Thermal and Burning Properties of Poly(lactic acid) Composites Using Cellulose-Based Intumescing Flame Retardants

Douglas M. Fox,[*,1,2,§] Srilatha Temburni,[1] Melissa Novy,[1] Laura Flynn,[1] Mauro Zammarano,[1,2,§] Yeon S. Kim,[2,§] Jeffrey W. Gilman,[3] and Rick D. Davis[2]

[1]Chemistry Department, American University, Washington, DC 20016
[2]Fire Research Division, Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8665
[3]Polymers Division, Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-1070
[§]Guest Researcher at NIST
[*]E-mail: dfox@american.edu

Poly(lactic acid) was flame – retarded using cellulose-based intumescing flame retardants. Cellulose was found to be an excellent carbon source, and when added in combination with ammonium polyphosphate (APP), PLA composites exhibited good thermal stabilities and UL-94 ratings of V-0. Nanofibrillated cellulose was phosphorylated to eliminate the need for APP. The fibers were further modified by quaternization and with glycidyl phenyl POSS to increase the char yield during pyrolysis. Fibers were analyzed by elemental analysis, potentiometric titration, and thermogravimetric analysis. The composites prepared without APP exhibited good thermal stability, but they failed the UL-94 vertical burn test.

Introduction

There has been a surge in research and product development of environmentally sustainable materials over the past twenty years. Company managers have learned how to manufacture products that are derived from renewable materials, are less toxic, and produce little waste while maintaining and, in some cases, increasing company profits (*1*, *2*). The production of polymer resins and use of polymers is the third largest industry globally, with 265 million tonnes produced annually (*3*). One of the more promising bio-derived and biodegradable polymers is poly(lactic acid), or polylactide (PLA) (*2*, *4*, *5*). A key disadvantage to the use of polymers is their inherent flammability. Depending on their use, most polymers, including PLA, require the addition of flame retardants to pass regulatory and safety requirements. Due to increasing regulatory pressures, public perceptions of the hazards and toxicities of the most commonly used flame retardants, and a perceived need for enhanced fire retardancy of materials, there is a need to develop more sustainable flame retardants with lower risks to the public and environmental health. Intumescing flame retardants (IFRs) have emerged as possible alternatives to address these issues.

One of the most effective methods for reducing flammability is the generation of carbonaceous char. One of the flame retardant classes that generates a foaming char barrier to heat and fuel transport is an intumescent (*6*, *7*). Intumescing flame retardants (IFRs) typically consist of three components: an acid source, a carbon source, and a blowing agent. Like many other flame retardants, a relatively high loading (15 % to 25 % by mass) for the polymer matrix is needed to successfully pass fire tests. As a result, the composites suffer significant reductions in both mechanical strength and melt viscosity (*8*, *9*). Furthermore, the components are often water soluble, leading to loss of the additives, hydrolysis reactions, and a loss in fire protection under warm, humid conditions (*10*, *11*). Finally, the lower thermal stability of the components than that of many high performance polymers, such as polyamides or poly(ethylene terephthalate), preclude their use as flame retardants in these systems.

These issues have been addressed by incorporating nanofibrillated cellulose fibers (NFC) in intumescing flame retardant formulations (*12*). This takes advantage of the reinforcing nature of fibers, while retaining the use of an underutilized, sustainable resource. In this study, cellulose fibers were modified to include an acid source and blowing agent on the fiber, producing an all – fiber IFR for polymers. Phosphorylation of cellulose using phosphoric acid was used to add an acid source to the fibers. This method produces only monosubstituted glucose units (*13*) and has been shown to be less efficient than other phosphorylation techniques, such as the use of phosphorus oxychloride (*14*, *15*), phosphorus trichloride (*14*), phosphorus pentachloride (*14*, *16*), organophosphoryl chlorides (*17*) or phosphoroamidates (*18*). However, these other phosphorylating agents are significantly more toxic, are more hazardous to handle, or involve more reaction steps. A primary goal of this study was to establish a greener process for flame retarding polymers, so it was determined that the less efficient pad-bake phosphorylating method presented here was the most appropriate procedure for initial studies.

The modified cellulose was characterized using potentiometric titration, elemental analysis, and thermogravimetric analysis (TGA). Composites were prepared by a melt blending technique. Thermal stability was determined using thermal gravimetric analysis (TGA) and flammability was characterized by UL-94 tests. Reinforcing effects were examined using dynamic mechanical analysis (DMA). The effects on flammability properties and the remaining challenges to producing an all-fiber IFR are discussed.

