

Thermal Analysis of Polyamide 6 Composites Filled by Natural Fiber Blend

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This study describes changes in the viscoelastic and thermal properties of composites made with various percentages (up to 20 wt.%) of a natural fiber blend (a mixture of flax, kenaf, and hemp fibers) and polyamide 6 (PA 6). According to the differential scanning calorimetry (DSC) analyses, the incorporation of natural fibers produced minor changes in the glass transition (T_g), melting (T_m), and crystallization temperature (T_c) of the PA 6 composites. Because of the reinforcing effect of natural fibers, the storage modulus (E') from dynamic mechanical thermal analysis (DMTA) increased as the natural fiber content increased. The E' values at room temperature and T_g were 3960 MPa and 1800 MPa, respectively, with the incorporation 20 wt.% fiber, which were 68% and 193% higher than the E' value of neat PA 6. As the natural fiber content increased, the thermal stability of the composites decreased, and thermogravimetric analysis (TGA) showed that the onset temperature of rapid thermal degradation decreased from around 440 (neat PA 6) to 420 °C (20 wt.% natural fiber blend). The addition of 20 wt.% single type fibers showed comparable DSC and TG results to the incorporation of 20 wt.% natural fiber blends.

Keywords: Engineering thermoplastic composite; Melt compounding; Dynamic mechanical thermal analysis (DMTA); Differential scanning calorimetry (DSC); Thermogravimetric analysis (TG); Thermal stability

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INTRODUCTION

Lightweight composites from sustainable sources, including renewable, biodegradable, and recycled materials are promising new materials. In automotive applications, lightweight sustainable composites lessen the dependence on petroleum resources and replacing dense (talc fillers) as well as man-made fillers (glass and carbon fibers) with more environmentally friendly materials (Leao *et al.* 1998; Zhao and Zhou 2014). Recently in Europe and North America, the use of natural fibers as fillers in plastic composites has received considerable attention in the automotive industry because of their low cost compared to carbon fibers, low density *versus* other fillers (2.5 g/cm³ for glass fibers and 2.75 g/cm³ for talc fillers), good mechanical properties, ease of fiber surface modification *via* functional groups, relative non-abrasiveness to compounding and processing tools, renewability, biodegradability, and world-wide availability (Joshi *et al.* 2004; Santos *et al.* 2008; Njuguna *et al.* 2011; Ozen *et al.* 2012). The future of the natural

fiber composites (NFCs) market looks attractive, and the global NFCs market is forecast to grow at a compound annual growth rate (CAGR) of 8.2% from 2015 to 2020 (Lucintel 2015). The automotive industry is expected to remain the largest application of NFCs because of the increasing concern for passenger safety, government mandates for better fuel economy (corporate average fuel economy (CAFE) regulations), and end-of-life vehicle directives (Lucintel 2015).

Polyamides (6, 6/6, 11, and 12) are the most widely used engineering thermoplastics in a number of critical areas in automotives, such as the engine, transmission, cooling systems, and fuel system components, where mechanical and thermal stability are required at temperatures of 90 to 150 °C or above; thermoplastics also provide higher oil and corrosive chemical resistance, good mechanical properties, and attractive surface qualities (MacDermont and Shenoy 1997; Graff 2005). However, their high melting points (over 220 °C for nylon 6 and 6/6) are usually problematic in producing NFCs, and thermal degradation is the primary cause of problems when working with natural fibers because it leads to reduced mechanical properties (Graff 2005; Vedoy 2012; Birch *et al.* 2015). Combined with their better mechanical properties than polyolefins (polypropylene (PP), polyethylene (PE), *etc.*) and easier recyclability, which is important for end-of-life vehicles directives, compared to thermoset polymers (epoxy, polyester, polyurethane, *etc.*), polyamides show great interaction with natural fibers. These interactions are attributed to their hydrophilic nature, making it possible to eliminate the use of coupling agents and surface modification of natural fibers, which are time consuming and increase the cost of the final composite materials (Graff 2005; Tajvidi and Feizmand 2009). Although there is considerable interest in nylon-based composites, there have been only a few studies of nylon-based NFCs, and the available literature focuses on mechanical and morphological properties (Santos *et al.* 2007; de Arcaya *et al.* 2009; Arsad *et al.* 2013; Ozen *et al.* 2013). There is a lack of information about the rheological and thermal properties of PA-based NFCs. The studied PA-based NFCs are generally single fiber feedstocks, and but the optimal material properties may be achieved using blends of natural fibers (Sherman 1999).

In a previous paper, the effects of a natural fiber blend on the mechanical and morphological properties of PA 6-based NFCs were investigated (Ozen *et al.* 2013). The aim of this study is to investigate the effect of a natural fiber blend (a mixture of flax, kenaf, and hemp) on the rheological and thermal properties of PA 6-based NFCs. Using thermal tests including differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA), the thermal stability, DTG max temperature, viscoelastic behavior (storage modulus and $\tan \delta$), T_g , T_m , and T_c of the neat PA 6 and PA 6-based NFCs were compared.

