In Situ Cellulose Nanocrystal-Reinforced Glycerol-Based Biopolyester for Enhancing Poly(lactic acid) Biocomposites

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ABSTRACT: Biobased, elastomeric polymer poly(glycerol succinate-co-maleate) (PGSMA) was produced using a "green" synthesis with added cellulose nanocrystals (CNCs) to create a novel PGSMA–CNC material. PGSMA–CNC was synthesized with the aim of developing a new strategy for successfully dispersing CNCs within a poly(lactic acid) (PLA) matrix for optimal reinforcement of tensile strength and modulus while having the added benefit of the proven toughness enhancements of PLA/PGSMA blends. Optical microscopy and fractionation in tetrahydrofuran showed that CNCs agglomerated during PGSMA–CNC synthesis and remained in agglomerates during PLA/PGSMA–CNC reactive blending. Fourier transform infrared, differential scanning calorimetry, and dynamic mechanical analyses also showed that PGSMA–CNC inhibited the formation of PGSMA crosslinks and PLA-g-PGSMA during reactive blending. These two effects resulted in loss of impact strength and only a 4% increase in tensile modulus over PLA/PGSMA at the highest CNC content. Further work in preventing CNC aggregation could help improve mechanical properties of the final blend.

INTRODUCTION

Increasing numbers of consumers and corporations alike are opting to move away from petroleum-based products and toward products that are made using renewable resources and/or can be recycled or composted at their end of life. This motivates research into development of new biobased and compostable materials that can compete with and replace petroleum-based plastics in a variety of applications. Poly(lactic acid) (PLA) is a compostable thermoplastic polyester that can be synthesized from renewable resources. PLA is one of the most promising biobased and biodegradable polymers for competing with petroleum-based plastics because of low production cost, good mechanical properties (Young’s modulus ~3 GPa), good thermal properties (melting temperature of ~170 °C and glass-transition temperature of ~60 °C), and good optical properties.¹² However, its brittleness (evidenced by very low elongation at break and poor impact strength) limits its use in applications requiring higher toughness and flexibility.¹³⁴ Thus, there has been much research interest in using a variety of methods to improve the properties of PLA.

PLA is commonly toughened by compounding with plasticizers or impact modifiers or by blending with soft/rubbery polymers.¹³⁴ Melt blending coupled with extrusion is the most widely used processing method for producing plastics on an industrial scale, as this is the most convenient and economical technique.¹¹ Improvement in elongation at break and impact strength of PLA has been achieved by melt blending with a variety of different soft polymers.¹⁻³ Melt blending soft polymers with PLA is even more effective when combined with a reactive extrusion process in which a radical initiator is used during melt blending. This creates compatibilizing graft polymers between the soft polymer and PLA and creates a cross-linked phase of the soft polymer. This technique has been used in previous research by Valerio et al. on poly(glycerol succinate-co-maleate) (PGSMA) as a toughness enhancer for PLA.⁷,¹⁰ In this work, reactive blends of 20 wt % PGSMA with PLA showed improved elongation at break and impact strength.⁷ The use of PGS and PGSMA has the added benefit of being a partially biobased blend.¹¹,¹²

