

POSS-Modified Cellulose for Improving Flammability Characteristics of Polystyrene

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Abstract

Due to its strength, charring ability, and biodegradability, cellulose-based reinforced polymers have received considerable attention. However, its high polarity, large molecular size, and solvent resistivity, have often resulted in immiscible or agglomerated composites. To improve the separation and dispersion of cellulose in hydrophobic commodity plastics, we have begun the study of polyhedral oligomeric silsesquioxane (POSS)-modified cellulose. The initial phase of this project focused on the optimization of the POSS-cellulose nanoparticle for incorporation into

polystyrene (PS). Fourier transform infrared spectroscopy (FTIR) was used to validate the inclusion of POSS in the cellulose fiber matrix, thermal gravimetric analysis (TGA) was used to assess the thermal stability and char yield of the materials, and differential scanning calorimetry (DSC) was used to examine changes in cellulose glass transition temperatures. Initial results suggest the POSS molecules are physically trapped within the cellulose network rather than covalently bonded at the hydroxyl sites. Polystyrene-cellulose composites were prepared, but solution blending resulted in poorly dispersed fibers.

Introduction

The reinforcement of polymers on the nanoscale has been shown to exhibit significant improvements in thermal, mechanical, electrical, and barrier properties over conventional microscale composites (Hussain et al. 2006, Viswanathan et al. 2006). Due to its strength, charring ability, and biodegradability, cellulose-based reinforced polymers have received considerable attention (Mohanty et al. 2000, Samir et al. 2005, Oksman and Sain 2006, Kamel 2007). However, its high polarity, large molecular size, and solvent resistivity, have often resulted in immiscible or agglomerated composites. To improve the separation and dispersion of cellulose in hydrophobic commodity plastics, we have begun the study of POSS-modified cellulose for improving polystyrene (PS) and polypropylene. Although cellulose is often overlooked as a flame-retardant for polymers due to its low thermal stability, the potentially high char yield could be advantageous in reducing the available fuel and peak-heat release in the event of an actual fire (Levchik and Wilkie 2000, Kandola and Horrocks 2000). Our primary goal in this project was to investigate the use of modified cellulose as a char-forming flame-retardant in commodity plastics.

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Polyhedral oligomeric silsesquioxane (POSS) is a macromolecule consisting of an inorganic Si-O cage and bulky organic groups surrounding this inorganic core. Most POSS monomers have one reactive organic substituent to allow for grafting onto a polymer backbone. POSS has a number of advantages as an organic modifier for nanofiller incorporation into hydrophobic polymers. First, the POSS cage (≈ 1 nm) is ten times as large as organosilanes; so fewer molecules are required to alter the nanoparticle hydrophobicity. Second, the inner structure of the POSS cage is a silicon-oxygen network that provides both thermal and oxidative barrier enhancements (Gilman et al. 1996, Li et al. 2001, Bourbigot et al. 2006). Third, POSS molecules exhibit low toxicity levels in drug carrier and decomposition studies (McCusker et al. 2005, Li et al. 2001). Finally, the rigidity of POSS molecules imbues surface toughness that may reduce interfacial stress (Zhang et al. 2002). The most promising benefit of POSS-modified polymers is the reduction in polymer flammability (Li et al. 2001, Bourbigot et al. 2006, Fina et al. 2006). For instance, Liu et al. (2007) found that the addition of 30% by mass octa(tetramethylammonium) POSS to PS significantly improved the fire retardancy of the polymer by reducing the peak heat-release rate by more than half, increasing the peak decomposition temperature by 10°C , and increasing char yield by 25%. Furthermore, flame retardant effects were noticeable with as little as 5% by mass POSS. The mechanisms have been identified as the formation of a silica rich, ceramic-like char layer at the surface of the burning front of the material (Fina et al. 2006, Bourbigot et al. 2006). Furthermore, this improvement in flammability properties does not come at an expense of processability (Li et al. 2001).

