Title: Crystal structure transformation and induction of shear banding in Polyamide 11 by surface modified Cellulose Nanocrystals

Authors: Shane X. Peng¹, Shikha Shrestha¹, and Jeffrey P. Youngblood ^{*,1}

Authors address:

¹ School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907, United States

* Corresponding author

Email: jpyoungb@purdue.edu, Phone: +1 765-496-2294, Fax: +1 765 494-1204

Abstract

Polyamide 11 (PA11) nanocomposites reinforced with Cellulose Nanocrystals (CNC), dodecanoic acid surface modified CNC (CNC_d), and CNC with methyl laurate (CNC+ML) as plasticizer were fabricated. With the addition of CNC alone, tensile modulus and strength of the PA11 were improved, but the toughness decreased at high CNC concentration. Using CNCs that were surface modified, the tensile modulus and strength both increased while the toughness of PA11 was preserved. CNC_d also led to the formation of shear band like structures during uniaxial tensile testing. When PA11 and nanocomposites were annealed near their melting point, a higher T_m peak indicated that smaller crystals were melted and recrystallized. The addition of CNC inhibited this transformation, while CNC_d promoted it at early stages of annealing. Overall, the combination of shear banding and crystal transformation inducing properties of surface modified CNC provides an intriguing option for future improvement of CNC polyamide nanocomposites.

Keywords: Cellulose Nanocrystal, Polyamide, Surface Modification, Plasticizer, Shear bands, Annealing, Crystalline structure,

1. Introduction

Global environmental protection efforts and limited petroleum feedstocks have led to increasing research and development on bio-based polymers and composites in the past two decades.[1] Poly(lactic acid) (PLA), poly(butylene succinate), poly(caprolactone), polyhydroxyalkanoates (PHA), and poly(trimethylene terephthalate (PTT) are just a few examples of polymers that can be produced from bio-derived monomers.[1,2] Polyamide 11 (PA11), produced from castor oil, is a performance thermoplastic polymer that is likewise derived from renewable resources.[3] Current applications for PA11 include pipes, tubing, and fuel lines for automotive and offshore oil applications. PA11 is a semicrystalline polymer with good thermal stability and chemical resistance.[3,4] Compared to other polyamides, such as PA6 and PA6/6, it also has good resistance to moisture and is generally used as a replacement for PA12 during supply shortage.[5] Many research studies have been focused on improving the properties of PA11 by making composite materials with graphene oxide,[6] glass,[7] silica,[8,9] clay,[10–13] and different types of carbon nanotubes (CNT) [14–17] being some of the commonly investigated fillers. The addition of these fillers usually leads to improved mechanical properties and thermal stability. Nevertheless, reinforcing nanoparticles derived from renewable sources are more desirable to keep the inherent sustainability of PA11.

Cellulose nanocrystals (CNCs) are whisker shaped nanoparticles (3-10 nm wide and 50-500 nm long) derived from biomass such as woods, plants, and algae.[18] Their unique combination of mechanical, thermal, and optical properties have led to numerous research studies in different fields in the past decade.[18–25] The utilization of CNCs as reinforcing

fillers for polymer nanocomposites are at the forefront of CNC research.[22,24–26] Many studies have been conducted on nanocellulose-based composites of the polyamide family of polymers.[27–32] Correa et al. focused on improving the processability and thermal stability of CNC during high temperature processing by coating CNC with PA6 first.[30] Nicharat et al. achieved a similar goal by using phosphoric acid hydrolyzed CNC in PA12 composite.[32] Panaitescu et al. fabricated PA11/CNC nanocomposites by melt mixing, and reported an increase in modulus and strength.[29,31] One common trend found among all the studies on CNC/polyamide nanocomposite was the reduction of ductility of polyamide with addition of CNC, a common trade-off for nanocomposite materials, likely due to aggregation and poor interfacial interaction.[33] By comparison, a hydrophobic surface can passivate interactions and prevent embrittlement. Interfacial engineering is the key to improve nanocomposite properties. For example, Nie et al. reported increased strength and toughness of CNT/PA11 composite through improved interfacial load transfer by utilizing a nanohybrid shish kebab structure, which was synthesized through controlled crystallization of PA11 on the CNT surface.[14] In recent years, there have been numerous studies that surface functionalize CNC in attempts to enhance nanocomposite properties.[34–39]

In this study, surface modification was performed on CNCs to improve their interfacial interaction and dispersibility in PA11. CNCs were modified with fatty acid side chains via esterification, a common surface modification moiety, and then dispersed in a co-solvent blend with PA11. Nanocomposite films were fabricated by solvent casting, followed by melt compression molding. To study the mechanism of action, an ester of aliphatic fatty acid with similar structure to the side chains of modified CNCs was added with unmodified CNC. The

mechanical and thermal properties of different types of CNC/PA11 nanocomposite were investigated.

2. Methods

2.1 Materials

11.8 wt% never-dried CNC suspension in water was provided by USDA Forest Service-Forest Products Laboratory (FPL), Madison, WI, USA.[40] Dimethyl Sulfoxide (DMSO, anhydrous 99.9%), 1'-Carbonyldiimidazole (CDI, reagent grade), Acetone, (ACS reagent), Dodecanoic acid (98%), Methyl laurate (ML, 98%), Formic acid (95%), Dichloromethane (DCM, 99.5%), and PA11 ($M_v = 20,000$) were purchased from Sigma Aldrich, St. Louis, MO, USA. Ethanol (200 proof) were purchased from VWR, West Chester, PA, USA.

2.2 Surface Modification of CNC

CNCs were modified using CDI and dodecanoic acid to generate dodecanoyl grafted CNC (CNC_d). The detailed reaction procedure can be found elsewhere.[41] Briefly, CNCs were first solvent exchanged from never-dried water suspension to acetone and then to DMSO. Dodecanoic acid was first mixed with CDI for 24 hours. Subsequently, CNC/DMSO suspension was added to initiate the modification reaction. The reactions were carried out at 90 °C for 72 hours. CNC_d was purified and stored in ethanol. Elemental analysis of CNC_d samples was conducted by Galbraith Laboratories (Knoxville, TN, USA). Carbon, hydrogen, and oxygen

contents were measured for CNC_d and used to calculate degree of substitution and the weight fraction of grafted side chain in the sample.

2.3 Fabrication of CNC/PA11 nanocomposite

CNC/PA11 nanocomposites were fabricated via solvent casting followed by compression molding. PA11 pellets were dissolved in 50/50 v/v% formic acid/DCM suspension using an ultrasonication bath.[42] For unmodified CNC/PA11 nanocomposite, CNCs were solvent exchanged from never-dried CNC suspension in water to acetone first and then redispersed in formic acid. Acetone was removed using a rotary evaporator. For CNC_d/PA11 nanocomposite, CNC_d was solvent exchanged from ethanol to formic acid and redispersed in DCM. For CNC+ML/PA11 nanocomposite, ML was added to CNC/formic acid suspension so that the ML to CNC weight ratio was the same as the grafted side chain to CNC ratio in CNC_d samples. The CNC+ML/PA11 suspension was further agitated with a vortexer allowing uniform dispersion of CNC and ML. These CNC, CNC_d, and CNC+ML suspensions were combined with PA11 suspensions. The formic acid and DCM volume ratio were adjusted to be consistent for all samples. The nanocomposite suspensions were cast in glass petri dishes. Solvents were removed via vacuum oven at 100°C for 8 hours to generate a nanocomposite pre-film.

To fabricate nanocomposite films, pre-films were compressed at 190 °C under a hot press between two PTFE interlayers. The samples were pre-heated at 190 °C for 5 minutes, compressed under 1000 psi pressure for 2 minutes, and subsequently water quenched to room temperature. A separate set of CNC_d nanocomposite specimens was compressed at 210 °C

following the same procedure. Table 1 lists the final composition of CNC/PA11, CNC_d/PA11, and CNC+ML/PA11 nanocomposite films. The final film thickness was around 150 μm .