Although melt blending of PLA with soft polymers can yield dramatic improvements in elongation at break and impact strength, there is a corresponding decrease in tensile strength...
Because of the incorporation of a soft phase.\(^1\) Another strategy for improving PLA toughness involves the incorporation of rigid fillers to counteract a loss in stiffness (however, the incorporation of fillers will also correspond to a decrease in elongation at break).\(^1\) The right filler can also further increase toughness by enhancing PLA crystallization.\(^13\) For example, the addition of nanoclay to PLA/poly-(butylene succinate) (PBS) blends increases the tensile strength from 1.08 to 1.94 GPa while decreasing the elongation at break from 71.8 to 3.6%, but using an epoxy-functionalized organoclay that was able to react with terminal carboxylic acid groups of PLA and PBS gave a composite with high tensile strength and elongation at break of 118%.\(^14\) A good filler must be able to provide increased stiffness while being compatibilized to minimize losses in elongation at break. Cellulose nanocrystals (CNCs) have been studied by a variety of researchers as a reinforcing filler for PLA and other plastics. CNCs can dramatically increase the tensile strength of a composite at small loadings and have a large amount of surface hydroxyl groups that can be used for compatibilizing reactions with PLA and other blended polymers.\(^15\) CNCs are of particular interest for PLA composites because they are a plant-based reinforcing filler and thus produce fully biobased composites with PLA. PLA–CNC nanocomposites have been prepared using surfactant-modified CNCs through melt extrusion followed by film formation, resulting in a composite with a 600 MPa increase in Young’s modulus over neat PLA.\(^16\) PLA/surface-acetylated CNC nanocomposites have also been prepared that exhibited dramatic increases in tensile strength and modulus over neat PLA, obtaining an 150% increase in Young’s modulus with a loading of 10 wt % acetylated CNCs.\(^17\) CNCs have also been previously used by Medeiros et al. as a reinforcement for PGSMA films that resulted in 20 and 40% improvements in tensile strength and Young’s modulus, respectively.\(^18\)

Despite the significant improvements in mechanical properties CNC reinforcement can produce, there are challenges incorporating them into polymer blends. The high proportion of surface hydroxyl groups on CNCs lend a strong tendency to hydrogen-bond with other CNC molecules, forming agglomerations rather than a dispersion of nanocellulose.\(^19\) Processing techniques that keep CNCs in solution have shown promise in maintaining dispersion,\(^20\) such as film casting from solvent evaporation or melt compounding combined with liquid feeding.\(^21\)

In this work, an attempt to improving the tensile strength and modulus of toughened PLA/PGSMA blends by the addition of CNCs is explored while utilizing a new method to prevent CNC agglomeration during extrusion processing of the composite. Research by Dorris and Gray found that CNC suspensions could be formed in glycerol with minimal agglomeration.\(^22\) Here, a suspension of CNCs in glycerol is used in the synthesis of PGSMA to form PGSMA–CNC, which is then used in reactive melt blending with PLA. Ideally, this method would keep the CNC well dispersed during the melt processing, as it is introduced via the soft PGSMA. There is also the potential for reactions between PGSMA and CNC that could work to better compatibilize CNC with PLA for optimized reinforcement.

**RESULTS AND DISCUSSION**

**Synthesis of PGSMA–CNC.** PGSMA–CNC was synthesized using a 1:0.75:0.25 glycerol/succinic acid/maleic anhydride molar ratio with 1, 3, and 5 wt % CNC added.
neat PGSMA: The signal from the small amount of any potential new PGSMA–CNC bonds is too weak. The only noticeable change in the spectra is a slight change in the broad hydroxyl peak at ∼3425 cm\(^{-1}\) in PGSMA–5%CNC, which can be attributed to increased hydroxyl signals due to increased CNC content.

To better determine the presence of any new bonds in PGSMA–CNC, the polyester was fractioned in tetrahydrofuran (THF). Neat PGSMA is fully soluble in THF, whereas CNC is not, leaving an insoluble "gel". PGSMA–3%CNC and PGSMA–5%CNC left a gel fraction much larger than the weight percent of CNC (17.72 ± 2.85 and 11.09 ± 0.17% respectively; see Table S1), suggesting that the gel fraction is composed of some PGSMA as well as CNC. Therefore, there must be some sort of interaction between PGSMA and CNC (either hydrogen bonding or formation of PGSMA-g-CNC), which modifies some PGSMA so that it is no longer soluble in THF. It is also interesting to note that PGSMA–5%CNC has a lower gel content than that in PGSMA–3%CNC, despite PGSMA–5%CNC having a higher CNC content. This could be explained by increased agglomeration of CNCs in PGSMA–5%CNC, as agglomerations of CNCs would have reduced surface area to react with PGSMA, reducing the amount of insoluble PGSMA-g-CNC formed and thus the insoluble gel content.

