# THERMAL AND MECHANICAL PROPERTIES OF PLA /PEG BLEND AND ITS NANOCOMPOSITES

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## Abstract

*In this study, the nanocomposites of polylactic acid-polyethylene glycol (PLA-PEG) blend and cellulose nanocrystals were prepared. Cellulose nanocrystals were produced by sulphuric acid hydrolysis of microcrystalline cellulose (MCC). The composite system, wherein cellulose nanoparticles were added, were prepared by melt extrusion technique to improve the mechanical and thermal properties of PLA. The surface of cellulose nanoparticles were modified in order to achieve homogeneous dispersion in the polymer matrix. The thermal and mechanical properties of these nanocomposites were investigated by Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and tensile tests. As a result, the mechanical properties are not greatly affected in the presence of cellulose nanocrystals. On the other hand, composites containing the treated nanocellulose show better tensile strength properties compared to composites with untreated cellulose nanocrystals.*

## 1. Introduction

Environmental pollution, high price of crude oil and global warming have led to increasing interest in replacing petroleum based polymers with biodegradable biopolymers. Moreover, much efforts have been made for the development of advanced materials for solving these problems. In this context, PLA is one of the most promising biodegradable polymer due to its good mechanical properties, renewability and biodegradability which make it suitable for use in biomedical, agricultural and packaging applications [1]. However, inherent brittleness, poor thermal resistance and limited gas barrier properties limit its large scale commercial applications. For this reason, its properties must be improved to make it competitive with petroleum based synthetic polymers. Several studies have carried out to improve mechanical properties of PLA including copolymerization of PLA with other monomers, blending with other polymers and plasticization using biocompatible plasticizers [2,3]. Blends of PLA with different polymers have been demonstrated that only moderate improvements are achieved in mechanical properties. PLA is relatively a brittle and rigid polymer. Therefore, it needs to be plasticized to increase its ductility. Plasticizers such as citrate esters, polyethylene glycol (PEG), glycerol and oligomeric lactic acid are widely used to improve the flexibility and processability of PLA. It has been found that incorporation of low molecular weight PEG within PLA can be provided a significant increase in elongation at break and impact resistance of PLA [3]. Also, the addition of PEG reduces the glass transition temperature and melting temperature.

One of the other solution to improve the properties of PLA is the addition of nanosized reinforcement within PLA matrix. The impressive mechanical properties, abundance, low weight, and biodegradability of nanocellulose make them ideal to use in polymer nanocomposites. Nanocellulose can be used as reinforcement in composite materials because of enhanced mechanical and thermal properties of composites. Therefore, there has been a great research effort on the development of nanocellulose reinforced polymer nanocomposites. However, very few studies have been reported concerning the processing of nanocellulose reinforced nanocomposites by extrusion methods. Because the main challenge is related to the homogeneous dispersion of hydrophilic nanocellulose within the hydrophobic polymeric matrix like PLA [4]. In order to prevent agglomeration of nanocellulose and to improve their dispersion and compatibility within matrix, nanocellulose can be modified. Methods of surface modifications including surfactant usage, surface silanization, polymer grafting have been reported in literature [1,5].

The objective of this study was to prepare biobased nanocomposites using PLA-PEG as a matrix phase and cellulose nanocrystals as additives. Cellulose nanocrystals were produced by sulphuric acid hydrolysis of (MCC). Acid hydrolysis of MCC fibers provide extraction of cellulose nanowhiskers by hydrolyzing the amorphous region whereas crystalline region remain intact. The surface silanization method was used to improve the dispersion/compatibilization of nanocellulose with the non-polar polymer, PLA-PEG matrix. The mechanical properties of composites were studied in order to evaluate the effects of concentration and modification of nanoparticles on the composites modulus, tensile strength and elongation at break values. The influence of nanocrystal addition on the thermal characteristics of PLA was evaluated by DSC and TGA analysis.

## 2. Materials and testing methods

### *2.1. Materials*

Poly(lactic acid) granules was supplied by Nature Plast and commercialized under the trade name of PLE 005. PEG with molecular weight 400 was purchased from Merck. Microcrystalline cellulose (MCC, a powder with particle size of 10-15 µm) used for the production of nanocellulose and 3-aminopropyltriethoxysilane, used as the silane coupling agent, were obtained from Sigma Aldrich.