EXPERIMENTAL

PA 6 with a density of 1.13 g/cm³ was kindly supplied by Entec Polymers LLC, Orlando, FL, USA. The lubricant used as processing aid was supplied by Struktol Company (Stow, OH, USA). Natural fibers (flax, hemp, and kenaf) were kindly supplied by Bast Fibers LLC (Cresskill, NJ, USA) and were milled into small particles using a lab scale grinder; the uniform particle size distribution facilitated mixing during melt compounding. Natural fibers were milled into small particles using a lab-scale grinder and passed through a 5-mm screen to obtain particles of uniform size. The same amount of natural fiber particles (most of the natural fiber particles 86 wt.% were less than 850 μm . based on sieve

analysis) from different fibers was packed in an air-tight container and mixed in a high-speed mixer (2000 rpm, 2 min) to obtain a uniform mixture. A Brabender Prepmixer® (South Hackensack, NJ, USA) was used to compound the PA 6 with the natural fiber blend or individual fiber types. Mixing was performed for 15 min at 250 °C and a rotor speed of 60 rpm. Melt compounding was followed by grinding and injection molding for all composite materials. The materials and sample preparation methods used in this study are described in more detail elsewhere (Ozen *et al.* 2013). The NFCs nomenclature and compositions are shown in Table 1. A DMTA IV rheometer from Rheometric Scientific® (Patel Scientific Corporation, Piscataway, NJ, USA) was used to determine the viscoelastic properties of the composites. The experiments were conducted in three point bending mode at a frequency of 1 Hz from -50 to 150 °C at a scanning rate of 5 °C/min. DSC measurements were performed using a PerkinElmer Pyris DSC (Waltham, MA, USA), and each 10 mg sample was scanned from -10 °C to 250 °C at a heating rate of 5 °C/min under nitrogen flow (20 mL/min) to prevent sample oxidation. The specimens' X_c was calculated according to the following equation,

$$X_c = (\Delta H_f \times 100) / (\Delta H_f^\circ \times \omega) \quad (1)$$

where ΔH_f is the heat of fusion of the PA 6 and PA 6-based NFCs, ΔH_f° the heat of fusion for 100% crystalline PA 6 ($\Delta H_{100}=190$ J/g), and ω is the mass fraction for PA 6 in the composites (Wu *et al.* 2001).

TGA measurements were performed using a Mettler Toledo analyzer (Columbus, OH, USA), and each 10 mg sample was scanned from room temperature to 600 °C at a heating rate of 10 °C/min under nitrogen flow (20 mL/min) to prevent sample oxidation. At least three specimens were tested for each composition for DSC, DMTA, and TGA tests, and the results are presented as an average of tested samples. More details on DSC, DMTA, and TGA can be found elsewhere (Kiziltas *et al.* 2010; Kiziltas *et al.* 2011).

Table 1. Nomenclature and Compositions of PA 6-NFCs

Sample Name	PA 6 (wt.%)	Flax (wt.%)	Hemp (wt.%)	Kenaf (wt.%)	NFB (wt.%)	Lubricant (wt.%)
PA 6	97	-	-	-	-	3
5% M	92	-	-	-	5	3
10% M	87	-	-	-	10	3
20% M	77	-	-	-	20	3
20% F	77	20	-	-	-	3
20% H	77	-	20	-	-	3
20% K	77	-	-	20	-	3

NFB = natural fiber blend, mixture of flax, hemp, and kenaf fibers

M = mixture, F = flax, H = hemp, K = kenaf

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves of the neat PA 6 and PA 6-based NFCs. The T_g of the neat PA 6 was approximately 38 °C, and the T_g values of composites changed, but only marginally in Fig. 1. PA composites containing glass fibers, microcrystalline cellulose, montmorillonite, and organoclay exhibit similar T_g behavior, and previous reports showed that the T_g values of PA-based NFCs are strongly affected by the matrix polymer but not the fillers (Cho and Paul 2001; Kiziltas *et al.* 2011).

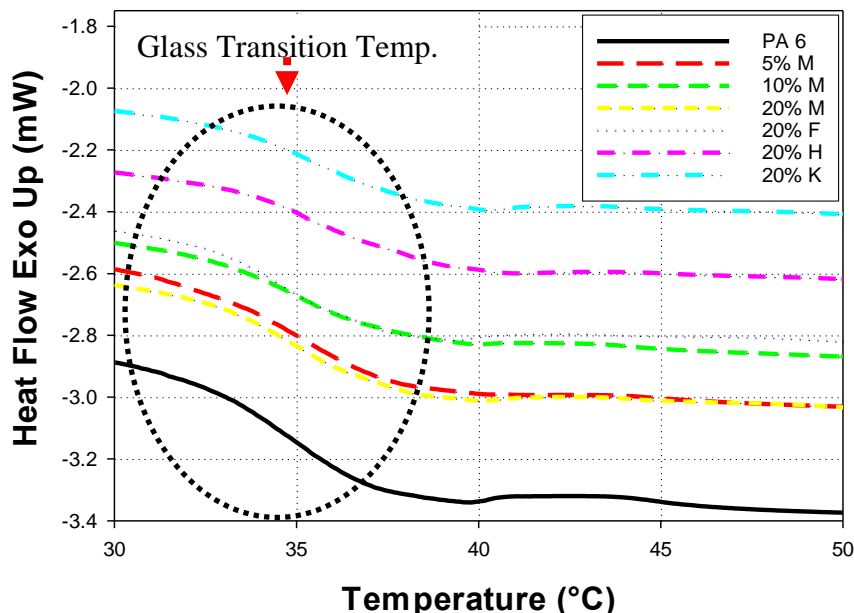


Fig. 1. Glass transition temperatures (T_g) from DSC for neat PA and PA 6-based NFCs

