



## Dynamic mechanical behavior and thermal properties of microcrystalline cellulose (MCC)-filled nylon 6 composites

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### ABSTRACT

The dynamic mechanical behavior and thermal properties of nylon 6 composites containing from 2.5 wt.% to 30 wt.% MCC were investigated using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). The DSC results indicated that there was no consistent or significant change in the glass transition ( $T_g$ ), melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) of the composites with the addition of MCC. The DSC results also indicated that the crystallinity ( $X_c$ ) decreased with high MCC loading level (more than 20 wt.%) because of the inability of polymers chains to be fully incorporated into growing crystallinity lamella. With increasing MCC content, storage modulus from DMTA improved because of the reinforcing effect of the MCC. The  $\tan \delta$  peak values from DMTA were not significantly changed as the MCC content increased. DMTA also indicates that the magnitude of the  $\tan \delta$  maximum peak of MCC filled composites was significantly decreased around the glass transition temperature. Thermogravimetric analysis also indicated that the MCC did not show significant initial degradation under 300 °C, which implies thermal stability so that MCC-filled composites could be used for high temperature circumstances, like in “under the hood” applications in the automobile industry.

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### 1. Introduction

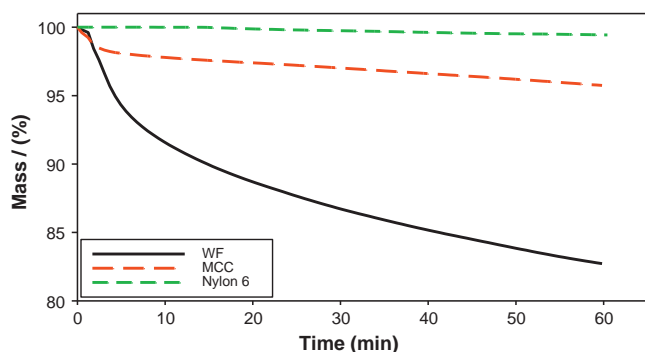
Over the past several decades, interest in the development of new composite materials derived from wood fiber and thermoplastic polymer matrices has received remarkable attention in the marketplace. Wood fiber filled thermoplastic composites are lightweight, low cost, offer high strength to weight ratios, less abrasive to processing equipment than mineral and glass fillers and can be recycled [1,2]. In spite of these attractive properties, the processing temperature of these composites is restricted to about 200 °C because the hemicellulose component of wood fibers degrade above 180 °C and the melting temperature of selected plastics should not be over 200 °C, which restricts the use of engineering thermoplastics such as nylon and polyethylene terephthalate [1–6]. Thermogravimetric analysis studies of wood component polymers show that the purified cellulosic component of is thermally more stable than other wood component polymers [1–6]. Because of greater thermal stability compared to wood fibers,

microcrystalline cellulose could be used with engineering thermoplastics. Fig. 1 shows that MCC is thermally more stable and has less mass loss in comparison with similar sized wood flour at 250 °C.

Natural and synthetic polymers are exposed to thermal degradation reactions under the effect of increased temperatures [7]. Because of the high processing temperatures of engineering thermoplastics, cellulose might be degraded and its mechanical properties decreased during melt processing. Therefore, it is extremely important to have information about the impact of processing temperatures during the manufacturing of cellulose reinforced composite materials with engineering thermoplastic matrices [7]. Essential statements regarding the processing temperatures and thermal stability of natural and synthetic polymers are obtained from thermal analysis techniques including dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These techniques measure the thermal behaviors and interfacial characteristics of composite materials as a function of temperature [8–11]. DMTA has been used extensively and is an important technique in terms of determining the viscoelastic properties of composite materials as a function of temperature. DSC which can be used to determine melting temperature ( $T_m$ ), glass transition temperature ( $T_g$ ), crystallization temperature ( $T_c$ ) and crystallinity

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**Fig. 1.** Mass change in % vs. time of MCC, wood flour and nylon 6 by isothermal TGA at 250 °C.

( $X_c$ ) of composite materials, is a widely used thermal analysis technique. TGA can be used to determine the moisture content, mass change, thermal degradation temperature and thermal stability of composite materials [9–11].

