Novel Nanocellulose Based Supports for PHBV composites – Synthesis and Properties

Kavan Sheth[1], Ting Zheng[1], James Sternberg[1], Craig Clemons[2], Srikanth Pilla[1]
[1]Clemson Composites Center, Clemson University, Greenville, South Carolina 29607, United States
[2]USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin 53726, United States

Abstract

Novel nanocellulose based nanostructures modified with hyperbranched polymers were prepared by using isocyanate linking chemistry. The chemistry was investigated using FTIR spectroscopy. The composites were homogenized utilizing solvent casting followed by injection molding of the samples. The thermal properties of the prepared samples were investigated using DSC and TGA.

Introduction

PHBV (poly (3-hydroxybutyrate-co-3-hydroxyvalerate)) is a bacterially derived linear polyester containing randomly arranged 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV) segments [1]. PHBV belongs to a family of polymers called PHA (polyhydroxyalkanoates). PHAs have been a critical area of research as they are bio-based as well biodegradable in nature. PHBV, like other PHAs, faces the same drawbacks as it does not have mechanical properties comparable to petroleum-based polymers [2]. The melting temperature (T_m) of PHBV is close to its degradation temperature, making processing these polymers by conventional means complicated [2]. Various properties of PHBV like mechanical properties, crystallinity, degradation rate, thermal stability, and hydrophilicity need to be tailored in order to achieve a polymer with real-world applications [3].

There are various strategies to improve PHBV performance, like blending with natural as well as synthetic materials and chemical modifications like grafting and block copolymerization [4]. One such modification is the incorporation of CNC (crystalline nanocellulose) into PHBV. There have been numerous studies on the benefits of using CNC to modify the properties of PHBV [1,3,5–7].

CNCs are also of interest to researchers due to the high abundance of cellulose and attractive mechanical properties associated with CNCs [8]. CNCs are hydrophilic in nature and need to be surface modified in order to be compatible with some polymers [9].

The current study modifies the CNC using diisocyanates and links them with hyperbranched polymers (HBP) via a urethane linkage. The chemical linkage is investigated using FTIR spectroscopy. These CNC-HBP nanostructures are incorporated into a PHBV matrix employing solvent casting. The thermal properties of the PHBV after CNC modification have been studied using DSC and TGA.

Materials and Methods

Materials

PHBV pellets (ENMAT Y1000P, 8% HV content, injection molding grade) were purchased from Tianan Biological Materials, China. The CNC was prepared by the USDA Forest Products Laboratory in Madison, WI, via sulfuric acid hydrolysis with the dimensions of the length of 271±47 nm and width of 6.17±2.00 nm. CNC was freeze-dried prior to solvent casting and reacting. Commercially available Toluene Diisocyanate (Sigma Aldrich) and Boltorn H30 Regular (Polymer Factory) were purchased.

Support Preparation

The freeze-dried CNC was dispersed in toluene utilizing ultrasonication. The sonicated suspension was checked for stability using cross

polarizers for birefringence. The suspension was heated to 90 °C and held for an hour to get rid of any water in the solution by means of azeotropic distillation. The temperature was reduced to 45 °C, and three equivalents of the toluene diisocyanate were introduced into the system. The reaction was carried out for 5 hours. Following the reaction, the suspension was centrifuged at 6000 rpm for 10 mins. The precipitated product was washed with toluene four times to eliminate unreacted isocyanates and other side products. Following this, the isocyanate functionalized nanocellulose was dispersed in tetrahydrofuran. The suspension was heated to 60 °C. One eq. of HBP was added to the suspension and reacted for 5 hours. After the reaction, the product was centrifuged and separated and washed with THF four times.

Specimen Preparation

The CNC-HBP nanostructures were dispersed in Chloroform using ultrasonication. After ultrasonication, PHBV was added to the suspension and heated to 60 C. The mixture was stirred for 4 hours prior to being solvent cast. The solvent cast specimens were ground and then injection molded using a DSM Xplore microinjection molding unit. Standard type-V tensile specimens (ASTM D638,20 thickness = 1.12 mm) were injection molded with a barrel temperature of 170°C and a mold temperature of 60°C. The injection pressure and holding pressure were both 4.5 bar, and the holding time was 15s.

Characterization

Differential scanning calorimetry (DSC, DSC250, TA Instruments) was carried out on each sample (~5 mg) under a heating−cooling−heating cycle in N_2 from −25 to 200°C at a rate of 20°C/min. The melt temperature (T_m) and glass transition temperature (T_g) was determined from the second heating scan, and the crystallization temperature (T_c) was determined from the cooling scan. Thermogravimetric analysis (TGA, TGA5500, TA Instruments) was carried out on the samples under a ramp of 20°C/min from 25-500 °C. The FTIR data was collected using an ATR-FTIR (Nicolet iS50 FTIR, Thermo Scientific).

