

MODIFICATION AND FLUORESCENCE MONITORING OF CELLULOSE

PHOSPHATE FOR INTUMESCENT FLAME RETARDANT

APPLICATION IN POLY LACTIC ACID

By

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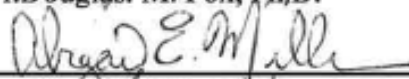
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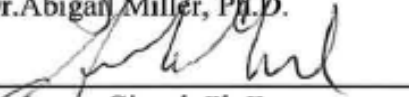
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DEDICATION

I would like to dedicate this thesis to my parents, who showed me the path of education and encouraged me all through my life. It is also dedicated to my husband for his unwavering and healthy support all through my study.

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ABSTRACT

This thesis focuses on the synthesis of Intumescent Flame Retardant (IFR) from a sustainable resource that is abundant, environmentally less toxic than standard IFRs, biodegradable and economical. For this purpose Nano Fibrillated Cellulose (NFC) was used as a carbon /char producing source. Modification by phosphorous and nitrogen compounds as acid and gas producing agents resulted in the synthesis of IFR. Fourier Transform Infrared Spectroscopy (FTIR) was used to confirm the modification of the cellulose. Thermo Gravimetric Analysis (TGA) was performed to check the thermal stability of modified cellulose. Estimation of cellulose phosphate was measured by Potentiometry. The modified cellulose composites with Poly Lactic Acid (PLA) were obtained by using a melt blending technique. The composites were analyzed for viscoelastic/stiffness properties using Dynamic mechanical analyzer (DMA). The

composites were found to exhibit horizontal burn (HB) flammability ratings.

Additionally, to study the interfacial and dispersion properties of nano fibrillated cellulose in PLA two thermally stable fluorescent tagged celluloses with amino-methyl Coumarin and Fluoresceinamine (FA) dyes in PLA were synthesized. The Amino methyl Coumarin tagged cellulose showed good thermal stability even after blending with PLA and showed absorbance in UV-Visible Spectrophotometer; the FA tagged cellulose was thermally stable before blending with PLA but showed reduced quantum yield once it was blended in PLA.

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MODIFICATION OF CELLULOSE FOR INTUMESCENT FLAME RETARDANT APPLICATION

Introduction

Intumescent Flame Retardants

The term “to intumesce” was used by the tragedian John Webster (1580–1624) during the Elizabethan period with two meanings: “to grow and to increase in volume against the heat” or “to show an expanding effect by bubbling”. When heating beyond a critical temperature, intumescent materials begin to swell and then to expand. The result of this process is a foamed cellular charred layer on the surface which protects the underlying material from the action of the heat flux or the flame ¹⁻³. The proposed mechanism is based on the charred layer acting as a physical barrier which slows down heat and mass transfer between gas and condensed phases.

Condensed Phase Charring

The mode of fire protection action of intumescence occurs in the condensed phase of the material during combustion. A complete description of intumescence requires analysis of both chemical and physical process.

Physical Mode of Intumescence

The mechanism of intumescent flame retardation is by the formation of a foamed multicellular char on the polymer surface that hinders the polymer from further burning. The char foam acts as an effective barrier against heat and oxygen which slows down the diffusion of gaseous pyrolysis products to the combustion zone ⁴. Figure 1 shows the mechanism of intumescent flame retardant.

When plastic or other materials which contain ammonium polyphosphate (APP) are exposed to an accidental fire or heat, the flame retardant APP starts to decompose, commonly into polymeric phosphoric acid and ammonia. The polyphosphoric acid reacts with hydroxyl or other groups of a synergist to form a non stable phosphate ester. In the next step, phosphate ester dehydrates. Carbon foam is built up on the surface against the heat source (charring). The carbon barrier acts as an insulation layer, preventing further decomposition of the material.

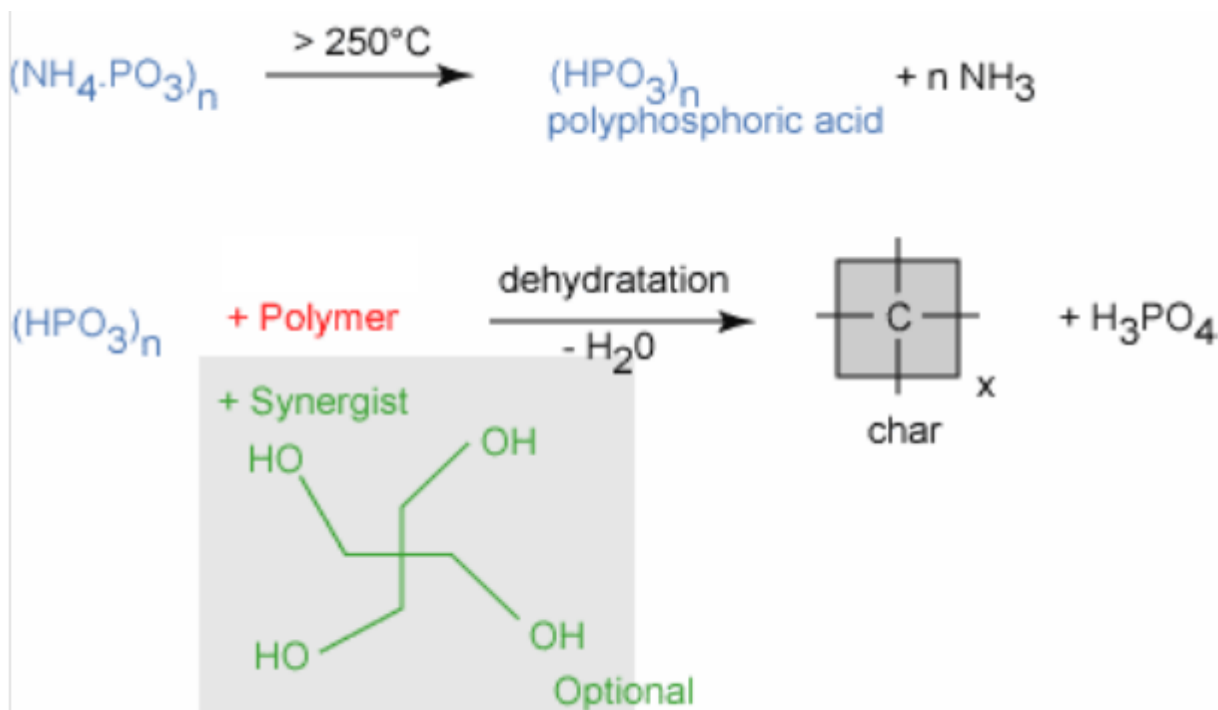


Figure 1: Mechanism of Intumescent Flame Retardant

(Courtesy: Specialchem4polymers)

Chemical Mode of Intumescence

Intumescent flame retardant's (IFR) are used in paints and coating industries. Typical IFR formulation consists of phosphorous compounds such as, Ammonium Polyphosphate, a char forming source such as pentaerythritol and a blowing agent such as melamine. A binder such as polyolefin, methyl styrene or poly lactic acid is used to keep the mixture intact.

Therefore, a burning polymer which is flame retarded with intumescent materials, can be considered to be a block with several separated layers. A top char layer is adjacent to an intumescent front where the foaming reaction occurs; below that is the unburned polymer coating layer that contains a flame retardant; the bottom layer consists of polymer substrate that is being protected by intumescent coating. The char foam produces a physical barrier to heat and mass transfer and thus interferes with combustion process. It also lowers the rate of temperature increase on the surface and hinders the diffusion of oxygen to the site of combustion.

Melamine, which is used as a blowing agent, contributes to the expansion of the char layer in the intumescent process. The char layer acts as a barrier between oxygen and polymeric decomposition gases. Char stability is enhanced by multi-ring structures like melem and melon, formed during self-condensation of melamine. In combination with phosphorous synergists melamine can further increase char stability through the formation of nitrogen-phosphorous synergism. Last but not least, melamine can act as blowing agent by increasing char volume and enhancing the heat barrier functionality of the char layer.

Therefore for a mixture to be an efficient IFR it requires;

- An Acid Source
- A carbon rich polyhydric material as a char forming source
- A blowing agent also called as a spumific

Objective

Flame retardants (FR) are chemicals used in thermoplastics, thermo sets, textiles and coatings that inhibit or resist the spread of fire. One of the standards FR for plastics is organohalogen compounds including organo chlorine derivatives such as chlorendic acid and chlorinated paraffin's; organobromines such as decabromodiphenyl ether (decaBDE), decabromodiphenyl ethane (a replacement for decaBDE), polymeric brominated compounds such as brominated polystyrenes, brominated carbonate oligomers (BCOs), brominated epoxy oligomers (BEOs), tetrabromophthalic anyhydride, tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD)⁵. These FR's are all petroleum based products which have negative impact on health and the environment for their disposal. They are non-biodegradable, toxic and obtained from a non sustainable resource, such as petroleum. These FR's are under scrutiny due to their toxicity and increasing regulations, thus making them less desirable.