Table 1. Summary of Nanocomposite compositions

Filler Type	Structure	Filler wt%	CNC wt%	Side chain wt%	ML wt%
CNC		1	1		
		3	3		
		5	5		
		7	7		
		10	10		
CNC_d		1	0.55	0.45	
		3	1.65	1.35	
		5	2.75	2.25	
		7	3.85	3.15	
		10	5.5	4.5	
CNC+ML		1	0.55		0.45
		5	2.75		2.25
		10	5.5		4.5

2.4 Tensile testing

Tensile testing specimens were prepared by laser cutting dog-bone shapes out of nanocomposite films, following ASTM D638 Type IV sample dimensions proportionally decreased by 50%. The gauge length was 12.5 mm. The specimens were tested using a MTS insight universal tensile testing machine (MTS system Corp., Eden Prairie, MN, USA) at 2 mm/min. Ten replicates were tested for each type of specimen. The average and standard deviation were reported. Student *t*-tests were conducted with threshold level set at 0.05. The tensile testing process was recorded using a Canon 60D digital camera. The fractured specimens were observed using a Carl Zeiss (Thornwood, NY, USA) inverted microscope.

2.5 Scanning Electron Microscopy (SEM)

The fracture surface morphologies of PA11 and nanocomposites were investigated using a Phenom Pro Desktop SEM (Phenom-World B.V., Eindhoven, The Netherlands). The fracture surface of each specimen was mounted on carbon tape and sputter-coated with gold.

2.6 Dynamic mechanical analysis (DMA)

Neat PA11, CNC/PA11, CNC_d/PA11, and CNC+ML/PA11 nanocomposites were analyzed by DMA (Q800 TA instruments, New Castle, DE, USA). The specimens were cut into 20 mm by 6.4 mm strips with gap separation of 10-11mm and tested under tension. Tests were conducted from -100 °C to 150 °C with a heating rate 10 °C/min, strain amplitude of 15 µm, and frequency of 1 Hz.

2.7 Differential Scanning Calorimetry (DSC)

2.7.1 Processing history study

DSC measurements were conducted on Neat PA11, CNC/PA11, CNC_d/PA11, and CNC+ML/PA11 nanocomposite specimens using TA Q100 (TA instruments, New Castle, DE, USA). 8-10 mg of each sample were measured under Nitrogen atmosphere in aluminum pans. The samples were first equilibrated at -50 °C, followed by heating to 250 °C at 10 °C/min, then cooled to -50 °C at 10 °C/min, and finally heated back up to 250 °C at 10 °C/min. The degree of crystallinity (X_c) of PA11 and nanocomposites were calculated using Equation 1:

$$X_c(\%) = \frac{\Delta H_f}{w \times \Delta H_o} \times 100 \quad (1)$$

ΔH_f and ΔH_o are the heat of fusion of nanocomposites and 100% crystalline PA11, which is 226.4 J/g, respectively.[43] w is the weight fraction of PA11 in the nanocomposites.

2.7.2 Isothermal annealing study

To explore the potential crystal structure changes, an isothermal annealing study was conducted on PA11 and nanocomposite specimens. The specimens were first fabricated via solvent casting as described in Section 2.3. These specimens were then heated rapidly to 187 °C in DSC and held at 187 °C isothermally for different amounts of time. The specimens were then cooled at 20°C/min to 0 °C, followed by heating to 220 °C at 10 °C/min. The final heating ramp was used to monitor the crystal structure change by measuring the melting temperature and the heat of fusion (ΔH_f) of the crystalline peaks. ΔH_f was calculated by integrating the crystalline peaks with OriginPro 2015.

2.8 Thermogravimetric Analysis (TGA)

The TGA experiments were conducted with a TA Q50 (TA Instruments). 10-15 mg of specimen was heated to 800 °C at 10 °C/min. under nitrogen atmosphere.

3. Results and discussions

To better disperse CNCs in PA11, CNCs were surface modified with dodecanoic acid and CDI to create dodecanoyl CNC (CNC_d). The detailed structure of CNC_d is presented elsewhere.[41] Solid state nuclear magnetic resonance spectroscopy, X-ray diffraction, and elemental analysis were conducted on the CNC_d used here which can be found in the supplementary information. From elemental analysis, the degree of substitution (DS) was calculated to be 0.72 using the method proposed by Vaca-Garcia et al.[44] The weight fraction of CNC and grafted side chain in the CNC_d samples were calculated to be approximately 55 wt% and 45 wt%, respectively. To isolate the effect of side chains, methyl laurate (ML) was chosen as an analogous structure to the dodecanoyl side group of CNC_d. Keeping the same weight ratio of CNC and aliphatic group, ML was added to PA11 along with CNC to create CNC+ML nanocomposite specimens as a comparison. ML was expected to freely disperse in PA11 matrix as opposed to the side chains of CNC_d, which were covalently attached to the surface of CNC. After solvent casting and before compression molding, the nanocomposite films along with neat PA11 were analyzed with TGA to investigate their thermal stability. The TGA thermograms were shown in Figure S4 of the Supplemental Information. All samples were stable up until 200 °C indicating stability during molding and that there is little free fatty acid in the polymer as an impurity or from liberation during composite fabrication.

3.1 Tensile properties

Uniaxial tensile tests were performed on neat PA11 and nanocomposite specimens. The results are summarized in Figure 1. Some of the representative curves are illustrated in Figure 2. As shown in Figure 1a, the CNC and CNC_d have similar effects on Young's Modulus of PA11 except at high concentration, where CNC continues to stiffen PA11, yet CNC_d reinforced samples reach a plateau. This may be due to potential aggregation of CNC_d at high loading concentrations, although why this is the case with the more hydrophobic surface modified CNCs as opposed to unmodified material is unclear. One of the potential reasons is that surface modification reaction might have changed the intrinsic mechanical properties of CNC and led to the reduction of its reinforcing performance in nanocomposites. The CNC+ML specimens have different effects on modulus compared to CNC and CNC_d specimens. Statistical analysis indicates that there is no significant change in Young's Modulus when CNC+ML specimens are compared with neat PA11, except for specimens with 10 wt% loading. Previous study has shown that linear aliphatic plasticizers can lead to a decrease in Young's Modulus.[45] The results of CNC+ML specimens are likely due to the competing effects of CNC as reinforcing material and ML as plasticizer such that the CNC cancels the reduction in modulus from the plasticizer. For ultimate tensile strength (UTS) of the samples, the trend is similar for all three types of nanocomposites with steady increases in UTS with CNC content, although again, CNC_d shows a plateau, this time at intermediate contents and pure CNC ultimately showing the highest strengths. Interestingly, the CNC+ML also shows higher UTS indicating that CNC is reinforcing PA11 more than plasticization is decreasing UTS. Strain at failure (SAF) and work of fracture (WOF) results are shown in Figure 1c and 1d, respectively. The WOF of the specimens was calculated as the integral area under the stress-strain curve. The plasticizing effects of ML can be clearly found in the CNC+ML specimens, as SAF and WOF of these specimens have statistically

significant increases compared to neat PA11 and other nanocomposite specimens. Both CNC and CNC_d specimens display initial increases in toughness at low loading percentage, follow by decreases at high loading percentage, possibly due to aggregation. Noticeably, the slight decrease in toughness reaches a plateau for CNC_d samples, where it continues to decrease for CNC specimens. This may be attributed to the plasticizing effects of the dodecanoyl side chain of CNC_d. Overall, it is apparent that the best results are from CNC+ML where large increases in strength, ductility and toughness can be realized with a small increase in stiffness. However, if stiffness is desired, the better interfacial interaction of between CNC_d and PA11 can lead to good increases in stiffness and strength without embrittlement.

