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Kinetics of Thermal Degradation of Polypropylene/Nanoclay/Wood Flour Nanocomposites

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ABSTRACT : As a part of enhancing the performance of wood-plastic composites (WPC), polypropylene (PP)/ nanoclay (NC)/ wood flour (WF) nanocomposites were prepared using melt blending and injection molding process to evaluate their thermal stability. Thermogravimetric analysis (TGA) was employed to investigate thermal degradation kinetics of the nanocomposites both dynamic and isothermal conditions. Dynamic scans of the TGA showed an increased thermal stability of the nanocomposites at moderate wood flour concentrations (up to 20 phr, percentage based on hundred percent resin) while it decreased with the addition of 30 phr wood flour. The activation energy (E_a) of thermal degradation of nanocomposites increased when nanoclay was added and the concentration of wood flour increased. Different equations were used to evaluate isothermal degradation kinetics using the rate of thermal degradation of the composites, expressed as weight loss (%) from their isothermal TGA curves. Degradation occurred at faster rate in the initial stages of about 60 min., and then proceeded in a gradual manner. However, nanocomposites with wood flour of 30 phr heated at 300 °C showed a drastic difference in their degradation behavior, and reached almost a complete decomposition after 40 min. of the isothermal heating. The degree of decomposition was greater at higher temperatures, and the residual weight of isothermal degradation of nanocomposites greatly varied from about 10 to 90 %, depending on isothermal temperatures. The isothermal degradation of nanocomposites also increased their thermal stability with the addition of 1 phr nanoclay and of wood flour up to 20 phr. But, the degradation of PP100/NC1/MAPP3/WF30 nanocomposites with 30 phr wood flour occurs at a faster rate compared to those of the others, indicating a decrease in their thermal stability.

Keywords: nanocomposites, thermogravimetric analysis, thermal kinetics, dynamic degradation, isothermal degradation

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1. Introduction

Recently, a great deal of attention has been paid to polymer nanocomposites using nanoclayas they often exhibit physicochemical properties dramatically different from those of their microcomposite and macrocomposite counterparts. A number of experimental investigations on the nanoclay have indicated that they exhibit improved strength, enhanced modulus, decreased thermal expansion coefficient, increased thermal stability and reduced gas permeability compared to pure polymer or conventional composites [1-3]. Generally, the performance improvement of the nanocomposites depends, to a large extent, firstly, on the distribution and arrangement of the mineral layers as a result of intercalation or exfoliation, and secondly, on the interfacial bonding between the mineral layers and the thermoplastic polymer by a compatibilizer [4-6]. Nanoclay as an inorganic filler has been widely studied, primarily, because of significant enhancement in mechanical and thermal properties. The previous work attempted to manufacture plastic/wood composites by adding nanoclay through melt blending and injection molding [7].

Much effort has been devoted to developing a new mathematical method for kinetic analysis using TGA [8,9]. The X-ray photoelectron spectra of PVC/clay nanocomposites showed that clay could enhance the thermal stability by delayed loss of allylic species [10]. Several attempts have been made to understand the thermal, mechanical and physical properties of nanocomposites with polypropylene (PP) [11,12], polyimide [13], polyamide-66(PA-66) [14], PS [15,16] and poly(1-caprolactone) [17]. However, the effect of nanoclay to the thermal stability of the PP/wood flour composite has not been evaluated, which requires to investigate thermal degradation kinetics of the composites. But limited studies

have been directed towards isothermal kinetic aspects of the PP/NC/WF hybrid nanocomposites. Moreover, a kinetic study of the thermal degradation provides useful information for the optimization of the successive material in order to avoid or at least limit thermal degradation. Various analytical methods of calculating the kinetics of thermal degradation have been reported in the literatures [18-20].