To make a polymer flame resistant, IFRs must be added at relatively high loading (15 % to 25 % by mass) to successfully pass fire tests, and as a result, the polymer composites generated suffer significant losses in mechanical strength and melt viscosity⁶. Ammonium Polyphosphate/Pentaerythritol (APP/PER) is a powder based standard IFR, which reduces mechanical strength. Furthermore, APP/PER is water soluble, leading to loss of the additives, hydrolysis reactions, and a loss in fire protection under warm,

humid conditions⁷. Finally, the lower thermal stability of the APP/PER than many high performance polymers, such as polyamides or poly (ethylene terephthalate), preclude their use in these systems.

Penta- erythritol is a classic polyol that can be used as a char producing agent and it is water soluble. As a result, APP/PER readily absorbs moisture⁸, and under high temperature and UV radiation APP initiates its conversion to phosphoric acid⁹. This leads to the hydrolysis of wood based Cellulose. PER has reduced strength at ambient temperatures and low glass transition temperature and viscosity.

To overcome these issues nano fibrillated cellulose (NFC) was used as a carbon source in an intumescent flame retardant formulation. The NFC fibers were phosphorylated to introduce an acid source and to potentially eliminate the need for either APP or PER. This approach takes advantage of the reinforcing nature of fibers, while retaining the use of an underutilized, sustainable resource.

Design and Synthesis

Due to the increasing public awareness of the environment, a less toxic, environmentally friendly, and economical compound obtained from sustainable source, was used to synthesize an Intumescent Flame Retardant.

To address these issues, NFC was used as the char producing carbon source; this was modified with phosphoric acid to add as an acid source and nitrogen as a blowing agent which also enhances the heat barrier functionality of char. Composites were prepared by melt blending technique using PLA a bio-based polymer.

Cellulose

Cellulose is obtained from biomass such as plants. It is economical, biodegradable and non-toxic and when burned, it produces carbonaceous char. It consists of a linear polymer of 10,000 to 14,000 1, 4- β -D Glucose molecules [10](#). It has a great number of hydroxyl groups, higher flexibility and strength [11](#) when it is compared to other types of cellulose materials such as; microcrystalline cellulose. Based on strength and purity, the thermal stability of fibers range from 230°-300° C, and when burned, they produce char yields of 5 to 30% [12,13](#)

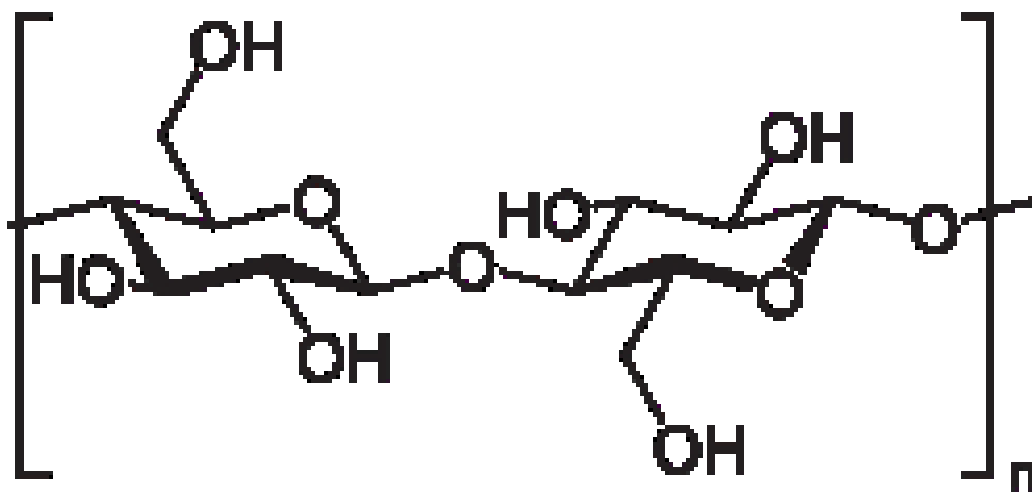


Figure 2: Cellulose

(Courtesy Wikipedia)

Nitrogen Source

NFC was modified with phosphoric acid and nitrogen sources like urea, ammonia and quaternary ammonium salts were used. The nitrogen source acts as blowing agent which increases the char formation and enhances the intumescent behavior of the final product phospho- ammonium cellulose, an IFR. Figure 3 shows the typical reaction between fibers, phosphoric acid and urea. This reaction is carried out using a pad bake procedure at 150° C in the oven for a bake time of 15 min.

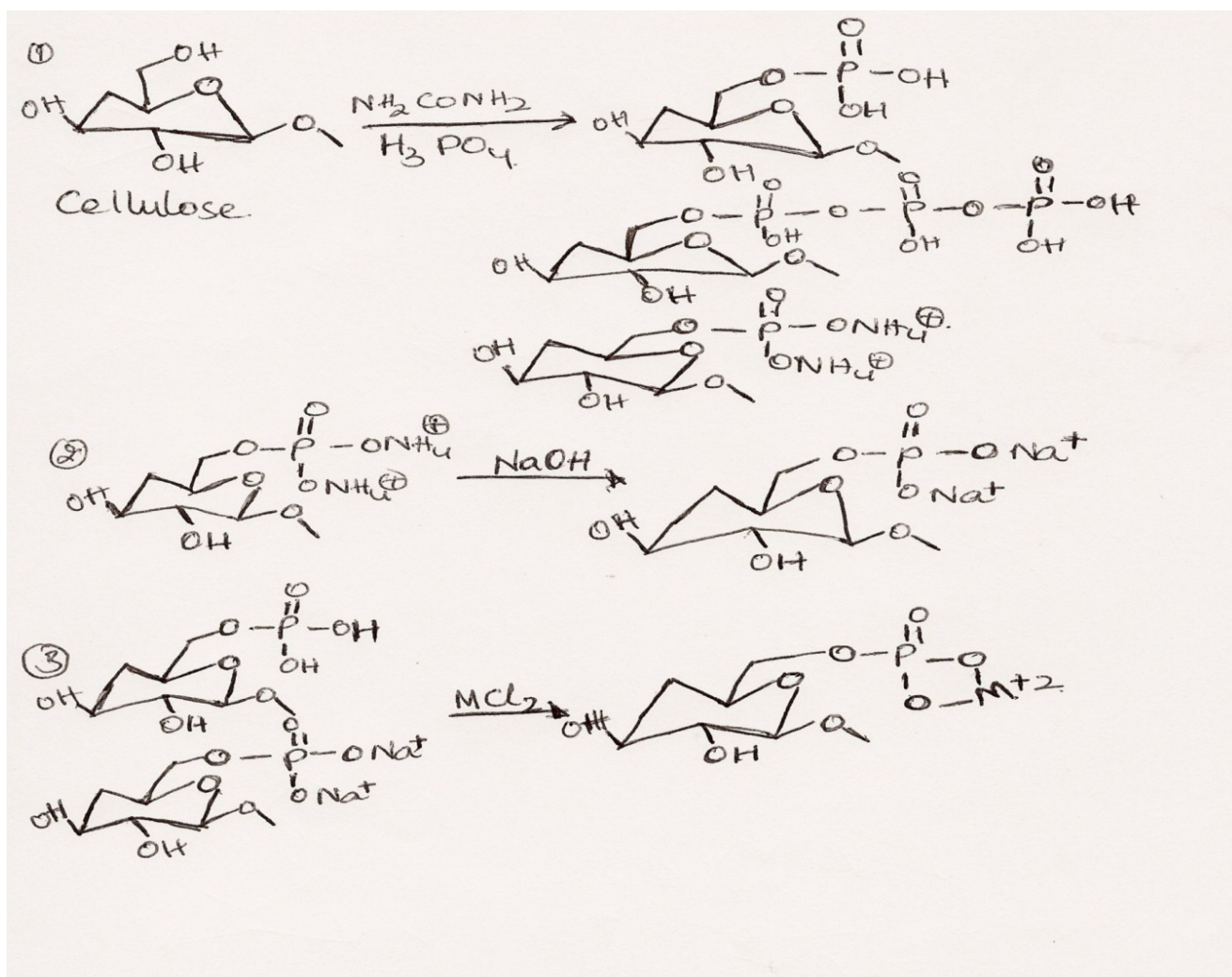


Figure 3: Schematic Diagram Showing the Pad Bake Reaction of Fibers with Phosphoric Acid and Urea

Rice Hull Flour (RHF)

In recent years polymer composites reinforced with natural fibers such as wood, corn stalk, hemp wheat straw, sunflower stalk and bagasse fiber have been used

extensively because of their recyclability, renewability and biodegradability¹⁴. They also have excellent durability, superior dimensional stability, high rigidity and low density¹⁵. RHF has a potential to enhance flame retardant behavior because of its relative high Si content. Also, RHF is conveniently obtained from natural agro waste. So, phosphorylation of RHF was also carried out so that the thermal stability and flammability properties of the resulting polymer could be measured.