MCC is a naturally occurring substance obtained from purified, partially depolymerised cellulose, prepared by treating alpha-cellulose, obtained as a pulp from fibrous material with mineral acids and it is used extensively in the pharmaceutical, food, paper and composite manufacturing industries [3]. According to TGA results, MCC is thermally stable until 300 °C which is much higher than melting temperature of nylon 6 (223 °C). Today, MCC is also commercially available and price of MCC ( $\approx$ \$4/kg from J. Rettenmaier & Sohne (JRS), Germany) comparable or less than some other engineering should be fillers. (aramid and glass). MCC filled polyethylene and polystyrene polymer composites have been studied [12–15]. However there is lack of information about MCC filled engineering thermoplastics. Aliphatic polyamides are well known engineering plastics in industry [16]. Nylon 6 is in a major class of aliphatic polyamides and has several advantages including good chemical resistance, good abrasion resistance, and good mechanical and thermal properties [17]. Because of these advantages, nylon 6 is widely used in many areas such as automobile, construction markets and textile industries [17]. A variety of inorganic materials such as clay minerals, glass fiber, talc and kaolin have been used in nylon 6 composites [18,19]. The automobile and construction markets also need high specific strength and modulus, low density and inexpensive reinforcements for engineering thermoplastics. Because of the high specific strength and modulus, low density and thermally stable structure of MCC, it could be a good candidate as reinforcement for engineering thermoplastics. In spite of the technological interest in nylon 6, only a few studies of nylon 6/cellulose polymer composites have been published [4–6]. Most were concerned with mechanical properties and there is not enough information related to thermal properties of nylon 6/cellulose composites in the literature.

The objective of this study was to investigate the effect of microcrystalline cellulose on the dynamic thermomechanical behavior and thermal properties of an engineering thermoplastic, nylon 6, composites with melting point over the 220 °C. Microcrystalline cellulose was incorporated over a content range from 0 to 30 wt.%.

Analyses were conducted using thermal tests including DMTA, DSC, and TGA. The thermal stability, DTGmax, viscoelastic behavior (storage modulus and  $\tan(\delta)$ )  $T_m$ ,  $T_g$ ,  $T_c$  and  $X_c$  of the neat nylon 6 and composites were compared. In the present study, nylon based composites were prepared with microcrystalline cellulose as the filler phase by injection molding.

## 2. Experimental procedure

### 2.1. Materials

The nylon 6 used as the thermoplastic matrix polymer, was supplied by Entec Co., USA. Nylon 6 has a density of 1.13 g/cm<sup>3</sup> and has a mold shrinkage of 0.015 in./in. The MCC used as the reinforcement was a powder with a particle size range from 26  $\mu$ m to 96  $\mu$ m. The average particle size was 50  $\mu$ m. The MCC is highly crystalline cellulose supplied by Sigma–Aldrich Co. The MCC was stored in sealed containers after being oven dried for at least 16 h at 105 °C to obtain low moisture content which is less than 1%. The lubricant (TPW 113) used as an additive to improve processing conditions, was supplied by Struktol Co.

### 2.2. Sample preparation

The MCC and nylon 6 were dried to moisture content less than 1% using an oven at 105 °C for 16-h. The matrix polymer, nylon 6, was mixed with the MCC. The compounding was conducted using a Brabender Prep-mixer<sup>®</sup> equipped with a bowl mixer and the process temperature and torque changes were measured in real time. Melt temperature and torque changes for every run were recorded to determine optimum processability for the nylon 6–MCC composites. The basic processing parameters are listed in Table 1. The temperature was set to 250 °C and rotor speed at 60 rpm. MCC was added to the mixer when the polymer melt appeared well mixed. After addition of the MCC, the melt temperature dropped sharply to 200 °C and increased again as the mixing progressed. The melt mixture was released from the mixture immediately after the temperature reached 230 °C. These temperature ranges and MCC residence times, approximately 3 min, were recognized as a relatively safe temperature range to prevent severe thermal degradation with a guarantee of composite processability. The nylon 6–MCC compounds were granulated using a lab scale grinder. The ground particles were dried at an oven at 105 °C for 16 h before being injection molding into ASTM test specimens. All materials were injection molded using a barrel temperature of 250 °C mold temperature of 250 °C injection pressure of 2500 psi. The compositions of composites are shown in Table 2.

### 2.3. Statistical analysis

The relative crystallinity, melting and crystallization enthalpy and melting, glass transition, and crystallization temperature data were compared using a one-way analysis of variance followed by Tukey–Kramer Honestly Significant Differences (HSD) test with JMP statistical analysis program [20].