### *2.2. Production of nanocellulose (NS)*

Nanocellulose was isolated from MCC by acid hydrolysis. The isolation procedure was described by Bondeson et al. [6]. Briefly, the aqueous MCC suspension was mixed with sulphuric acid (64 wt.%) at 44°C for 2 h. The resulting suspension was centrifuged (15 min at 12000 rpm) several times until the pH of suspension reached up to 5 and then dialyzed against distilled water. The final suspension was filtered using filter paper Whatman no 1. and sonicated for 5 min in an ice bath.

### *2.2.1. Silanization of nanocellulose (SLNS)*

Nanocellulose suspension was treated with 80/20 (v/v) ethanol/water solution containing 10 wt% APS for 2 h. After mixing, two centrifugation steps (5000 rpm, 20 min) were applied. Then, modified nanocellulose were dried by using freeze drying process and heated under vacuum at 120°C for 4 h to promote actual chemical coupling. The nanostructure of NS was examined by scanning electron microscopy (Zeiss Supra 50 VP).

### 2.3. *Production of nanocomposites*

PLA was vacuum dried at 80°C for 24 h and NS was vacuum dried at 30 °C for 24h before processing. PEG content was kept constant at 20 wt% in all compositions. The untreated nanocellulose (SN) and silane treated nanocellulose (SLNS) at 1.5 and 3 wt. % concentrations were added to the plasticized PLA (PLA-PEG) matrix. The composites were prepared by using a twin screw extruder (DSM Xplore, Micro Compounder). The extrusion process was performed at 170 $^{o}$C and a screw speed of 100 rpm. Specimens for tensile test were prepared by using injection molding device (DSM Xplore, Micro 10 cc Injection Molding Machine) at 7 bars. The temperature of the sample holder and mold was 180 and 30 $^{o}$C, respectively.

### *2.3.1. Characterization of nanocomposites*

The thermal analyses were conducted by TGA and DSC. In DSC analysis the samples were heated from 30 to 200 °C at a rate of 10 °C/min. The samples were kept at 200 °C for 1 minute and subsequently cooled to 30 °C and then heated to 200 °C with the same rate. The glass transition ($T_g$) and melting temperatures ($T_m$'s) were determined from the second heating cycle. The crystallinity (%) of the PLA was estimated from the corrected enthalpy for PLA content in the nanocomposites by using the following equation:

$$X_c = (\Delta H_m / \Delta H_f) \times w^{-1} \times 100 \quad (1)$$

where $\Delta H_m$ is melting enthalpy of the sample (J/g) and $\Delta H_f$ is theoretical melting enthalpy of 100 % crystalline polymer. The theoretical value of enthalpy for 100 % crystalline PLA is 93 J/gram [7]. w is the mass ratio of PLA in the whole composite.

TGA thermograms were carried out under nitrogen flow with a temperature range from room temperature to 600°C at a heating rate 10°C/min. Tensile tests were performed by using Instron 5944 tensile testing machine on ISO 527-2 5A standard.

## 3. Results and Discussion

Figure 1 presents a typical micrograph of cellulose nanocrystals. The nanocrystals are well individualized in the nanoscale region. Aggregates of a few nanocrystals is observed, which was expected as a result of the presence of hydroxyl groups on the surface of cellulose promoting the hydrogen bonding formed in drying process.

The mechanical properties of the prepared PLA-PEG blend and its nanocomposites are presented in Figure 2. The composites show no increase in tensile strength compared to PLA-PEG. There is a slight decrease in tensile strength and modulus with the addition of nanocrystals. The reason is the agglomerated morphology and lack of good interaction between the matrix and the cellulose nanocrystals. There are some improvements in the tensile strength and modulus properties of the silane treated nanocomposite materials compared to untreated nanocomposites. The elongation at break is decreased with the addition of nanocrystals. The reason is that cellulose nanocrystals cause local stress concentrations and failure at reduced strain [5]. It seems that the interfacial adhesion between the polymer matrix and cellulose nanocrystals is not properly enhanced.