Poly Lactic Acid

Polylactic acid (PLA) is thermoplastic aliphatic polyester derived from renewable resources, such as corn starch or sugar cane. It is an environmentally friendly polymer that does not produce toxic gases when it is burned. PLA has good visco-elasticity, high melting point, strength and is a bio-degradable polymer¹⁶.

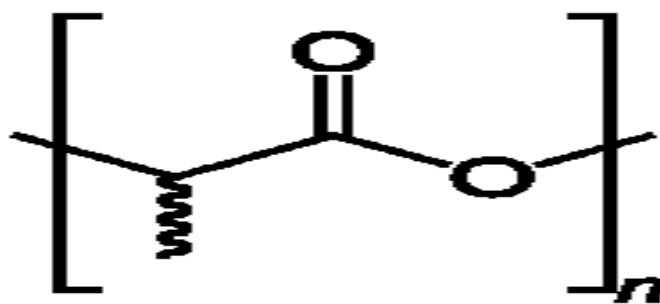


Figure 4 : Poly Lactic Acid

(Courtesy Wikipedia)

Experimental

Nano fibrillated cellulose (NFC), prepared from Lyocell fibers with a precursor length of 6 mm and low degree of nanofibrillation (≈ 500 nm diameter), and was obtained from Engineered Fibers. Rice hull flour (RHF) was obtained from Composition Materials Co., 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, ≥ 98.6 %) was purchased from Fluka and ammonium hydroxide (ACS reagent, 14.8 M) was purchased from Fisher Scientific. Poly (lactic acid) (PLA) was purchased from Nature Works (PLA2002D grade) and dried 60 min at 90 °C prior to use.

Synthesis of Phosphorylated Cellulose

Cellulose phosphate fibers were prepared by soaking in a 1 M H_3PO_4 / 3 M urea solution for 90 min, filtering until the solution uptake was 4 times the mass of fibers, and placing in a 150 °C oven for 15 and 40 min. The excess phosphoric acid was neutralized with either 1 M NaOH (NFC- PO_4) or 1 M NH_4OH (NFC- PO_4NH_4).

Synthesis of Rice Hull Flour Phosphate

RHF phosphate (RHF-PO₄) was also prepared in the same manner as phosphorylated cellulose. It was baked for 40 min and neutralized with NH₄OH. Filtration for this product took a longer time.

Quarternization of Cellulose

The homogeneous Quarternization was carried out by dissolving cellulose in 15% wt, aqueous solution of NaOH and adding it to a 1:3 ratio of (3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHPTAC) as a etherification agent. Under alkaline conditions, epoxide is produced in-situ from CHPTAC, and quaternized cellulose is then formed through the reaction between cellulose sodium alkoxide and epoxide of CHPTAC as shown in the Figure 5. Next, 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 were obtained. All reactions were performed consecutively prior to manual shredding the fibers which were then dried at 90°C in oven.

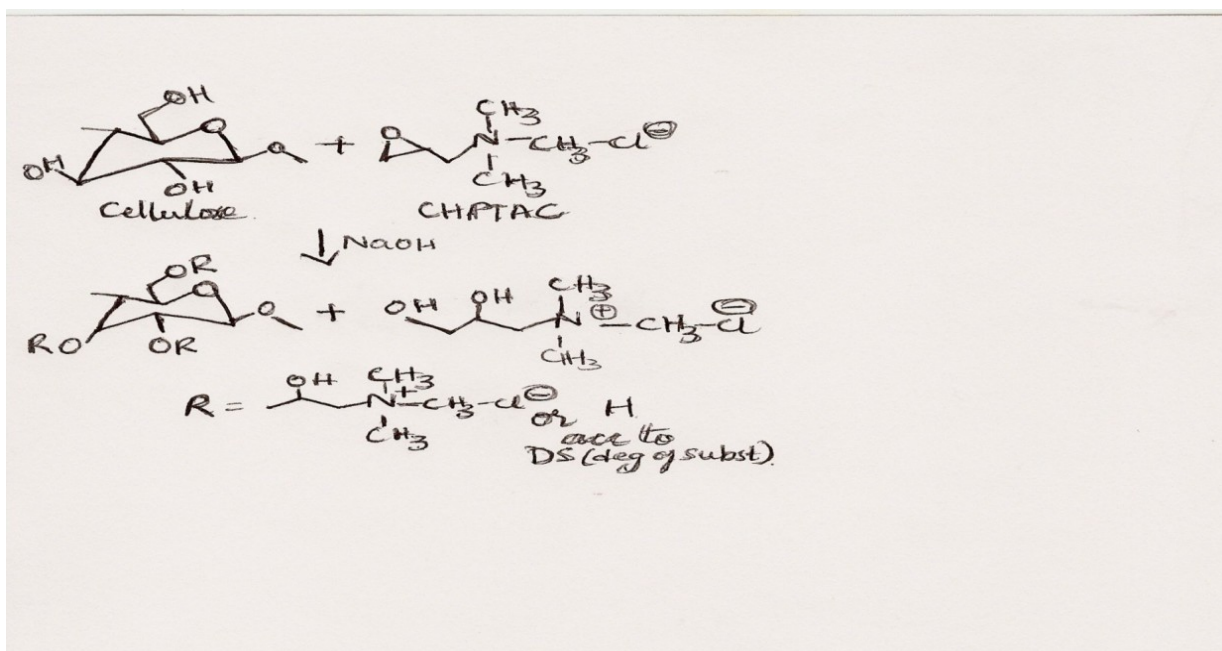


Figure 5 : Schematic Diagram of Quaternization of Cellulose with 3-Chloro-2-Hydroxypropyl-Trimethylammonium Chloride in NaOH/Urea Aqueous Solutions

Estimation of phosphoric acid in the fibers was performed by Potentiometry using a pH electrode connected to an Orion 5 Star multimeter. Typically, 0.05 g of phosphorylated fibers was titrated using standard sodium hydroxide solution. Potassium Hydrogen Phthalate ($C_8H_5KO_4$) was used as a primary standard to standardize NaOH.

To determine the chloride ion concentration, 100% pure Sodium Chloride (NaCl) was dried in oven for 30 min at 90°C. Then, solutions with concentrations ranging from 5ppm-250ppm of sodium chloride were prepared and the voltage was measured. This was used as the standard. About 0.05 g of quaternized cellulose sample was added to 20 ml of water and voltage was measured. The concentration was calculated from the standard curve.

Instrumentation

FTIR Analysis

The above prepared fibers were subjected to FTIR analysis, using a Bruker Alpha instrument with the platinum-ATR attachment and a diamond crystal. Air was used as background.

Potentiometric Estimation

Estimation of acid concentration in the fibers was performed by acid-base titrations using an Orion 5-Star meter, equipped with an AquaPro pH combination electrode and chloride ion estimation was determined by an Ion Plus chloride ion selective electrode. Once the titration of the fibers was done the degree of substitution (DS_p) of the phosphate group was determined from the corresponding equivalence point volume and the following relation.

$$DS_p = 162 \cdot V_b \cdot M_b / M_d - 80 \cdot V_b \cdot M_b$$

Where, V_b = volume of the base at equivalence point in mL

M_b = Conc. of the base

M_d = Wt of the sample taken in g

Composite Preparation

The acidified cellulose sample and PLA was weighed out and dried in the oven at 90°C for 30 min and PLA composites were prepared by melt blending at 180 °C and 200 rpm for 5 min in an Xplore 15 mL twin-screw co-rotating mini-compounder (DSM).

Thermo Gravimetric Analysis

Thermo gravimetric Analysis (TGA) measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. This technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration.

Thermal stabilities were measured by our colleagues in the Fire Research Division at NIST using a Netzsch TG449 F1 Jupiter Thermo-nanobalance or a TA Instruments Q-500 thermo gravimetric analyzer. 5.0 mg $\pm$ 0.3 mg samples were placed in open ceramic pans and heated at a scan rate of 10°C/min while purged with 100 mL/min of nitrogen gas. 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

Horizontal and Vertical burn tests were conducted in a fume hood according to ASTM standards. In the vertical flame test, a flame is applied to the base of the specimen that is held in the vertical position and the extinguishing times are measured after removal of the test flame. In the horizontal flame tests, the flame is applied to the free end of specimens held in horizontal position for 30 seconds and the rate of burning is determined as the flame front progresses between two bench marks. All methods described in the UL-94 specification involve the use of a standard specimen size of 3mm in thickness and length between 125mm with benchmarks at 25 and 100mm positions and a controlled heat source of methane gas. Composite samples were hot pressed (25 MPa) into 125 mm x 13 mm x 3 mm molds at a temperature of 180 °C.

Dynamic Mechanical Analysis (DMA)

Storage modulus, storage loss, and $\tan \delta$ were determined using a TA Instruments Q-800 Dynamic Mechanical Analyzer. Samples were hot pressed into 36 mm x 13 mm x 2 mm plate molds at 180 °C and 25 MPa using a Carver hydraulic heated press. They were quench cooled with forced air, annealed at 100°C for 60 min, 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 displacement

amplitude of 15 μm and frequency of 1 Hz. Storage modulus and T_g had uncertainties of $\sigma = \pm 100 \text{ MPa}$ and $\sigma = \pm 1 \text{ }^\circ\text{C}$, respectively.