**Table 1**

Basic operating parameters of the Brabender Rheomixer for the nylon 6 and MCC-filled-nylon 6 composites.

Stage level set	Temp.	Melt temp.	RPM	Mix melt temp.	Reaction time
1st stage (nylon 6)	250	240	60–70	–	7 min
2nd stage (with MCC)	230	200 240	50	Cont. under 240	3 min

Temperature values are °C.

**Table 2**  
Composition of the MCC-filled nylon 6 composites.

Sample code	MCC content	Nylon 6	Lubricant
Neat nylon 6	0	95	5
Nylon 6–MCC 2.5	2.5	92.5	5
Nylon 6–MCC 10	10	85	5
Nylon 6–MCC 20	20	75	5
Nylon 6–MCC 30	30	65	5

Values are percentage by weight (wt.%).

## 2.4. Thermal properties

### 2.4.1. Differential scanning calorimetry (DSC)

DSC analysis was carried out using a PerkinElmer Instrument Pyris DSC with a sample weight of 8–10 mg. All samples were held at 5 °C for 5 min, heated at a rate of 5 °C/min to 250 °C, subsequently held for 5 min to erase thermal history, then cooled at a rate of 5 °C/min to –10 °C, subsequently held for 5 min and heated again at a rate of 5 °C/min to 250 °C under a nitrogen atmosphere.  $T_m$  and  $T_g$  were determined from a second scan. The  $T_m$  was taken as the peak temperature of the melting endotherm. The  $T_g$  was taken as the inflection point of the specific heat increment at the glass–rubber transition. The specimens'  $X_c$  was calculated according to the following equation [21].

$$X_c = \frac{\Delta H_f \times 100}{\Delta H_f^\circ \times \omega}$$

where  $\Delta H_f$  is the heat of fusion of the nylon blend and composites,  $\Delta H_f^\circ$  the heat of fusion for 100% crystalline nylon 6 ( $\Delta H_{100} = 190$  J/g) and  $\omega$  is the mass fraction for nylon 6 in the composites [22]. At least five randomly picked specimens from ground samples were tested for each composition, and the results are presented as an average for tested samples.

### 2.4.2. Dynamic mechanical thermal analysis (DMTA)

The viscoelastic properties of the composites were determined with a Rheometric Scientific DMTA IV. The experiments were conducted in three point bending mode under isochronal conditions at a frequency of 1 Hz. The strain amplitude was fixed at 0.01% to be in the domain of the linear viscoelasticity of the composites. The samples were rectangular with dimensions about 42 mm × 3.2 mm × 3 mm. The temperature range was from 0 to 150 °C at a scanning rate of 5 °C/min. The storage modulus ( $E'$ ), loss modulus ( $E''$ ) and loss factor ( $\tan \delta$ ) of the samples were measured as a function of temperature. At least three specimens were tested for each composition, and the results are presented as an average for tested samples.

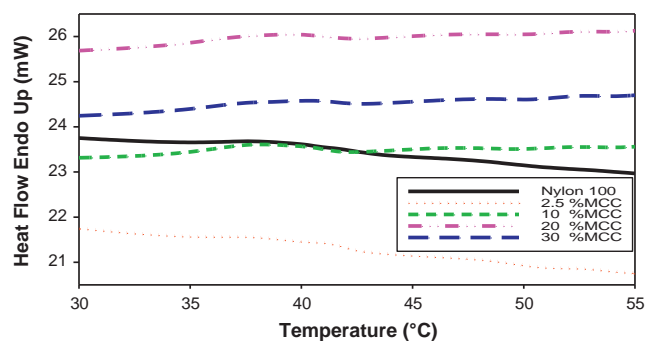
### 2.4.3. Thermogravimetric analysis (TGA)

TGA measurements were carried out using a Mettler Toledo analyzer on samples of about 10 mg. Each sample was scanned over a temperature range from room temperature to 500 °C at a heating rate of 10 °C/min under nitrogen with a flow rate 20 ml/min to avoid sample oxidation. The samples used for the TGA measurement were randomly picked 5 individual samples from ground samples.