Results

CNC – HBP Nanocomposites

The FTIR spectrum of the support (CNC-HBP-Support) was compared to the FTIR spectrum of CNC (CNC-Freeze Dried) as well as HBP (HBP Boltorn H30 Regular). The spectra clearly showed the existence of a urethane linkage, the presence of carbonyl groups from the hyperbranched polymer, and characteristic peaks for the CNC. The IR spectra of the three have been highlighted in Fig. 1. The FTIR results align with the expected results based on previous CNC functionalization studies [10,11]. Table 1 shows characteristic peaks and their wavenumbers key to our nanostructures. Isocyanate functionalization of the CNC is a challenge as the isocyanates are sensitive to moisture, and the presence of moisture leads to self polymerization of the toluene diisocyanate forming a polyurea [8]. For the peaks associated with the CNC unit of the nanocomposite, the broad peak between 3100-3500 cm^{-1} corresponds to the characteristic O-H stretching and inter and intramolecular hydrogen bonding. The band at 2833 cm^{-1} corresponds to the aliphatic C-H stretching in the CNC units. The peak at 1428 cm^{-1} can be assigned to the CH_2 symmetrical bending and scissoring motion in CNC. The peak at 1160 cm^{-1} can be assigned to the CNC unit's C–O–C stretching. The band at 1110 cm^{-1} represents the stretching of the glucose unit in the CNC. For the HBP unit – the prominent carbonyl in its backbone is represented by a peak at 1729 cm^{-1}. The urethane linkage binding the CNC and HBP can be attributed to the peak at 1652 cm^{-1}. Previous studies on surface modification of CNC's with isocyanates have reported the carbonyl peak corresponding to the urethane linkage in between 1600-1700 cm^{-1} [12]. The table below highlights key functional groups associated with the FTIR studies. The goal of surface modification of

CNCs is to increase their processability in non-polar mediums.

Table 1 Key IR peaks

Chemical Group	Wavenumber (cm^{-1})
Cellulose Hydroxyl	3100-3500
HBP Carbonyl	1729
Urethane Carbonyl	1652
Cellulose C-H	1030-1050

The suspensions of modified CNCs are more stable in solvent systems than unmodified CNCs [10–12]. The role of HBP in the composite is to aid in miscibility in the PHBV matrix. The hydrogen bonding due to an abundance of OH groups in the HBP structure with the polar groups of the PHBV polyester aids in the formation of a well-dispersed composite [13,14]. HBPs also have been attributed to reduced melt viscosity and their use as toughening agents and stabilizers. Achieving a nanostructure with the benefits of HBPs as well as CNCs as shown in the IR as a support to the PHBV matrix was the goal of the current study.

Thermal Properties

The thermal properties were assessed using DSC and TGA. Figure 2 shows the DSC and TGA graphs for the PHBV and PHBV composite. The DSC graph showed very similar results for the PHBV without the support and the PHBV with the support. The glass transition temperature was recorded to be around -2.94 °C for the PHBV with the support and -7.98 °C for pure PHBV. Moreover, the onset temperatures were 158 °C and 159 °C for the PHBV without and with the support, respectively. Previous DSC studies have shown PHBV melting temperatures in the range of 170 °C [6,15].

The TGA shows that PHBV degrades at a slightly higher temperature with the filler compared to pure PHBV. There is a sharp decomposition step in between 280-320 °C and no other steps. Previous TGA studies on CNCs show a degradation step in the range of 300-340 °C [16]. This is the same temperature range in which the PHBV shows its degradation step. The TGA thermograms indicate that the properties of the PHBV are not altered significantly and can be processed using existing methods.

Injection Molding

Square samples and tensile specimens were injection molded using the conditions specified above. Figure 3 shows the specimens processed using a microinjection molding machine. The specimens visually show a uniform dispersion and homogeneity. This shows that PHBV composites can be processed using a traditional injection molding setup.