The present work deals with the kinetics of dynamic thermal degradation at three different heating rates and isothermal degradation at four different temperatures of polypropylene (PP)/nanoclay (NC)/wood flour (WF) hybrids nanocomposites. This study also focuses on the effect of different constituents combinations (i.e., wood flour, nanoclay and compatibilizer) on the thermal stability of the resultant nanocomposites.

2. Materials and methods

2.1. Materials

Polypropylene (PP 5014, Mw= 180,000 g/mol) was obtained from the Korea Petrochemical Ind. Co., Republic of Korea. Neat PP was in the form of powder with a melt flow index of 3.2 g/10min and a density of 0.9 g/cm^3. The wood flour (Lignocel C120, particle size of 100-120 mesh per 2.54 cm^2) prepared from European softwood was supplied from J. Retenmaier & Sohne Co. (Germany). Maleated polypropylene (MAPP; PH-200, Honam Petrochemical Co., Republic of Korea) was used as a compatibilizer. The molecular weight and maleic anhydride grafting level of MAPP were 40,000 g/mol and 5 %, respectively. Nanoclay (NC) (Cloisite®15A), chemicallymodified with a quaternary ammonium salt was purchased from Southern Clay Products, Inc. (Texas, U.S.). The clay was a fine powder with a cation exchange capacity of 125 mequiv/100g. The density and layer distance of clay were

1.6 g/cm^3 and 3.03 nm, respectively.

2.2. Melt compounding

The PP/NC/WF hybrid nanocomposites were prepared by adding 1 phr (percent based on hundred resin) nanoclay and wood flour (10 to 30 phr) using either a one-step or a two-step melt compounding with a co-rotating twin-screw extruder (Bautek Co, Korea). The extruder had a screw diameter of 19 mm with an L/D ratio of 40. The compounding temperature of 190 °C and the screw speed of 100-150 rpm were used for compounding. The loading level of compatiblizer was 3 phr. The neat PP as a control, PP/NC, and PP/NC/MAPP hybrid composites were also compounded using the one-step method. The two-step method was used to compound wood flour with PP/NC/MAPP hybrids. The PP/NC/MAPP hybrids were compounded, pelletized, and then blended with the wood flour. The extrudate in the strand form was air-cooled and pelletized with a pelletizer (Bautek Co., Korea).

2.3. Thermogravimetric analysis (TGA)

Thermal decomposition behavior of the hybrid composites was observed using thermogravimetric analyzer (SDT Q600, TA Instrument, USA). The dynamic thermal degradation was performed at a heating rate of 10 °C/min in a programmed temperature range from 30 to 600 °C, in nitrogen atmosphere. A sample of 5 to 10 mg was used for each run. The weight change was recorded as a function of temperature and time. Peak temperature (T_p) was a maximum temperature acquired from the differentiation of the weight change by time. To determine the activation energy, hybrid composites were measured at heating rates of 5, 10, 15 to 20 °C/min.

This multi-heating rate method was employed to determine the activation energy (E_a) of the thermal degradation of hybrid composites using the Kissinger equation [20] expressed as:

$$-\ln(\beta/T_p^2) = E_a/RT_p - \ln(R/E_a) \quad \cdots\cdots\cdots\cdots (1)$$

where β is heating rate (°C/min.) and T_p is the peak temperature. R is the gas constant (8.313 KJ/mol). The E_a can be calculated from the slope and the pre-exponential factor from the intercept of a plot of $-\ln(/T_p^2)$ versus $1/T_p$.

Isothermal experiments were performed at temperatures of 240, 260, 280 and 300 °C under nitrogen atmosphere. Prior to heating at each isothermal temperature, the sample was heated from room temperature to the target temperature at a rate of 80 °C/min and was scanned at each selected temperature for 120 min.