To further distinguish the contribution of CNC from the side chain in the nanocomposite, the mechanical properties were normalized and compared in terms of their actual CNC content accounting for the added mass of the side chain. The results are illustrated as dotted lines in Figure 1. CNC_d leads to a higher increase in Young's modulus at lower weight percentage than unmodified CNC which is likely associated with a better dispersibility of CNC_d in the PA11 matrix. Halpin-Tsai model was used to predict the Young's modulus of the nanocomposite. The parameters used in the model are elaborated in the Supplemental Information. As shown in Figure 1a, the model gives the closest prediction to normalized CNC_d data until around 3 wt%, where the normalized CNC_d values starts to plateau. The model overestimates the unmodified CNC data. This could be attributed to the model assuming unidirectional orientation of the fillers and perfect adhesion between the filler and matrix. Nevertheless, the good correlation between the normalized CNC_d data and the model prediction could indicate that the surface modified CNC had good interfacial adhesion with PA11 and low loading concentration. In addition, the

compression molding process can potentially lead to orientation of the fillers, which is also in consensus with the model assumption.

Previous studies have shown that simultaneous increase of toughness and modulus could be achieved for CNT reinforced polymer composite with either surface grafted dispersant [46] or bulk addition of dispersant. [47] In both studies, the dispersant had a chemical structure similar to the matrix polymer, hence improved interfacial interaction between CNT and the matrix polymer. For our study, both ML and dodecanoyl side chain have a similar aliphatic structure as PA11. However, drastic improvement of both toughness and stiffness are not observed in this case. This could be attributed to the different interaction mechanism of CNC and CNT with their respective polymer matrix. Previous study focused on CNT and PMMA, which is an amorphous polymer.[46] The study suggested that the entanglement of polymer chains at the interfacial region of CNT and PMMA led to stronger interfacial bonding and better stress transfer. For a semi-crystalline polymer like PA11, the existence of ordered crystalline domain in the polymer matrix could have restricted the polymer chain motion and limited the likelihood of entanglement with the surface chains of grafted CNC. Therefore, the interfacial bonding is less robust. Another possibility could be attributed to the amide hydrogen bonding network governing the mechanical performance of PA11 and dominating the interfacial interaction between CNC and PA11. As shown in Figure 1d, unmodified CNC also led to improvement of toughness at 1-3 wt%. To investigate potential hydrogen bonding between CNC and PA11, the FT-IR spectra of our nanocomposites specimens were collected. However, as shown in Figure S3 of supplementary information, there is no clear shifts in the N-H stretches indicates hydrogen bonding. This could attribute to the low CNC content in nanocomposites. Nevertheless, it is clear from the trends observed in the mechanical property results that unmodified CNC and grafted

CNC had different reinforcing mechanisms in PA11 nanocomposite, although the origin of these phenomena is yet unclear.

Figure 1. Mechanical properties of PA11 nanocomposites. a) Young's Modulus, b) Ultimate tensile strength (UTS), c) Strain at failure (SAF), and d) Work of fracture (WOF). The dotted lines represent the results that were normalized to the actual CNC content in the nanocomposite.

Figure 2. Example stress-strain curves of uniaxial tensile tests for neat PA11 and a) 1wt%, b) 5wt%, c) 10wt% of CNC, CNC_d, and CNC+ML.

3.2 Morphology of fracture surface

To further investigate the mechanical behavior of PA11 and its nanocomposites, the resulting fracture surfaces after tensile testing were investigated using SEM, as shown in Figure 3. Different morphologies of the fracture surfaces are observed. In Figure 3a, neat PA11 has areas of both brittle fracture surface and fibrillation, although brittle fracture surfaces dominate most of the areas. For the CNC_d PA11 specimen, there are also fibrillation and pull-out regions on the fracture surface, as shown in Figure 3b. In areas without fibrillation, a highly porous

surface is observed. These pores could have been formed during the compression molding process. Another possibility is that they are attributed to cavities formed within the specimen during the tensile test. The forming of these cavities could help dissipate additional energy. Similar mechanisms were also found in rubber toughened PA for which the cavities elongated and evolved into fine fibrils.[48] These cavities could have originated from the stress-whitened zones.[48,49] They could have been generated either due to crazing or intrinsic local inhomogeneous deformation, which is associated with the transformation of polymer crystal from spherulitic structure to fibrillar structure.[50] Another possibility is the presence of agglomerates that are below critical flaw size and leads to particle-matrix debonding that creates voids. This phenomenon has been previously observed in isotactic polypropylene filled with CaCO_3 particles.[51] For CNC PA11 nanocomposites in Figure 3c, the fracture surface is similar to that of neat PA11 but with fibrillation in most of the areas. For CNC+ML nanocomposites (Figure 3d), there is nearly no brittle fracture surface, which is likely due to these specimens being severely plasticized and undergoing ductile failure during tensile testing. Similar to the CNC_d specimen, areas of voids and cavities are also found in CNC+ML specimens. However, the concentration of these voids is lower and the size of fibrils generated is larger for CNC+ML specimens.

Figure 3. Fracture surface of a) neat PA11 and PA11 nanocomposite with b) 5wt% CNC_d, c) 5wt% CNC, and d) 5wt% CNC+ML. Scale bar is 20 μm

3.3 Shear banding phenomenon of the tensile specimen

In addition to changing the mechanical properties of PA11, the CNC_d reinforced nanocomposite also generated shear band structures near the fracture zone. Figure 4 illustrates the pictures of broken tensile specimen of PA11 with different types of reinforcement. The darkened color of some specimens is due to presence of CNC, which turns brown after exposure to high temperature. Micrographs of neat PA11 and CNC_d specimens between crossed polarizers are shown in Figure 5. There is no indication of phase separation or large scale aggregate formation, at least at the micro-level. At 1 and 3 wt% of CNC_d, the shear band structures are dense and more concentrated near the fracture tip, where at 5 and 7 wt% of CNC_d, these structures are sparser and more dispersed throughout the specimen. For 1 wt% CNC_d specimen, necking of the specimen is also observed. In Figure 5f, the 5 wt% CNC_d specimen was observed under two crossed polarizers at 0 and 90°. The samples are the brightest at 45°

from the polarizers, which indicates that the polymer chains were aligned with the elongation axis. Figure 5f also shows that these shear band structures were generated at angles less than 45° to the elongation axis. This is similar to the conventional shear bands formed during compression of polymers, which propagated at angles between 35° to 42° to the compressive axis. [50] The process of shear banding formation in CNC_d nanocomposite was also investigated through video capturing of the tensile test. Figure 6 presents the screen shots of neat PA11 and 5 wt% CNC_d nanocomposite tensile tests. The videos of the tensile tests can be found in the supplementary information section. For neat PA11 in Figure 6a, a necking event is observed, followed by failure in the necking region. For the 5wt% CNC_d specimen in Figure 6b, as the shear bands were formed, they led to localized stress whitening, which caused the sample to appear less transparent as the test progressed. Some of the shear bands were nucleated from small defects or notches along the edge of the specimen. These defects and notches were formed when the specimens were cut from a bulk nanocomposite film. Similar stress whitening effects are also found in CNC+ML nanocomposite specimens, as the macrograph in Figure 4c indicates. However, these whitening zones were more concentrated. The sparse shear band like structure was not observed. These stress whitening effects were likely associated with the alignment of the polymer chains near the fracture zone. CNC_d/PA11 nanocomposite samples with thickness ranges from 120 to 250 μm were evaluated. Shear bands were observed in all samples indicating that, at least in the thickness range here, the formation of shear bands in CNC_d/PA11 nanocomposite is independent of the thickness of the sample.

