

Effect of Cellulose Fiber Reinforcement on the Temperature Dependent Mechanical Performance of Nylon 6

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ABSTRACT: In order to quantify the effect of temperature on the mechanical properties of pure nylon 6 and its composite with cellulose fibers (containing 25 wt% cellulose fibers), the materials were sampled and tested at three representative temperatures of 256, 296, and 336 K. Flexural and tensile tests were performed and the reductions in mechanical properties were evaluated. The highest reductions were observed in stiffness (modulus) values and the cellulose fibers remarkably enhanced the high temperature resistance of nylon. The reductions in mechanical properties were well explained by a simple quadratic curve fitting procedure applied to experimental data. Dynamic mechanical analysis (DMA) was also performed to study the effect of temperature on mechanical performance. No shifting in glass transition temperature was observed, but the composite material showed less viscous behavior as seen by its lower mechanical loss factor ($\tan \delta$) values in the rubbery state. The results of the present study will be helpful in determining the end-use application of these composite materials.

KEY WORDS: composites, mechanical properties, temperature, nylon, cellulose.

INTRODUCTION

THE CHOICE OF plastic for the production of wood plastic composites (WPCs) is restricted to the so-called 'commodity thermoplastics' such as polypropylene and polyethylene, mainly due to the higher melting points of engineering plastics such as nylon which would bring about thermal degradation of wood components [1]. The fact that engineering plastics are also more costly than commodity plastics has contributed to this limitation as well. However, there are certain 'under-the-hood' applications in the automobile industry where conditions are too severe for commodity plastics to withstand [2]. Having a high melting point and high stiffness, nylon is an alternative to commodity plastics as the

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polymeric matrix of the WPCs where resistance to high temperatures is of great significance. Although recent efforts have promised the feasibility of producing extruded nylon/wood composites [3], the presence of thermally instable hemicelluloses in wood may confine the lignocellulosic fraction to pure cellulose fibers rather than wood particles.

The use of nylon as the polymeric matrix in WPCs presents some advantages and disadvantages. The disadvantages are related to the potential thermal degradation of wood fibers at high temperatures whereas the advantages are mostly pertinent to the higher mechanical properties of nylon as compared with polyolefins. Another advantage is that thanks to its hydrophilic nature, the compatibility between the polymer and wood is good. This will eliminate the need to use a compatibilizer or coupling agent.

Scientific research reports on natural fiber nylon composites are rare. This is mainly due to the difficulties in producing the composites without considerable thermal degradation of the wood/cellulose fibers. It has been suggested that using nylon 12, which has considerably lower melting point than nylon 6 or nylon 6.6, can be a good alternative to overcome the problem [4]. As an alternative method, McHenry and Stachurski [5] manufactured nylon/wood fiber and polypropylene/wood fiber composite materials using a hot press technique.

The first step in understanding the behavior of nylon/natural fiber composites in under-the-hood applications is to have basic knowledge on the effects of temperature of their mechanical performance. The present paper deals with the effects of cellulose fiber reinforcement on static and dynamic mechanical properties of nylon 6 at varying temperatures.

EXPERIMENTAL

Materials

The evaluated materials were injection molded specimens of industrial grade pure nylon 6 (designated as NY) and its composite containing 25 wt% pure cellulose fibers (designated as NYCF).

Mechanical Testing

Mechanical tests were performed at three different temperatures (256, 296, and 336 K). Static flexural tests were performed according to ASTM D-790-07 specification [6]. Nominal specimen dimensions were $130 \times 8 \times 3.2$ mm. A span of 100 mm was used which gave a span/depth ratio of at least 30. An Instron testing machine Model 4486 equipped with a 10 kN load cell was used and the crosshead speed was 8 mm/min. Flexural strength and flexural modulus were calculated from the load–deflection curves. Tensile tests were carried out according to ASTM D-638-03 specification on dumbbell-shaped specimens [7]. The tests were performed using the same Instron machine at a crosshead speed of 5 mm/min. Strain was measured in the mid-span of the specimens using an Instron extensometer mounted on the specimens. Tensile modulus (E) and tensile strength (TS) were calculated using the stress–strain curves. Five specimens of each formulation were tested.