In this study, we report our progress in the preparation of POSS-functionalized cellulose nanofibrils. The resultant fibers are analyzed using Fourier-transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). The effects of excess NaOH (aq) and reaction solvent are discussed.

Experimental Methods

Nanofibrillated cellulose (NFC) was obtained from Engineered Fibers Technology (Shelton, CT) and microcrystalline cellulose (MCC) was obtained from Sigma-Aldrich (Milwaukee, WI). Two different NFC fibers were used in this study: Lyocell fibers with a precursor length of 6 mm and a low degree of nanofibrillation (≈ 500 nm diameter) and Lyocell fibers with a precursor length of 4 mm and a high degree of nanofibrillation (≈ 50 nm diameter), designated as L040-6 and L010-4, respectively. Toluene (anhydrous, 99.8%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), glacial acetic acid (HAc, 99.8%), 1,2-epoxy-3-phenoxypropane (99%), toluene-d₈ (99.8 atom%D), and KBr (FT-IR grade, 99+%) were purchased from Sigma-Aldrich, sodium hydroxide (ACS reagent, $\geq 98.6\%$) was purchased

from Fluka, ethanol (dehydrated, 200 Proof) was purchased from Pharmco (Brookfield, CT), and OctaPhenyl POSS, GlycidylPhenyl POSS, and POSS Amic Acid-Phenyl were purchased from Hybrid Plastics, Inc. (Hattiesburg, MS).

The NFC contained some residual solvent (N-methylmorpholine-N-oxide) from the production process and was neutralized with 0.5 mol/L acetic acid, then thoroughly washed with de-ionized water and ethanol to a neutral pH. All other chemicals were used as received.

Cellulose (1 g) was alkaliated using 15% by mass NaOH (20 mL) for 1 h. The Na-cellulose was filtered using a sintered glass crucible until its final wet uptake was 400 to 500% by mass. For some studies, the prepared Na-cellulose was thoroughly washed with dry ethanol and filtered until its wet uptake was 200% by mass. The Na-cellulose was placed in a solvent (20 mL water, toluene, and DMF) and GlycidylPhenyl POSS (1 g) was added. The reaction mixture was heated to between 85 and 95°C for 24 h. The reaction mixture was filtered (filtrate saved for analysis) and washed with fresh solvent, followed by a 60:40 (v:v) ethanol-de-ionized water mixture. The product was then neutralized with 0.5 mol/L acetic acid (40 mL) and soxhlet extracted 24 h with 60:40 (v:v) ethanol-de-ionized water to remove trace ions. The final product was dried in a vacuum oven at 40°C for 24 h.

Infrared spectra were measured using a Shimadzu FTIR-8300 with a diffuse reflectance sample accessory (DRIFT). Samples were diluted to 3 to 5% by mass with dried KBr and ground five minutes to about $75\text{-}\mu\text{m}$ particle size. ^{13}C - and ^1H -NMR of the product filtrates were performed using deuterated toluene in a Bruker 400 MHz NMR Spectrometer (Ettlingen, Germany). Thermal stabilities were measured using a TA Instruments Q-500 Thermogravimetric Analyzer (New Castle, DE). 5.0 ± 0.3 mg samples were placed in open platinum pans and heated at a scan rate of $10^\circ\text{C}/\text{min}$ while purged with 100 mL/min N_2 or compressed air. The mean of typically three replicate measurements was reported. The temperature of both the onset (5% mass fraction loss) and peak mass loss rate have an uncertainty of $\sigma = \pm 2^\circ\text{C}$. All samples were held at 90°C for 30 min. prior to each scan to remove any residual water and to remove any residual oxygen from the furnace. Glass transition and water absorption properties were characterized using a TA Instruments Q-2000 differential scanning calorimeter connected to a refrigerated cooling system. 3.0 ± 0.3 mg samples were placed in open aluminum pans and were heated and cooled at a scan rate of $50^\circ\text{C}/\text{min}$ while purged with 50 mL/min N_2 . Data were collected during the second consecutive scan. Glass transition temperatures have an uncertainty of $\sigma = \pm 1^\circ\text{C}$

Results and Discussion

The nanofibrillated cellulose fibers were found to contain some impurities from their manufacturing process.