3. Results and discussion

3.1. Dynamic thermal degradation

Representative TGA thermograms shown in Fig. 1 clearly indicate that the weight loss has occurred in one-step degradation process in the range of 300-480 °C for all the composites. When PP was modified with nanoclay, there was not much change in the thermal stability of the composite. In the case of PP/NC/WF nanocomposites treated with the MAPP, the initial decomposition temperature (IDT) was around 320 °C, which is similar to that of neat PP. However, the decomposition of pure PP reached a faster completion (about 450 °C), as compared to those of nanocomposites modified with MAPP (~480 °C). This result confirmed that PP composed of the carbon-carbon bonds in the main-chain allowed a temperature increase to promote random scission, with associated thermal degradation and thermal depolymerization occurring at the weak sites of the PP main chains [21,22]. Above 300 °C, the quantity of PP residue was very small,

and sometimes it was lost due to the further breakdown, owing to thermal degradation materials into gaseous products at higher temperature.
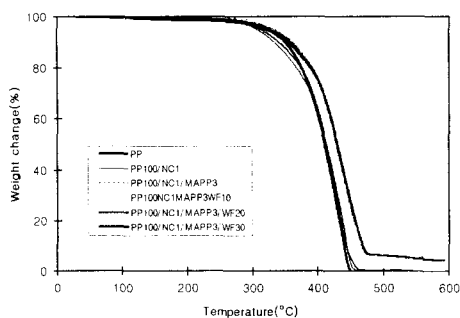

Fig. 1. Dynamic TGA thermograms of neat PP and PP100/NC1/MAPP3/WF(10~ 30 phr) nanocomposites.

The thermal stability and degradation temperature of MAPP-treated composites was slightly greater than that of neat PP, which eventually increased with increasing of wood flour loading. An improved thermal stability of the compatibilizer-treated composites could be due to enhanced interfacial adhesion and additional intermolecular bonding. It was already reported that an esterification reaction between hydroxyl groups of wood flour and the anhydride functional group of MAPP had been occurred [23,24]. The temperature corresponding to initial 10 % of weight loss (T_{10}), 50 % of weight loss (T_{50}), peak temperature (T_P) and residual weight obtained at 600 °C from TGA experimental curves are given in Table 1. This data reveals that PP/NC composites show a decrease in T_{10}(°C), which further increased with the addition of wood flour. The probable reasons may be attributed to anintimate contact between the polymer molecules and the inorganic nanoclay with large surface area as well as the presence of highly crystalline cellulose of wood flour in nanocomposites [25, 26]. At the same time, poor dispersion of nanoclay has lead to a catalytic effect that has boosted the initial degradation process at the early stages of heating. However, PP/NC added with wood flour at 10 and 20 phr show higher IDT (353 and 350 °C), and char yield at 600 °C, as compared to PP with 30 phr wood flour. The increase of initial decomposition temperature can also be ascribed to the hindered diffusion of volatile decomposition products caused by the clay particles and wood flour. By contrast, this kind of behavior was not observed at the higher concentration of wood flour (30 phr).

Dynamic heating of samples was performed at the constant heating rates of 5, 10, 15 and 20 °C/min (Fig. 2). The TGA thermograms

Table 1. Dynamic TGA data of neat PP and PP/NC/MAPP/WF nanocomposites

Hybrids	Temp. of 10% wt. loss (°C)	Temp. of 50% wt. loss (°C)	T_p (°C)	Residual weight at 600°C (%)	E_a (kJ/mol)
PP	349.9	410.1	415.1	−1.95	101.8
PP100/NC1	341.8	414.6	432.1	0.09	188.3
PP100/NC1/MAPP3	336.7	415.6	436.3	0.07	166.9
PP100/NC1/MAPP3/WF10	360.6	428.9	416.9	0.21	157.4
PP100/NC1/MAPP3/WF20	356.8	430.0	427.2	4.27	168.1
PP100/NC1/MAPP3/WF30	334.8	413.2	437.1	0.64	191.5

T_p is a peak temperature.

