Thermal Analysis of Polyamide 6 Composites Filled by Natural Fiber Blend

Esra Erbas Kiziltas, a,b,* Han-Seung Yang, c Alper Kiziltas, a,d Sevda Boran, a,e Ertan Ozen, a,d and Douglas J. Gardner a

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 (CAFÉ) 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 automobiles, 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 δ), Tg, Tm, and Tc 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’ T_g was calculated according to the following equation,

\[ T_g = \frac{\Delta H_f \times 100}{\Delta H_{f0} \times \omega} \]  

where \( \Delta H_f \) is the heat of fusion of the PA 6 and PA 6-based NFCs, \( \Delta H_{f0} \) the heat of fusion for 100% crystalline PA 6 (\( \Delta H_{f0} = 190 \) J/g), and \( \omega \) 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

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>PA 6 (wt.%)</th>
<th>Flax (wt.%)</th>
<th>Hemp (wt.%)</th>
<th>Kenaf (wt.%)</th>
<th>NFB (wt.%)</th>
<th>Lubricant (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 6</td>
<td>97</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>5% M</td>
<td>92</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>10% M</td>
<td>87</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>20% M</td>
<td>77</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>20% F</td>
<td>77</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>20% H</td>
<td>77</td>
<td>-</td>
<td>20</td>
<td>-</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>20% K</td>
<td>77</td>
<td>-</td>
<td>-</td>
<td>20</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

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).
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), Goitisolo et al. (2008), and Cho and Paul (2001) for PA6/filler composites. In addition, the enthalpies of crystallization, $\Delta H_c$, 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).

**Fig. 1.** Glass transition temperatures ($T_g$) from DSC for neat PA and PA 6-based NFCs
The shifting of $T_g$ was between 51 and 63 °C. neat PA 6 had a tan $\delta$ value of 20 wt.% natural fiber blend, which were 68% and 193% higher than the modulus with the incorporation of natural fiber blend compared to the neat polymer. The increase in the modulus was explained by the decreasing mobility of the polymer chain. 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 δ 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 δ max), is shown in Fig. 4. The neat PA 6 had a tan δ 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

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA 6</td>
<td>218.8 (1.3)</td>
<td>193.9 (1.0)</td>
<td>79.8 (0.1)</td>
<td>79.7 (0.2)</td>
<td>42.0 (0.1)</td>
</tr>
<tr>
<td>5% M</td>
<td>217.7 (0.5)</td>
<td>192.5 (1.6)</td>
<td>76.1 (2.0)</td>
<td>77.7 (1.6)</td>
<td>42.1 (1.1)</td>
</tr>
<tr>
<td>10% M</td>
<td>216.6 (2.1)</td>
<td>190.7 (2.9)</td>
<td>69.6 (2.4)</td>
<td>71.8 (0.1)</td>
<td>40.7 (1.4)</td>
</tr>
<tr>
<td>20% M</td>
<td>216.7 (1.2)</td>
<td>193.0 (0.3)</td>
<td>64.9 (3.8)</td>
<td>65.2 (1.0)</td>
<td>42.7 (2.5)</td>
</tr>
<tr>
<td>20% F</td>
<td>217.8 (1.5)</td>
<td>193.2 (0.2)</td>
<td>64.3 (1.8)</td>
<td>67.4 (1.3)</td>
<td>42.3 (1.2)</td>
</tr>
<tr>
<td>20% H</td>
<td>216.5 (3.0)</td>
<td>192.4 (0.2)</td>
<td>64.9 (2.0)</td>
<td>64.5 (1.4)</td>
<td>42.7 (1.3)</td>
</tr>
<tr>
<td>20% K</td>
<td>216.1 (0.4)</td>
<td>193.0 (0.1)</td>
<td>57.3 (3.3)</td>
<td>66.1 (1.5)</td>
<td>37.7 (2.8)</td>
</tr>
</tbody>
</table>

Parenthesis indicates standard deviation

Table 2. DSC Summary of $T_m$, $T_c$, $\Delta H_m$, $\Delta H_c$, and $X_c$ for the neat PA6 and PA 6-NFCs (modified from Ozen et al. 2012)
PA 6 chains attributable to mixing of natural fibers (Huda et al. 2008). The tan δ 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
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_delta) 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. 3.** Storage modulus at room temperature and glass transition temperature of neat PA 6 and PA 6-based NFCs

**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

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

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.

![Graph](https://example.com/graph.png)

**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 δ\textsubscript{max} peak temperatures from DMTA were not significantly shifted as the natural fiber blend content increased, while tan δ\textsubscript{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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