These impurities resulted in a broadening of their decomposition temperature ranges and a char yield of 30% by mass. The impurities were effectively removed after washing the fibers with ethanol and 0.5 mol/L acetic acid, followed by soxhlet extraction. The resulting decomposition temperatures closely followed the decomposition profile of microcrystalline cellulose. The thermal stability of the different cellulose sources is shown in **Fig. 1**. The slightly higher thermal stability for the nanofibrils is consistent with conventional lyocell fibers, indicating that the nanofibrillation process does not change the crystalline structure or thermal stability of the fibers (Carrillo et al. 2004).

The microcrystalline and fibrous celluloses have different crystalline structures, which can alter their overall structure. This results in slightly different FTIR spectra, as shown in **Fig. 2**. Differences in the regions between 2800 and 3600 cm^{-1} and between 1000 and 1500 cm^{-1} are likely due to the differences in crystalline structure between the microcrystalline and nanofibrillated forms of the cellulose. The observed differences in the former have been attributed to the $-\text{OH}$ stretching intramolecular hydrogen bonds found in cellulose II, but not cellulose I (Carrillo et al. 2004).

The reaction of Na-cellulose with GlycidylPhenyl POSS in toluene produced cellulosic fibers with significant POSS content (**Fig. 3**). Evidence of POSS in the cellulose product was identified by examining FTIR associated with the benzyl rings on the POSS molecules. The appearance of peaks at 3000, 1510, 1450, 750, and 710 cm^{-1} with an accompanying decrease in the O-H stretching peak at 3420 cm^{-1} has been attributed to the vibrations of benzyl rings in benzyl cellulose (Zemke et al. 1996). We found similar variations in the FTIR spectra of GlycidylPhenyl POSS modified L040-6 (**Fig. 3b**). Reactions in water and *N,N*-dimethylformamide (DMF)—solvents with greater ability to swell cellulose—showed no FTIR evidence of POSS incorporation. In addition, washing Na-cellulose with ethanol prior to the etherification reaction to remove excess water and NaOH did not affect the product in either solvent. The washing failed to produce POSS-modified cellulose in DMF and there was still evidence of POSS when reacted in toluene.

The pyrolysis behavior of the modified cellulose fibers was measured using TGA (**Fig. 4**). The TGA shows that the modified cellulose exhibits a slight decrease in the decomposition onset and peak temperatures, but that the char yield is significantly increased (24% by mass vs. negligible for unmodified cellulose). The reaction product contains at least 50% by mass cellulose, yet the char yield is greater than half of the pure POSS. Furthermore, the second and third decomposition steps associated with the POSS molecule occur at slightly higher temperatures in the POSS-cellulose. These are indications that the decomposition mechanisms are altered from both the

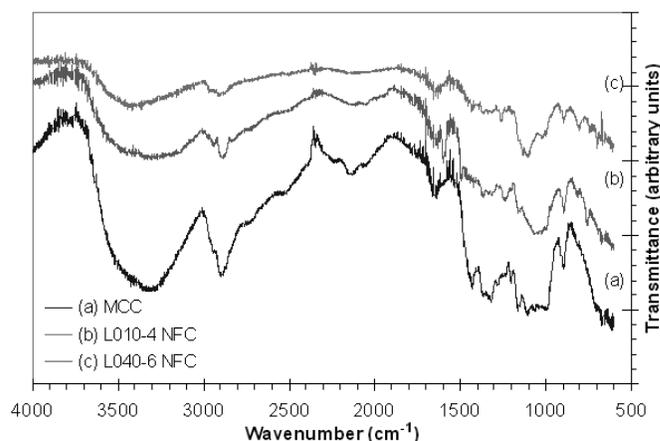


Figure 1. ~ Thermal stability of washed cellulose sources using a TA Q-500 thermal gravimetric analyzer in Pt pans under a flow of 100 mL/min N_2 .