Experimental

Materials

Nanofibrillated cellulose (NFC), prepared from Lyocell fibers with a precursor length of 6 mm and low degree of nanofibrillation ($\approx$ 500 nm diameter), was obtained from Engineered Fibers. Rice hull flour (RHF) was obtained from Composition Materials Co. Toluene (anhydrous, 99.8 %), N,N-dimethylformamide (DMF, anhydrous, 99.8 %), glacial acetic acid (HAc, 99.8 %), orthophosphoric acid (99 %), urea (99 %), and (3-chloro-2-hydroxypropyl) trimethylammonium chloride (97 %) were purchased from Sigma-Aldrich. Sodium hydroxide (ACS reagent, $\geq$ 98.6 %) was purchased from Fluka, ammonium polyphosphate (APP, EXOLIT AP422 (NH_4PO_3)$_{1000+}$) was purchased from Clariant, pentaerythritol (PER, > 98%) was purchased from Avacado, ammonium hydroxide (ACS reagent, 14.8 M) was purchased from Fisher Scientific, ethanol (dehydrated, 200 Proof) was purchased from Pharmco, and glycidyl isobutyl POSS and glycidyl phenyl POSS were purchased from Hybrid Plastics, Inc. Poly(lactic acid) (PLA) was purchased from NatureWorks (PLA2002D grade) and dried 60 min at 90 °C prior to use.

POSS – modified nanofibrillated cellulose (PNFC) was prepared as previously described (*19*). Cellulose phosphate fibers were prepared by soaking in a 1 M H_3PO_4 / 3 M urea solution for 90 min, filtering until the fibers retained enough solution to equal 4 times the mass of fibers, and placing in a 150 °C oven for 15 min or 40 min. The excess phosphoric acid was neutralized with either 1 M aqueous NaOH (NFC-PO4) or 1 M aqueous NH_4OH (NFC-PO4NH4). RHF phosphate (RHF-PO4) and PNFC phosphate (PNFC-PO4) were prepared in the same manner, baking for 40 min and neutralizing with an aqueous NH_4OH solution. Nitrogen was added to the fibers by mixing a 1:3 ratio of (3-chloro-2-hydroxypropyl) trimethylammonium chloride to fibers in 15% by mass aqueous NaOH solution for 60 min. The quaternized cellulose (QNFC) and quaternized cellulose phosphate (NFC-PO4Q) were neutralized by dialysis in 3.5 kDa cellulose SnakeSkin tubing. Dialysis water was replaced daily for 3 days, or until pH = 7 was obtained. POSS – modified QNFC (QPNFC) was prepared by adding ethanol to the pre-dialyzed solution, filtering until the solution uptake was 2 times the mass of fibers, then reacting in toluene in the same manner as PNFC. All reactions were performed consecutively prior to manual shredding the fibers and drying them overnight at 90°C.

Instrumentation

Duplicate elemental analyses of the fibers were performed by Galbraith Laboratories. Carbon, hydrogen, and nitrogen contents were analysized by combustion. Silicon and phosphorus contents were measured using an ICP – OES technique. Carbon, hydrogen, and nitrogen analyses were performed in duplicate on 2 mg ± 0.3 mg samples and phosphorus and silicon analyses were performed on 75 mg ± 2 mg samples. The repeated measurements were within 5% of each other, and the mean values are reported here. Acid-base titrations and chloride ion concentrations were measured using an Orion 5-Star meter, equipped with an AquaPro pH combination electrode and an IonPlus chloride ion selective electrode. PLA composites were prepared by melt blending at 180 °C and 21 rad/s for 5 min in an Xplore 15 mL twin-screw co-rotating mini-compounder (DSM Instruments). Thermal stabilities were measured using a Netzsch TG449 F1 Jupiter Thermo-nanobalance or a TA Instruments Q-500 thermogravimetric analyzer. Samples (5.0 mg ± 0.3 mg) were placed in open ceramic pans and heated at a scan rate of 10°C/min while purged with nitrogen at a rate of 100 mL/min. The mean of typically two replicate measurements was reported. The temperature of both the onset (5 % mass fraction loss) and peak mass loss rate have an uncertainty of $\sigma = \pm 2$ °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. Horizontal and vertical burn tests were conducted in a fume hood using UL-94 standard procedures. Composite samples were hot pressed (25 MPa) into 125 mm x 13 mm x 3 mm molds at a temperature of 180 °C using a Carver hydraulic heated press. The reported burn rate had an uncertainty of $\sigma = \pm 0.2$ mm/min. Storage modulus, storage loss, and tan δ were determined using a TA Instruments Q-800 Dynamic Mechanical Analyzer. Samples were hot pressed into 36 mm x 13 mm x 3 mm plate molds at 180 °C and 25 MPa. They were quench cooled with forced air, annealed at 90 °C for 45 min to induce crystallization, and clamped into the 35 mm single/dual cantilever attachment. The samples were heated from 35 °C to 130 °C at a rate of 3 °C/min using the single cantilever mode (17.5 mm) with a displacement amplitude of 15 μm and frequency of 1 Hz. Storage modulus and T_g had uncertainties of $\sigma = \pm 100$ MPa and $\sigma = \pm 1$ °C, respectively.