Figure 2 shows the FTIR spectra in two key regions of the PGSMA–CNC gel fraction compared to those of CNC and PGSMA. The primary functional group in CNC is the OH group, producing a distinctive broad peak in the range of 3400 cm\(^{-1}\) with three smaller peaks visible within (3483, 3439, and 3336 cm\(^{-1}\)). A distinctively shaped, broad OH peak at 3425 cm\(^{-1}\) is observed in the spectra of PGSMA. The other primary functional groups in PGSMA are the C=O (present in ester linkages and terminal carboxylic acids), producing a sharp peak at 1718 cm\(^{-1}\); the C≡C, producing a smaller peak at 1643 cm\(^{-1}\); and the C–O stretch, producing a sharp peak at 1153 cm\(^{-1}\). The FTIR spectra of the PGSMA–3%CNC and PGSMA–5%CNC gel fractions show a broad peak containing three smaller peaks at exactly the same wavenumbers this is observed in the spectrum of neat CNC (Figure 2a). The C≡O peak is still present at a slightly higher wavenumber than observed in neat PGSMA (Figure 2b). This suggests that the terminal carboxylic acids of PGSMA may have formed ester linkages with CNC surface hydroxyl groups, thereby altering the C=O environment and producing a signal at a higher wavenumber. Figure 3 shows the proposed reaction scheme between PGSMA and CNC.

**Reactive Extrusion Blending of PGSMA–CNC and PLA.** The synthesized PGSMA–CNC with varying CNC content was blended with PLA to create the different composites outlined in Table 1. The use of maleic anhydride in addition to succinic acid as monomers in PGSMA synthesis creates a polyester with C≡C double bonds, allowing for the use of a radical initiator during blending with PLA. The formed free radicals could attack C≡C bonds on PGSMA, creating macroradical PGSMA, which can either react with other macroradicals to form cross-linked PGSMA or abstract hydrogens from PLA to form PLA-g-PGSMA copolymers (Figure 4).\(^9,26,27\) It is also possible that a transesterification between PLA and PGSMA ester groups may occur or an esterification reaction between terminal OH and COOH groups on PLA or PGSMA may occur. However, these reactions have been found to occur mostly in the presence of a catalyst with much higher residence times; thus, it is unlikely that they occur to a significant extent.\(^28–30\) The use of a radical initiator has also previously been used to compatibilize PLA–CNC nanocomposites by forming CNC-g-PLA through a reactive extrusion under temperatures and residence times similar to those in this study.\(^31,32\) However, the total concentration of CNCs in the PLA/PGSMA–CNC blend is at most 1 wt %; thus, the PLA-g-PGSMA grafting reactions are much more likely to be favored.
Figure 5 shows the FTIR spectra of PLA/PGSMA–CNC reactive blends. The spectra of the blended polymers show the same characteristic peaks as those of PLA with the addition of a small, broad hydroxyl peak at 3480 cm$^{-1}$. The spectra remain the same with the increasing CNC content, and only a slight change in the hydroxyl peak in the PLA/(PGSMA–3%CNC) and PLA/(PGSMA–5%CNC) spectra due to signals from dispersed CNC is observed (Figure 5a). The PLA/PGSMA–CNC blends were fractioned in THF to determine the extent of cross-linking due to the radical initiator. PLA, PLA-g-PGSMA, and uncrosslinked PGSMA are soluble in THF, whereas cross-linked PGSMA and CNCs are not, leaving an insoluble “gel”.

Figure 3. Proposed reaction mechanism of PGSMA–CNC synthesis.