## 3. Results and discussion

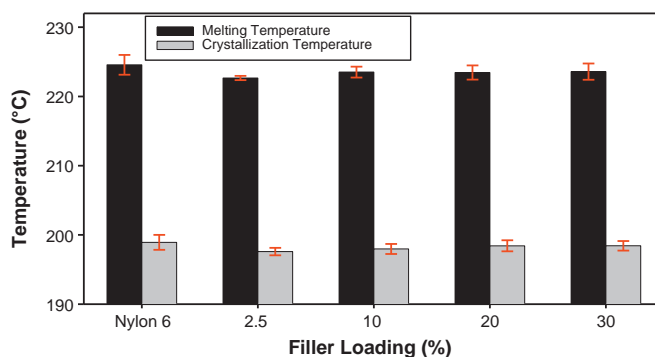
### 3.1. Differential scanning calorimetry (DSC)

The values of  $T_g$ ,  $T_m$ ,  $T_c$  and corresponding melting enthalpies ( $\Delta H_m$ ) and crystallization enthalpies ( $\Delta H_c$ ) are presented in Table 3. The DSC measurements indicate that the presence of MCC does not affect the  $T_g$  of the nylon 6 matrix, which occurs approximately at 42 °C in Fig. 2. A similar behavior was observed in glass



**Fig. 2.** Glass transition temperatures from DSC for nylon 6 and MCC-filled nylon 6 composites at different filler loadings.

fiber, montmorillonite and organoclay filled nylon 6 composites [19,23]. There are also small peaks at around 35 °C which is the effect of lubricant. Fig. 3 shows the crystallization temperature of neat nylon 6 and composites. The figure illustrates that adding MCC does not change the  $T_c$  of the composites or it has a slight effect at most. However, increasing the MCC content, in all cases, results in smaller heats of crystallization,  $\Delta H_c$  in Table 3. Similar phenomena were also observed for the addition of nontreated silica in nylon 6 composites [24]. The melting point was taken as the main peak of the endothermic curve. The melting point of neat nylon 6 is 225 °C. The effect of MCC on  $T_m$  of the composites is presented in Fig. 3. It can be seen for Fig. 3 that the melting points of composites are between 222 °C and 225 °C. The addition of the MCC to composite does not have significant influence on the  $T_m$  of the composites. From these results, it can be concluded that the  $T_g$  and  $T_m$  values of the composites were strongly influenced by the matrix polymer. Furthermore, the  $T_m$  of the composites plays an important role in determining their processing temperature and thermal properties [9,10]. The degree of crystallinity of composites was calculated using the heat of fusion determined from DSC measurements and the one corresponding to a 100% crystalline nylon reported by Wu et al. [22]. These values are reported in Table 3. For low loading levels of MCC up to 20 wt%, increasing the MCC content does not have significant change in percent crystallinity as seen in Table 3. For high loading contents above 20 wt%, increasing the MCC content results in a small decrease in percent crystallinity. It is believed that the decreased crystallinity with increasing MCC level results from the inability of polymer chains [16]. A similar effect was reported by Wu et al. [22], Fornes and Paul [16] for nylon 6/clay composites.



**Fig. 3.** The effect of MCC loading on the melting and crystallization temperatures for nylon 6 and MCC-filled nylon 6 composites from DSC.

**Table 3**DSC summary of  $T_g$ ,  $T_m$ ,  $T_c$ ,  $\Delta H_m$  (J/g),  $\Delta H_c$  (J/g), and  $X_c$  for the nylon 6 and MCC-filled nylon 6 composites.

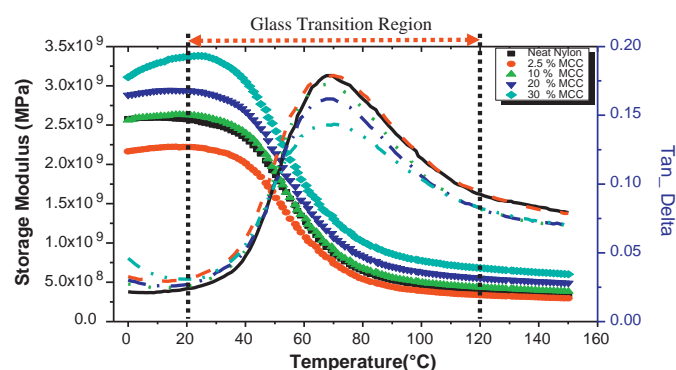
Sample code	$T_g$	$T_m$	$T_c$	$\Delta H_m$ (J/g)	$\Delta H_c$ (J/g)	$X_c$ (%)
Neat nylon 6	41.5 (0.9) A	224.6 (1.4) A	198.9 (0.8) A	50.2 (2.7) A	-63.7 (4.8) A	26.4 (1.4) A
Nylon 6–MCC 2.5	41.9 (0.2) A	222.7 (0.3) A	197.6 (0.4) A	46.1 (3.2) AB	-62.6 (3.4) AB	24.9 (1.7) A
Nylon 6–MCC 10	41.2 (1.4) A	223.5 (0.9) A	198.0 (0.3) A	42.9 (1.0) B	-57.5 (2.1) BC	25.1 (0.6) A
Nylon 6–MCC 20	41.3 (0.7) A	223.5 (1.0) A	198.4 (0.7) A	36.2 (3.7) C	-50.9 (2.6) C	23.8 (2.5) AB
Nylon 6–MCC 30	41.5 (0.4) A	223.6 (1.1) A	198.4 (0.4) A	27.4 (3.4) D	-40.4 (3.7) D	20.6 (2.5) B