Dynamic Mechanical Analysis

Dynamic mechanical analysis was performed using a Rheometric Scientific DMTA V analyzer. A dual cantilever mode was selected and the samples were scanned over a

temperature range of 193–423 K. Nominal specimen dimensions were $52 \times 8 \times 2$ mm. Frequency of the oscillations were fixed at 1 Hz and the strain amplitude was 0.1%, which was well within the linear viscoelastic region. The heating rate was $2^\circ\text{K}/\text{min}$ for all temperature scan tests. An 8 min soak time was applied before the first measurement in order to let the specimens equilibrate. Storage modulus (E'), loss modulus (E''), and mechanical loss factor ($\tan \delta$) were collected during the test and were plotted vs. temperature. At least three specimens for each formulation were analyzed and average values were reported.

RESULTS AND DISCUSSION

Flexural Properties

Flexural load–deflection curves of both formulations are presented in Figure 1, where the effect of temperature on mechanical behavior can be observed. As expected, the slopes of the curves become smaller at elevated temperatures indicating lower stiffness at higher temperatures. Maximum load is also lower at higher temperatures. At all temperatures the composite material presents higher slopes and maximum load, indicating the enhancement in mechanical performance of nylon 6. The highest slope of the curves corresponds to the composite formulation at 256 K whereas the lowest one is seen for the pure nylon at 336 K. It should be also mentioned that neither the pure plastic nor the composite formulation broke under flexural load at 10 mm flexural deflection, where the test was stopped due to excessive deformation.

Effect of temperature on the flexural strength of the formulations is presented in Figure 2. Temperature strongly affects flexural strength as seen in the reductions in Table 1, which shows that this property drops around 78 and 47% at 296 K for

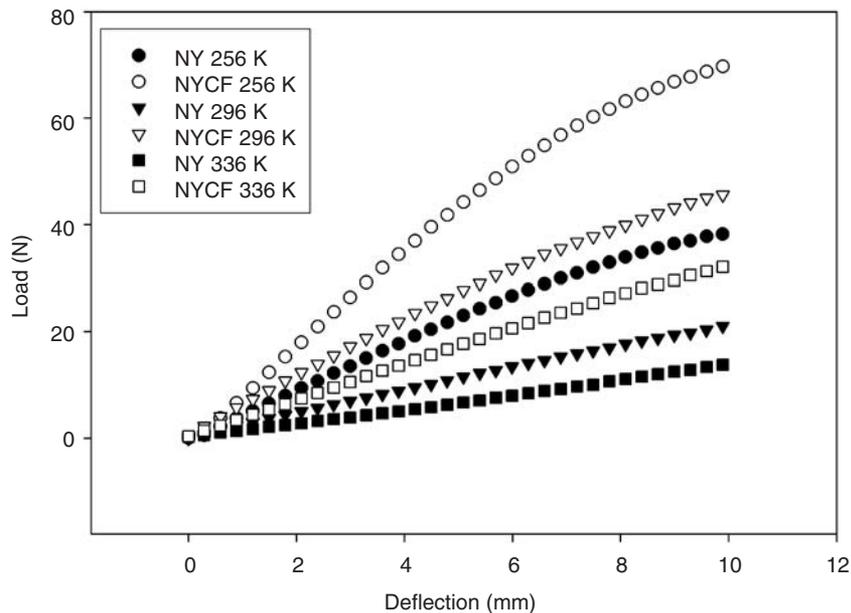


Figure 1. Flexural load–deflection curves of pure nylon and its composite at various temperatures.