The crystallization temperatures of neat PA 6 and PA 6-based NFCs are shown in Table 2. The T_c values of neat PA 194 °C and the PA 6-based NFCs were between 191 and 193 °C. Thus, the presence of natural fibers had little or no effect on the T_c of the PA 6-based NFCs. Table 2 also shows the T_m of neat PA6 and PA 6-based NFCs. The melting temperature of neat PA 6 was around 219 °C. For PA 6-based NFCs, the melting temperatures were between 216 and 218 °C, showing that the natural fibers had little effect on the T_m of the NFCs. The minor effect on the T_m can be explained with a small change in crystallite size in the presence of natural fibers (Cho and Paul 2001). Correlation among different natural fiber blend contents was not possible, and from a practical standpoint, this result suggests that the incorporation of natural fiber does not affect the T_m of the PA 6. Similar results were also reported by Kiziltas *et al.* (2011), Goitisoló *et al.* (2008), and Cho and Paul (2001) for PA6/filler composites. In addition, the enthalpies of crystallization, ΔH_c , of natural fiber blend-Nylon 6 composites decreased as the natural fiber content increased (Table 2). The addition of non-treated silica to PA 6 composites showed similar crystallization behavior, and this behavior is explained by the reduction in the molecular chain movement of the PA 6 through physical bonding or through confinement with the addition of natural fibers (Racz *et al.* 2004).

The crystallinity index (%) (X_c) of the neat PA 6 and PA 6-based NFCs is shown in Table 2. Increasing the natural fiber content slightly increased the crystallinity index at low loading levels of natural fiber blend from 5 to 20 wt.%. The incorporation of 20 wt.% kenaf fiber alone resulted in a considerable decrease in percent crystallinity, and the lower percent crystallinity was partially explained by the restriction of polymer chains (Fornes and Paul 2003). A similar effect was reported in clay-Nylon 6 composites (Wu *et al.* 2001; Fornes and Paul 2003).

Table 2. DSC Summary of T_m , T_c , ΔH_m , ΔH_c , and X_c for the neat PA6 and PA 6-NFCs (modified from Ozen *et al.* 2012)

Sample Name	T_m (°C)	T_c (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)
PA 6	218.8 (1.3)	193.9 (1.0)	79.8 (0.1)	79.7 (0.2)	42.0 (0.1)
5% M	217.7 (0.5)	192.5 (1.6)	76.1 (2.0)	77.7 (1.6)	42.1 (1.1)
10% M	216.6 (2.1)	190.7 (2.9)	69.6 (2.4)	71.8 (0.1)	40.7 (1.4)
20% M	217.6 (1.2)	193.0 (0.3)	64.9 (3.8)	65.2 (1.0)	42.7 (2.5)
20% F	217.8 (1.5)	193.2 (0.2)	64.3 (1.8)	67.4 (1.3)	42.3 (1.2)
20% H	216.5 (3.0)	192.4 (0.2)	64.9 (2.0)	64.5 (1.4)	42.7 (1.3)
20% K	216.1 (0.4)	193.0 (0.1)	57.3 (3.3)	66.1 (1.5)	37.7 (2.8)

Parenthesis indicates standard deviation

The variation in storage modulus (E') and loss factor ($\tan \delta$) for neat PA6 and PA 6-based NFCs is shown in Fig. 2. The increase of E' with increasing cellulose content was most significant within the glassy region (< 20 °C) where the E' remained almost constant. The glass transition region of the nylon phase was partially responsible for the decrease in E' around 30 °C. The magnitude of the decrease in E' was small, which was related to the high degree of crystallinity of Nylon 6. The E' curves at higher temperatures beyond the glassy region (> 35 °C) showed a significant drop in E' because of the decreased viscosity and higher polymer chain mobility (Kim *et al.* 2005; Kim *et al.* 2006; Petersson *et al.* 2007). The decrease in the E' curves continued until reaching the rubbery plateau, and then the E' curves leveled out. The PA 6-based NFCs showed a similar viscoelastic behavior and had a higher modulus over the entire temperature span compared with neat PA 6, and this increase in the modulus was explained by reinforcing effect of natural fibers. Similar results have been reported for PA 6-clay nanocomposites (Xie *et al.* 2005; Miri *et al.* 2008). Furthermore, 20 wt.% natural fiber incorporated into the PA 6 exhibited greater temperature stability than the neat polymer in the rubbery region. In the $\tan \delta$ curves as a function of temperature (Fig. 2a), the presence of natural fibers slightly changed the glass transition temperature of the PA 6 based-NFCs. Moreover, there was not a clear shift in the peak of the $\tan \delta$ max. The reinforcing effect is likely attributable to natural fibers networks and/or strong interactions between natural fibers in the PA 6 matrix (Kim *et al.* 2005, 2006; Seydibeyoglu and Oksman 2008). The temperature range from -40 to 125 °C is critical for under-the-hood applications of NFCs in the automotive industry, especially at higher concentrations, which exhibited higher E' over the entire temperature range (Fig. 2a). The E' value of the natural fiber blend-filled Nylon 6 composites was enhanced as the natural fiber content increased at both room (20 °C) and glass transition temperatures (Fig. 3). The highest E' was seen in the case of 20 wt.% natural fiber blend content. This result was attributed to improved stress transfer at the fiber interface, which leads to an increased modulus with the incorporation of natural fiber blend compared to the neat polymer. The E' of DMTA increased as the natural fiber content increased. The E' values at room temperature and T_g were 3960 MPa and 1800 MPa, respectively, with the incorporation 20 wt.% natural fiber blend, which were 68% and 193% higher than the E' of neat PA 6.