Results and Discussion

FTIR Analysis of the Compounds

FTIR of Phosphorylated Cellulose

Reaction of nano fibrillated cellulose with phosphoric acid/urea mixture was successively performed. By comparing the FTIR figures 6 and 7 of cellulose fibers and cellulose phosphate fibers, the FTIR peak at 820 cm^{-1} confirmed phosphorylation of the cellulose, corresponding to the P-O-C bond. The bands at 2370 cm^{-1} are caused by an absorbance by P-H bond, at 1210 cm^{-1} caused by absorption of P=O bonds, and a shoulder at $920\text{-}1000 \text{ cm}^{-1}$ caused by absorption of a P-OH group. The FTIR data showed that the cellulose was successfully phosphorylated.

FTIR of Quaternary Cellulose Phosphate

The Figure 8 confirms the FTIR of quaternized cellulose with a characteristic absorption peak at 1482 cm^{-1} which correspond to the methyl group of ammonium. The peaks positioned at 1414 cm^{-1} correspond to the C-N stretching vibration. A broad band at

3400 cm^{-1} is the stretching vibration mode of cellulose and bands at 2900 and 1370 cm^{-1} correspond to $-\text{CH}_2-$ groups.

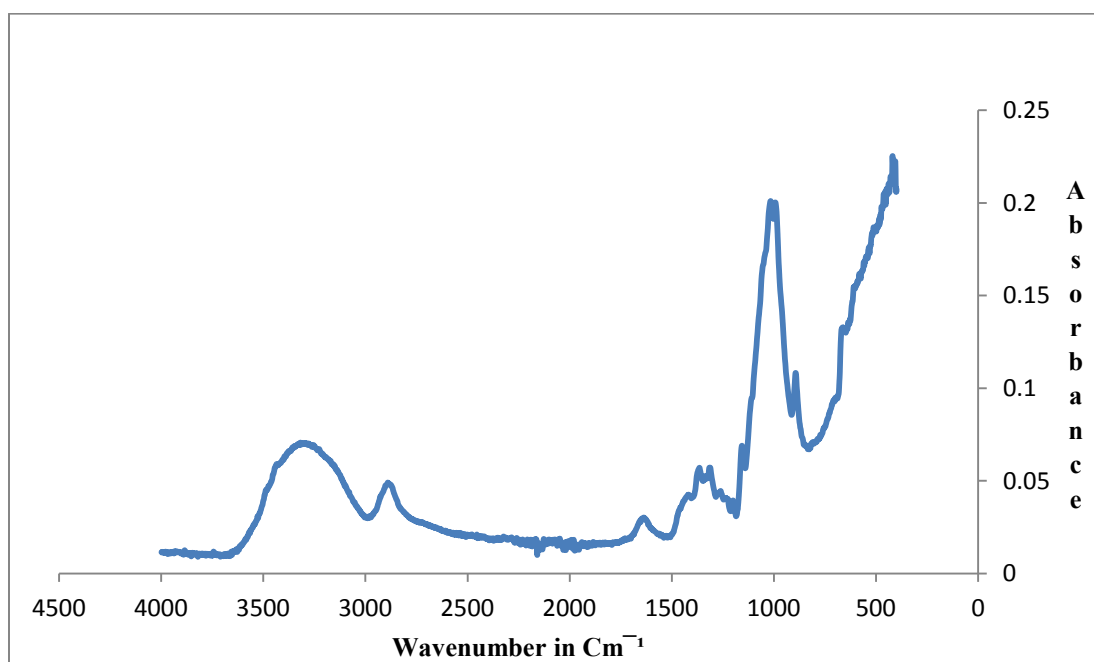


Figure 6 : FTIR of Cellulose Fibers

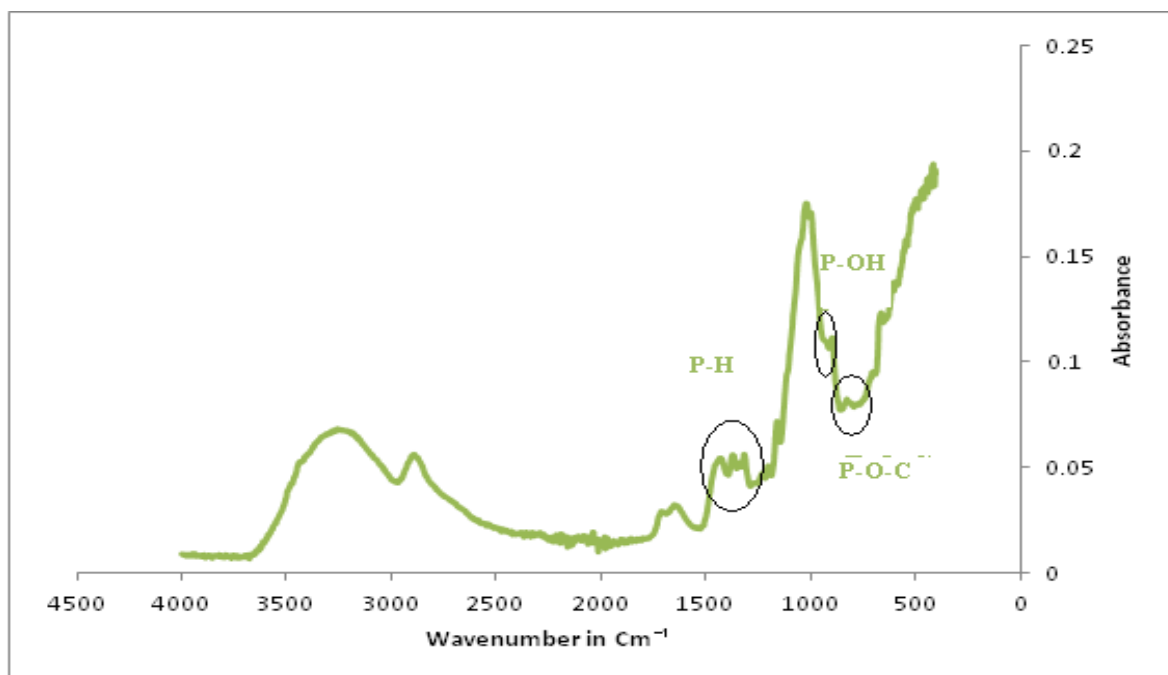


Figure 7 : FTIR of Cellulose Phosphate Fibers

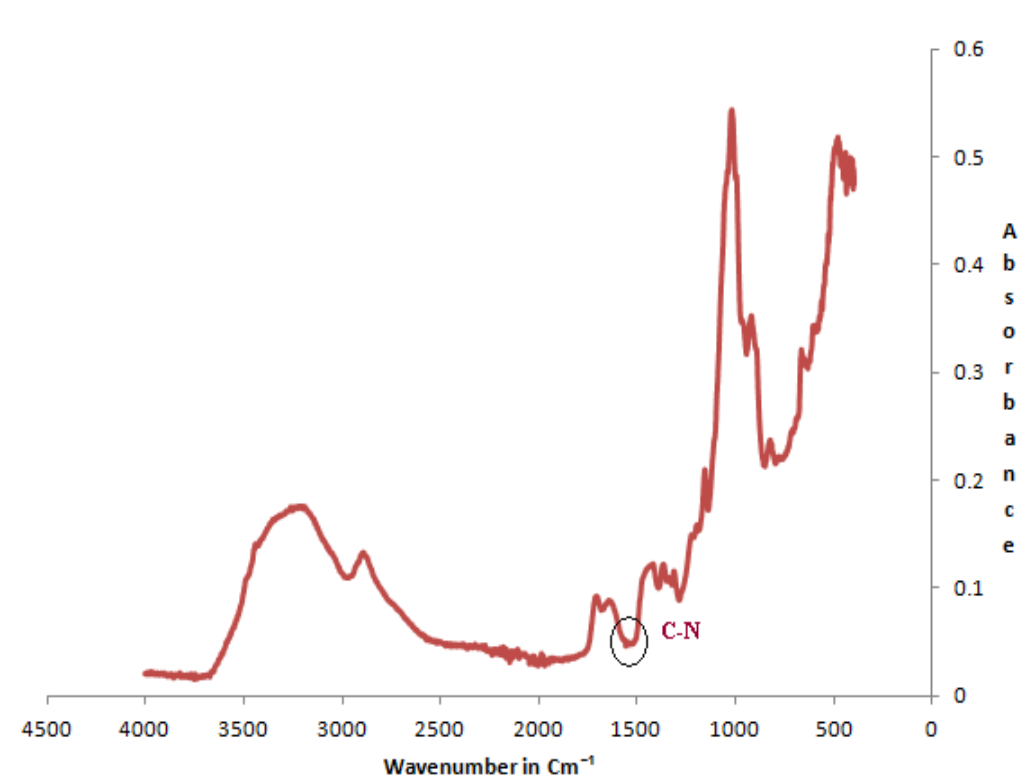


Figure 8 : FTIR of Quaternized Cellulose Fibers

FTIR of Rice Hull Flour Phosphate

Figures 9 and 10 showed multiple number of peaks which made the identification of phosphate difficult as the rice hull has lignin and silica in major amounts and the cellulose content in a minute amount. The FTIR of lignin and silica show similar peaks at 820 cm^{-1} , 1210 cm^{-1} and at 2300 cm^{-1} thus skewing the phosphorylated product.