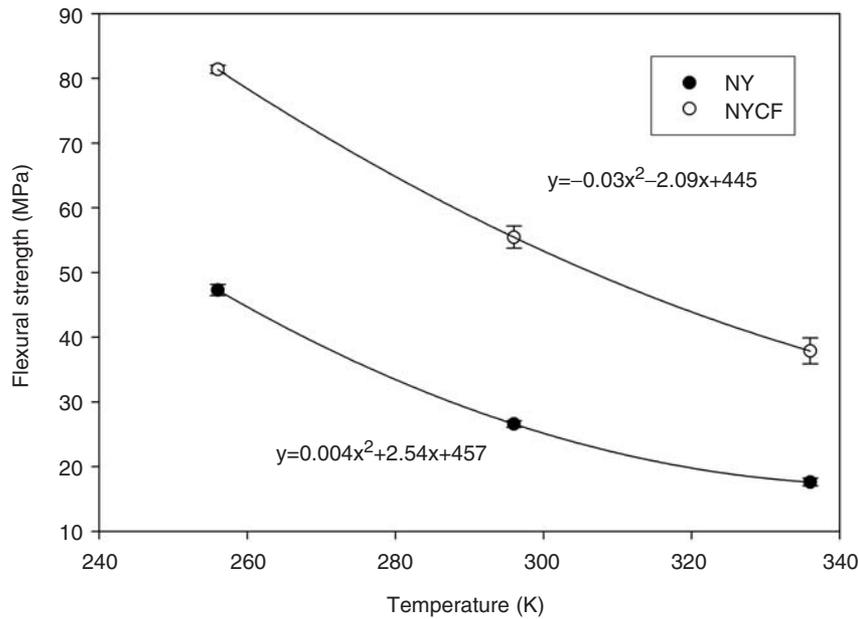


Figure 2. Effect of temperature on the flexural strength.

Table 1. Percent reduction in mechanical properties at elevated temperatures in comparison with the properties at 256 K.

Sample	Temperature (K)	Flexural strength	Flexural modulus	Tensile strength	Tensile modulus
NY	296	77.9	110.2	13.7	121.3
	336	168.6	272.2	1.0	326.9
NYCF	296	46.8	72.0	13.3	65.4
	336	114.9	173.3	30.0	101.0

pure plastic and composite formulation, respectively. However, as the temperature is raised to 336 K, the corresponding reductions are 169 and 115%, respectively. The reductions are considerably lower for the composite material. Clearly, there is non-linearity in the effect of temperature on flexural modulus, which can be expected considering the load–deflection curves in Figure 1. A simple quadratic function was fit to the experimental data and R^2 values of unity were obtained, indicating that the effect of temperature on flexural strength can be quantitatively explained using the obtained equation (Figure 2).

Effect of temperature on the flexural modulus of the formulations along with the predictive equations are presented in Figure 3. Flexural modulus is also strongly affected by temperature and its reduction is much larger as compared with that of flexural strength. Table 1 exhibits that flexural modulus drops around 110 and 72% at 296 K for pure plastic and composite formulation, respectively. As the temperature is raised to 336 K, the corresponding reductions are 272 and 173%, respectively. The reduction in flexural modulus is larger for pure plastic as it is inherently more sensitive to temperature than natural fibers due to higher viscoelasticity [8].

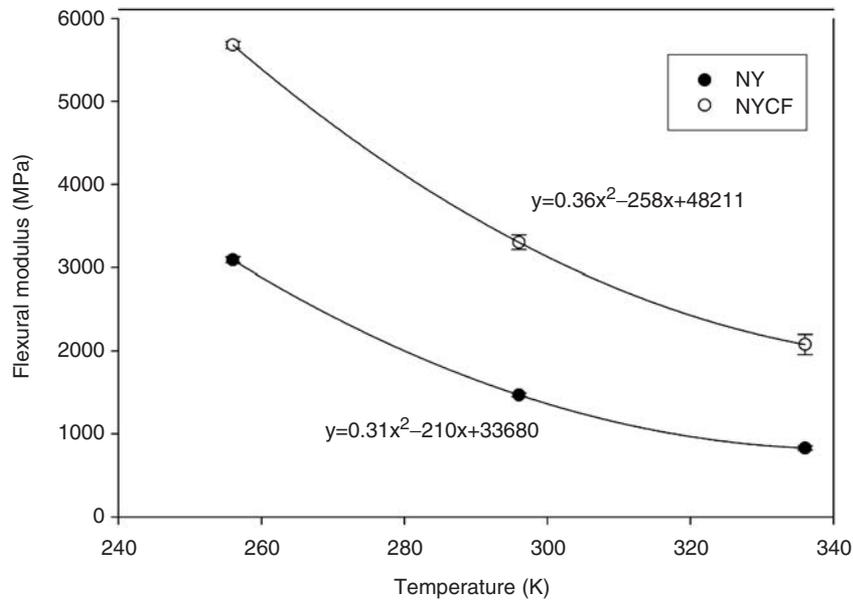


Figure 3. Effect of temperature on flexural modulus.