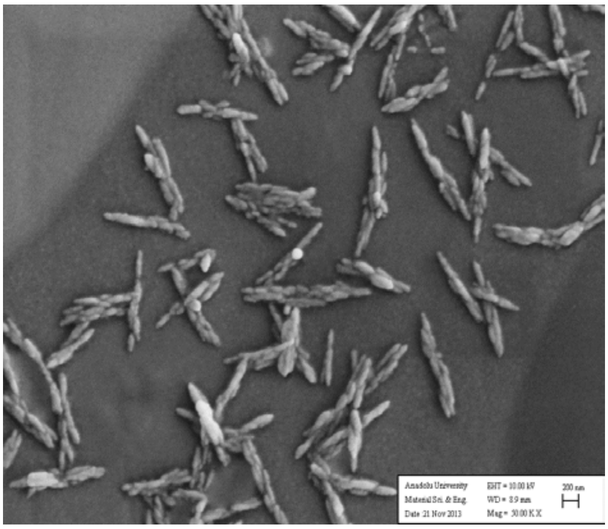

**Figure 1.** SEM micrograph of cellulose nanocrystals

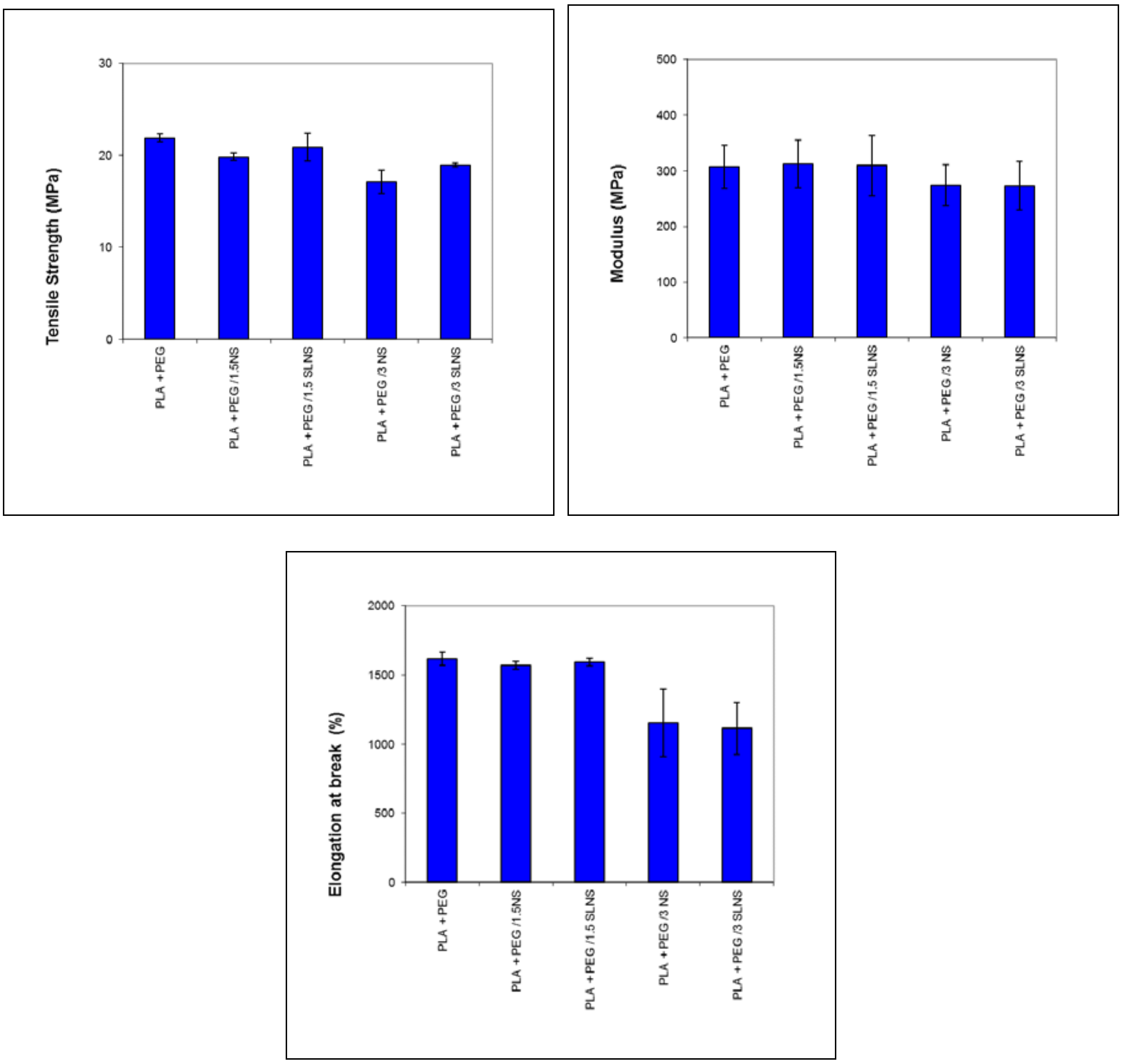

**Figure 2.** The mechanical properties of PLA-PEG blend and its nanocomposites

The thermal behavior of PLA-PEG based nanocomposites was determined using DSC measurements (Fig. 3). The glass transition temperature ($T_g$), melting temperatures ($T_m$), melting enthalpy ($\Delta H_m$), crystallization temperature ($T_c$) and crystallization enthalpy ($\Delta H_c$) are determined for the PLA-PEG and the nanocomposites (Table 1). In the first heating scan all samples show an exothermic peak which is indicating the cold crystallization during heating. Under the investigated conditions, the samples present only a glass transition temperature close to 60 °C, which is predominantly the $T_g$ of the neat PLA. $T_g$ value for the resulting nanocomposites are not affected by the presence of nanocellulose. It reveals that no plasticizing effect is provided by the cellulose additives [4]. PLA-PEG and PLA-PEG/NS composites show two melting peaks. The observation of  double melting peaks indicates the formation of two different crystal types [2]. From Table 1 it is observed that melting temperatures ($T_m$), total melting enthalpy ($\Delta H_{mTot}$) decrease with the addition of nanocellulose. The crystallinity values of nanocomposites are lower when compared to PLA-PEG blend whatever cellulose nanofibers were silanized or not .