Figure 4. Optical macrographs (pictures) of fractured a) neat PA11 and CNC_d/PA11 nanocomposite, b) CNC/PA11 nanocomposite, and c) CNC+ML/PA11 nanocomposite.

Figure 5. Optical micrographs of fractured a) neat PA11 and CNC_d PA11 nanocomposite with b) 1 wt% CNC_d, c) 3 wt% CNC_d, d) 5 wt% CNC_d, e) 7 wt% CNC_d. In part f), 5wt% CNC_d Polyamide11 nanocomposites were observed and rotated under crossed polarizers. Micrographs in part f) has the same magnification as part d).

Figure 6. Freeze frames of videos of a) neat PA11 and b) 5wt% CNC_d/PA11 nanocomposite uniaxial tensile tests

It is very difficult to isolate the mechanism that led the formation of shear bands in CNC_d/PA 11 nanocomposites. Shear band phenomena have long been observed for glassy amorphous polymers such as polystyrene (PS) and poly(methylmethacrylate) (PMMA).[52] For glassy polymers, there are generally two intrinsic deformation modes: shear yielding and crazing. These two failure modes are often competing with each other.[52] Crazing is usually caused by formation of a thin region of craze that consists of interconnected microvoids and fibrils. Polymers that undergo craze failure typically show limited ductility.[53,54] On the other hand,

shear yielding is the formation of shear bands that are typically caused by localized plastic deformation. Ultimately, ductile failure is usually observed.[53,54] The generation of one phenomenon over the other is governed by a number of factors, such as type of polymer, temperature, testing mode, and strain rate.[52] For semi-crystalline polymers, studies on the formation of shear bands are very limited. Most of the studies have focused on shear band formation under compression and impact testing.[50,55,56] In the case of polyamide, studies have focused on shear band formation in rubber modified polyamide.[48,55,56] The low modulus rubber particle acts as a stress concentrator, and enhances both craze and shear band formation, which increases the toughness of polyamide. However, it is difficult to correlate the shear band-inducing effects of rubber particles to surface modified CNC nanoparticles due to the large size differences and as these CNC_d nanoparticles are considered high modulus filler and stiffen the polymer matrix, as seen in Figure 1a. Also, as shown in Figure 1c, toughness does not increase for most of CNC_d specimens that have shear bands. The main toughening mechanism was rather due to the necking of the specimen, as shown in Figure 5b. Nevertheless, introducing plasticizer into a thermoplastic polymer usually reduces the shear yield stress more than the stress needed for craze formation.[57,58] CNC_d, which has plasticizing groups attached to the nanoparticle surface, may have caused localized reduction of the critical shear yielding stress and acted as shear band nucleators. By contrast, CNC+ML, which has plasticizer ML freely dispersed in PA11, had changes in bulk material properties instead of shear band formation. Overall, it is difficult to conclude that the origin of the shear band formation in CNC_d nanocomposite specimens was due to structure of CNC_d having a high modulus CNC core and plasticizing surface chains, which have competing effects on the brittle-ductile transition of the matrix polymer. Nevertheless, nucleation of shear bands may be a promising route to toughening

for future CNC based polyamide nanocomposites as unlike with rubber toughening, both modulus and strength can be retained.

3.4 DMA analysis

The mechanical properties of PA11 and nanocomposites were further studied using DMA. Storage modulus (E') as a function of temperature is illustrated in Figure 7 and Figure 8, respectively. For the CNC reinforced PA11 in Figure 7a, E' increases at temperatures above and below the glass transition temperature (T_g). This result agrees with other studies of CNC reinforced polymer nanocomposites.[22,25,32] For CNC_d reinforced PA11, E' curve also shifts to the right when compared with neat PA11, indicating increases throughout the entire temperature range, as shown in Figure 7b. For the CNC+ML reinforced PA11 in Figure 7c, E' is lower at temperatures below T_g at 1 wt% loading. As loading increased to 5 wt%, E' is increased both above and below T_g . However, at 10 wt%, the E' above T_g does not increase significantly compared to 5 wt% CNC+ML. This may be attributed to the decrease in T_g with the addition of ML. Overall, these results indicate that ML plasticized the PA11 matrix and has effects competing against CNC on E' of the nanocomposite. As shown in Figure 7d, as different types of nanocomposite specimens with similar amounts of CNC content are compared, E' above T_g increases for all the nanocomposites. This result shows that CNC has a more dominating effect on E' above T_g regardless the addition of plasticizers. For CNC_d and CNC+ML specimens in Figure 7d, the E' below T_g does not have the same amount of improvement as specimens with only CNC added. This indicates that the plasticizing effects of the plasticizers is more significant when PA11 is in glassy state rather than rubbery state. Despite having the same amount of plasticizer as CNC+ML specimens, CNC_d specimens are not severely plasticized. This result

indicates that having plasticizers grafted to the surface of CNC minimized their effects on the polymer matrix at temperatures above and below T_g .

Relaxations of PA11 and nanocomposites are investigated using the Tan δ data illustrated in Figure 8. For the α relaxation that is associated with T_g and centered around 50 to 70 °C, there is a shift to higher temperature in all types of nanocomposite specimens. However, as shown in Figure 8d, CNC_d has the highest increase in T_g when specimens with similar amounts of CNC were compared. The peak around centered at -100 to -50 °C is associated with the β relaxation of PA11. It represents the local chain motion and conformational change. [59] For all specimens, a slight increase in the β relaxation temperature is observed, which indicates the CNC potentially leads to a reduction of free volume in PA11 by hindering chain motion and conformational changes. In addition, at high CNC loadings in Figure 8a, the shape of Tan δ peak becomes broader and lower in height indicating restrictions of molecular chain motions of PA11 which leads to more elastic response of the nanocomposite. This effect is not very apparent in CNC_d and CNC+ML samples due to presence of plasticizer and aliphatic side chain that potentially cause more damping effects.

Figure 7. Storage modulus of neat PA11 along with nanocomposite reinforced with CNC a), CNC_d b), and CNC+ML c). In part d), PA11 nanocomposites with different types of filler at similar amount of CNC were compared.

Figure 8. Tan δ of neat PA11 along with nanocomposite reinforced with CNC a), CNC_d b), and CNC+ML c). In part d), PA11 nanocomposites with different types of filler with similar amount of CNC were compared.

3.5 DSC characterization

DSC characterization was conducted on PA11 and its nanocomposites in order to explore the addition of fillers on thermal and crystallization properties of PA11. All specimens used in the DSC study underwent the same processing procedure as the tensile testing specimens, which was solvent casting followed by compression molding. A heat/cool/heat cycle was adopted in order to evaluate the glass transition, crystallization, and melting process of PA11 of different types of nanocomposites. T_g of the specimen was measured during the first heating ramp, since slow cooling rates lead to a lower T_g in the second heating ramp. Similar to the DMA results, T_g increases slightly when compared to the neat PA11 for unmodified CNC nanocomposites. In addition, the CNC+ML specimen has lower T_g than neat PA11. No additional endothermic peaks were observed prior to the melting peaks of PA11, unlike other studies of PA11 cast from formic acid, possibly due to the heat and vacuum treatment of our materials during processing, which removed the residual solvents.[30] This indicates that the depression of T_g in CNC+ML was not caused by residual water, DCM, or formic acid, but rather ML. On the other hand, the CNC_d specimens have increased T_g , which indicates that plasticizers needed to be freely dispersed in the polymer matrix in order to take effect. Attaching them to a stiffening filler like CNC minimizes their effects. The detailed results of T_g are listed in TableS3 of the supplementary information.