Results and Discussion

Fiber Characterization

Fibers were analyzed for C, H, N, P, and Si content by elemental analysis. (cf Table 1) All fibers had higher than expected hydrogen content, which is likely due to surface absorbed water. The phosphorylation process was found to be inefficient, resulting in the incorporation of only about 20% of the expected phosphorus. The nitrogen content was below the instrument detection limit for almost all fibers. It has been noted that elemental analysis underestimates the

degree of quaternization in cellulose (*20*). Since carbon, hydrogen, and nitrogen contents were determined by combustion, the lower than expected carbon content in POSS – containing fibers is likely due to the large amount of char that results during combustion (*19*).

The degree of substitution for the modified fibers were determined from the elemental analysis and by potentiometric techniques, and is shown in Table 2. Phosphate content by potentiometric titration were slightly lower than those from elemental analysis, but values were comparable. On average, the phosphorylation adds a phosphate group about every 5 glucose units. Implied nitrogen content by potentiometric Cl⁻ concentrations were lower than those suggested by elemental analysis, indicating that potentiometric Cl⁻ content is an ineffective method for determining the extent of the quaternization reaction. The higher phosphorus and silicon content for PNFC-PO4 may suggest that some of the phosphate ions cross-link with the trisilanols that form during the PNFC reaction, similar to what was found for APP-PNFC mixtures (*12*).

Table 1. Elemental Analysis of Modified Fibers

Fiber	*%C expt (theor)*	*%H expt (theor)*	*%N expt (theor)*	*%P expt (theor)*	*%Si expt (theor)*
NFC	41.6 (44.4)	6.4 (6.2)	---	---	---
RHF	38.8 (38.7)	5.5 (5.4)	0.9 (0.7)	0.3 (0)	7.6 (6.8)
PNFC	41.9 (50.3)	6.1 (5.0)	0 (0)	---	3.2 (13.0)
NFC-PO4	39.5 (29.8)	6.2 (4.5)	0.9 (0)	2.1 (12.8)	---
NFC-PO4NH4	41.7 (27.8)	6.3 (5.4)	0 (5.4)	0.6 (12.0)	---
QNFC	46.2 (46.0)	6.4 (6.8)	0 (1.8)	---	---
QPNFC	32.4 (50.5)	4.1 (5.3)	0 (0.8)	---	5.4 (12.1)
NFC-PO4Q	39.7 (31.6)	6.4 (6.0)	0.9 (6.1)	1.7 (10.2)	---
RHF-PO4	37.0 (30.4)	5.4 (4.6)	0.7 (3.4)	3.2 (6.3)	7.8 (6.8)
PNFC-PO4	37.2 (43.0)	5.3 (4.9)	1.1 (2.1)	3.6 (4.6)	6.7 (11.1)

The thermal stabilities of cellulose phosphate prepared under different reaction conditions are shown in Figure 1. Phosphorylating cellulose resulted in a 50 °C decrease in both onset and peak degradation temperatures, and the char yield significantly increased to over 20% of the original mass. Increasing the pad bake time decreased the thermal stability and increased char yield only slightly, despite nearly doubling the phosphate concentration. Neutralizing the product with ammonium hydroxide solution increased the char yield without significantly altering the thermal stability.