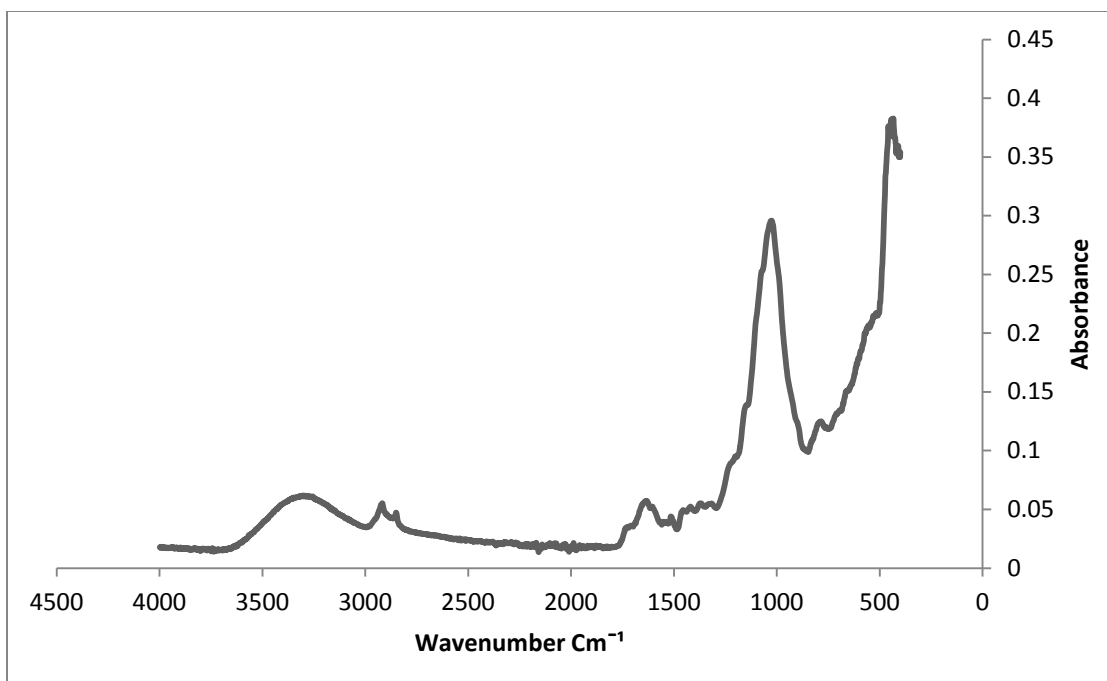


Figure 9: FTIR of Rice Hull Flour

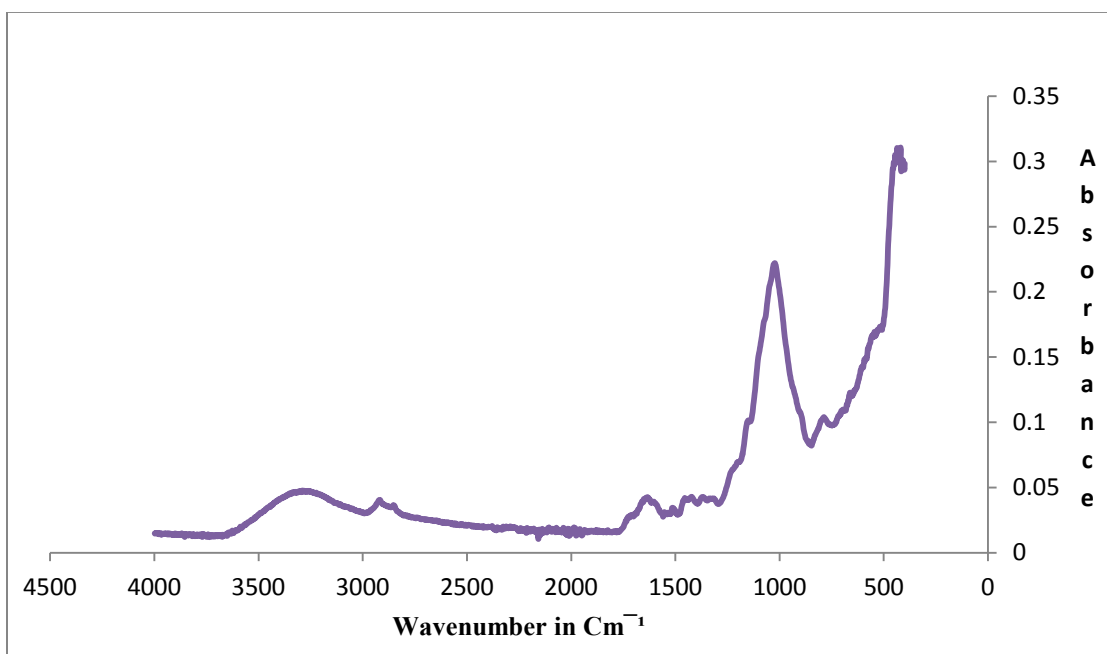


Figure 10 : FTIR of Rice Hull Phosphate

Potentiometry Estimation

Estimation of Phosphorous Content

The degree of substitution (DSp) for various modifications was determined by potentiometric technique, and is shown in Table 1. The DSp is calculated by using the volume of the base obtained at equivalence point (Ve) in mL, concentration of the base in moles (Mb) and weight of the sample (Md) in gm. Phosphate content by potentiometric titration was markedly less than those reported theoretically. On average, phosphorylation method adds a phosphate group about every 300 glucose units which is much less than the theoretical 1 phosphate for every glucose unit.

Table 1 : Degree of Substitution of Phosphorous in Various Modified Cellulose Fibers

Type of Phosphate	DSp	Ve(ml)	Md (gm)	Mb
NFC-PO4	.0008	25	.05	.00001
NFC-PO4 (Ammono wash)	.003	10	.05	.0001
QNFC-PO4	.003	10	.054	.0001
RHF-PO4	.004	12	.05	.0001

Estimation of Nitrogen Content

The concentration of nitrogen in the fibers was calculated from the calibration curve found in Figure 11. The concentration of NFC-PO₄Q was found to be 0.43 ppm. This was markedly less than those reported theoretically. The DS_N was found to be 0.00046. The DS_N by potentiometric analysis of chloride ion requires very high purity water to ensure no ions other than the chloride ions are present as the counter ions. Thus, it was concluded that th method is ineffective for these fibers.