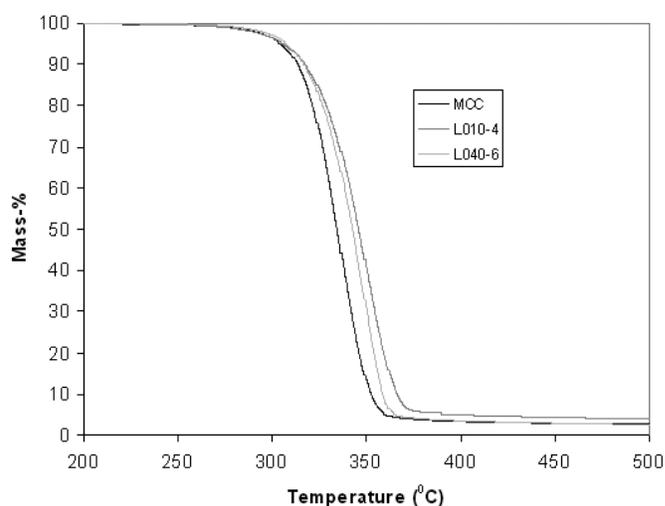


Figure 2. ~ FTIR of cellulose sources using a Shimadzu A-8300 and DRIFT accessory. Samples have been diluted to 5% by mass using dried FTIR grade KBr. Plots are vertically shifted for clarity.

pure cellulose and pure POSS compounds. The higher char yield is promising for the application of polymer fire retardancy. Washing Na-cellulose with ethanol did not significantly change the characteristics of the product fibers. As shown in **Fig. 4**, the char yield is only slightly lower in these products.

The thermal characteristics of cellulose were monitored using DSC. The cellulose and POSS-cellulose fibers did exhibit a large endotherm during the first heating cycle, but this has been well documented as the release of bound water. As shown in **Fig. 5**, there was a slight change in the first glass transition temperature ($\approx 1^\circ\text{C}$) in the product fibers and an increase in the time required for fibers to undergo the glass transition just prior to decomposition ($\approx 200^\circ\text{C}$). This increase is a result of the POSS molecules impeding relaxation of the cellulose fiber chains.