Parentheses indicate standard deviation. Temperature values are °C. The same letters indicates no statistical difference between properties of composites and those around it.

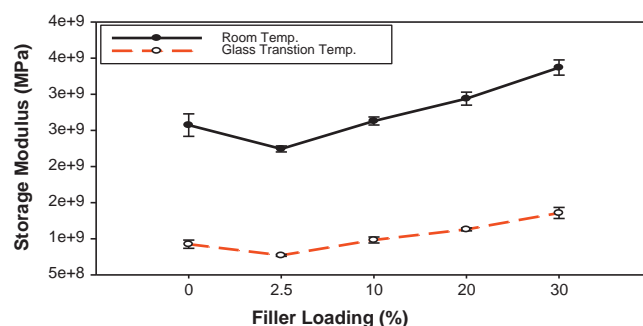
### 3.2. Dynamic mechanical thermal analysis (DMTA)

Fig. 4 shows the temperature dependence of the  $E'$  and  $\tan \delta$  of nylon 6 and related composites. The neat nylon 6 shows a typical behavior of semi crystalline polymer with three distinct regions that could be identified glassy, glass transition and rubbery regions. In the glassy region (temperature is smaller than 25 °C), the storage modulus remains roughly constant. Around 30 °C, the modulus decrease is related to the glass transition region of the nylon amorphous phase. The magnitude of this storage modulus decrease is small due to high degree crystallinity of the blend. At higher temperatures after the glassy region (temperature is higher than 35 °C) the storage modulus decreases sharply because of the increased viscosity and polymer chain mobility [9,10,21]. The sharp decrease in the storage modulus is continued until the rubbery region. MCC filled composites show a similar behavior and have a higher modulus for the all temperature ranges compared to unfilled composites except the addition of 2.5 wt.% MCC. It is believe that the decrease in the modulus of 2.5 wt.% MCC filled composites should be related to poor dispersion. The higher modulus for the composites could be a result of the highest degree of crystallinity of nylon 6 in the composite formulations, but DSC measurements show that the degree of crystallinity of the composites decreases with the addition of MCC [21]. It is hypothesized that the increase of the modulus should be related to a reinforcing effect of MCC. A similar observation was reported for polylactic acid (PLA)/MCC composites [25].

Fig. 5 shows that the storage modulus of the composites increased with increasing MCC percent at high filler loading both at room (20 °C) and glass transition temperatures. At 30 wt% MCC loading, the storage modulus increased significantly. As the MCC loading increases, the stress is more evenly distributed throughout the composite and therefore the modulus increases with the addition of MCC compared to the neat nylon 6. The temperature dependence of  $\tan \delta$  vs. for the MCC filled nylon composites as a function of temperature at a frequency of 1 Hz is presented in Fig. 4. The shift in  $\tan \delta$  peak temperature can provide information about molecular interactions between nylon 6 and MCC [25]. The main mechanical relaxation associated with the glass transition of the

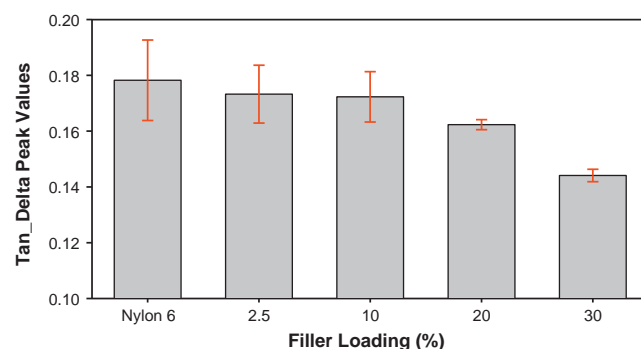


**Fig. 4.** DMTA storage modulus and  $\tan(\delta)$  of nylon 6 and MCC-filled nylon 6 composites from 0 to 150 °C as a function of temp.