Tensile Properties

Tensile stress–strain curves for both formulations at the three studied temperatures are presented in Figure 4. A similar behavior to that of flexural load–deflection curves can be seen as the great impact of the temperature on stress–strain behavior. However, a different behavior is seen as for the elongations at break. The composite formulation fails at much lower elongation values than the pure plastic. The shapes of the curves are distinctly different at different temperatures. At the lowest temperature, an almost linear portion is seen at low strain values. As the temperature goes higher, this linear region tends to become shorter and at the highest temperature the entire curve is almost non-linear. This is true both for pure plastic and composite specimens but it is more evident for pure plastic.

An interesting phenomenon is observed in Figure 5 where the effect of temperature on the tensile strength of both formulations is presented. For the composite formulation, tensile strength linearly decreases at higher temperatures. However, this not true for the pure nylon where tensile strength is resumed at the highest temperature. This phenomenon is due to the necking of the pure nylon specimens at 336 K, which leads to an increase in maximum load and in turn tensile strength. As presented in Table 1, tensile strength drops around the same value (13%) for both formulations at 296 K. On the contrary, when the temperature is raised to 336 K, the corresponding reductions are 1 and 30% for pure plastic and composite formulation, respectively.

Effect of temperature on the tensile modulus of the formulations is presented in Figure 6. The predictive equations are also presented, which have very good fits ($R^2 = 1$). Tensile modulus is more adversely affected by temperature as compared with tensile strength. As seen in Table 1, at 296 K tensile modulus drops around 121 and 65% for pure plastic and composite formulation, respectively. At 336 K, the corresponding reductions are 327 and 101%, respectively. Therefore, the temperature had the most adverse effect on tensile modulus as compared with other properties.

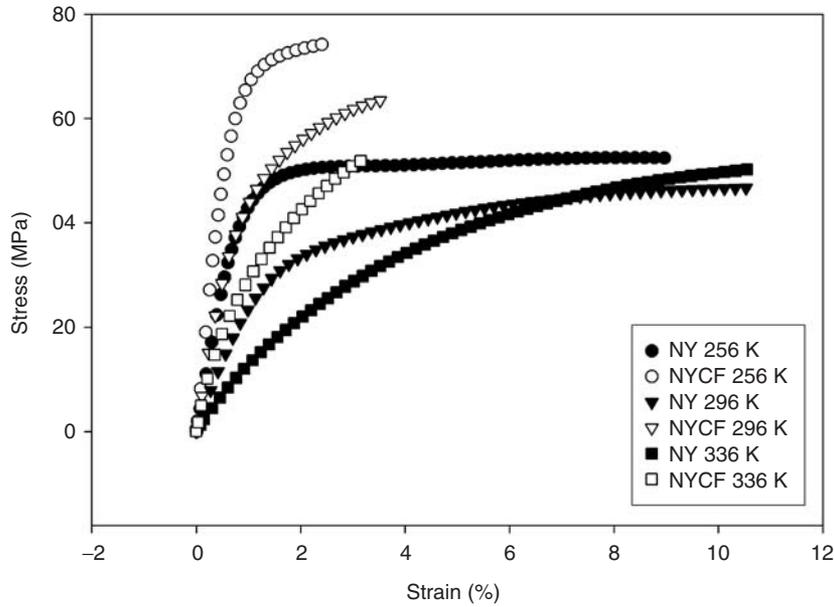


Figure 4. Tensile stress–strain curves of pure nylon and its composite at various temperatures.