Table 1. Naming of PLA/PGSMA–CNC Blends Produced in this Study

| blend name               | blend composition                                        |
|-------------------------|----------------------------------------------------------|
| PLA/PGSMA               | 8 g PLA + 2 g PGSMA + 0.2 phr radical initiator          |
| PLA/(PGSMA–1%CNC)      | 8 g PLA + 2 g PGSMA–1 wt % CNC + 0.2 phr radical initiator|
| PLA/(PGSMA–3%CNC)      | 8 g PLA + 2 g PGSMA–3 wt % CNC + 0.2 phr radical initiator|
| PLA/(PGSMA–5%CNC)      | 8 g PLA + 2 g PGSMA–5 wt % CNC + 0.2 phr radical initiator|

Figure 4. Potential reactions during reactive extrusion of PLA and PGSMA–CNC.
Therefore, this gel will consist of cross-linked PGSMA, CNCs, and PGSMA–CNC polymers. By weight percent, PLA/PGSMA and PLA/(PGSMA–1%CNC) were found to have the largest gel content of ∼9 wt % and PLA/(PGSMA–3%CNC) and PLA/(PGSMA–5%CNC) had a gel content of ∼3 wt % (Table S1). A gel content of ∼9 wt % is in agreement with gel fractions obtained for reactive PLA/PGSMA blends without CNC in previous works by Valerio et al.9,10 A gel fraction of ∼3 wt % is still higher than the total CNC content in the blend (0.6–1 wt %) but much less than the typical gel content of reactive blends without CNC. This suggests that there is some PGSMA cross-linking adding to the insoluble PGSMA–CNC fraction, but PGSMA–CNC could be somewhat inhibiting radical-initiated PGSMA cross-linking, resulting in a smaller gel fraction. In previous work by Valerio et al., the small shoulder peak at ∼1643 cm⁻¹ (corresponding to C==C bonds) is less intense in the FTIR spectra of reactive PLA/PGSMA blends than in the FTIR spectra of neat PGSMA because of the disappearance of PGSMA double bonds during cross-linking.10 This peak does not decrease noticeably in the spectra of PLA/(PGSMA–3%CNC) or PLA/(PGSMA–5%CNC) (Figure 5b), which also suggests that PGSMA–CNC is inhibiting cross-linking. Furthermore, dynamic mechanical analysis (DMA, Figure 6) shows that PLA/PGSMA–CNC has a lower first glass-transition temperature (∼4 °C compared to 10.98 °C in reactive PLA/PGSMA without CNC). A higher glass-transition temperature has been correlated with increased cross-linking density in poly(glycerol sebacate) polyesters and in PGSMA, suggesting that there is less PGSMA cross-linking in PLA/PGSMA–CNC compared to that in PLA/PGSMA.33,10

The formation of PLA-g-PGSMA molecules has previously been shown to cause the appearance of a secondary PLA melting peak in differential scanning calorimetry (DSC) curves at a lower temperature because of the formation of imperfect PLA crystals.34,10 This peak can be seen as a shoulder on the PLA melting peak at ∼159 °C on the DSC curve for the PLA/PGSMA reactive blend (see Figure 7). This shoulder is also present with a similar intensity in the PLA/(PGSMA–1%CNC) blend (Figure 7), suggesting that PLA-g-PGSMA molecules are being formed in PLA/PGSMA–CNC blends as well. Scanning electron microscopy (SEM) imaging of PLA/PGSMA–CNC blends processed with and without a radical initiator (Figure 8) further supports that there is some graft polymer formation, as there is a noticeable compatibilization between PLA and PGSMA–CNC phases when using the radical initiator (the PLA/PGSMA–CNC blend created through reactive extrusion shows a much more uniform surface with smaller particle sizes of the dispersed PGSMA phase, as was also seen in previous work by Valerio et al.).9 As CNC content increases, PLA-g-PGSMA formation appears to be inhibited, as evidenced by the disappearance of the PLA melting peak shoulder in the DSC curves for PLA/(PGSMA–3%CNC) and PLA/(PGSMA–5%CNC) (Figure 7). Furthermore, FTIR analysis of the insoluble gel fraction from PLA/(PGSMA–3%CNC) (Figure 9) shows a single peak at 1722 cm⁻¹ corresponding to the C==O groups in cross-linked PGSMA. However, in the work by Valerio et al.,10 the FTIR
spectra of the gel fraction of PLA/PGSMA reactive blends showed a small shoulder evident on the C=O peak, which is deconvoluted into signals for PGSMA and PLA C=O functionalities, indicating the presence of PLA-g-PGSMA (PLA-g-PLA polymers are soluble in THF, but if PGSMA participates in PGSMA cross-linking as well, the PLA fragment will remain in the insoluble gel fraction, resulting in a PLA C=O signal in the gel fraction FTIR spectrum). Because this PLA signal is not evident in the PLA/PGSMA−CNC gel fraction FTIR spectra (Figure 9), this reinforces that PLA-g-PLA formation is inhibited in higher-CNC-content PLA/PGSMA−CNC blends.