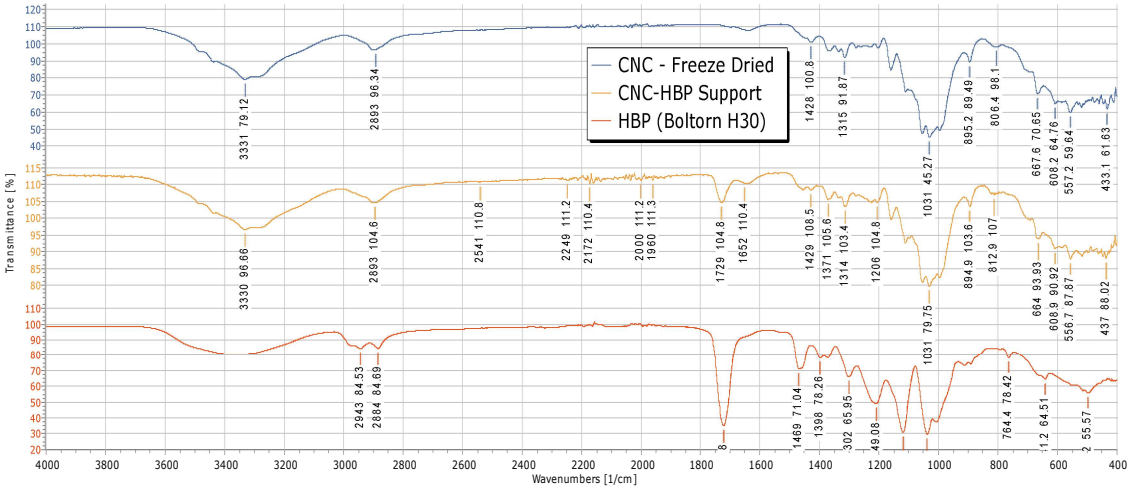

Figure 1 FTIR Spectra of CNC, HBP, and Support

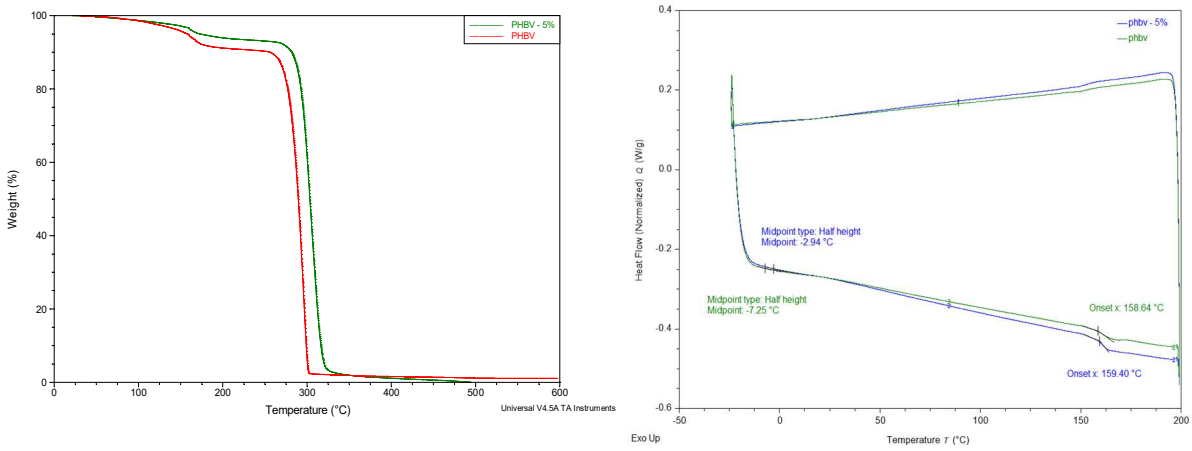

Figure 2 TGA and DSC for PHBV composites

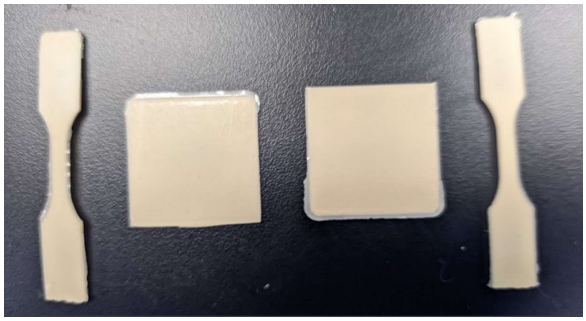

Figure 3 Samples prepared by injection molding

Conclusion

The project focuses on preparation and characterization of CNC-HBP composites which can potentially improve the properties of PHBV. The FTIR clearly showed the linking of the hydroxyl groups on the CNC and HBP using isocyanate (urethane) chemistry. Solvent casting led to a good dispersion of CNC-HBP in the PHBV matrix. The injection molded samples prepared from the solvent cast blocks were uniform and homogenous. The thermal analysis on the samples confirmed that they can be processed using existing methods used for processing unmodified PHBV. The authors expect the CNC-HBP support to improve mechanical properties of PHBV, but the analysis of those has been left to a future study.

References

[1] H.Y. Yu, Z.Y. Qin, Y.N. Liu, L. Chen, N. Liu, Z. Zhou, Simultaneous improvement of mechanical properties and thermal stability of bacterial polyester by cellulose nanocrystals, Carbohydr. Polym. 89 (2012) 971–978. https://doi.org/10.1016/j.carbpol.2012.04.053.

[2] S. Malmir, B. Montero, M. Rico, L. Barral, R. Bouza, Morphology, thermal and barrier properties of biodegradable films of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) containing cellulose nanocrystals, Compos. Part A Appl. Sci. Manuf. 93 (2017) 41–48. https://doi.org/10.1016/j.compositesa.201

6.11.011.