The influence of the natural fiber incorporation on the glass transition temperature (T_g), as obtained by the peak position of the loss factor ($\tan \delta$ max), is shown in Fig. 4. The neat PA 6 had a $\tan \delta$ max peak temperature of about 58 °C; for the PA 6-based NFCs, this value was between 51 and 63 °C. The most pronounced effect of the fiber had been the shifting T_g to higher temperature with the presence of the 20 wt.% mixture of natural fibers. The shifting of T_g to higher temperature can be explained by the decreasing mobility of the

PA 6 chains attributable to mixing of natural fibers (Huda *et al.* 2008). The $\tan \delta$ max peak height values of the PA 6-based NFCs decreased (from 0.19 for PA 6 to 0.12 for the 20 wt.% NFCs) as the natural fiber content increased at around the glass transition temperature, potentially because the incorporation of natural fibers restricted the polymer melt mobility (Xie *et al.* 2005; Kim *et al.* 2006; Chow and Mohd Ishak 2007), which leads to reduced damping of the composite material.

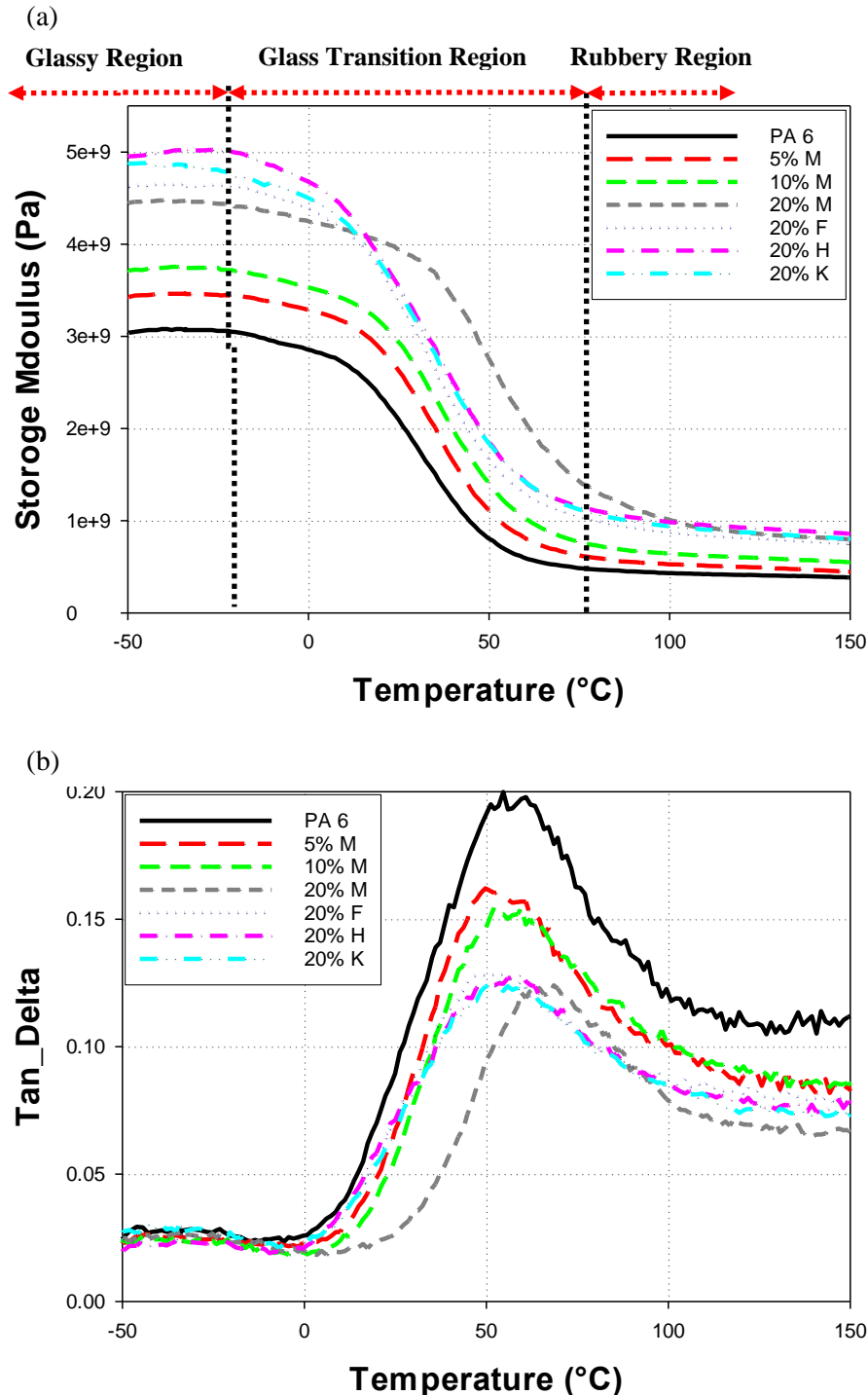


Fig. 2. Storage modulus (a) and $\tan \delta$ (b) of neat PA 6 and PA 6-based NFCs