**Morphology.** In SEM photos (Figure S1) of PLA/PGSMA−CNC blends, it is possible to differentiate between two separate phases (the PLA matrix and dispersed PGSMA particles), but it is less easy to see any indication of dispersed CNCs (usually observed as white dots). Furthermore, there is minimal change in morphology with increasing CNC content (Figure S1). From atomic force microscopy (AFM) images, it is again possible to see a good dispersion of PGSMA within neat PLA, as evidenced by the small, uniform holes left by pulled-out PGSMA−CNC (Figure S2). However, there is no indication of a high-modulus CNC polymer (Figure S3). This could be the result of CNC particles only staying in the PGSMA phase and thus being pulled with PGSMA, or due to the fact that the amount of CNC is small and potentially agglomerated and not well dispersed, it may be present only in small areas not imaged during AFM or SEM. To better determine the dispersion of CNC within PGSMA and whether agglomeration had occurred, optical microscopy of the PGSMA−CNC alone was done to determine the dispersion of CNCs within the polyester (Figure 10). CNCs can easily be seen as large, white agglomerates, ranging in size from 10 to 20 μm wide by 10 to 50 μm long. As shown by previous researchers, it is very difficult to successfully re-disperse CNCs by melt processing (i.e., extrusion of dried CNCs with PLA). If optical microscopy shows CNC agglomerations in PGSMA−CNC, it is very unlikely that these agglomerations were broken up during extrusion and therefore would still exist in the final PLA/PGSMA−CNC composite.

From Figure 10, the dispersion of CNC within the PLA/PGSMA−CNC composite is not uniform. Because of a high surface area and the presence of many −OH groups on CNCs, they have a strong tendency to hydrogen-bond one another and form microscale agglomerations rather than a nanoscale dispersion of crystalline cellulose. A variety of processing
techniques can be used when creating nanocomposites with CNCs to avoid agglomeration: surface modification of CNCS, solvent casting, and liquid feeding during melt processing. Water-soluble polymer matrices or solution methods are usually used to prepare nanocomposites with CNC. The use of powdered, freeze-dried CNCs dispersed in polar glycerol by sonication was expected to give a stable suspension of CNCs that could then be used for dispersing CNCs within a PGSMA matrix, similar to the work of Medeiros et al. However, CNC has a tendency to agglomerate during drying, and it is difficult to disperse these agglomerations. In the work by Khoshkava and Kamal, freeze-dried CNCs when dispersed in water by sonication and then blended with polypropylene produced a morphology of large, flake-like agglomerates, similar to the dispersion observed from optical microscopy of PGSMA–CNC (Figure 10). It appears that dissolving in a polar medium (glycerol) with sonication is not enough to overcome hydrogen bonding between CNC chains and disperse the nanocrystalline cellulose.