shifted to higher temperature as the heating rate increased, although the shapes of the curves were quite similar. As expected, this shift in the onset of degradation to higher temperature is due to a shorter time required for a sample to reach a given temperature at the faster heating rates.
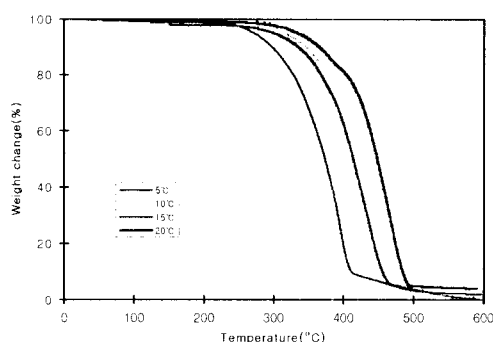

Fig. 2. TGA thermograms of PP100/NC1/ MAPP3/WF30 nanocomposites heated at different heating rates.

The activation energy (Ea) for the thermal degradation as a function of the weight-loss fraction (%) for the pure PP and the hybrid composites is shown in Table. 1. The data clearly indicate that the Ea values vary in a wide range from 101 to 188 kJ/mol. It is interesting to note that the activation energy values for degradation vary depending on the composition of wood flour. Neat PP possessed the lowest Ea value of 101 kJ/mol. The addition of wood flour to PP/NC composites gradually increased the energy of activation. The highest value of Ea was observed for wood flour of 30 phr (191.5 kJ/mol), probably due to its higher hydrophilic property. The terminal polar group is higher, and then it promoted the intermolecular hydrogen bonds, with the consequent difficulty to the mobility of the segments of the polymer chain. It is obvious that the addition of coupling agent has further improved their thermal stability via an improved interfacial adhesion.

3.2. Kinetic modeling of isothermal degradation

The degree of degradation (%) has been calculated based on the weight loss that has occurred in the isothermal TGA curves at a particular time, using the following equation:

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where W_0, W and W_f denote initial, actual and final values of the weight loss occurred during the isothermal period, respectively. The Prout-Tompkins (P-T) model was used to calculate the kinetic parameters of the degradation process as shown:

$$\ln[\alpha/(1-\alpha)] = k(T)t + C \quad \cdots\cdots\cdots\cdots\cdots (3)$$

where t indicates the time needed to reach each degree of degradation and the graphs of $\ln[\alpha/(1-\alpha)]$ versus t were presented in Fig. 3. Rate constants k(T) were determined from the slope of the linear part of the curve for each degradation temperature and were summarized in Table 2.

It is evident from the dynamic TGA experiment that the decomposition of PP, NC, MAPP and wood flour nanocomposites starts above 300°C. Therefore, we have chosen four isothermal different temperatures of 240, 260, 280 and 300 °C for the TGA analysis of materials. The samples were kept at the selected temperature for a period of 120 min. The pattern of weight loss of the isothermal TGA curves was assumed of corresponding to the degradation of nanocomposite material. They were analyzed to follow the decomposition process, depending on the effect of isothermal temperature, time, and the effects of addition of reactant substituents (clay, compatibilizer and wood flour) on the decomposition pattern.

Fig. 3 shows the isothermal TGA curves of PP, clay, MAPP and wood flour

Table 2. Kinetic parameters of the isothermal degradation of nanocomposites determined by the Prout-Tompkins model.

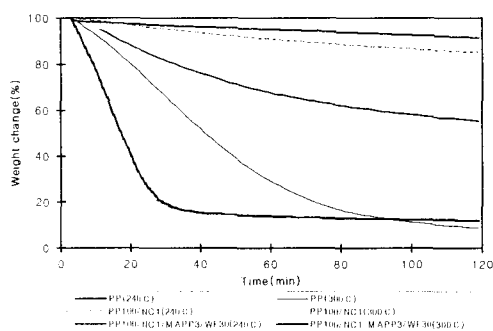| Hybrids	α	Temp. (°C)				R^2	lnA
		240	260	280	300		
		k(T)/min					
PP100	0.2-0.9	43.6	43.6	61.2	58.4	0.737	1.72
PP100/NC1	0.5-0.7	35.8	37.1	37.6	34.4	0.085	1.24
PP100/NC1/MAPP3	0.4-0.9	39.0	37.4	36.5	37.1	0.688	1.22
PP100/NC1/MAPP3/WF10	0.5-0.9	36.0	33.9	34.7	38.4	0.216	1.34
PP100/NC1/MAPP3/WF20	0.3-0.9	30.5	36.2	39.5	36.7	0.644	1.50
PP100/NC1/MAPP3/WF30	0.4-0.9	29.0	40.6	61.0	33.3	0.146	1.60