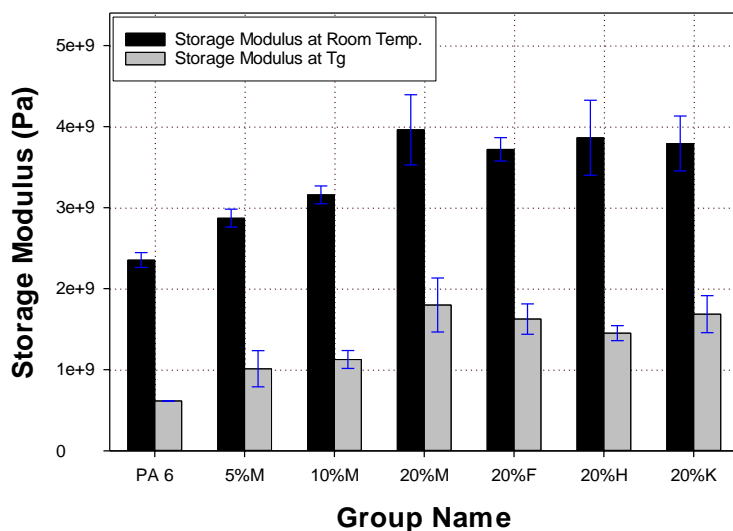


Fig. 3. Storage modulus at room temperature and glass transition temperature of neat PA 6 and PA 6-based NFCs

There was not a good correlation between T_g obtained from DSC and DMTA (Fig. 4). The T_g obtained by DMTA and loss factor (\tan_{Δ}) measurements was up to 20 °C higher than those calculated by DSC measurements. However, a 10 to 20 °C difference from DSC measurements is also seen in many different materials (Wunderlich 2005). The T_g from DMTA exhibited different effects in comparison with T_g from DSC because of the oscillating frequency effect in the DMTA. It is believed that the frequency effect changed molecular relaxations of polymer chains and provided different T_g behavior (Karsli and Aytac 2013).

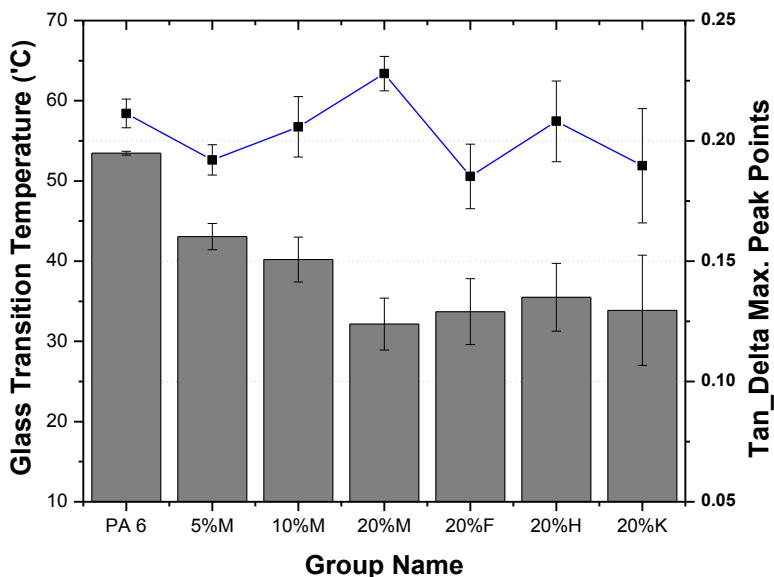


Fig. 4. The tan delta max peak (glass transition) temperatures (blue line) and peak height values (gray bars) of neat PA 6 and PA 6-based NFCs

Thermogravimetric analysis (TGA) provides a useful method of determining the thermal stability of the natural fibers during the heating process based on mass change; therefore, it is important that natural fibers show considerable thermal stability at high temperature (220 °C) at least for a few minutes. Figure 5(a) shows the characteristic thermal behavior data of the natural fiber blend, single-type fibers, and PA 6-based NFCs in an inert TGA atmosphere. Three stages of mass loss were observed for all natural fibers, including single fibers and natural fiber blend. The initial stage extended up to 120 °C and corresponded to the evaporation of moisture, free water, *etc.* The second occurred between 270 and 290 °C during the thermal depolymerization or decomposition of hemicelluloses. Cellulose decomposes in the range of 350 to 375 °C, which corresponds to the third weight loss stage (Monteiro *et al.* 2012; Ozen *et al.* 2013). The TGA curves of natural fiber blend-filled Nylon 6 composites were also divided into three regions. In the first region, the initial weight loss of less than 7 wt.% was below 200 °C, and the second region showed 70 wt.% loss up to 500 °C. The third region extends to 600 °C and corresponded to >75 wt.% loss. Thus, the degradation temperatures of neat polymer and natural fiber blend-Nylon 6 composites were different. From the published literature, nylon 6 showed a single-stage degradation at 452 °C, while natural fiber blend-Nylon 6 composites showed two degradation stages between 372 and 450 °C (Kiziltas *et al.* 2011). As the natural fiber content increased, the thermal stability of the PA 6-based NFCs decreased slightly. It was concluded that natural fibers have lower rapid thermal degradation onset temperatures compared with Nylon 6 composites because of the higher onset temperature of PA 6. The results in Fig. 5(b) confirmed that as the fiber content increased, the main DTG peak shifted to a lower temperature for PA 6-based NFCs.

In contrast, the final ash contents (residual weight at the end of TGA measurement) of the composite samples were proportionally increased from around 2 (neat PA 6) to 9% (20 wt.% natural fiber blend content) as the natural fiber content increased (Table 3), which indicated that even if rapid thermal degradation onset occurred earlier, the composite materials became more resistant in extreme environments as their natural fiber content increased. The temperatures at 10% weight loss (T_{10}) and 50% weight loss (T_{50}) for the natural fibers, neat PA 6 and the PA 6-based NFCs composites are shown in Table 3.