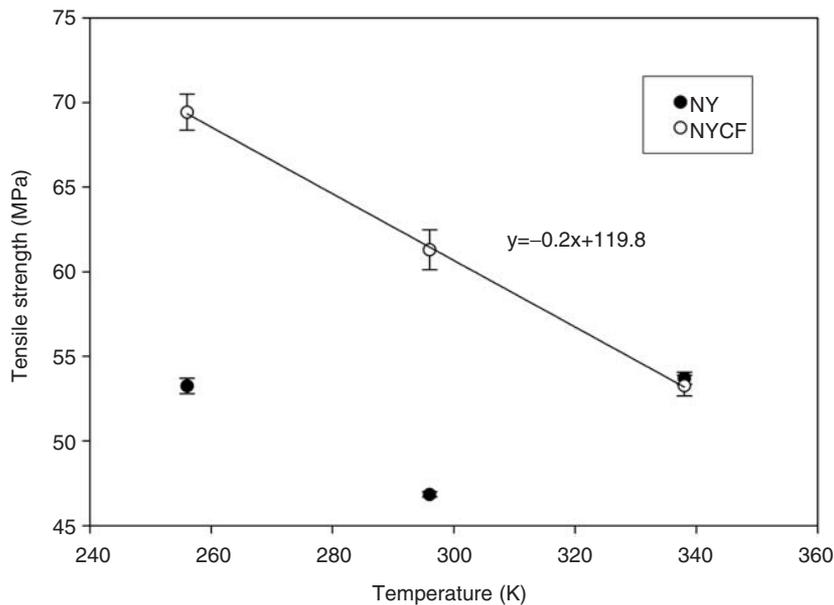


Figure 5. Effect of temperature on the tensile strength.

Generally it was found that the effect of temperature was the highest for stiffness of the composite and pure nylon (both flexural and tensile) as compared with that of strength values. This is mainly because of the fact that stiffness of the composite is directly related to the stiffness of the constituents, which heavily depend on temperature. Strength values are mainly governed by interfacial adhesion which is less influenced by temperature.

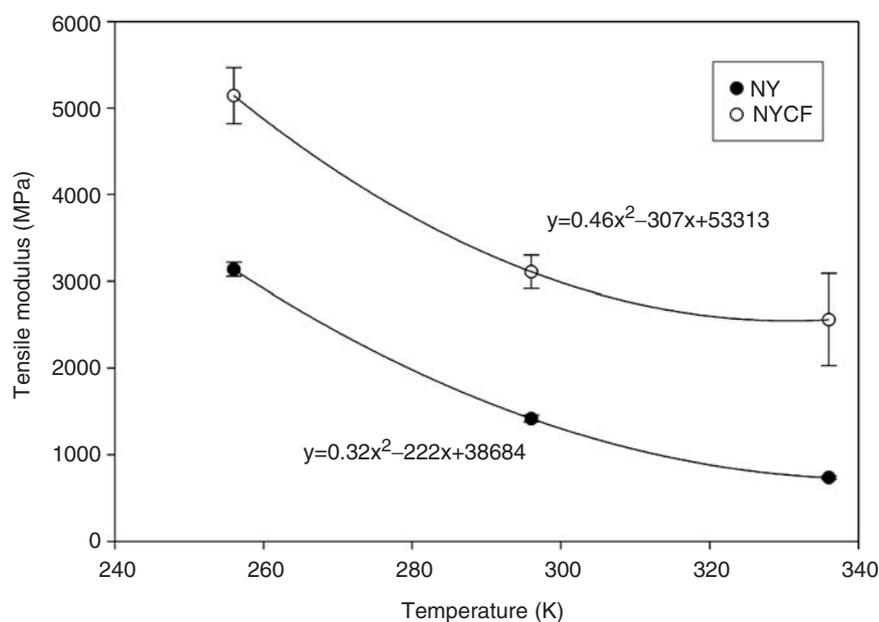


Figure 6. Effect of temperature on the tensile modulus.

Dynamic Mechanical Properties

Changes in the storage modulus of the formulations due to the increase in temperature are presented in Figure 7, along with the curves depicting the ‘modulus retention term’ which is calculated by dividing the storage modulus at any given temperature by its initial value at the lowest temperature (highest stiffness). As is clearly seen, the composite material has higher modulus values over all the studied temperature range. The modulus retention term shows how much of the stiffness is retained at any given temperature. As seen, this term is higher for the composite material over all the studied temperature range which indicates better mechanical performance of the composite material at elevated temperatures.

Nylon 6 is a semi-crystalline polymer and the reduction of stiffness beyond glass transition temperature is quite considerable [9]. Glass transition temperature can be determined from storage modulus (Figure 7), loss modulus, and $\tan \delta$ curves (Figure 8) but they would not necessarily give similar values as these curves represent different stages in phase transition. The glass transition temperatures of the pure nylon and the composite material were determined using all the three curves and the results are presented in Table 2. As seen, the highest values correspond to the peak $\tan \delta$ curve whereas the lowest values are determined from the storage modulus curves. Chen and Gardner [3] state that from a mechanical point of view, the glass transition temperature determined from storage modulus curves should be considered as it relates directly to the stiffness of the material. Nevertheless, the important point is that very little change was observed as to the location of glass transition temperature, indicating that the presence of cellulose fibers did not affect phase transition.

