reinforced PP composites can quantify the periodic intercalated structures of inorganic crystalline layers in the  $2\theta$  range of 2 to 10°. Therefore, the clay product with a d-spacing of 30.3 Å ( $2\theta = 2.91$ ), was compared with hybrid composites. Figure 4a and Table 2 illustrate the



**Figure 4.** WAXD patterns of selected composite systems. (a) clay and PP/clay hybrids; (b) clay, PP/clay, PP/clay/MAPP, and PP/clay/MAPP/wood flour hybrids

**Table 2.** Interlayer distance of clay by wide angle X-ray diffraction

Systems	PP/clay	Value at $2\theta$ [°]	$d_{001}$ spacing [Å]
S1 <sup>a</sup>	100/0	2.91	30.3
S2 <sup>a</sup>	100/1	2.59	34.1
S3 <sup>a</sup>	100/2	2.95	29.9
S4 <sup>a</sup>	100/3	3.10	28.5
S5 <sup>a</sup>	100/4	3.05	29.0
S6 <sup>a</sup>	100/5	3.00	29.4

<sup>a</sup>hybrid systems made using a one-step compounding method

comparison of WAXD patterns of hybrid composites with different levels of clay. The (001) peak of the hybrid with 1 phr clay was shifted to a lower value ( $2\theta = 2.95$ ,  $d$ -spacing = 34.1 Å), which indicates an increase of  $d$ -spacing for clay layers. On the other hand, the (001) peaks of hybrids with 2 to 5 phr clay were shifted to a higher value (minimum  $2\theta = 3.10$ ,  $d$ -spacing = 28.5 Å), which indicates a decrease in  $d$ -spacing for clay layers. This decrease of the  $d$ -spacing of clay layers is presumably due to the low compatibility at interfaces between neat PP and clay.

Through the enhancement of the compatibility between neat PP and clay, the polymer chains could be well diffused into the clay layers and the  $d$ -spacing of clay layers might be increased (Figure 4b). Therefore, the peaks disappeared when 3 phr MAPP was incorporated, representing the intercalation of PP into the clay layers or the partial exfoliation of the clay layers. The (001) peaks of WAXD of the composites with the MAPP showed a broad and weak peak intensity compared to the (001) peaks of WAXD without MAPP. The (001) peaks of WAXD with wood flour/MAPP/clay hybrid prepared by the two-step compounding method are shown in Figure 4b. The addition of wood flour with clay and MAPP gave much wider peaks, indicating the improved compatibility of wood flour and PP matrix by adding MAPP and the enhancement of intercalation from the better shear action by adding wood flour during the compounding process.

### 3.3.2. TEM results

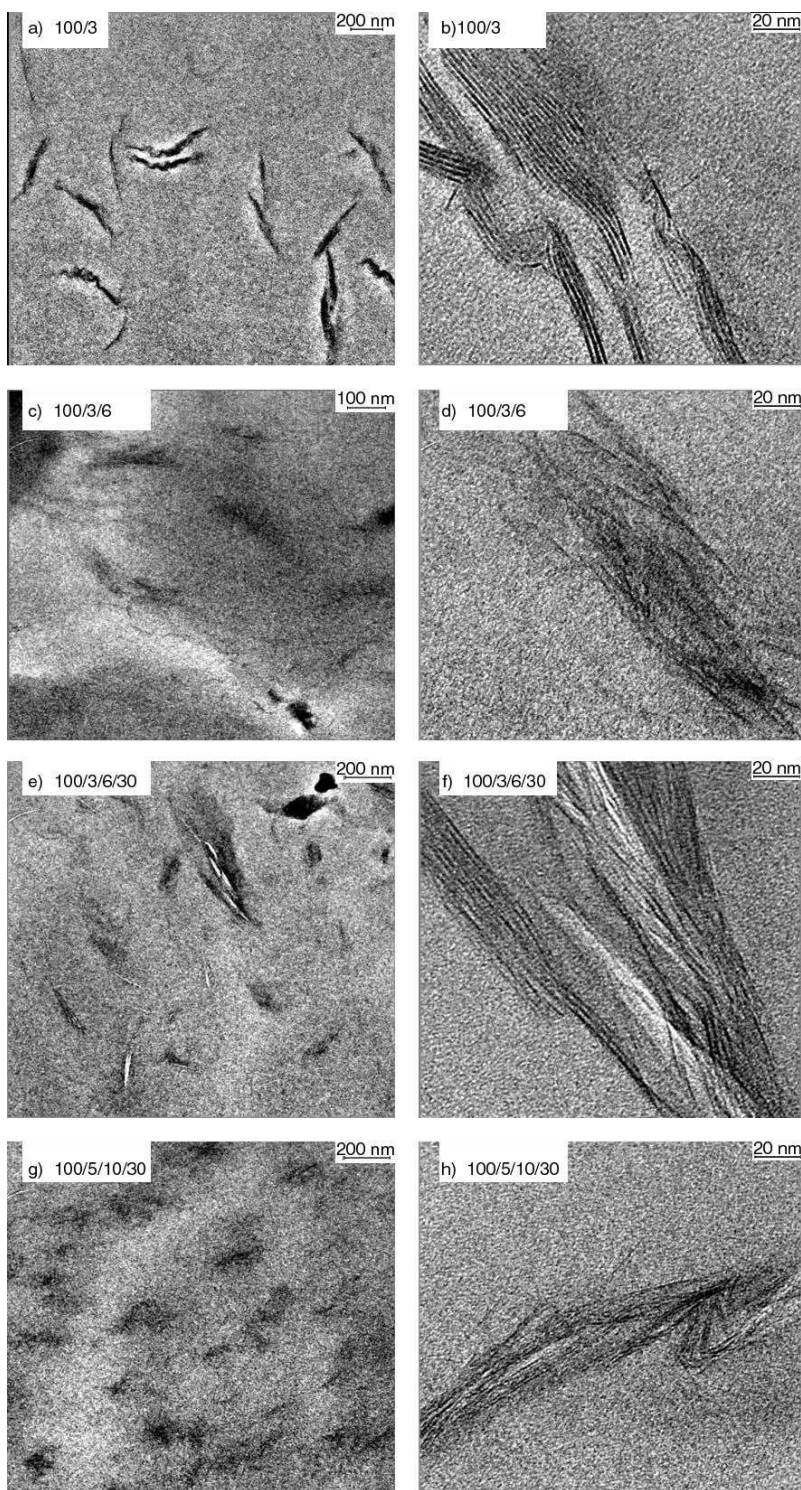
The TEM photomicrographs of the hybrids with clay, MAPP and wood flour prepared by the one-step and two-step compounding are shown in Figures 5a–5h. The dark lines in Figures 5a and 5b