Table 3. T_{10} , T_{50} , and Ash Content at 600 °C for the Neat PA6 and PA 6-NFCs from TGA Curve

Sample Name	Temperature at 10% Mass Loss (°C)	Temperature at 50% Mass Loss (°C)	Ash Content at 600 °C (%)
M	279.4 (0.7)	357.9 (0.5)	18.5 (0.3)
F	269.2 (2.9)	355.9 (0.8)	22.4 (0.6)
H	285.0 (1.9)	357.8 (1.1)	17.2 (1.6)
K	281.2 (1.8)	360.7 (0.5)	20.8 (0.4)
PA 6	399.6 (1.2)	437.3 (3.0)	1.7 (0.3)
5% M	377.0 (1.0)	431.0 (1.0)	2.8 (0.1)
10% M	362.1 (1.9)	421.8 (3.8)	4.3 (0.1)
20% M	348.5 (1.9)	420.9 (2.5)	8.7 (1.0)
20% F	341.1 (2.0)	416.0 (1.3)	7.8 (0.4)
20% H	349.7 (0.8)	416.0 (3.1)	7.3 (0.1)
20% K	346.1 (2.7)	417.2 (2.5)	8.2 (0.1)

Parenthesis indicates standard deviation

Both T_{10} and T_{50} values for the PA 6-based NFCs composites decreased from neat PA (400 and 437 for T_{10} and T_{50} , respectively) to addition of a 20 wt.% natural fiber blend (348 and 421 for T_{10} and T_{50} , respectively). The decrease in the T_{10} and T_{50} values in PA 6-based NFCs reflected the higher thermal stability of PA 6 compared with natural fibers.

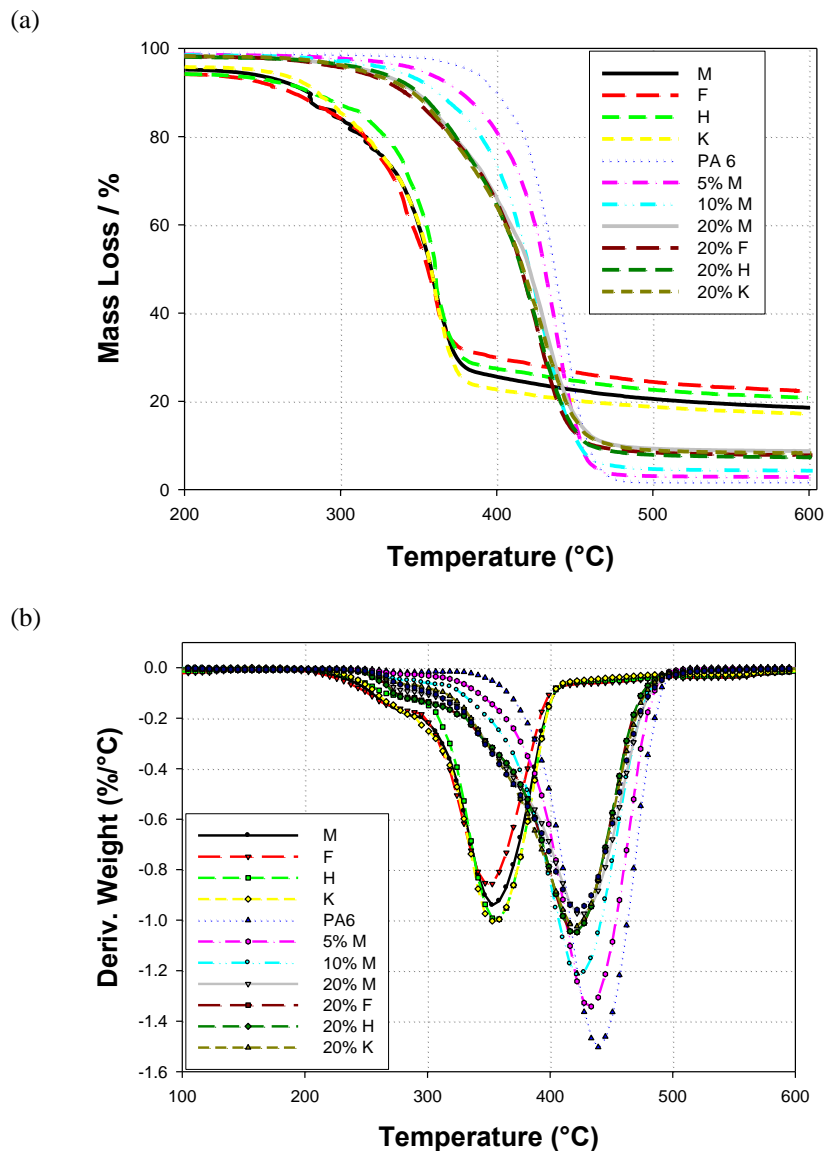


Fig. 5. TGA (a) and derivative TGA (b) curves of natural fibers, neat PA 6 and PA 6-based NFCs

CONCLUSIONS

1. No significant differences were observed in the T_g , T_m , and T_c temperatures of the PA 6-based NFCs composites as the natural fiber blend content increased.
2. As the natural fiber blend content increased, the E' value of the PA 6-based NFCs increased, and the highest E' was observed in the case of 20 wt.% natural fiber blend content.