Therefore, from the three temperatures used for the study of the effect of temperature on the static mechanical properties of the formulations, only the lowest one (256 K) is below

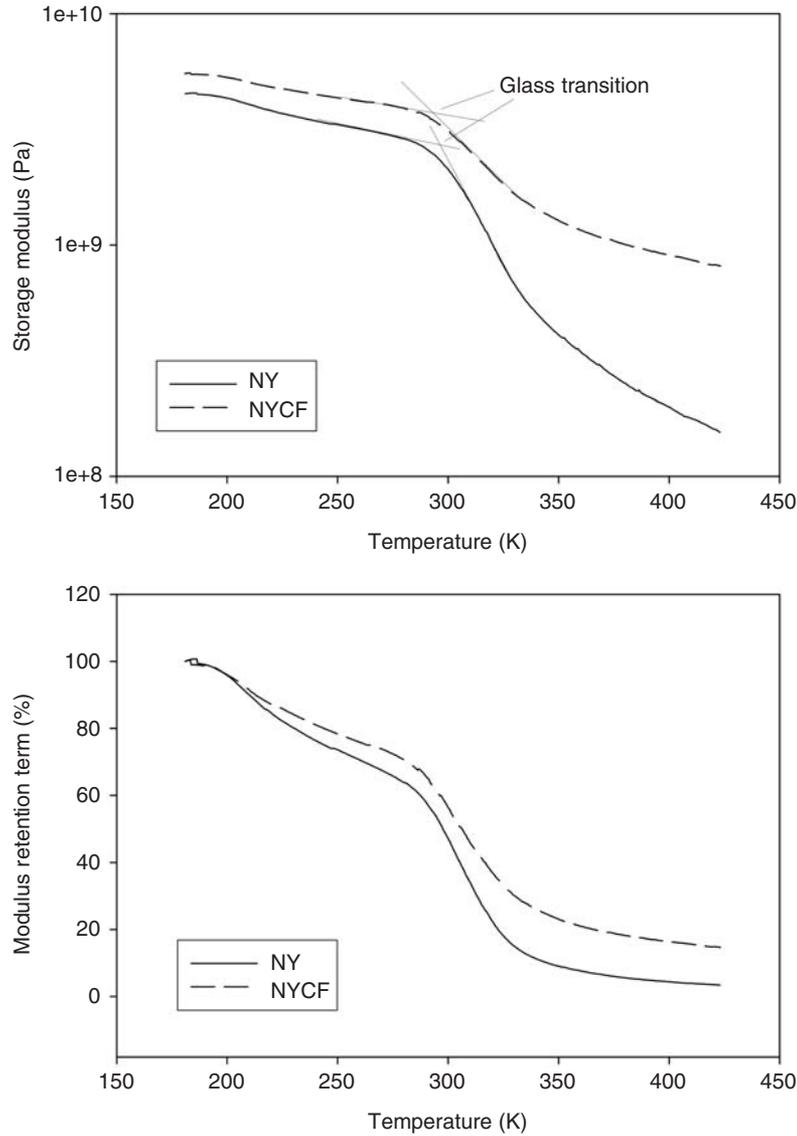


Figure 7. Storage modulus spectra of the formulations (top) and the modulus retention term (bottom).

glass transition temperature. This clearly explains the remarkable stiffness reductions at the two other temperatures.

Figure 8 shows that the mechanical loss factor is almost the same for both pure nylon and its composite before the glass transition temperature. However, the $\tan \delta$ values are remarkably lower for the composite after glass transition when the material is in a rubbery status. As far as the study of the viscoelasticity of the materials is concerned, $\tan \delta$ is a better indicator to be considered than storage or loss modulus, as its value is independent of sample geometry [8]. The presence of 25% cellulose fiber has considerably reduced damping, indicating that the composite material is more elastic than pure nylon at elevated temperatures.