**Table 1.** DSC of PLA-PEG blends and its nanocomposites derived from cooling and second heating scans

| *SAMPLE* | $T_g$ | $T_c$ | $\Delta H_c$ | $T_{m1}$ | $\Delta H_{m1}$ | $T_{m2}$ | $\Delta H_{m2}$ | $\Delta H_{mTot}$ | $X_c$ |
|---|---|---|---|---|---|---|---|---|---|
| PLA + PEG | 58 | 99 | 30.83 | 139 | 9.71 | 150 | 23.79 | 33.50 | 45 |
| PLA + PEG /1.5 NS | 61 | 98 | 28.49 | 137 | 8.43 | 149 | 21.42 | 29.85 | 41 |
| PLA + PEG /1.5 SLNS | 59 | 99 | 32.5 | 132 | 7.37 | 141 | 20.79 | 28.16 | 39 |
| PLA + PEG /3 NS | 59 | 99 | 29.26 | 136 | 8.27 | 148 | 20.09 | 28.36 | 40 |
| PLA + PEG /3 SLNS | 60 | 99 | 33.74 | 135 | 7.67 | 148 | 20.02 | 27.69 | 39 |

Table 2 summarizes the decomposition temperature (peak maximum for the first derivative, $T_{max}$) and the peak onset temperatures ($T_{onset}$) of all samples. Table 2 shows the temperature at which the PLA-PEG blend starts to decompose at 289 °C. Beyond this temperature, the weight loss increases and $T_{max}$ is at 289 °C. However, with the addition of nanocellulose, the decomposition temperature of the PLA-PEG seems to decrease.

**Table 2**. The decomposition temperature ($T_{max}$) and the peak onset temperatures ($T_{onset}$) of PLA-PEG and the composites

| SAMPLE | $T_{onset}$ | $T_{max}$ |
|---|---|---|
| PLA + PEG | 289 | 374 |
| PLA + PEG /1.5 NS | 284 | 374 |
| PLA + PEG /1.5 SLNS | 272 | 370 |
| PLA + PEG /3 NS | 269 | 372 |
| PLA + PEG /3 SLNS | 268 | 371 |