The melting behavior of the specimens was also investigated. Figure 9a illustrates the major endothermic events during the first heating ramp of the specimen. The degree of crystallinity of PA11 was calculated for neat polymer and different types of nanocomposite using both the first and second heating ramp. The results are summarized in Table S3 of the supplementary information. There are no drastic changes in the overall crystallinity with the addition of CNC and its derivatives. This could be attributed to the relatively low loading of fillers in the nanocomposite. This also indicates the increase in mechanical properties of the nanocomposite was not due to the increase of degree of crystallinity of PA11, but the interaction between PA11 and the fillers. The crystallization process of PA11 and its nanocomposite were also studied from the cooling ramp of the DSC curve. The crystallization curves of PA11 and its nanocomposite are shown in Figure 9b. The temperatures of the major crystallization peak are listed as T_c in Table S3. Compared to neat PA11, there is a slight decrease in the main T_c for CNC and CNC+ML nanocomposites, while a smaller shoulder peak forms at a slightly higher temperature. This result indicates that there were two different crystallization events, possibly from heterogeneous and homogenous crystallization of PA11. Previous studies have reported that the presence of nanoparticles usually leads to heterogeneous nucleation and shifting of the crystallization peak to a higher temperature.[12,15,30] For CNC_d specimens, only one peak is found, and there is a slight increase in the T_c . CNC_d specimens have a sharper crystallization peak, which appeared at slightly higher temperature as compared to other types of specimens indicating an ability of CNC_d to increase crystallization rate of PA11.

Figure 9. DSC curves of compression molded neat PA11 and nanocomposites during the first heating ramp a) and cooling ramp b). In part c), the first heating ramp of compression molded PA11 nanocomposites with different amounts of CNC_d.

Interestingly, for the CNC_d PA11 nanocomposite in Figure 9a, the DSC melting pattern during the first heating ramp is drastically different from that of neat PA11, CNC, and CNC+ML nanocomposite. For neat PA11 and most of the other nanocomposite samples, there are two melting peaks around 177 °C and 186 °C, respectively. Similar patterns of peaks were observed during the second heating. However, for the CNC_d nanocomposite, there is an additional melting peak at around 190 °C and the 177 °C lower melting peak either disappears or is

subsumed by a broader peak at 186 °C. During the second heating ramp, this additional peak disappeared and the melting pattern resembled that of neat PA11 and other nanocomposites. The change in the melting pattern after the first heating ramp indicates that this newly formed melting peak is related to the nanocomposite fabrication process. In Figure 9c, DSC graphs of PA11 nanocomposites with different amounts of CNC_d are displayed. As CNC_d content increases, the newly formed peak becomes larger indicating that the structural change is dependent upon CNC_d concentration. At the same time, the α' crystal peak becomes smaller and broader indicating that some transformation is happening. The heat of fusion (ΔH_f) data of the original and the new peaks of CNC_d nanocomposite is listed in Table S4 of the supplemental information.

There are a few possible reasons for this newly formed melting peak in DSC. It could be related to a crystal phase transformation of PA11, similar to that of the Brill transition, which is a reversible phase transformation upon heating.[60] Previous reports identified six different crystal structures for PA 11: α , α' , β , γ , δ , δ' . [15,30,60–62] Different processing procedures are required to obtain each of these crystal structures. For this study, the only possible structures are α and α' polymorphs. The α crystalline structure is usually obtained from solvent casting and is the most thermodynamically stable form. The α' polymorph is very close in structure to α and is typically obtained from slow cooling from the melt. The DSC melting patterns for all the specimens except CNC_d/PA11 nanocomposite in Figure 9a resemble that of the α' structure of PA11, as seen in previous work likely due to the relatively slow cooling from compression molding.[60] To the best of our knowledge, there are no previous DSC studies that report this type of melting pattern for any of the known PA11 polymorphs, making the possibility of a new phase unlikely. Regardless, X-ray diffractograms were collected for all the compression molded

specimens. As shown in Figure S5 of the supplemental information, the XRD patterns for neat PA 11 and different types of nanocomposites are similar, indicating the same crystal structure for all specimens. There have been previous studies on CNT/PA11 nanocomposite with a similar melting peak patterns.[14,15] The authors reported a nano-hybrid shish kebab (NHSK) structure of PA11, crystallized on the surface of CNT, which led to the formation of two sizes of crystal lamellae. The NHSK consisted of an inner layer of crystal grown on the CNT surface, which had a higher melting point due to its lamella having larger longitudinal thickness. The kebab structure was subsequently crystallized on this inner layer.[14,63] It is possible that a similar structure was formed on the surface of CNC_d. However, no microscopy data could be obtained to solidify this hypothesis. Another possibility is that PA11 underwent an isothermal annealing event near its melting point. As CNC_d/PA11 nanocomposites were compression molded at 190 °C, there could be a small portion of large sized PA11 crystals that underwent annealing while the smaller sized PA11 crystals were melted. As well, Gogolewski previously conducted an isothermal annealing study of PA11 at 180 °C for different amounts of time up to 2000 hours.[64] No crystal phase transformation was observed. However, the original melting peak at 190 °C became smaller, while a new melting peak at up to 20 °C higher temperature was generated after hours of annealing. Gogolewski suggested this was due to increased PA11 crystal perfection and lamellae thickness as annealing was prolonged. A similar phenomenon could have occurred during our processing steps of PA11 nanocomposites. To further explore this phenomenon, annealing studies of neat PA11 and different types of nanocomposites were conducted.

3.6 Annealing study

To mimic the annealing event during compression molding, solvent-cast neat PA11 and 5wt% nanocomposite specimens were annealed at 187 °C in the DSC for different times, quenched to 0 °C, and subsequently analyzed by DSC. The melting patterns of annealed specimens are illustrated in Figure 10. Solvent-cast specimens that were directly heated to 220 °C under the same heating rate are listed as ‘Unannealed’ in Figure 10. The ‘Unannealed’ samples show only one peak around 187 °C, resembling that of the typical α polymorph DSC thermogram.[60] After annealing, a new peak was formed around 193 °C for all the specimens. The melting temperatures of both original and newly formed peaks are listed in Figure 11a. For Neat PA11, as annealing time is increased, the original melting peak shifted to lower temperature, broadens and is reduced, while the new melting peak shifted to higher temperature and grows larger. This possibly indicates that there was a critical threshold for the size of the PA11 crystals. Below this size threshold, the crystals were melted, became smaller, and led to the left shift of the original melting peaks. Above this size threshold, the crystals became larger due to annealing and led to right shift of the newly formed peaks. For the CNC nanocomposite in Figure 10b, this change in crystal structure seems to be inhibited. The newly formed peak around 193 °C is much smaller compared to neat PA11, yet there is also a new peak generated around 183 °C, possibly due to the transformation of α to α' polymorph. A similar phenomenon is also observed in CNC+ML nanocomposite at low annealing time in Figure 10d. The new high melting peak is also observed to be much larger than in the CNC nanocomposite, indicating the plasticization effect, although the peak is still smaller than in neat PA11. Interestingly, in comparison to the molded specimens where the time of heating, albeit inexact is 420 seconds, the isothermally annealed pure PA11 attains half transformation, while the molded materials have little to no

transformation. However, the CNC_d composites both show full transformation. The discrepancy is likely due to differences in actual time at temperature and cooling rates.

Figure 10. DSC melting curves of neat PA11 a) and nanocomposite with 5 wt% of CNC b), CNC_d c), and CNC+ML d) after different amounts of annealing time at 187 °C.

Figure 11. The changes in melting temperature a) and heat of fusion b) of the original and newly generated melting peaks of PA11 and nanocomposites after different amounts of annealing time at 187 °C.