**Fig. 5.** The storage modulus of nylon 6 and MCC-filled nylon 6 composites at the room temperature and glass transition temperature from DMTA.

nylon 6 in composites is quite similar and in agreement with several reports regarding nylon 6/clay nanocomposites [8,26,27]. From the peak in the  $\tan \delta$  curve, we can see that the incorporation of MCC does not significantly affect the glass transition temperature of the composite, but it does have a significant effect on the magnitude of  $\tan \delta_{\max}$  peak values. This means that the overall chain mobility is not sensitive to the presence of MCC despite the high filler loading [8]. The  $\tan \delta_{\max}$  peak temperatures correspond to the glass transition temperature and these values are not significantly changed as the MCC content is increased because the viscoelastic properties of the composite are strongly influenced by the matrix polymer. The neat nylon 6 presents a  $\tan \delta_{\max}$  peak temperature of about 68 °C and the composites present  $\tan \delta_{\max}$  peak temperatures between 68 and 69 °C. Fig. 4 indicates that the  $\tan \delta$  peak did not experience a temperature shift which indicates that there are no molecular interactions between the polymer matrix and MCC. Fig. 6 shows that the magnitude of the  $\tan \delta_{\max}$  peak values of the MCC filled composites were significantly decreased around the glass transition temperature and it is believe that the decrease in  $\tan \delta_{\max}$  peak value results from restriction in the chain segment mobility in the amorphous region of nylon 6 brought about by the incorporation of MCC [9].

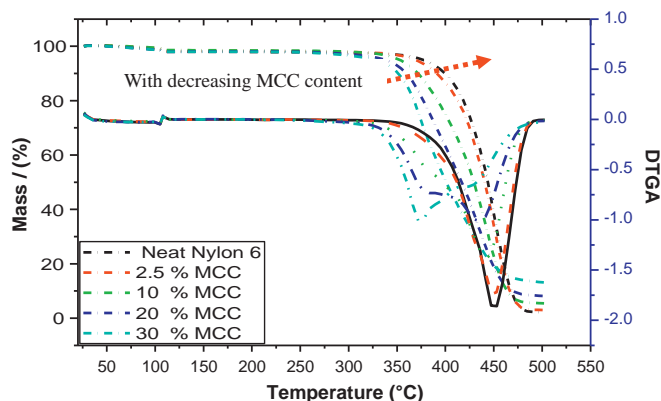


**Fig. 6.** The effect of MCC loading on  $\tan \delta$  peak values for nylon 6 and MCC-filled nylon 6 composites from DMTA.

**Table 4**  
Thermogravimetric data for the nylon 6 and MCC-filled nylon 6 composites at 500 °C.

Sample code	DTGA temp. (°C)		Mass loss (%)	Residue (%)	
MCC	348.7 (0.1)		65.6 (1.1)	12.9 (0.7)	
Neat nylon 6	451.2 (0.9)		56.3 (0.3)	2.2 (0.1)	
Nylon 6–MCC 2.5	450.5 (0.4)		60.9 (0.5)	3.1 (0.4)	
Sample code	DTGA temp. (°C)		Mass loss (%)		Residue (%)
	1st peak	2nd peak	1st peak	2nd peak	
Nylon 6–MCC 10	385.1 (0.5)	441.9 (0.2)	15.5 (0.4)	65.8 (0.1)	5.5 (0.2)
Nylon 6–MCC 20	380.6 (0.7)	434.9 (1.1)	20.5 (0.6)	68.1 (1.4)	8.2 (0.5)
Nylon 6–MCC 30	375.9 (2.2)	431.3 (2.6)	24.4 (0.1)	71.1 (1.9)	13 (0.9)