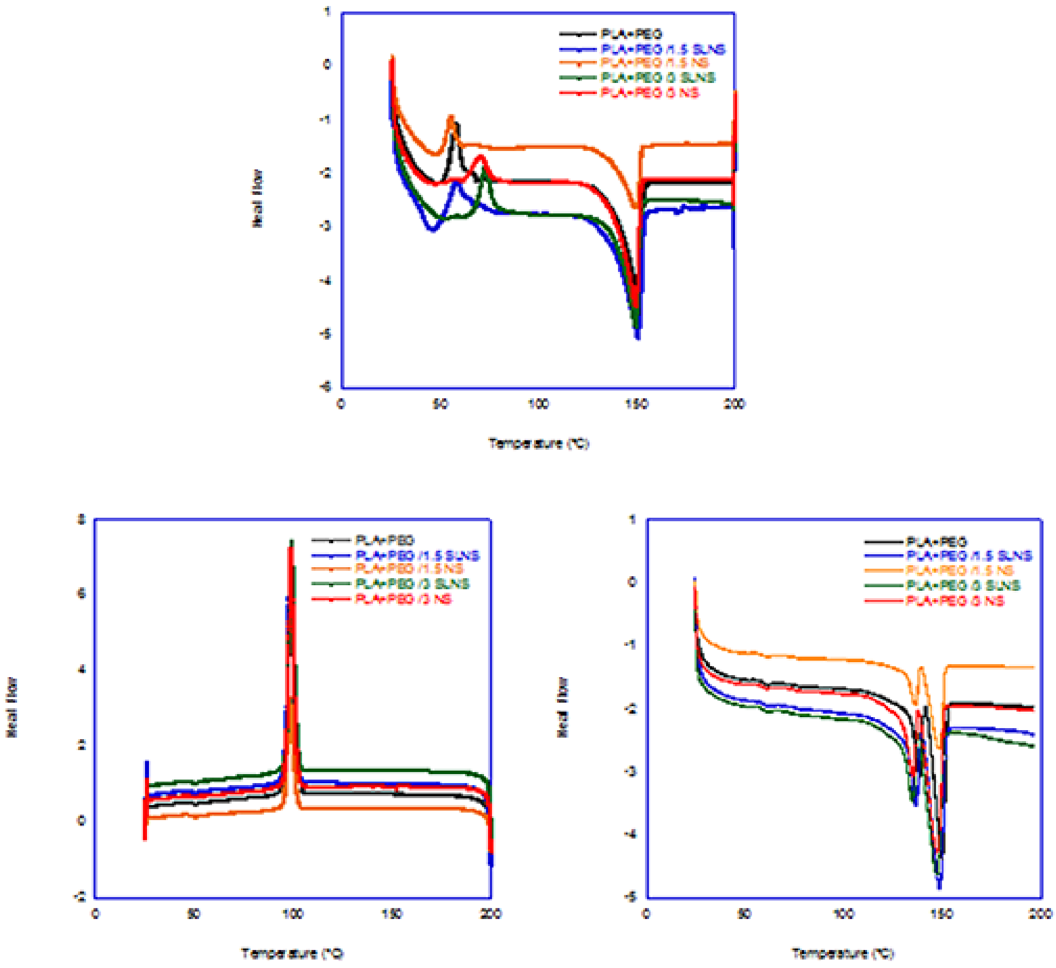

**Figure 3.** DSC curve of (a) first heating (b) cooling and (c) second heating scans of PLA-PEG blends and the nanocomposites.

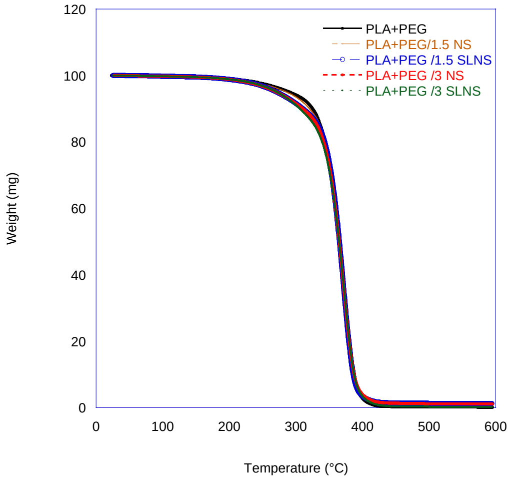

**Figure 4.** TGA thermogram of PLA-PEG blends and the nanocomposites

## Conclusions

In this study, cellulose nanocrystals were prepared by acid hydrolysis method from microcrystalline cellulose (MCC). The effect of silane treatment and nanocellulose concentration on the mechanical and thermal properties of PLA-PEG blend was investigated. PEG was used as plasticizer and the composites were prepared by melt extrusion. Addition of cellulose nanocrystals increase slightly the tensile strength and the modulus of PLA-PEG. The elongation at break of PLA-PEG is reduced in the presence of nanocrystals. DSC measurements reveal that the $T_g$ and $T_m$ values does not change with the incorporation of nanocellulose. The increase in the concentration of cellulose nanocrystals results in a slight decline in the crystallinity of PLA-PEG blend. TGA thermograms show that the thermal stability of the blend is not affected with the nanocellulose addition.

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