To further analyze the annealing event, the heat of fusion (ΔH_f) was calculated by integrating the area under the melting peaks and normalizing to the weight fraction of PA11. The results for the original peaks and the new peak are plotted separately in Figure 11b as a function of annealing time. The total ΔH_f of the peaks are shown in Figure 11c. The ΔH_f at zero annealing time represents the ΔH_f of original solvent-cast specimens without annealing. In neat PA 11, ΔH_f for the original peak decreased as the new peak in increased as annealing time increases. This indicates there may be a transformation event. As the original solvent generated PA11 crystals started to melt, there are large PA11 crystals above the size threshold that become

thicker. They utilize materials from the smaller PA11 crystals that are just melted. As shown in Figure 11c, there is an initial decrease to the total ΔH_f . This is likely due to the slower initiation rate for the transformation compared to the melting rate of the crystals. As annealing time increased, there is no drastic change in total ΔH_f . Noticeably, for all specimens, the total ΔH_f are lower for annealed samples comparing to that of the solvent-cast samples (zero annealing time). This is likely due to the solvent-casting method leading to higher overall crystallinity. For the CNC nanocomposites, there are no drastic changes in ΔH_f of the original melting peak as the annealing time increased. As expected, ΔH_f for the newly generated peak in CNC nanocomposites is also small suggesting that CNC may be inhibiting the PA11 crystal size transformation by acting as heterogonous nucleator and leading to formation of crystals with smaller size or possibly preventing crystal growth/recrystallization directly by acting as a barrier to chain motion. Regardless, addition of CNC to PA11 effectively inhibits the recrystallization in PA11. As seen in Figure 11b, the CNC+ML nanocomposites show a similar trend to neat PA11 indicating that CNC+ML did not affect the crystal size transformation event fundamentally. However, as compared to neat PA11, ΔH_f of the new peak for CNC+ML nanocomposites is smaller and does not increase as rapidly. This is likely attributed to the presence of CNC in the specimen inhibiting formation as before. However, the presence of ML plasticizer seems to allow for higher new peak ΔH_f as compared to CNC only, which is likely the result of enhanced chain mobility. Regardless, overall crystallinity is less with ML plasticizer than all others, as expected. For the CNC_d nanocomposite, a different kinetics is observed in Figure 11b. ΔH_f for the new peak for CNC_d specimens is higher than neat PA11 at low annealing time, but it falls and reaches a plateau at high annealing time. This is possibly due to CNC_d acting as a nucleator for the crystal size transformation at low annealing time. At long annealing times, it is unknown

why the transformation plateaus and total ΔH_f decreases. However, the effect may at least partially be artificial as it is known that larger, more perfect crystals have an effect on the enthalpy of melting and heat of fusion. In this case we are assuming that the apparent heat evolution scales linearly with crystallinity, however, if the actual heat of fusion changes due to crystalline changes, then the crystallinity we assume would be different. Regardless, it is clear that CNC_d greatly enhances the transformation ability of PA11 crystallites allowing full transformation in a matter of minutes rather than hours. Thus, CNC_d is a promising recrystallization nucleator for such processes as injection molding.

It is possible that the shear band inducing effects of CNC_d was related to the larger PA11 crystals formed during annealing. To investigate this relationship, CNC_d nanocomposite was compression molded at 210 °C following the same procedure in order to completely melt the crystals and eliminate any possible annealing event. These types of specimens also generated shear bands as shown in Figure S6 of the supplementary information. This indicates the shear band inducing effects were not related to the larger PA11 crystals. Nevertheless, the two unrelated but simultaneous effects of CNC_d on PA11 can be further explored in future manufacturing, processing, and performance enhancement of polyamide nanocomposite.

4. Conclusion

In this study, unmodified CNC, dodecanoic acid modified CNC (CNC_d), and CNC with methyl laurate as an additive (CNC+ML) were used to create nanocomposites of PA11 via solution casting followed by compression molding. For mechanical properties, CNC_d acted as an intermediate between CNC and CNC+ML. CNC_d improved Young's modulus of PA11 as well as maintained the toughness. The CNC and CNC+ML nanocomposites had to sacrifice one

for the other. In addition, shear band like structures were formed for the CNC_d nanocomposites during tensile testing, suggesting a potential alternative toughening mechanism for PA11. Thermal analysis of PA11 and its nanocomposite suggested CNC_d minimized the glass transition temperature depression effect of the plasticizer. The addition of CNC_d to the PA11 also led to higher crystallization rate and initiated crystal structure changes of PA11 crystals to form crystals that melted at higher temperature, although we found this crystal transformation unrelated to the shear-banding effect. Overall, surface modified CNC could maintain the reinforcing effects of CNC in PA11 while providing added benefits of creating a new toughening mechanism and initiating crystal structure change. However, it is not known whether these effects are specific to this system or can be broadened to other polyamides and/or surface modifiers.

5. Supplemental Information

Videos of uniaxial tensile test of neat PA11, 1wt%, 5wt%, and 7wt% of CNC_d nanocomposite, ^{13}C solid-state NMR spectra of unmodified and dodecanoyl grafted CNC, Table of elemental analysis results and degree of substitution calculation of unmodified and dodecanoyl grafted CNC, XRD diffractograms of unmodified and dodecanoyl grafted CNC, Haplin-Tsai model and its parameters, FT-IR spectra of PA11 and different types of PA11 nanocomposite, Table of DSC data of compression molded PA11 and nanocomposite, XRD diffractograms of compression molded PA11 and nanocomposite, Micrographs of broken CNC_d/PA11 nanocomposite tensile specimens that were compression molded at 210 °C.

6. Acknowledgement

The authors would like to thank John Harwood from Purdue Interdepartmental NMR Facility for obtaining the ^{13}C solid-state NMR spectra and John Howarter from Purdue University Materials Engineering department for providing suggestions and corrections to the manuscript. This research was supported by the National Science Foundation IGERT sustainable electronic grant#1144843-DGE and the Forest Products Laboratory under USDA grant# 11-JV-11111129-118

7. References

- [1] G.Q. Chen, M.K. Patel, *Plastics Derived from Biological Sources: Present and Future*, Chem. Rev. n/a (2012) n/a.
- [2] S. a. Attaran, a. Hassan, M.U. Wahit, *Materials for food packaging applications based on bio-based polymer nanocomposites: A review*, J. Thermoplast. Compos. Mater. (2015). doi:10.1177/0892705715588801.
- [3] G. Wypych, PA-11 polyamide-11, in: *Handb. Polym.*, Elsevier, 2012: pp. 235–238. doi:10.1016/B978-1-895198-47-8.50002-3.
- [4] R. Greco, L. Nicolais, *Glass transition temperature in nylons*, Polymer (Guildf). 17 (1976) 1049–1053. doi:10.1016/0032-3861(76)90005-7.
- [5] K. Marchildon, *Polyamides - Still strong after seventy years*, Macromol. React. Eng. 5 (2011) 22–54. doi:10.1002/mren.201000017.
- [6] D. Yuan, B. Wang, L. Wang, Y. Wang, Z. Zhou, *Unusual toughening effect of graphene oxide on the graphene oxide/nylon 11 composites prepared by in situ melt polycondensation*, Compos. Part B Eng. 55 (2013) 215–220. doi:10.1016/j.compositesb.2013.05.055.