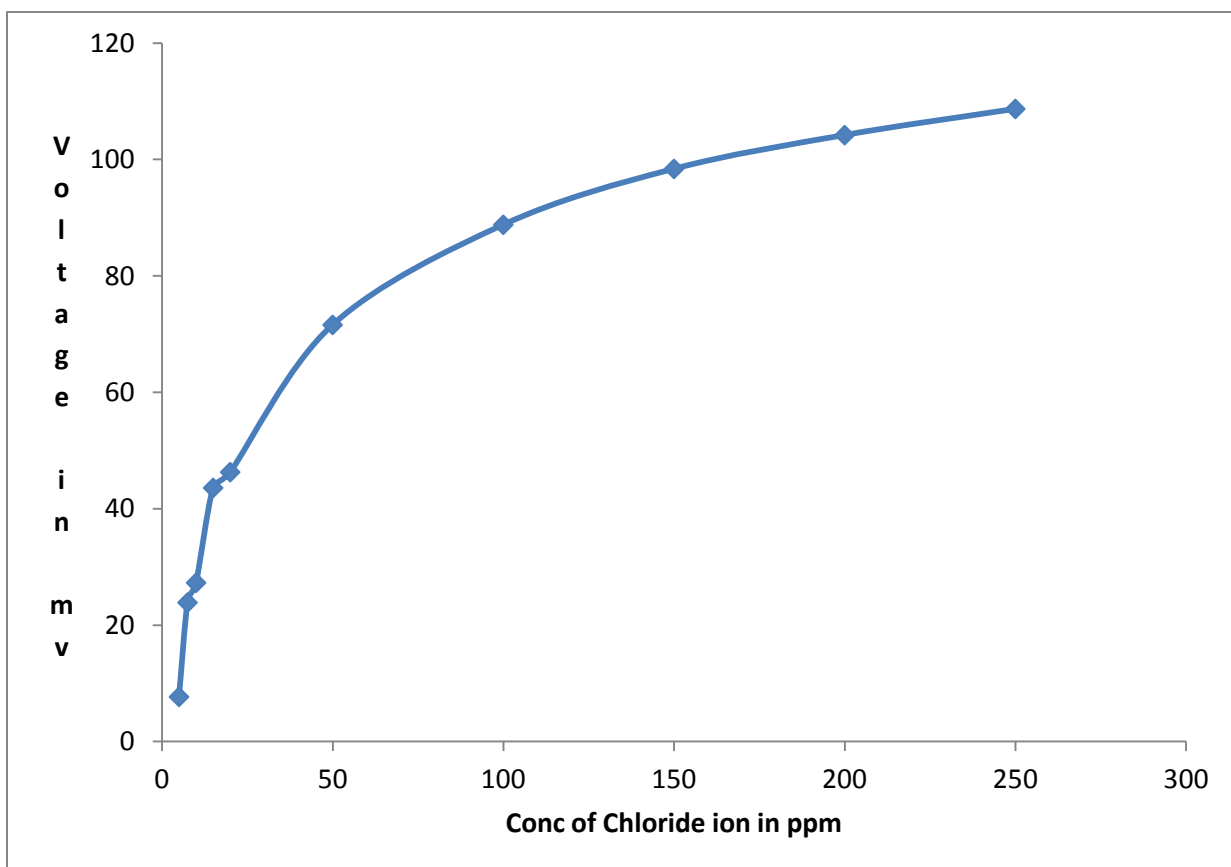


Figure 11 : Standard Curve for Chloride Ion Determination

Thermo Gravimetric Analysis

Thermo Gravimetric Analysis of Fibers

The thermal stabilities of cellulose phosphate prepared under different reaction conditions are shown in Figure 12. Phosphorylated cellulose results in a 50 °C decrease in both onset and peak degradation temperatures, but significantly increases char yield to over 20% of the original mass. Increasing the pad bake time, decreases the stability and increases char yield only slightly, despite nearly doubling the phosphate concentration. Neutralizing the product with ammonium hydroxide increases the char yield by 20% without significantly altering the thermal stability.

The addition of phosphate by phosphoric acid hydrolysis adds an acid source to the cellulose fibers. The thermal stability of the cellulose phosphate depends significantly on the other modifications performed, as shown in Figure 12. Quaternizing the fibers with glycidyltrimethylammonium ions slightly increased the thermal stability of the fibers by 20°C, but reduced the char yield at all temperatures. Rice hull flour phosphate had a nearly identical thermal profile to nanofibrillated cellulose phosphate. This may be because some of the lignin and hemicelluloses found in RHF was removed during hydrolysis with phosphoric acid, producing predominantly cellulose phosphate. This illustrates the slightly lower thermal stabilities that are common with intumescing

flame retardants and indicates that the increased char yield with higher thermal stability of the char may be effective as an IFR.

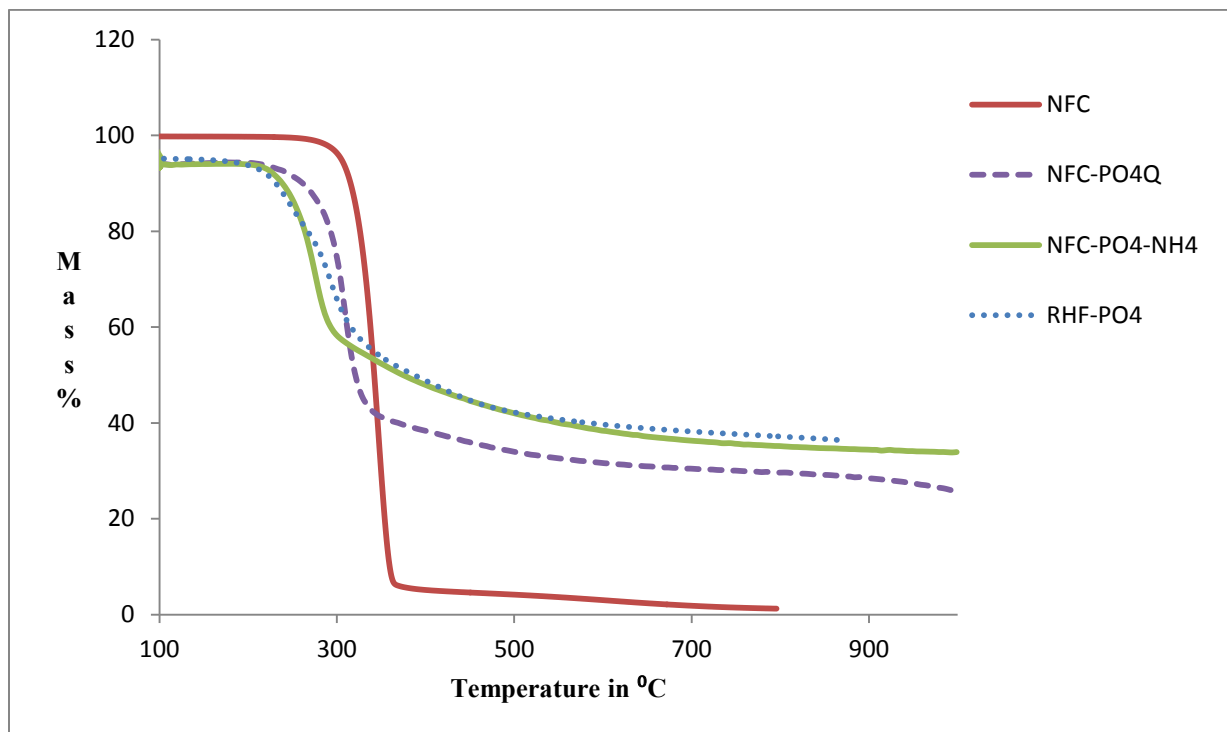


Figure 12: Thermal Stability of Cellulose Phosphate Fibers with Different Modifications Under a Flow of N₂ at 10°C/min

Thermo Gravimetric Analysis of PLA Composites

Intumescent flame retarded PLA composites were prepared by melt blending. Thermal stabilities of cellulose phosphate based IFRs are shown in Figure 13. Previous studies have shown that APP-NFC has distinct advantages over using APP-PER, so this study compares results only to APP-NFC. 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, the fibers may show some intumescent behavior during burning.

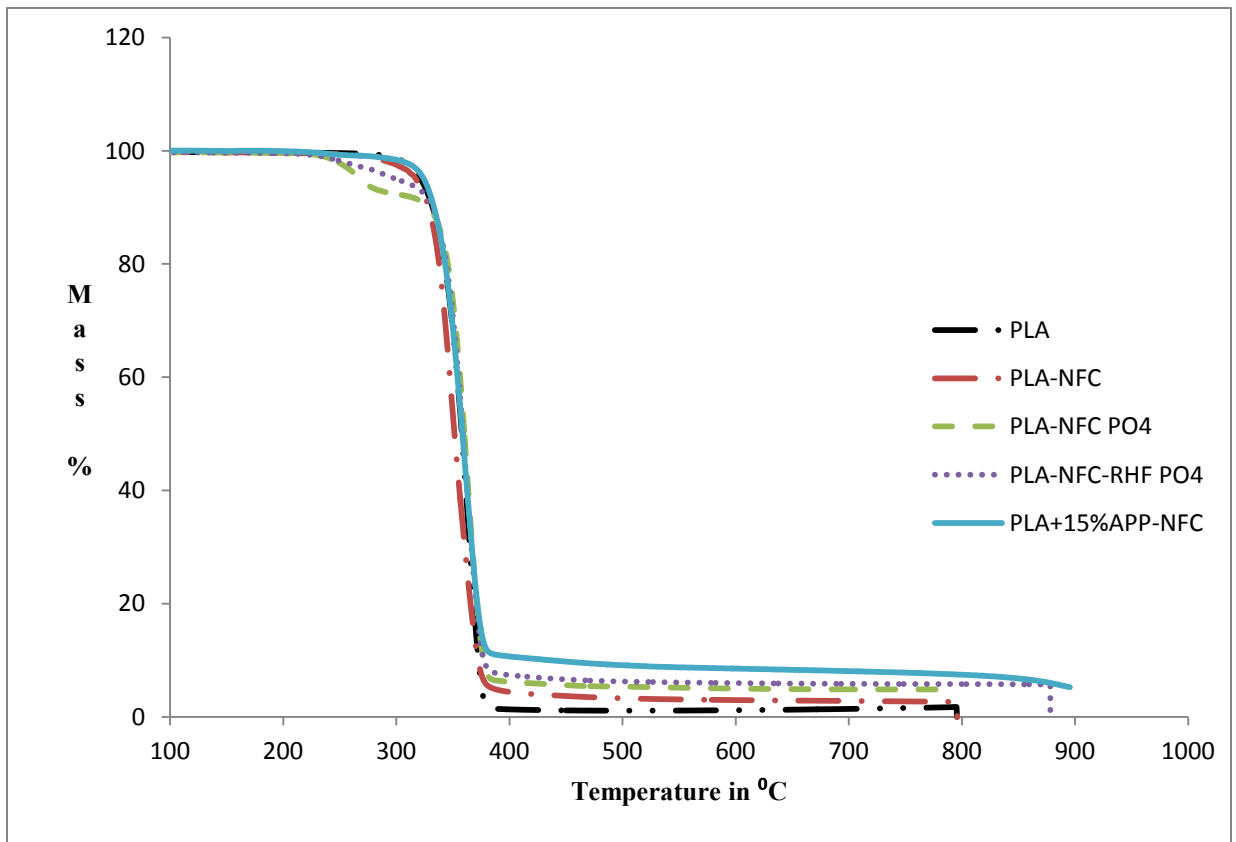


Figure 13 : Thermal Stability of PLA Composites Using Cellulose Phosphate Fibers as an IFR Under a Flow of N₂ at 10°C/min