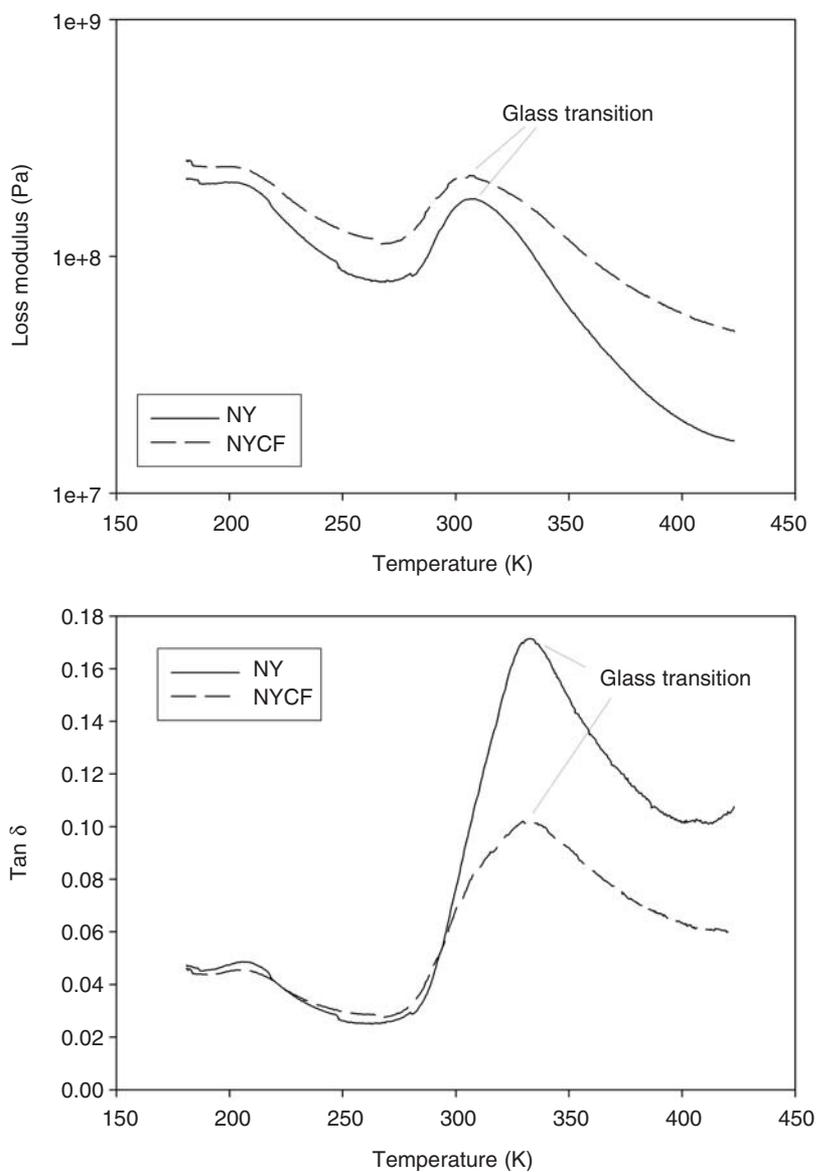


Figure 8. Loss modulus spectra of the formulations (top) and the mechanical loss factor ($\tan \delta$) (bottom).

Table 2. Glass transition temperatures determined using different methods (K).

Formulation	Determination method		
	Storage modulus tangent intersection	Loss modulus peak	$\tan \delta$ peak
NY	295	307	333
NYCF	293	305	333

CONCLUSIONS

The effect of operating temperature on static and dynamic mechanical properties of nylon 6 and its composite with cellulose fibers was studied in the present research and the following conclusions could be drawn from the results and discussion presented above:

- Flexural strength, flexural modulus, tensile strength, and tensile modulus of both formulations drop remarkably at higher temperatures.
- The effect of temperature is the highest for stiffness of the composites (both flexural and tensile) as compared with that of strength values.
- The composite material possesses better temperature resistance than pure nylon.
- Glass transition was not influenced by the presence of fibers. However, damping was considerably lower at higher temperatures for the composite formulation.
- The reductions in mechanical properties could be best predicted using a simple quadratic curve fitting procedure.

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