3. The $\tan \delta_{\max}$ peak temperatures from DMTA were not significantly shifted as the natural fiber blend content increased, while $\tan \delta_{\max}$ peak values decreased from 0.19 for PA 6 to and 0.12 for 20 wt.% natural fiber blend-filled PA 6 composites.
4. As the natural fiber blend content increased, the thermal stability of the PA 6-based NFCs decreased; however, the residual weight increased from ~ 2% for the neat polymer to 9% for addition of 20 wt.% natural fiber.
5. Incorporation of a 20 wt.% natural fiber blend showed comparable DSC and TGA results to the addition of 20 wt.% single type fibers.
6. Higher E' from sub-ambient temperatures to 125 °C and thermal stability until 275 °C from TGA curves suggested that PA 6-based NFCs are superior for critical under-the-hood applications in the automotive industry.

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REFERENCES CITED

- de Arcaya, P. A., Retegi, A., Arbelaiz, A., Kenny, J. M., and Mondragon, I. (2009). "Mechanical properties of natural fibers/polyamides composites," *Polym. Composite*. 30(3), 257-264. DOI: 10.1002/pc.20558
- Arsad, A., Suradi, N. L., Rahmat, A. R., and Danlami, J. M. (2013). "The influence of kenaf fiber as reinforcement on recycled polypropylene/recycled polyamide-6 composites," *IJPT* 17(2), 149-162. DOI: 10.1007/s12588-013-9055-7
- Birch, A., Dal Castel C., Kiziltas, A., Mielewski, D., and Simon, L. (2015). "Development of cost effective and sustainable polyamide blends for automotive applications," in: *SPE Automotive Composites Conference & Exhibition*, Troy, MI, USA, pp. 1-10.
- Cho, J. W., and Paul, D. R. (2001). "Nylon 6 nanocomposites by melt compounding," *Polymer* 42(3), 1083-1094. DOI: 10.1016/S0032-3861(00)00380-3
- Chow, W. S., and Mohd Ishak, Z. A. (2007). "Mechanical, morphological and rheological properties of polyamide 6/organo-montmorillonite nanocomposites," *Express. Polym. Lett.* 1(2), 77-83. DOI: 10.3144/expresspolymlett.com
- Fornes, T. D., and Paul, D. R. (2003). "Crystallization behavior of Nylon 6 nanocomposites," *Polymer* 44(14), 3945-3961. DOI: 10.1016/S0032-3861(03)00344-6
- Goitisoló, I., Eguiazabal, J. I., and Nazabal, J. (2008). "Effects of reprocessing on the structure and properties of polyamide 6 nanocomposites," *Polym. Degrad. Stabil.* 93(10), 1747-1752. DOI:10.1016/j.polymdegradstab.2008.07.030

- Graff, G. (2005). "Under-hood applications of nylon accelerate," (<http://www.omnexus.com/resources/articles/article.aspx?id=9660>), Accessed 22 February 2016.
- Huda, M. S., Drzal, L. T., Ray, D., Mohanty, A. K., and Mishra, M. (2008). "Natural-fiber composites in the automotive sector," in: *Properties and Performance of Natural-Fibre Composites*, K.L. Pickering (Ed.), CRC Press LLC, Boca Raton, FL, USA, pp. 221-261.
- Joshi, S. V., Drzal, L. T., Mohanty, A. K., and Arora, S. (2004). "Are natural fiber composites environmentally superior to glass fiber reinforced composites?" *Compos. Part. A-Appl. S.* 35(3), 371-376. DOI: 10.1016/j.compositesa.2003.09.016
- Karsli, N. G., and Aytac, A. (2013). "Tensile and thermomechanical properties of short carbon fiber reinforced polyamide 6 composites," *Compos. Part. B. Eng.* 51, 270-275. DOI:10.1016/j.compositesb.2013.03.023
- Kim, H. S., Yang, H. S., Kim, H. J., Lee, B. J., and Hwang, T. S. (2005). "Thermal properties of agro-flour-filled biodegradable polymer bio-composites," *J. Therm. Anal. Calorim.* 81(2), 299-306. DOI: 1388-6150/S20.00
- Kim, H. S., Kim, S., Kim, H. J., and Yang, H. S. (2006). "Thermal properties of bio-flour-filled polyolefin composites with different compatibilizing agent type and content," *Thermochim. Acta* 451(2), 181-188. DOI: 10.1016/j.tca.2006.009.013
- Kiziltas, A., Gardner, D. J., Han, Y., and Yang, H. S. (2010). "Thermal properties of microcrystalline cellulose-filled PET-PTT blend polymer composites," *J. Therm. Anal. Calorim.* 103(1), 163-170. DOI: 10.1007/s10973-010-0894-6
- Kiziltas, A., Gardner, D. J., Han, Y., and Yang, H. S. (2011). "Dynamic mechanical behavior and thermal properties of microcrystalline cellulose (MCC)-filled nylon 6 composites," *Thermochim. Acta* 519(1-2), 38-43. DOI: 10.1016/j.tca.2011.02.26
- Leao, A. L., Rowell, R., and Tavares, N. (1998). "Applications of natural fibers in automotive industry in Brazil-thermoforming process," in: *Science and Technology of Polymers and Advanced Materials: Emerging Technologies and Business Opportunities*, Prasad, P. N., Mark, J. E., Kandil, S. H., and Kafafi, Z. H. (eds.), Plenum Press, New York, NY, USA, pp. 763-781.
- Lucintel. (2015). *Global Natural Fiber Composite Market 2015-2020: Trends, Forecast, and Opportunity Analysis*, Lucintel LLC, Irving, TX, USA, (http://www.lucintel.com/reports/chemical_composites/global_natural_fiber_composite_market_2015_2020_trends_forecast_and_opportunity_analysis_december_2015.aspx).
- MacDermont, C. P., and Shenoy, A. V. (1997). *Selecting Thermoplastics for Engineering Applications* (2nd Ed.), CRC Press, Boca Raton, FL, USA.
- Miri, V., Elkoun, S., Peurton, F., Vanmansart, C., Lefebvre, J. M., Krawczak, P., and Seguel, R. (2008). "Crystallization kinetics and crystal structure of nylon6-clay nanocomposites: Combined effects of thermomechanical history, clay content, and cooling conditions," *Macromolecules* 41(23), 9234-9244. DOI: 10.1021/ma801804y
- Monteiro, S. N., Calado, V., Rodriguez, R. J. S., and Margem, F. M. (2012). "Thermogravimetric behavior of natural fibers reinforced polymer composites – An overview," *Mater. Sci. Eng: A* 557, 17-28. DOI: 10.1016/j.msea.2012.05.109
- Njuguna, J., Wambua, P., Pielichowski, K., and Kayvantash, K. (2011). "Natural fibre-reinforced polymer composites and nanocomposites for automotive applications," in: *Cellulose Fibers: Bio- and Nano-Polymer Composites*, Kalia, S., Kaith, B. S., and Kaur, I. (eds.), Springer, New York, NY, USA, pp. 661-700.