Dynamic Mechanical Analysis

Dynamic mechanical analysis was used to assess the changes in semi-crystalline composite stiffness and polymer mobility. As noted in Table 2, the storage modulus of composites made with PLA-15%APP-NFC and PLA-15%NFC showed similar stiffness properties, but the glass transition temperature for the NFC composite was higher than the APP-NFC composites. This was as expected, since the addition of fibers has a reinforcing effect on polymer composites. Use of rice hull flour did not improve these properties, and is likely due to the lower aspect ratio of the filler. Use of phosphorylated fibers resulted in lower composite stiffness and reduced glass transition temperature as compared with NFC.

Table 2 : Storage Modulus, Tan δ Peaks and Loss Modulus of Modified PLA Composites

Composite	Storage Modulus (MPa)	Tan δ Peak(Tg, °C)	Loss Modulus (MPa)
PLA-15%APP-NFC	2600	67.6	223
PLA-15% NFC	2123	63.86	236.5
PLA-15%NFCPO ₄	1796	66.27	182
PLA-15%RHFPO ₄	2410	63.86	232

Horizontal and Vertical Burn Tests

Horizontal and vertical burn tests were conducted on the PLA composites. In the horizontal burn test, pure PLA was self extinguishing prior to reaching the starting point. It showed resistance to the flame and showed some burning drips. The NFC composite burned completely within 4 min and showed dripping behavior and the char was glowing after falling down. The burning rate was 22 mm/min. The RHF-PO₄ also burned completely within a min or 40 seconds, showing reduced flame retardancy and showed burning drips. The NFC-PO₄ composite showed higher thermal stability and flame retardance and did not burn at all thus passing the HB rating. There were no burning drips and bubbling of the char was seen attributed to the intumescent behavior. In the Vertical burn test the PLA composite burned completely with burning drips and afterglow flame. The same behavior was observed in the case with PLA+NFC composite. The PLA+NFC-PO₄ composites were self extinguished after the flame was removed, but produced burning drips and failed the VB test. However, the charring behavior observed was similar to the action of intumescence. Therefore, further modification of these fibers by the addition of small amount of additives (Clay) may result in an efficient IFR based solely on cellulose fibers.

Table 3 : UL-94 Test for PLA Composites

Composite	Horizontal Burn rate (mm/min)	Time in sec	Vertical Burn T(s)	UL-94
PLA+NFC	22	complete	complete	NR
PLA+NFC- PO ₄	DNB		DNB but showed burning drips.	HB, VB-NR
PLA+RHF- PO ₄	DNB, but showed burning drips.	complete	DNB but showed burning drips.	NR
PLA	DNB		complete	HB, VB-NR

DNB=did not burn; NR= Not rated;

Conclusion

Cellulose fibers were modified by phosphoric acid/urea and glycidyltrimethylammonium chloride to increase char yield, gas generation, and thermal oxidative stability upon pyrolysis. The fibers were used as intumescent flame retardants for poly (lactic acid). Potentiometric titrations indicated that the modifications resulted in a fairly low degree of substitution. Despite the low DS, the additions, especially of phosphate and ammonia wash, resulted in significant increases in char yield with only small decreases in thermal stabilities. Composites using phosphorylated celluloses instead of APP formulations exhibited similar thermal properties, and passed the HB rating. The composites were observed to exhibit intumescent behavior and did extinguish the flame prior to complete combustion. Dynamic mechanical analysis illustrated that the use of fibers in intumescent formulations prevented losses in stiffness and increased glass transition temperatures.

Suggestions

Even though, the NFC modified with phosphoric acid/urea mixture and adding CHPTAC as a nitrogen source showed lower degree of substitution and failed the UL-94 test but, by modifying APP/NFC with polyhedral oligomeric silsesquioxanes (POSS) the composites may show a greater degree of thermal stability, higher storage modulus,

greater stiffness and increased glass transition temperature. The POSS modified cellulose and APP mixture, was given a V=O rating by the UL-94 test [17](#). Flammability may also improve by using a small amount of additive known to minimize the deterioration of polymer mechanical properties, such as addition of 1-5% clay. This maintains materials that are obtained from sustainable resources, less toxic and environmentally friendly resources.

MONITOR INTERFACE AND DISPERSION IN POLYMER NANO-COMPOSITE USING FORSTER RESONANCE ENERGY TRANSFER (FRET)

Introduction

Previously, studies were done to evaluate the dispersion of fiber particles at nanoscale level using a mesoscale macroscopic technique ¹⁸. This study helps in the characterization of the morphology in macroscopic systems ¹⁹. For this, Forster resonance energy transfer (FRET) combined with spectroscopic analysis or LSCM (Laser scanning confocal microscopy) is used. FRET is an energy transfer mechanism between two fluorescent molecules. In this, a fluorescent donor is excited at its specific fluorescent excitation wavelength. By a long range dipole-dipole coupling mechanism, this excitation energy is then non-radiatively transferred to a second molecule, the acceptor, while the donor returns to the electronic ground state. The efficiency of this energy transfer decreases quickly with the sixth power of the inverse distance, therefore the distance between the donor and acceptor molecules can be deduced from observing the fluorescence of the acceptor and comparing it to the reference intensity. This energy transfer mechanism is termed as “Forster resonance energy transfer” (FRET) after the

German scientist Theodor Forster. When both the molecules are fluorescent, the term fluorescence resonance energy transfer is often used, although the energy is actually not transferred by fluorescence [20](#).

To monitor the complex formation between two molecules, one of them is labeled with a donor and the other with an acceptor. FRET efficiency is measured and used to identify interactions between the labeled complexes.

One method of measuring FRET efficiency is to measure the acceptor emission intensity. When the donor and acceptor are in proximity (1–10 nm) due to the interaction of the two molecules, the acceptor emission will increase because of the intermolecular FRET from the donor to the acceptor.

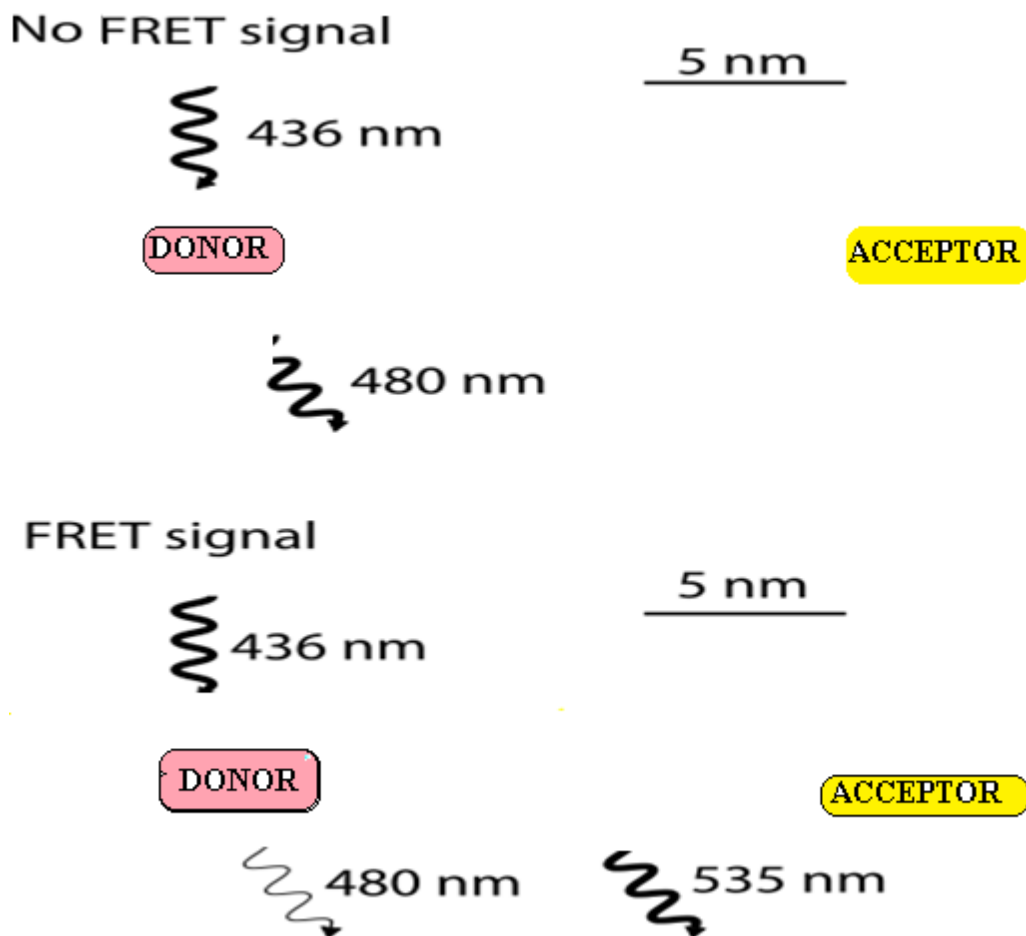


Figure 14 : Schematic diagram showing FRET between Donor and Acceptor Molecule

Figure 14 shows a system containing a donor and acceptor molecule which is excited at 440nm wavelength. The fluorescent peak of donor overlaps the excitation peak of acceptor. Because the two systems are adjacent to each other, the energy transfer is significant-a large proportion of the energy from donor is transferred to acceptor and creates a much larger acceptor emission peak of 535nm.