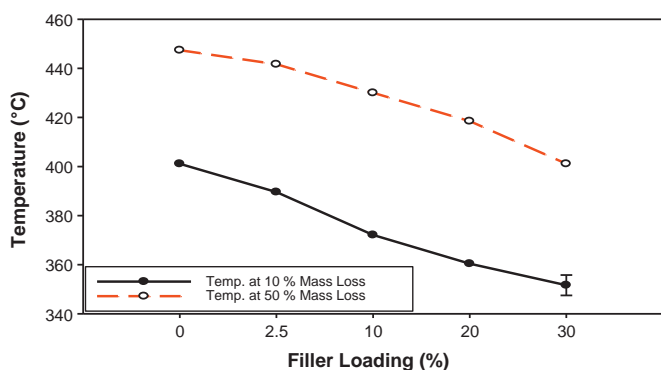
Parentheses indicate standard deviation.



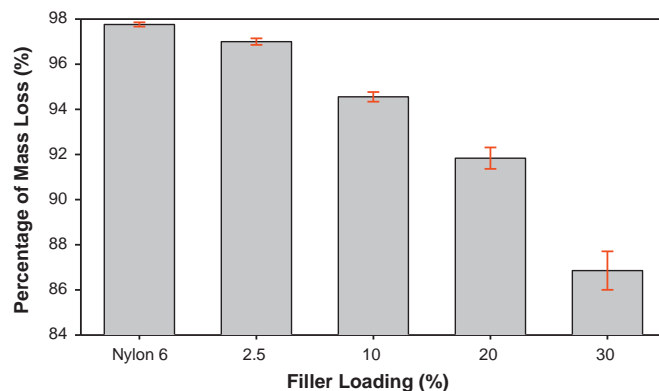
**Fig. 7.** TGA and DTGA curves of nylon 6 and MCC-filled nylon 6 composites.

### 3.3. Thermogravimetric analysis (TGA)

The TGA and DTGA curves for nylon 6 and MCC filled composites are shown in Fig. 7. Fig. 7 indicates that the onset temperature of rapid thermal degradation decreases with increasing MCC loading. As the filler loading increased, the thermal stability of the composites slightly decreased, whereas the final ash content monotonically increased from around 2% to 13% for the 30 wt% MCC addition. The degradation temperatures of neat nylon 6 and composites are different. The nylon 6 exhibited single stage degradation with a peak at 452 °C whereas MCC filled composites show two degradation peaks in the range of 372–450 °C. The temperature at 10% mass loss ( $T_{10}$ ) and the temperature at 50% mass loss ( $T_{50}$ ) for neat nylon 6 and the composites are shown Fig. 8. Both  $T_{10}$  and  $T_{50}$  values for the composites decreased monotonically from neat nylon 6 to the 30 wt% MCC addition. It is also obvious from Fig. 9 that the percentage of mass loss for composites decreased monotonically from



**Fig. 8.** TGA temperatures at 10% and 50% mass loss for nylon 6 and MCC-filled nylon 6 composites.



**Fig. 9.** Ultimate percentage of mass loss for nylon 6 and MCC-filled nylon 6 composites from TGA.

around 98% for neat nylon 6 to 87% for 30 wt% MCC addition. The results also show that as the filler loading increased, the thermal stability of the composites slightly decreased as the MCC content increased because of lower thermal stability of MCC compared to the neat nylon 6. A summary of mass loss (%), peak temperature and residual weight after 500 °C of the composites is given in Table 4.

## 4. Conclusions

There was not a significant change in the glass transition ( $T_g$ ), crystallization ( $T_c$ ) and melting ( $T_m$ ) temperatures of the composites with increased MCC loading. The storage modulus ( $E'$ ) of the MCC filled nylon 6 composite system was higher than that of neat nylon and increased with increasing MCC content except for the 2.5 wt% MCC loading. This is because the reinforcement effect of the MCC. The  $\tan \delta$  maximum peak temperatures values are not significantly changed as the MCC content increased because the viscoelastic properties of the composite are strongly influenced by the matrix polymer. Thermogravimetric analysis indicated that as the filler loading increased the thermal stability of the composites slightly decreased, whereas the final ash content monotonically increased from around 2% for the neat nylon 6 to 13% for the 30 wt% MCC addition. It is believed that the formulation containing only nylon 6 and MCC (without lubricant) will show better storage modulus and thermal stability and less change in the melt behavior of composites in comparison with lubricant added nylon 6 blend and MCC formulation. In this study, lubricant used only as an additive to improve processing conditions.

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