- [7] H. Chung, S. Das, Processing and properties of glass bead particulate-filled functionally graded Nylon-11 composites produced by selective laser sintering, *Mater. Sci. Eng. A*. 437 (2006) 226–234. doi:10.1016/j.msea.2006.07.112.
- [8] E. Petrovicova, R. Knight, L.S. Schadler, T.E. Twardowski, Nylon 11 / Silica Nanocomposite Coatings Applied by the HVOF Process . I . Microstructure and Morphology, Optimization. (2000) 1684–1699.
- [9] H. Chung, S. Das, Functionally graded Nylon-11/silica nanocomposites produced by selective laser sintering, *Mater. Sci. Eng. A*. 487 (2008) 251–257. doi:10.1016/j.msea.2007.10.082.
- [10] Y. Hu, L. Shen, H. Yang, M. Wang, T. Liu, T. Liang, J. Zhang, Nanoindentation studies on Nylon 11/clay nanocomposites, *Polym. Test*. 25 (2006) 492–497. doi:10.1016/j.polymertesting.2006.02.005.
- [11] G. Zhang, Y. Li, D. Yan, Polymorphism in Nylon-11/Montmorillonite Nanocomposite, *J. Polym. Sci. Part B Polym. Phys*. 42 (2004) 253–259. doi:10.1002/polb.10680.
- [12] Q. Zhang, M. Yu, Q. Fu, Crystal morphology and crystallization kinetics of polyamide-11/clay nanocomposites, *Polym. Int*. 53 (2004) 1941–1949. doi:10.1002/pi.1581.
- [13] T. Liu, K.P. Lim, W.C. Tjiu, K.P. Pramoda, Z.K. Chen, Preparation and characterization of nylon 11/organoclay nanocomposites, *Polymer (Guildf)*. 44 (2003) 3529–3535. doi:10.1016/S0032-3861(03)00252-0.
- [14] M. Nie, D.M. Kalyon, F.T. Fisher, Interfacial load transfer in polymer/carbon nanotube nanocomposites with a nanohybrid shish kebab modification., *ACS Appl. Mater. Interfaces*. 6 (2014) 14886–93. doi:10.1021/am501879q.
- [15] G. Mago, D.M. Kalyon, F.T. Fisher, Nanocomposites of polyamide-11 and carbon

- nanostructures: Development of microstructure and ultimate properties following solution processing, *J. Polym. Sci. Part B Polym. Phys.* 49 (2011) 1311–1321.
doi:10.1002/polb.22311.
- [16] S. Huang, M. Wang, T. Liu, W.-D. Zhang, W.C. Tjiu, C. He, X. Lu, Morphology, thermal, and rheological behavior of nylon 11/multi-walled carbon nanotube nanocomposites prepared by melt compounding, *Polym. Eng. Sci.* 49 (2009) 1063–1068.
doi:10.1002/pen.21349.
- [17] J. Gao, M.E. Itkis, A. Yu, E. Bekyarova, B. Zhao, R.C. Haddon, Continuous spinning of a single-walled carbon nanotube-nylon composite fiber, *J. Am. Chem. Soc.* 127 (2005) 3847–3854. doi:10.1021/ja0446193.
- [18] R.J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, Cellulose nanomaterials review: structure, properties and nanocomposites., *Chem. Soc. Rev.* 40 (2011) 3941–94.
doi:10.1039/c0cs00108b.
- [19] J.A. Diaz, X. Wu, A. Martini, J.P. Youngblood, R.J. Moon, Thermal Expansion of Self-Organized and Shear-Oriented Cellulose Nanocrystal Films, *Biomacromolecules*. 14 (2013) 2900–2908. doi:10.1021/bm400794e.
- [20] J.A. Diaz, Z. Ye, X. Wu, A.L. Moore, R.J. Moon, A. Martini, D.J. Boday, J.P. Youngblood, Thermal Conductivity in Nanostructured Films: From Single Cellulose Nanocrystals to Bulk Films, *Biomacromolecules*. 15 (2014) 4096–4101.
doi:10.1021/bm501131a.
- [21] J.-C. Liu, R.J. Moon, A. Rudie, J.P. Youngblood, Mechanical performance of cellulose nanofibril film-wood flake laminate, *Holzforschung*. 68 (2014) 283–290. doi:10.1515/hf-2013-0071.

- [22] J.-C. Liu, D.J. Martin, R.J. Moon, J.P. Youngblood, Enhanced thermal stability of biomedical thermoplastic polyurethane with the addition of cellulose nanocrystals, *J. Appl. Polym. Sci.* 132 (2015) 41970. doi:10.1002/app.41970.
- [23] A.B. Reising, R.J. Moon, J.P. Youngblood, Effect of particle alignment on mechanical properties of neat cellulose nanocrystal films, *J. Sci. Technol. For. Prod. Process.* 2 (2012) 32–41.
- [24] S. Chen, G. Schueneman, R.B. Pipes, J. Youngblood, R.J. Moon, Effects of Crystal Orientation on Cellulose Nanocrystals–Cellulose Acetate Nanocomposite Fibers Prepared by Dry Spinning, *Biomacromolecules.* 15 (2014) 3827–3835. doi:10.1021/bm501161v.
- [25] S.X. Peng, R.J. Moon, J.P. Youngblood, Design and characterization of cellulose nanocrystal-enhanced epoxy hardeners, *Green Mater.* 2 (2014) 193–205. doi:10.1680/gmat.14.00015.
- [26] C. Miao, W.Y. Hamad, Cellulose reinforced polymer composites and nanocomposites: a critical review, *Cellulose.* 20 (2013) 2221–2262. doi:10.1007/s10570-013-0007-3.
- [27] a. Awal, M. Sain, M. Chowdhury, Preparation of cellulose-based nano-composite fibers by electrospinning and understanding the effect of processing parameters, *Compos. Part B Eng.* 42 (2011) 1220–1225. doi:10.1016/j.compositesb.2011.02.011.
- [28] A. Kiziltas, D.J. Gardner, Y. Han, H.-S. Yang, Dynamic mechanical behavior and thermal properties of microcrystalline cellulose (MCC)-filled nylon 6 composites, *Thermochim. Acta.* 519 (2011) 38–43. doi:10.1016/j.tca.2011.02.026.
- [29] D.M. Panaitescu, A.N. Frone, C. Nicolae, Micro- and nano-mechanical characterization of polyamide 11 and its composites containing cellulose nanofibers, *Eur. Polym. J.* 49 (2013) 3857–3866. doi:10.1016/j.eurpolymj.2013.09.031.

- [30] A.C. Corrêa, E. de Moraes Teixeira, V.B. Carmona, K.B.R. Teodoro, C. Ribeiro, L.H.C. Mattoso, J.M. Marconcini, Obtaining nanocomposites of polyamide 6 and cellulose whiskers via extrusion and injection molding, *Cellulose*. 21 (2014) 311–322.
doi:10.1007/s10570-013-0132-z.
- [31] D.M. Panaitescu, R.A. Gabor, A.N. Frone, E. Vasile, Influence of Thermal Treatment on Mechanical and Morphological Characteristics of Polyamide 11 / Cellulose Nanofiber Nanocomposites, *J. Nanomater.* 2015 (2015) 11. doi:doi.org/10.1155/2015/136204.
- [32] A. Nicharat, J. Sapkota, C. Weder, E.J. Foster, Melt processing of polyamide 12 and cellulose nanocrystals nanocomposites, *J. Appl. Polym. Sci.* 132 (2015) n/a-n/a.
doi:10.1002/app.42752.
- [33] K. Oksman, Y. Aitomäki, A.P. Mathew, G. Siqueira, Q. Zhou, S. Butylina, S. Tanpichai, X. Zhou, S. Hooshmand, Review of the recent developments in cellulose nanocomposite processing, *Compos. Part A Appl. Sci. Manuf.* (2015).
doi:10.1016/j.compositesa.2015.10.041.
- [34] S. Eyley, W. Thielemans, Surface modification of cellulose nanocrystals., *Nanoscale*. 6 (2014) 7764–79. doi:10.1039/c4nr01756k.
- [35] Y. Habibi, Key advances in the chemical modification of nanocelluloses., *Chem. Soc. Rev.* 43 (2014) 1519–42. doi:10.1039/c3cs60204d.
- [36] C. Tan, J. Peng, W. Lin, Y. Xing, K. Xu, J. Wu, M. Chen, Role of surface modification and mechanical orientation on property enhancement of cellulose nanocrystals/polymer nanocomposites, *Eur. Polym. J.* 62 (2015) 186–197. doi:10.1016/j.eurpolymj.2014.11.033.
- [37] D. Yang, X. Peng, L. Zhong, X. Cao, W. Chen, S. Wang, C. Liu, R. Sun, Fabrication of a highly elastic nanocomposite hydrogel by surface modification of cellulose nanocrystals,