Effect of Addition of CNC on Thermal and Mechanical Properties of PLA/PGSMA Blends. The addition of CNCs to PLA typically yields a composite with improved thermal stability over neat PLA. Here, increasing CNC content shows minimal change in the onset of thermal decomposition over PLA/PGSMA (Figure S4). This lack of improvement in thermal stability could be due to a lower CNC loading (largest increase in thermal stability typically seen in composites with a higher CNC content) or due to poor interaction between CNC and PLA. The percent crystallinity (as calculated from DSC first heating cycles) of PLA/PGSMA–CNC blends increases slightly with increased cellulose content but only by 6% from lowest to highest CNC content blends (Table S2). A slight increase in crystallinity is expected, as both PGSMA droplets and CNC particles can act as heterogeneous nucleating sites to increase the crystallinity of the composite. However, the small increase in crystallinity observed here is too small to have any noticeable impact on mechanical properties of the blend. This is in line with typical DSC results for PLA/CNC nanocomposites (an increase in crystallinity but minimal change in glass-transition temperature or melting temperature). Similar results were also found by Bitinis et al. in PLA/natural rubber/CNC composites.

The addition of PGSMA with no CNC causes a 27% decrease in tensile strength from neat PLA, whereas giving a 27.7% increase in elongation at break and 57% increase in impact strength (Table S3). This decrease in tensile strength and modulus is expected, as adding PGSMA to PLA is incorporating an amorphous polymer into a semicrystalline polymer matrix. The increase in elongation at break and impact strength is promising, as these two properties are reflective of the blend’s toughness. With the addition of CNC, the impact strength lowers from 35.90 J/m in PLA/PGSMA to 29.03 J/m in PLA/(PGSMA–3%CNC) (the highest value out of the 3% CNC contents) (Table S3). This decrease in impact strength correlates with the observation that PGSMA cross-linking and PLA-g-PSMA formation are inhibited in PLA/PGSMA–CNC reactive blends, as the impact strength of reactive PL blends has shown to be dependent upon the extent of PGSMA cross-linking and formation of PLA-g-PSMA polymers in previous work by Valerio et al. The effect of secondary polymer cross-linking and PLA/secondary-polymer graft copolymer formation on reactive PL blends’ elongation at break and impact strength has also been observed in research by Zhang et al. Tensile strength and modulus in PLA/PGSMA–CNC blends remain close to their values in PLA/PGSMA, reaching the highest value in PLA/(PGSMA–3%CNC) (although this is only a 10 and 4% increase in strength and modulus, respectively). Elongation at break steadily decreases with increasing CNC content, from 32% in PLA/PGSMA down to 10% in PLA/(PGSMA–5%CNC) (Figure 11). In general, the incorporation of CNCs into various polymer matrices results in an increase in tensile strength and modulus and a decrease in the elongation at break, as observed here, but the increase in tensile strength and modulus is expected to be much larger.

Mechanical properties of CNC nanocomposites can often be much less than theoretically predicted due to agglomeration of CNCs: The strongly interacting surface hydroxyl groups of CNCs are what allow for their impressive reinforcing effect by forming rigid load-bearing percolating architectures for stress transfer. However, surface hydroxyl hydrogen bonding also causes CNC agglomeration. The commonly used CNCs isolated from wood pulp or cotton reach critical filler content at a higher CNC concentration, and CNCs begin to agglomerate at lower concentrations. In other studies where mechanical properties of polymers were not improved by the use of CNC, the nanocomposites were prepared by melt mixing, whereas successful nanocomposites are usually prepared by solution mixing methods or using surfactant-modified CNCs, which are better at preventing CNC agglomeration because competitive bonding with a hydrogen-bond-forming solvent (such as water) interrupts CNC hydrogen bonding and aggregations. Because CNCs in PGSMA have obviously aggregated, there is minimal effective reinforcing effect from the nanofiller to the composite.
CONCLUSIONS