Fig. 3. Isothermal TGA thermograms at different temperatures of PP100/NC1/MAPP3/WF (10~30 phr) nanocomposites.

nanocomposites recorded separately at four specified temperatures. They certainly indicate that the weight loss has occurred at somewhat faster rates in the initial stage up to about 60 min., and then proceeds in a gradual manner. The extent of weight loss depends on the temperature. That is, the higher the temperature is, the higher the weight loss is. For example, neat PP has the weight losses of 32.7, 47.7, 74.9 and 71.0 %, respectively, at 240, 260, 280 and 300 °C in the initial 60 min. In the remaining one hour of heating, the weight loss of all nanocomposites has occurred at a slow rate. The final weight losses were around 44.4, 61.2, 87.1 and 91.2 %. It may be appropriate to mention here that materials have shown various extents of weight losses in the isothermal period. Higher amount of weight changes are observed at higher temperatures. A difference of about 20 % mass change is witnessed between initial (60 min.) and final weight loss after 120 min. at higher temperature. Neat PP shows a weight loss of >90% at the isothermal heating of 300 °C. However, the addition of clay has improved the thermal stability of the PP to a large extent. PP100/NC1 nanocomposites has shown a weigh loss of 42.0 % at 300 °C even after 120 min. of heating. The thermal stability of PP, clay and wood flour composites modified by MAPP of 3 phr depends on the compatibility between PP and compatibilizer. The interfacial interaction between compatibilizer and either PP or wood flour are mainly due to polar groups (maleic anhydride) of the compatibilizer. There was not much change in the thermal stability of the hybrid nanocomposites with the addition of MAPP. An increase in the wood flour content has in turn resulted in a decrease in thermal stability at higher temperature. As shown in Fig. 3, it can be seen that, PP100/NC1/MAPP3/WF30 nanocomposites has >85% weight loss in the initial 30 min. of heating. The initial faster rate of decomposition can be attributed to the presence of more number of hydroxyl groups in the wood flour. Besides, it appears that the linear polymer chain of PP possessed the required freedom for the elimination of water from the hybrid composites. However at

lower concentration of wood flour, the hybridswere not much affected. The final weight loss after the completion of isothermal heating was around 41.0 and 53.3 % for PP100/NC1/MAPP3/WF10 and PP100/NC1/MAPP3/WF10 nanocomposites, respectively. The difference in the extent of decomposition is somewhat higher at initial time period. The final degradation behaviors of all the samples at different isothermal temperatures are shown in Fig. 4.
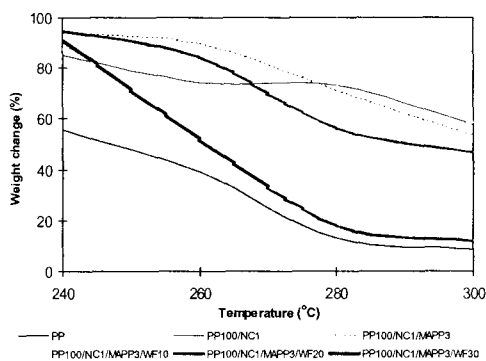

Fig. 4. Final weight loss (%) of neat PP and PP100/NC1/MAPP3/WF (10~30 phr) nanocomposites at different isothermal temperatures.