Table 2. Degree of Substitution of Modified Fibers

Fiber	DS$_P$ by pot	DS$_P$ by EA	DS$_N$ by pot	DS$_N$ by EA	DS$_{Si}$ by EA
PNFC	---	---	---	---	0.062
NFC-PO4 (15min)	0.10	---	---	---	---
NFC-PO4 (40min)	0.20	0.16	---	---	---
NFC-PO4NH4	0.03	0.05	---	---	---
QNFC	---	---	0.010	0	---
QPNFC	---	---	0	0	0.11
NFC-PO4Q	0.19	0.16	0.013	0.037	---
RHF-PO4	0.20		---	---	
PNFC-PO4	0.31	0.78	---	---	0.15
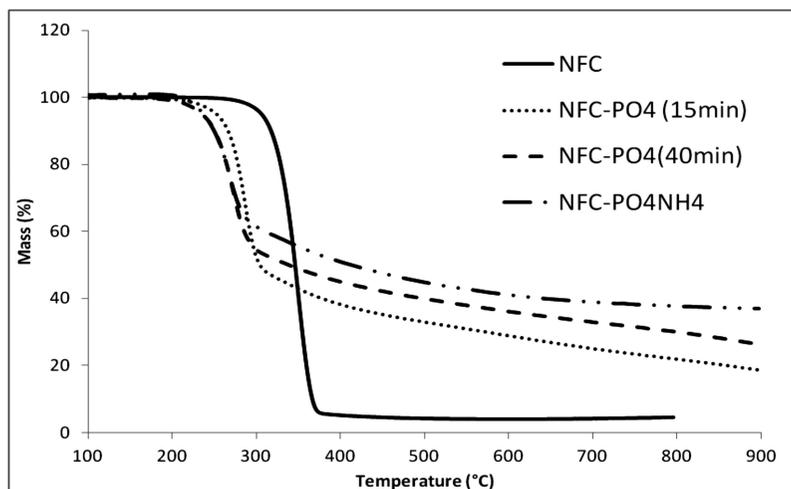
Figure 1. TGA of cellulose phosphate prepared under different reaction conditions under a flow of N_2 at 10°C/min.

The addition of phosphate by phosphoric acid hydrolysis added an acid source to the cellulose fibers. The thermal stability of the cellulose phosphate depended significantly on the other modifications performed, as shown in Figure 2. Quaternizing the fibers with glycidyltrimethylammonium ions slightly increased the thermal stability of the fibers, but reduced the char yield at all temperatures. Adding POSS to the fibers produced very high amounts of char (over 60% by mass), which were thermally stable to over 850 °C. Rice hull flour phosphate had

a nearly identical thermal profile to nanofibrillated cellulose phosphate. This was a bit surprising because RHF contains lignin and hemicelluloses (*21*), which both have significantly lower thermal stabilities and produce higher char yields than cellulose (*22*). It is likely that the lignin, which is water soluble, was removed from the final product during filtration, leaving predominately phosphorylated cellulose. Further characterization of these materials is under investigation.
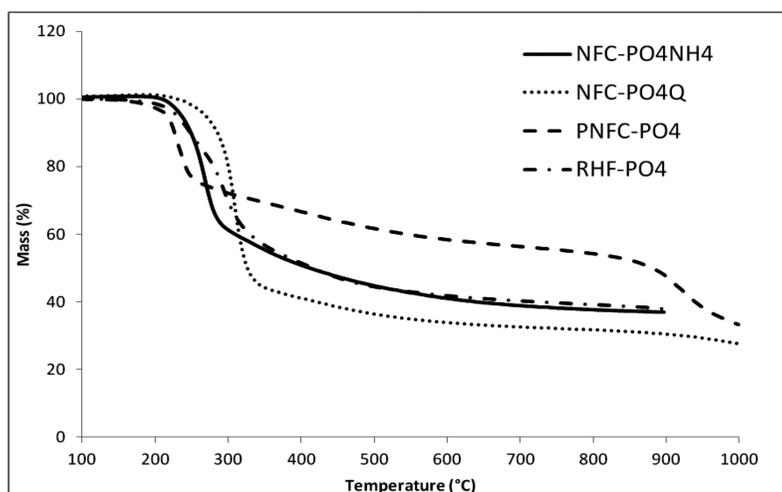

Figure 2. Thermal stability of cellulose phosphate fibers with different modifications while purged with a flow of N_2 at a heating rate of 10°C/min.