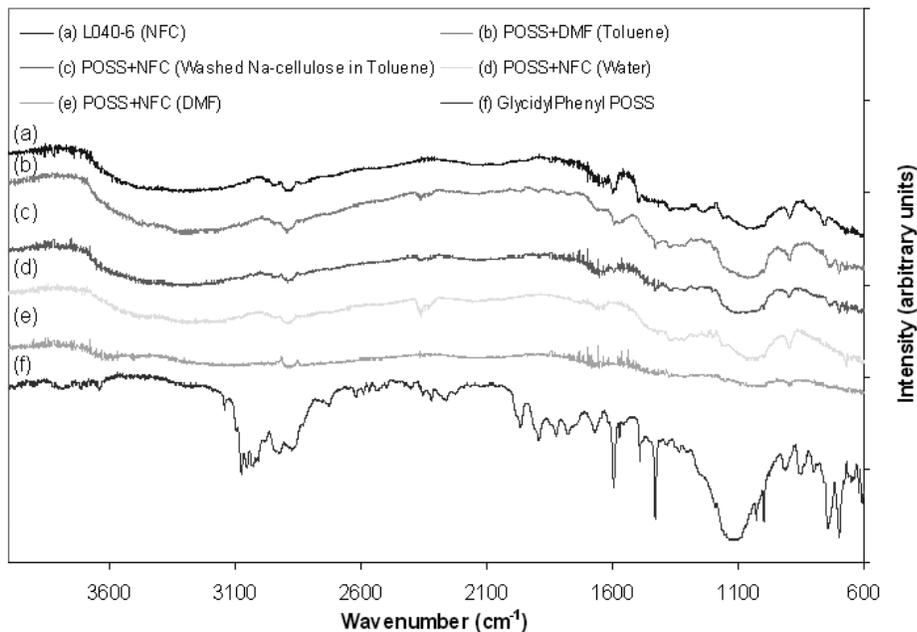
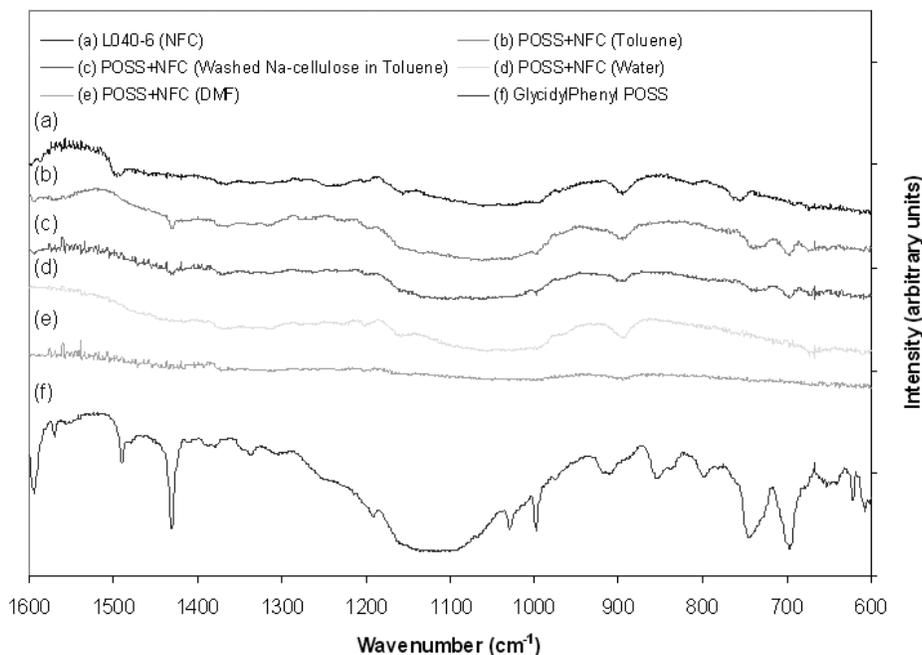


Figure 3. ~ FTIR of GlycidylPhenyl POSS modified L040-6 using a Shimadzu A-8300 and DRIFT accessory (a) between 600 and 4000 cm^{-1} and (b) between 600 and 1600 cm^{-1} . Samples have been diluted to 5% by mass using dried FTIR grade KBr. Plots are vertically shifted for clarity.



It is unclear at this point whether the POSS has covalently bonded through an etherification reaction or if the POSS molecules were simply trapped within the cellulose network. The failure to produce POSS-cellulose fibers in solvents with a strong ability to swell the cellulose suggests that the POSS-cellulose product formed in toluene was due to the physical trapping of POSS monomers within the cellulose chains as the swollen Na-cellulose structure collapses once in contact with the toluene. However, the thermal characterizations suggest there may be some chemical modifications, altering the glass transition and decomposition mechanisms. Further characterization using solid-state nuclear magnetic resonance (NMR) is planned to confirm this analysis.

We have begun preparing some cellulose-polymer composites using a solution-casting technique. Polystyrene composites were prepared from toluene and poly(lactic acid) (PLA) composites were prepared from DMF. We were unable to separate and disperse individual fibers using our sonication instrumentation, so these composites will need to be prepared using a melt-blending technique. Initial TGA results (not shown) are inconclusive, because residual toluene (the casting solvent) initiated some early decomposition in the PS composites. It does appear that the cellulose will decompose at a lower temperature than PS, but will leave some additional char in the composites (1.7% by mass char vs. 0% for pure PS). Furthermore, this char is equal to or greater than the