The degree of degradation (%) derived from these isothermal decomposition runs are presented in Table 2. The plot between $\ln[\alpha/(1-\alpha)]$ versus time at different temperatures is shown in Figs. 5(a)-(c). For neat PP there is not much change in the $\ln[\alpha/(1-\alpha)]$values till the initial 40 min, irrespective of temperature changes. However, after 50 min. there was little change in the degradation pattern. The similar kind of trend was observed for PP100/NC1 nanocomposites. A radical change in the degree of degradation was observed for PP100/NC1/MAPP3/WF30 nanocomposites at elevated temperatures of 280 and 300 °C. The pattern was quite similar to that other hybrid samples at lower temperatures. It is in analogous with dynamic TGA data that the degradation degree was

enhanced with an increase of wood flour concentration. In other words, the addition of more hydroxyl groups of wood flour can be volatilized easily at higher temperatures.
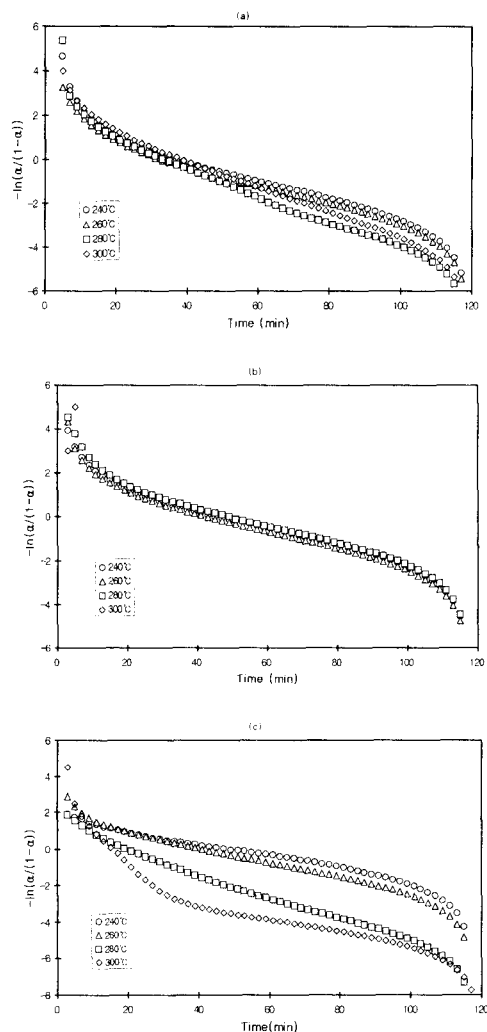

Fig. 5. Plot of $\ln[\alpha/(1-\alpha)]$ versus time of (a) neat PP, (b) PP100/NC1 and (c) P P 1 0 0 / N C 1 / M A P P 3 / W F 3 0 nanocomposite.

4. Conclusions

The study investigated the kinetics of thermal degradation of PP, clay and wood

flour nanocomposites under dynamic and isothermal heating conditions. In dynamic heating, thermal decomposition of nanocomposites occurs in a single stage in the temperature range of 300 to 480 °C. The rate of decomposition was greater at higher temperature. The PP/NC/WF nanocomposites were slightly more thermally stable when they were modified with the MAPP, owing to an enhanced interfacial adhesion and additional intermolecular bonding. Furthermore, the addition of wood flour to PP/NC nanocomposite gradually increased the energy of activation. In contrast, under isothermal condition, the addition of clay to neat PP resulted in an improvement of thermal stability to a large extent. It was observed that thermal degradation occurs at a faster rate in the initial 60 min. of heating and then proceeds gradually. The weight loss of about 20 % is witnessed between initial (60 min.) and final weight loss after 120 min. at higher temperature. Higher weight losses are observed at higher temperatures. A radical change in the degree of degradation was seen for PP100/NCl/MAPP3/WF30 nanocomposites at higher temperatures.

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