correspond to the intersection of clay layers of 3.15 nm thick clay layers, showing a large number of multi-layered stacks of clay platelets, and no clay platelets intercalated with polymer. The TEM photomicrographs in Figures 5c and 5d contain a large number of multilayered clay platelets intercalated with PP, corroborating the WAXD results [15]. This result is closely related to the enhancement of clay dispersion by MAPP and the intercalation of clay platelets with polymer. Moreover, the TEM photomicrographs in Figures 5e–5h reveal well-intercalated and partially exfoliated structures containing dispersed layers of clay, showing a larger number of platelets per unit area on average. With the addition of wood flour, the intercalated and partially exfoliated structures were clearly detected.

## 4. Conclusions

The effects of clay, wood flour and compatibilizer on the melting and crystallization behavior, mechanical properties and morphology of PP/clay/wood flour nanocomposites were studied. The addition of clay (1 to 5 phr), compatibilizer (5 to 10 phr) and wood flour (10 to 20 phr) increased the decomposition temperature and melting temperature of the hybrids. The crystalline peak temperature of the hybrids increased with the use of clay and wood flour compared to that of neat PP. The crystalline enthalpy largely decreased due to the increase of viscosity and the decrease of dispersion in the polymer as clay, compatibilizer and wood flour were added. The addition of clay to neat PP increased the tensile modulus and strength. The addition of clay and MAPP to neat PP increased the tensile modulus and strength, compared with the hybrids with only clay. The tensile modulus and strength of most hybrids were highly increased with the increased loading of clay, MAPP and wood flour, compared to the hybrids without wood flour. The increased tensile modulus is attributed to the increased stiffness and brittleness of hybrid composites by the addition of clay and wood flour. On the other hand, the high tensile strength is related to an intercalation phenomenon of clay layers and the increased bonding strength between wood flour and neat PP by MAPP. The WAXD pattern of the hybrids showed increased  $d$ -spacing of clay layers, indicating improved compatibility of





**Figure 5.** TEM images of PP/clay/MAPP/wood flour hybrids. a) and b) PP/clay: 100/3; c) and d) PP/clay/MAPP: 100/3/6; e) and f) PP/clay/MAPP/WF: 100/3/6/30; and g) and h) PP/clay/MAPP/WF: 100/5/10/30. Scale-bar of (a), (c), (e), and (g) was 100 nm, and scale-bar of (b), (d), (f), (h) was 20 nm

neat PP and clay by the addition of MAPP and the intercalation and partial exfoliation of clay layers. The TEM photomicrographs further illustrated the intercalated and partially exfoliated structures

formed by the addition of clay, MAPP and wood flour. From this study, the desired composite properties can be tailored by a synergetic combination



of clay and coupling agent with the presence of large-size wood flour.

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