[3] H. Yu, B. Sun, D. Zhang, G. Chen, X. Yang, J. Yao, Reinforcement of biodegradable poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with cellulose nanocrystal/silver nanohybrids as bifunctional nanofillers, J. Mater. Chem. B. 2 (2014) 8479–8489. https://doi.org/10.1039/c4tb01372g.

[4] Z. Li, J. Yang, X.J. Loh, Polyhydroxyalkanoates: Opening doors for a sustainable future, NPG Asia Mater. 8 (2016). https://doi.org/10.1038/AM.2016.48.

[5] H.Y. Yu, Z.Y. Qin, Z. Zhou, Cellulose nanocrystals as green fillers to improve crystallization and hydrophilic property of poly(3-hydroxybutyrate-co-3-hydroxyvalerate), Prog. Nat. Sci. Mater. Int. 21 (2011) 478–484. https://doi.org/10.1016/S1002-0071(12)60086-0.

[6] T. Zheng, C.M. Clemons, S. Pilla, Comparative Study of Direct Compounding, Coupling Agent-Aided and Initiator-Aided Reactive Extrusion to Prepare Cellulose Nanocrystal/PHBV (CNC/PHBV) Nanocomposite, ACS Sustain. Chem. Eng. 8 (2020) 814–822. https://doi.org/10.1021/acssuschemeng.9b04867.

[7] S. Malmir, B. Montero, M. Rico, L. Barral, R. Bouza, Y. Farrag, PHBV/CNC bionanocomposites processed by extrusion: Structural characterization and properties, Polym. Compos. 40 (2019) E275–E284. https://doi.org/10.1002/pc.24634.

[8] H. Abushammala, J. Mao, A Review of the Surface Modification of Cellulose, Molecules. 24 (2019) 1–18.

[9] B. Thomas, M.C. Raj, B.K. Athira, H.M. Rubiyah, J. Joy, A. Moores, G.L. Drisko, C. Sanchez, Nanocellulose, a Versatile Green Platform: From Biosources to Materials and Their Applications, Chem. Rev. 118 (2018) 11575–11625. https://doi.org/10.1021/acs.chemrev.7b00627.

[10] H. Abushammala, On the para/ortho reactivity of isocyanate groups during the carbamation of cellulose nanocrystals using 2,4-toluene diisocyanate, Polymers (Basel). 11 (2019) 1–12. https://doi.org/10.3390/polym11071164.

[11] H. Abushammala, A Simple Method for the Quantification of Free Isocyanates on the Surface of Cellulose Nanocrystals upon Carbamation using Toluene Diisocyanate, Surfaces. 2 (2019) 444–454. https://doi.org/10.3390/surfaces2020032.

[12] JG Gwon, H.J. Cho, S.J. Chun, S. Lee, Q. Wu, M.C. Li, S.Y. Lee, Mechanical and thermal properties of toluene diisocyanate-modified cellulose nanocrystal nanocomposites using semi-crystalline poly(lactic acid) as a base matrix, RSC Adv. 6 (2016) 73879–73886. https://doi.org/10.1039/c6ra10993d.

[13] SI. Bhat, Y. Ahmadi, S. Ahmad, Recent Advances in Structural Modifications of Hyperbranched Polymers and Their Applications, Ind. Eng. Chem. Res. 57 (2018) 10754–10785. https://doi.org/10.1021/ACS.IECR.8B01969.

[14] L. Boogh, G. Jannerfeldt, B. Pettersson, P.S. Chemicals, AB Perstorp, DENDRITIC-BASED ADDITIVES FOR POLYMER MATRIX COMPOSITES, System. (1999) 1–8.

[15] T. Zheng, Z. Zhang, S. Shukla, S. Agnihotri, C.M. Clemons, S. Pilla, PHBV-graft-GMA via reactive extrusion and its use in PHBV/nanocellulose crystal composites, Carbohydr. Polym. 205 (2019) 27–34. https://doi.org/10.1016/j.carbpol.2018.10.014.

[16] C.F. Bellani, E. Pollet, A. Hebraud, F. V.

Pereira, G. Schlatter, L. Avérous, R.E.S. Bretas, M.C. Branciforti, Morphological, thermal, and mechanical properties of poly(ε-caprolactone)/poly(ε-caprolactone)-grafted-cellulose nanocrystals mats produced by electrospinning, J. Appl. Polym. Sci. 133 (2016). https://doi.org/10.1002/APP.43445.

ANTEC® 2022 PROCEEDINGS - JUNE 16, 2022

Kavan Sheth
Graduate Research Assistant
Clemson University

Novel Nanocellulose Based Supports for PHBV Composites—Synthesis and Properties

Bioplastics and Renewable Technologies