PLA Composite Properties

Intumescing flame – retarded PLA composites were prepared by melt blending. Thermal stabilities of APP based IFR formulations using NFC, PNFC, RHF, and PER as the carbon source are shown in Figure 3. Thermal stabilities of cellulose phosphate based IFRs are shown in Figure 4. Addition of 15% by mass of the conventional IFR, APP-PER, to PLA increased the thermal stability by 2 °C and the char yield to 6 % of the original mass. Replacing the PER with a cellulose based carbon source further increased the thermal stability by 3 °C to 8 °C and resulted in char yields of 8% to 9% by mass. The onset of degradation temperature was increased by a few degrees, but the peak decomposition temperature remained unchanged in PLA composites containing 15% by mass cellulose fibers. The char yield only slightly increased. Phosphorylation of the fibers resulted in 5% to 10% loss in mass between 200 °C and 250 °C for the composites, but increased final char yield to about 6% of the original mass. Since less than the total mass of fibers degraded at the earlier stage, fiber char was likely formed and may show some intumescing behavior when burned.
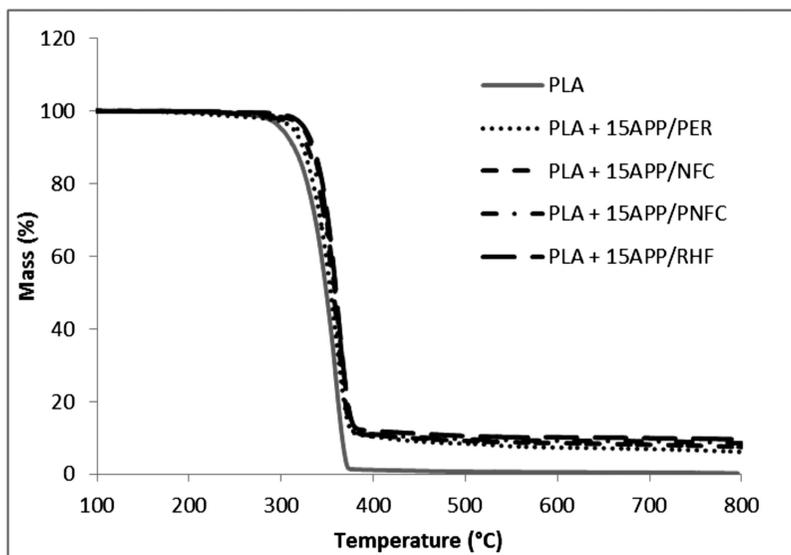
Figure 3. Thermal stability of PLA composites using APP-based IFRs with different cellulose carbon sources while purged with a flow of N_2 at a heating rate of 10°C/min.
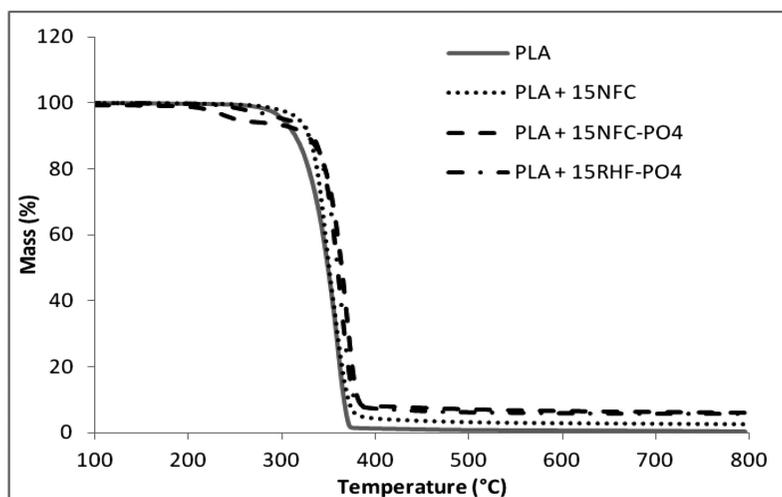

Figure 4. Thermal stability of PLA composites using cellulose phosphate fibers as an IFR while purged with a flow of N_2 at a heating rate of 10°C/min.