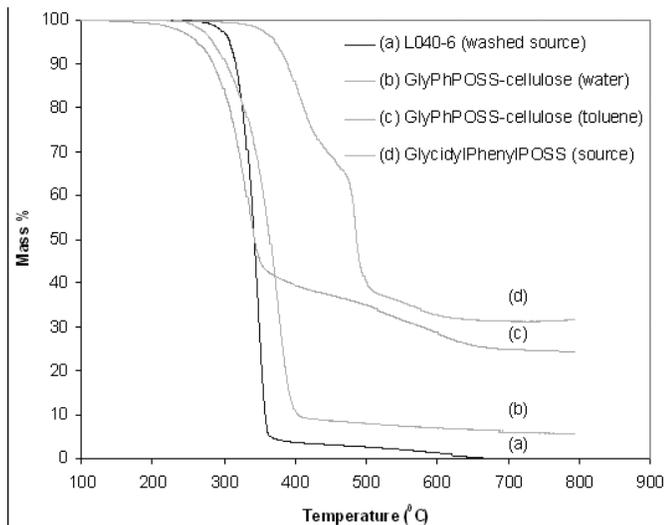


Figure 4. ~TGA of POSS-modified L040-6. Samples heated in Pt pans at 10°C/min under a flow of 100 mL/min N₂.

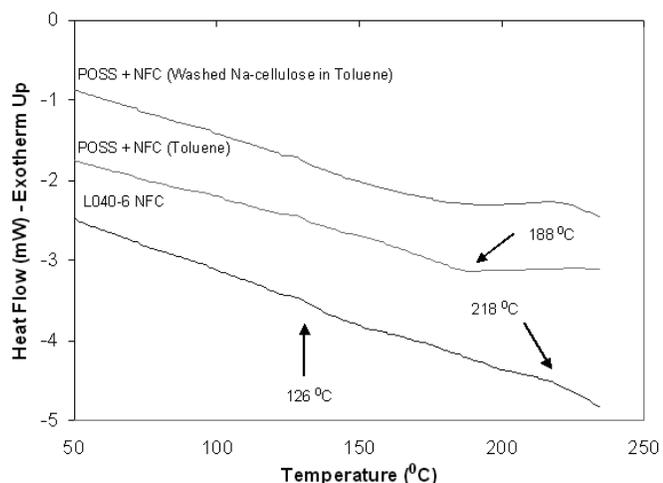


Figure 5. ~DSC of POSS-modified L040-6 heated and cooled in open Al pans at 50°C/min under a flow of 50 mL/min N₂. The second heating cycle is shown.

amount formed for POSS-PS composites, even though pure cellulose has less char than pure POSS (**Fig. 4**). Higher masses of additives may elucidate the charring synergies of the composites better.

Conclusions

Initial studies on the modification of cellulose with POSS molecules have produced mixed results. FTIR indicated that product fibers contain POSS reacted in toluene and TGA results show increases in char yield and inhibition of secondary decomposition mechanisms. However, reactions in DMF and water proved unsuccessful and TGA indicates a slight decrease in the initial decomposition temperature. The solvent effects suggest that POSS may be physically trapped during shrinkage in solvents which poorly swell cellulose. Further studies

to clarify the reaction products are currently underway in our laboratories.

Acknowledgments

The policy of the National Institute of Standards and Technology (NIST) is to use metric units of measurement in all its publications, and to provide statements of uncertainty for all original measurements. In this document however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements.

The authors wish to thank Em. Prof. Derek Horton from American University and Dr. Paul H. Maupin from the Department of Energy for the valuable discussions on the reactivity of potential modification procedures for cellulose. The identification of any commercial product or trade name does not imply endorsement or recommendation by NIST. Opinions, interpretations, conclusions, and recommendations are those of the authors and are not necessarily endorsed by NIST. This project is funded in part through the NIST-BFRL Extramural Fire Research Grants Program. This is an official contribution of the NIST, and not subject to copyright in the United States.

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