The reinforcement of PLA/PGSMA blends with CNCs by incorporating CNCs into the synthesis of PGSMA was investigated. Dry CNCs suspended in glycerol were added to the one pot, solvent-free synthesis of PGSMA, and the resulting PGSMA−CNC was blended with PLA by a reactive extrusion using a radical initiator. FTIR analysis of gel fractions showed that CNC had reacted with PGSMA chains to form ester linkages and hydrogen bonds between the two polymers. The reactive extrusion of PGSMA−CNC and PLA leads to PGSMA cross-linking and formation of PLA-g-PGSMA, although to a lesser extent than that in reactive PLA/PGSMA blends without CNC. The decrease in graft polymer formation and cross-linking correlates with the observed decrease in impact strength in PLA/PGSMA−CNC and PLA/PGSMA−CNC blends, explaining a lack of tensile strength improvement due to CNC reinforcement. Future work will focus on using new methods, such as solvent exchange from aqueous CNCs to a glycerol suspension, to obtain a better dispersion of CNCs within PGSMA.

EXPERIMENTAL SECTION

Materials. Technical glycerol (95 wt %) from biodiesel production was obtained from BIOX Corporation, Canada. Cellulose nanocrystals (CNCs) (freeze-dried, 0.85 wt % sulfur, sodium co-ion form) were obtained from the University of Maine Process Development Centre, Orono. Succinic acid (99 wt %, KIC Chemicals), maleic anhydride (99 wt %, Sigma-Aldrich, Canada), and tetrahydrofuran (THF) (99.8 wt %, Fisher Scientific, Canada) were purchased and used as received. Poly(lactic acid) (Ingeo 3251D) (NatureWorks) (melting point of 155−170 °C; melt flow index of 30−40 g/10 min at 190 °C, 2.16 kg) was purchased and used as received. 2,5-Bis(tert-butyl-peroxy)-2,5-dimethylhexane (Luperox 101) (technical grade 90%, Sigma-Aldrich, Canada) was used as a free radical initiator in reactive extrusion.

Synthesis of CNC-Reinforced Poly(glycerol succinate-co-maleate) (PGSMA−CNC). Varying amounts of CNCs (1, 3, and 5 wt %) were ground into a fine powder and then dispersed in glycerol (100.0 g, 1.086 mol) by sonication for 6 h. The weight percentage of CNCs was calculated as a fraction of the predicted final mass of PGSMA using an estimated mass yield of 89% based on yields obtained in previous PGSMA syntheses. The glycerol−CNC mixture was then combined with succinic acid (90.0 g, 0.762 mol) and maleic anhydride (25.0 g, 0.255 mol) in a 1 L reactor equipped with a mechanical stirrer (250 rpm), heating mantle (150 °C), nitrogen gas flow, and a Dean-Stark apparatus. Reaction progress was tracked by taking hourly viscosity measurements in a cone plate rheometer at 100 °C and 100 s⁻¹ (CAP 2000+, Brookfield). An initial synthesis was performed in which viscosity measurements were taken every 30 min until the material became an insoluble gel due to cross-linking (wrapping itself around the mechanical stirrer). On the basis of this reaction, it was determined that a viscosity of 300−500 P is the maximum achievable viscosity to obtain non-cross-linked liquid PGSMA. Once a viscosity in this range was reached, the reaction was stopped by removing the vessel from the heating mantle. The final product was a sticky, viscous, clear to opaque (depending on CNC content) yellow-white liquid. This product was used as is without further purification.

Reactive Melt Blending of PLA and PGSMA−CNC. PLA and PGSMA−CNC were blended by means of reactive extrusion. PLA was dried in an oven overnight at 80 °C, and PGSMA−CNC was kept in a plastic syringe heated to 85 °C with a syringe heater (New Era, NY) to melt the material for dispensing. PLA (8 g), PGSMA−CNC (2 g) (containing varying amounts of CNC: 1, 3, and 5 wt %), and a radical initiator (Luperox 101, 0.2 phr) were combined in a twin-screw extruder (Xplore, DSM, Netherlands) at a processing temperature of 180 °C and screw speed of 100 rpm. After 2 min of