Horizontal and vertical burn tests were conducted for the PLA composites. In the horizontal burn test, neat PLA burned at a rate of 9.4 mm/min and had a burn length between 0 mm and 20 mm. Since this polymer showed some resistance to burning, it was expected that the flame – retarded samples would not burn in the horizontal direction. So all other samples were burned only in the vertical direction, and the results are reported in Table 3. As expected, neat PLA completely burned in the test, producing burning drips. The use of APP-based intumescents eliminated burning, resulting in a V-0 rating, regardless of the carbon source used. It was observed, however, that APP/PER produced the most dripping, while APP/NFC and APP/PNFC produced only a few non-burning drips. APP/RHF exhibited a dripping behavior somewhat between that of the PER and cellulose fiber samples. The reduction in melt flow during burning was attributed to the higher aspect ratio of the carbon source. Replacing the APP with phosphorylated cellulose resulted in composites that produced burning drips and failed the UL-94 test. However, the charring behavior observed was similar to the action of an intumescent, and the flame in the NFC-PO4 composite did extinguish after about a minute, prior to reaching the holding clamp. This suggests that further modification of the fibers may result in an efficient IFR based solely on cellulose fibers.

Table 3. UL-94 Tests of PLA Composites[*]

Composite	HB rate (mm/min)	t_1 (s)	t_2 (s)	UL-94
PLA	9.4	complete		NR
PLA + 15APP/PER		DNB	DNB	V-0
PLA + 15APP/NFC		DNB	DNB	V-0
PLA + 15APP/PNFC		DNB	DNB	V-0
PLA + 15APP/RHF		DNB	DNB	V-0
PLA + 15NFC		complete		NR
PLA + 15NFC-PO4		DNB	73	NR
PLA + 15RHF-PO4		DNB	complete	NR

[*] - DNB = did not burn, NR = not rated.

Dynamic mechanical analysis was used to assess the changes in semi-crystalline composite stiffness and polymer mobility. As noted in Table 4, the addition of APP/PER reduced composite stiffness and increased the glass transition relative to pure PLA. This is consistent with the reduction in melt viscosity during extrusion that was visually observed. Other studies have noted losses in mechanical strength when incorporating PER in flame retarded polymers (*8*). Replacing the PER with fiber based carbon sources increased both storage

modulus and glass transition for the polymer. This was as expected, since the addition of fibers has a reinforcing effect on polymer composites. The addition of rice hull flour had the smallest increase in storage modulus and greatest increase in glass transition temperature. This is likely due to the lower aspect ratio of the filler. The storage modulus and glass transition temperatures of the composites containing phosphorylated cellulose fibers were similar to those of APP/fiber containing composites and slightly lower than the PLA + 15NFC composite. This is consistent with partial degradation of the polymer, which occurs during extrusion in the presence of acidic components. A more complete analysis of the role of IFR formulations in polymer degradation and in composite viscoelastic behavior is currently under investigation (*9*).

Table 4. Dynamic Mechanical Analysis of Composites

Composite	Storage Modulus (MPa)	tan δ peak (T_g, °C)
PLA	2050	61.8
PLA + 15APP/PER	1900	69.2
PLA + 15APP/NFC	2350	67.6
PLA + 15APP/PNFC	2450	69.9
PLA + 15APP/RHF	2300	71.7
PLA + 15NFC	2550	71.5
PLA + 15NFC-PO4	2400	70.6

Conclusions

Cellulose fibers were modified variously with phosphoric acid, glycidyltrimethylammonium chloride, and glycidylphenyl POSS to increase char yield, gas generation, and thermal oxidative stability upon pyrolysis. The fibers were used as intumescing flame retardants for poly(lactic acid). Elemental analysis indicated that the phosphorylation modifications resulted in a fairly low degree of substitution. Nitrogen elemental analysis by combustion and potentiometric analysis of Cl⁻ were both found to be ineffective for determining the extent of the quaternization reactions. Despite the low DS, the additions, especially of phosphate and POSS, resulted in significant increases in char yield with only small decreases in thermal stabilities. Using nanofibrillated cellulose fibers, POSS modified cellulose, or rice hull flour as the carbon source in APP based IFRs for PLA increased the thermal stability by up to 10 °C, increased char yield to nearly 10% of the original mass, and resulted in UL-94 ratings of V-0. Composites using phosphorylated celluloses instead of APP formulations exhibited similar thermal properties, but failed UL-94 tests. Despite poor UL-94

results, the composites were observed to exhibit intumescing behavior and did extinguish the flame prior to complete combustion. Dynamic mechanical analysis illustrated that the use of fibers in intumescing formulations prevented losses in stiffness normally observed for APP/PER containing composites. The glass transition temperatures were found to be 6 °C to 10 °C higher than the neat PLA, which is comparable to the composite containing APP/PER.

Acknowledgments

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