- Ozen, E., Kiziltas, A., Erbas Kiziltas, E., and Gardner, D. J. (2012). "Natural fiber blends-filled engineering thermoplastic composites for the automobile industry," in: *SPE Automotive Composites Conference & Exhibition*, Troy, MI, USA, pp. 1-12.
- Ozen, E., Kiziltas, A., Erbas Kiziltas, E., and Gardner, D. J. (2013). "Natural fiber blend—nylon 6 composites," *Polym. Composite*. 34(4), 544-553. DOI: 10.1002/pc.22463
- Petersson, L., Kvien, I., and Oksman, K. (2007). "Structure and thermal properties of poly(lactic acid)/cellulose whiskers nanocomposite materials," *Compos. Sci. Technol.* 67(11-12), 2535-2544. DOI: 10.1016/j.compscitech.2006.12.012
- Racz, L., Jr, B. P., Pozsgay, A., and Pukanszky, B. (2004). "Polyamide 6/montmorillonite nanocomposites: Effect of interaction on structure and properties," *Prog. Coll. Pol. Sci.* 125, 96-102. DOI: 10.1007/b13929
- Santos, P. A., Spinace, M. A. S., Feroselli, K. K. G., and De Paoli, M. A. (2007) "Polyamide-6/vegetal fiber composite prepared by extrusion and injection molding," *Compos. Part. A-Appl. S.* 38(12), 2404-2411. DOI: 10.1016/j.compositesa.2007.08.011
- Santos, P. A., Giriolli, J. C., Amarasekera, J., and Moraes, G. (2008). "Natural fibers plastic composites in automotive applications," in: *SPE Automotive Composites Conference & Exhibition*, Troy, MI, USA, pp. 1-9.
- Seydibeyoglu, M. O., and Oksman, K. (2008). "Novel nanocomposites based on polyurethane and micro fibrillated cellulose," *Compos. Sci. Technol.* 68(3-4), 908-914. DOI: 10.1016/j.compscitech.2007.08.008
- Sherman, L. (1999). "Natural fibers: The new fashion in automotive plastics," *Plastics Technology* (October 1999), (<http://www.ptonline.com/articles/natural-fibers-the-new-fashion-in-automotive-plastics>).
- Tajvidi, M., and Feizmand, M. (2009). "Effect of cellulose fiber reinforcement on the temperature dependent mechanical performance of nylon 6," *J. Reinf. Plast. Comp.* 28(22), 2781-2790. DOI: 10.1177/0731684408093875
- Vedoy, D. R. L. (2012). *Development of Methodologies for Improving Thermal Stability of Plant Fibers for Application in Thermoplastic Composites*, Ph.D. Dissertation, University of Waterloo, Waterloo, ON, Canada.
- Wu, Q., Liu, X., and Berglund, L. A. (2001). "An unusual crystallization behavior in polyamide 6/montmorillonite nanocomposites," *Macromol. Rapid Comm.* 22(17), 1438-1440. DOI: 10.1002/1521-3927(20011101)22:17<1438::AID-MARC1438>3.0.CO;2-U
- Wunderlich, B. (2005). *Thermal Analysis of Polymeric Materials*, Springer, New York, NY, USA, pp. 609-610.
- Xie, S., Zhang, S., Wang, F., Liu, H., and Yang, M. (2005). "Influence of annealing treatment on the heat distortion temperature of nylon-6/montmorillonite nanocomposites," *Polym. Eng. Sci.* 45(9), 1247-1253. DOI: 10.1002/pen.20359
- Zhao, D., and Zhou, Z. (2014). "Applications of lightweight composites in automotive industries," in: *Lightweight Materials from Biopolymers and Biofibers*, H. Xu, X. Yu, and Y. Yang, (Eds.), American Chemical Society, Washington, D. C., USA.

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