![Figure 11. Mechanical properties of PLA/PGSMA−CNC reactive blends with varying CNC content.](image-url)
extrusion, the blended material was collected in an injection device heated to 180 °C and injected into molds for mechanical testing specimens at 30 °C. The ratio of PLA/PGSMA–CNC (80/20) and amount of radical initiator was used as it was determined to give the best properties in previous work by Valerio et al.9

Mechanical Testing. All mechanical testing was completed 40 h after processing, and results are the average of five specimens. Flexural and tensile testing of polymer samples was performed using an Instron universal testing machine (Instron, Canada) according to ASTM D790 (flexural, 14.0 mm/min crosshead speed) and ASTM D638 (tensile, 50.0 mm/min crosshead speed, type IV specimens). Notched Izod impact testing was completed using an impact testing machine equipped with a 0.5–5 ft lbs hammer following ASTM D256. Impact samples were notched immediately following processing.

Fractionation of PLA/PGSMA–CNC Blends in Solvents. To determine the gel content of PLA/PGSMA–CNC blends, a sample of approximately 200 mg (m0) was dissolved in 30 mL of tetrahydrofuran (THF) at 40 °C for 2 h (THF dissolves the PLA and uncrosslinked fraction of PGSMA–CNC, whereas the cross-linked gel portion and CNCs are insoluble). The solution was then centrifuged for 10 min at 8000 rpm and washed again with 30 mL THF. The recovered gel portion was dried for 5 h at 80 °C and then weighed (m0). The gel fraction was calculated as gel fraction (wt %) = (m0 / m1) × 100.

FTIR Characterization. FTIR spectra of PGSMA–CNC, PLA/PGSMA–CNC composites, and gel fractions were collected in 64 scans at a resolution of 4 cm−1 using a Nicolet 6700 FTIR spectrometer with an attenuated total reflection accessory.

Thermal Characterizations. Differential scanning calorimetry (DSC) traces were obtained for samples of ~5 mg under a nitrogen flow of 50 mL/min (DSC Q200, TA instruments). The materials were equilibrated at −30.00 °C and then heated at a rate of 10.00 °C/min to 180 °C, cooled at a rate of 10.00 °C/min to −30.00 °C, held for 2 min, and then heated again at a rate of 10.00 °C/min to 180 °C. The crystallinity percentage of the samples was calculated from the first heating cycle using the following formula: Xc = (ΔHm − ΔHc)/ΔH100 × 100, where ΔHm and ΔHc are the enthalpies of melting and cold crystallization, respectively, and ΔH100 is the theoretical melting enthalpy of 100% crystalline PLA (93 J/g).27,45 Thermal decomposition was assessed using thermogravimetric analysis: 5–10 mg of sample heated from room temperature to 500 °C at a rate of 10 °C/min under a nitrogen flow of 50 mL/min (TGA Q500, TA Instruments).

Dynamic Mechanical Analysis. PLA/PGSMA–CNC samples were equilibrated at −100 °C for 10 min and then heated at 3 °C/min to 100 °C, applying a periodic deformation of 0.02% strain at 1 Hz in dual cantilever mode (Q800 DMA, TA Instruments). The storage (E') to loss (E') modulus ratio (tan δ) was plotted as a function of temperature.

Scanning Electron Microscopy. Scanning electron microscopy images of fractured impact specimens were taken using a Phenom ProX scanning electron microscope (Phenom-World VB, The Netherlands). Before imaging, the samples were coated with a thin layer of gold using a sputter coater to prevent degradation during imaging.

Atomic Force Microscopy. Samples were prepared at room temperature using a Leica RM microtome (Leica Biosystems, Germany) and analyzed using a Multi-Mode 8-HR atomic force microscope (AFM) (Bruker, Santa Barbra) in tapping mode.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00056.

Gel content, DSC, and mechanical properties data presented in tables and SEM and AFM images (PDF)

AUTHOR INFORMATION

Notes
The authors declare no competing financial interest.

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