- RSC Adv. 5 (2015) 13878–13885. doi:10.1039/C4RA10748A.
- [38] A. Junior de Menezes, G. Siqueira, A.A.S. Curvelo, A. Dufresne, Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites, *Polymer (Guildf)*. 50 (2009) 4552–4563. doi:10.1016/j.polymer.2009.07.038.
- [39] T. Lu, M. Jiang, Z. Jiang, D. Hui, Z. Wang, Z. Zhou, Effect of surface modification of bamboo cellulose fibers on mechanical properties of cellulose/epoxy composites, *Compos. Part B Eng.* 51 (2013) 28–34. doi:10.1016/j.compositesb.2013.02.031.
- [40] R.S. Reiner, A.W. Rudie, Process Scale-Up of Cellulose Nanocrystal Production to 25 kg per Batch at the Forest Products Laboratory, in: M.T. Postek, R.J. Moon, A.W. Rudie, M.A. Bilodeau (Eds.), *Prod. Appl. Cellul. Nanomater.*, TAPPI Press, Peachtree Corners, GA, 2013: pp. 21–24.
- [41] S.X. Peng, H. Chang, S. Kumar, R.J. Moon, J.P. Youngblood, A comparative guide to controlled hydrophobization of cellulose nanocrystals via surface esterification, *Cellulose*. 23 (2016) 1825–1846. doi:10.1007/s10570-016-0912-3.
- [42] K. Behler, M. Havel, Y. Gogotsi, New solvent for polyamides and its application to the electrospinning of polyamides 11 and 12, *Polymer (Guildf)*. 48 (2007) 6617–6621. doi:10.1016/j.polymer.2007.08.058.
- [43] M. Inoue, T.R. Company, Studies on Crystallization of High Polymers by Differential Thermal Analysis, *J. Polym. Sci. Part A*. 1 (1963) 2697–2709.
- [44] C. Vaca-Garcia, M.E. Borredon, A. Gaseta, Determination of the degree of substitution (DS) of mixed cellulose esters by elemental analysis, *Cellulose*. 8 (2001) 225–231. doi:10.1023/A:1013133921626.

- [45] A. Belous, R. Tchoudakov, A. Tzur, M. Narkis, D. Alperstein, Development and characterization of plasticized polyamides by fluid and solid plasticizers, *Polym. Adv. Technol.* 23 (2012) 938–945. doi:10.1002/pat.1988.
- [46] D. Blond, V. Barron, M. Ruether, K.P. Ryan, V. Nicolosi, W.J. Blau, J.N. Coleman, Enhancement of Modulus, Strength, and Toughness in Poly(methyl methacrylate)-Based Composites by the Incorporation of Poly(methyl methacrylate)-Functionalized Nanotubes, *Adv. Funct. Mater.* 16 (2006) 1608–1614. doi:10.1002/adfm.200500855.
- [47] W. Yuan, W. Li, Y. Mu, M.B. Chan-Park, Effect of side-chain structure of rigid polyimide dispersant on mechanical properties of single-walled carbon nanotube/cyanate ester composite, *ACS Appl. Mater. Interfaces.* 3 (2011) 1702–1712. doi:10.1021/am2002229.
- [48] O.K. Muratoglu, A.S. Argon, R.E. Cohen, M. Weinberg, Toughening mechanism of rubber-modified polyamides, *Polymer (Guildf).* 36 (1995) 921–930. doi:10.1016/0032-3861(95)93590-I.
- [49] H.-J. Sue, A.F. Yee, Toughening mechanisms in a multi-phase alloy of nylon 6,6/polyphenylene oxide, *J. Mater. Sci.* 24 (1989) 1447–1457. doi:10.1007/BF00553180.
- [50] K. Friedrich, Craze and shear bands in semi-crystalline thermoplastics, *Adv. Polym. Sci.* 52–53 (1983) 225–274. doi:10.1007/BFb0024059.
- [51] Y.S. Thio, A.S. Argon, R.E. Cohen, M. Weinberg, Toughening of isotactic polypropylene with CaCO₃ particles, *Polymer (Guildf).* 43 (2002) 3661–3674. doi:10.1016/S0032-3861(02)00193-3.
- [52] A.M. Donald, E.J. Kramer, The competition between shear deformation and crazing in glassy polymers, *J. Mater. Sci.* 17 (1982) 1871–1879. doi:10.1007/BF00540402.
- [53] R. Estevez, M.G.A. Tijssens, E. Van Der Giessen, Modeling of the competition between

- shear yielding and crazing in glassy polymers, *J. Mech. Phys. Solids* 48 (2000) 2585–2617. doi:10.1016/S0022-5096(00)00016-8.
- [54] B.P. Gearing, L. Anand, On modeling the deformation and fracture response of glassy polymers due to shear-yielding and crazing, *Int. J. Solids Struct.* 41 (2004) 3125–3150. doi:10.1016/j.ijsolstr.2004.01.017.
- [55] E. a. Flexman, Impact behavior of nylon-66 compositions: Ductile-brittle transitions, *Polym. Eng. Sci.* 19 (1979) 564–571. doi:10.1002/pen.760190807.
- [56] S.Y. Hobbs, R.C. Bopp, V.H. Watkins, Toughened nylon resins, *Polym. Eng. Sci.* 23 (1983) 380–389. doi:10.1002/pen.760230703.
- [57] B.Z. Jang, D.R. Uhlmann, J.B. Vander Sande, Ductile-Brittle Transition in Polymers., *J. Appl. Polym. Sci.* 29 (1984) 3409–3420. doi:10.1002/app.1984.070291118.
- [58] P.I. Vincent, The Tough-Brittle Transition in Thermoplastics, *Polymer (Guildf)*. 1 (1960) 425–444. doi:10.1016/0032-3861(60)90059-8.
- [59] G. Serpe, N. Chaupart, Relaxation–structure relationship in bulk and plasticized polyamide 11, *J. Polym. Sci. Part B Polym. Phys.* 34 (1996) 2351–2365. doi:10.1002/(sici)1099-0488(199610)34:14<2351::aid-polb5>3.0.co;2-z.
- [60] J. Pepin, V. Miri, J.-M. Lefebvre, New Insights into the Brill Transition in Polyamide 11 and Polyamide 6, *Macromolecules*. 49 (2016) 564–573. doi:10.1021/acs.macromol.5b01701.
- [61] J.O. Fernandez, G.M. Swallowe, S.F. Lee, Crystallization of Nylon 11 under compressive high strain rates, *J. Appl. Polym. Sci.* 80 (2001) 2031–2038. doi:10.1002/app.1301.
- [62] G.S. Hu, Z.Y. Ding, Y.C. Li, B.B. Wang, Crystalline morphology and melting behavior of nylon11/ethylene-vinyl alcohol/dicumyl peroxide blends, *J. Polym. Res.* 16 (2009) 263–

269. doi:10.1007/s10965-008-9225-z.
- [63] N. Ning, S. Fu, W. Zhang, F. Chen, K. Wang, H. Deng, Q. Zhang, Q. Fu, Realizing the enhancement of interfacial interaction in semicrystalline polymer/filler composites via interfacial crystallization, *Prog. Polym. Sci.* 37 (2012) 1425–1455.
doi:10.1016/j.progpolymsci.2011.12.005.
- [64] S. Gogolewski, Effect of annealing on thermal properties and crystalline structure of polyamides. Nylon 11 (polyundecaneamide), *Colloid Polym. Sci.* 257 (1979) 811–819.
doi:10.1007/BF01383352.

Surface modified CNC induced shear bands