Previously, studies were done using FRET in combination with LSCM, which provided a real space observation for interface formation in polymer nano composites, by generating energy transfer efficiency signals in nano fibrillated cellulose (NFC) labeled with 5-(4,6-dichlorotriazinyl)aminofluorescein (DTAF) and dispersed into polyethylene (PE), doped with Coumarin 30 (C30) ²¹. The effect of processing on NFC dispersion is monitored by measuring the extent of energy transfer with fluorescence spectroscopy. This was successfully performed in poly- ethylene (PE) but, DTAF is highly unstable at higher temperatures. Therefore, pairs of thermally stable dyes that can be blended with PLA were studied using Fluoresceinamine (FA) and Amino-methyl Coumarin.

Experimental

The Nano fibrillated Cellulose Fiber (NFC) used in this study were Lyocell fibers with a precursor length of 6 mm and moderate degree of Nano fibrillation (~50nm diameter), designated as L040-6. The NFC contained some residual solvent from the production process and was neutralized with 0.5 M acetic acid, then thoroughly washed with deionized water and ethanol to a neutral pH.

Around 2gms of NFC was subjected to periodate oxidation using sodium periodate (NaIO_4). The excess periodate was neutralized with ethylene glycol. The filtered product was subjected to a Schiff base reaction by adding 50mL of the amino dye Fluoresceinamine (Acceptor) and 50ml of acetate buffer for 16hrs. The product was

reduced using Sodium borohydride (NaBH_4) under nitrogen atmosphere at pH=10 with NaOH for 3hrs, excess hydride was neutralized with acetic acid and filtered. The sample was dialyzed in snake skin tubing for one week, until the pH is 7.0, dried in the oven and stored.

The above procedure was also used to synthesize Amino-methyl Coumarin tagged cellulose.

To determine the pH dependence of FA dye, buffer solutions ranging from a pH 4-8 were made using sodium phosphate (monobasic and dibasic) and adjusting the pH. The pH was monitored by an Aqua Pro pH probe connected to an Orion-5 star meter. The absorbance of the FA dye was monitored using UV-Visible spectrometer.

Instrumentation

The FA tagged cellulose was mixed with Coumarin-30 (donor) and PLA and dried in the oven at 90°C for 30min. PLA composites were prepared by melt blending at 180 °C and 200 rpm for 5 min in an Xplore 15 mL twin-screw co-rotating mini-compounder (DSM Instruments).

UV/Visible absorbance spectrometer, (Shimadzu UV- 2500) was used to measure the absorbance of the Coumarin and FA dyes from 250nm to 800nm wavelength.

Results and Discussion

The FA tagged cellulose showed good fluorescence under the UV lamp before it was added to PLA. But, when it was blended with PLA and composites were pressed, the acid hydrolysis of PLA resulted in acidic environment. Since, fluoresceinamine is pH dependent, fluorescent intensity significantly decreased after extrusion. At alkaline pH values, the FA units are strong absorbers and highly fluorescent, and excitation of the polymers results in strong emission from the FA acceptors and results in efficient FRET between the two species. But at acidic pH, FA is colorless and non fluorescent, and elimination of FRET pathway leads to the emission of the donor itself. Thus, quantum yield decreases with acidity. The absence of fluorescence is likely due to this, which reduces the quantum yield once in the PLA melt. Hence this dye cannot be used for FRET analysis since no signal was obtained. Figure 15 shows the effect of FA at lower pH conditions ranging from pH=4 to pH=8. The absorbance decreased drastically as the pH was lowered from 8 to 4.

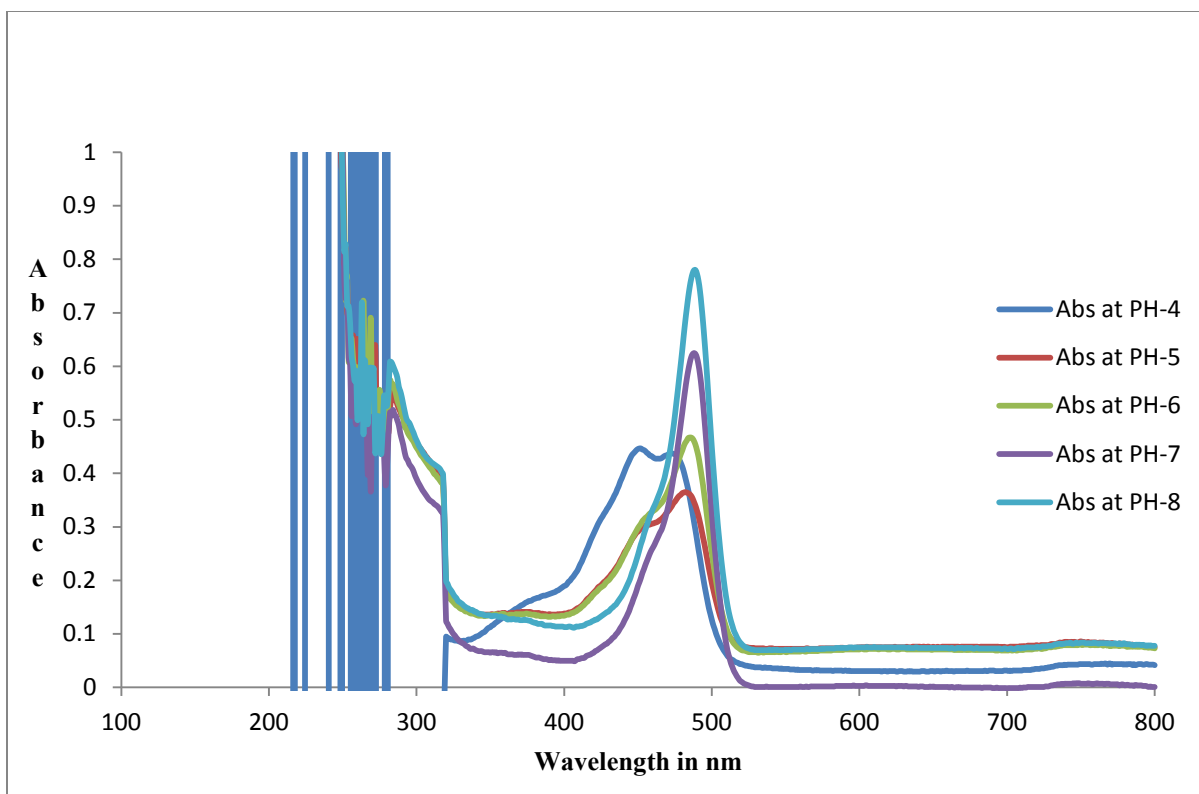


Figure 15 : Absorbance of FA at Acidic pH from 4-8

The Amino methyl Coumarin tagged cellulose showed good thermal stability even after blending in PLA and showed good quantum yield and absorbance in UV-Visible spectroscopy. The FRET studies are still under investigation.

Conclusion

Cellulose fibers were successfully modified by FA dye which, showed good thermal stability, but, once it was added to PLA, lost its stability due to the lower pH environment of PLA. It could not be used for FRET analysis to monitor the dispersion and interface properties. The Amino-methyl Coumarin tagged PLA composites were less sensitive to pH and may be used for FRET analysis to study dispersion and interface properties in fibers

Suggestions

Even though FA failed the dye modification; research was done on Di-Chloro-Fluorescein and Di-Flouro-Fluorescein and they proved to retain thermal stability even after blending with PLA. Relative intensities were observed with backlight but spectral studies are under investigation. So, the Di-Flouro-Fluorescein, PLA and Amino-methyl-Coumarin tagged cellulose can be used for FRET analysis to monitor the dispersion and interface properties in fibers.

APPENDIX A:

POTENTIOMETRIC ESTIMATION

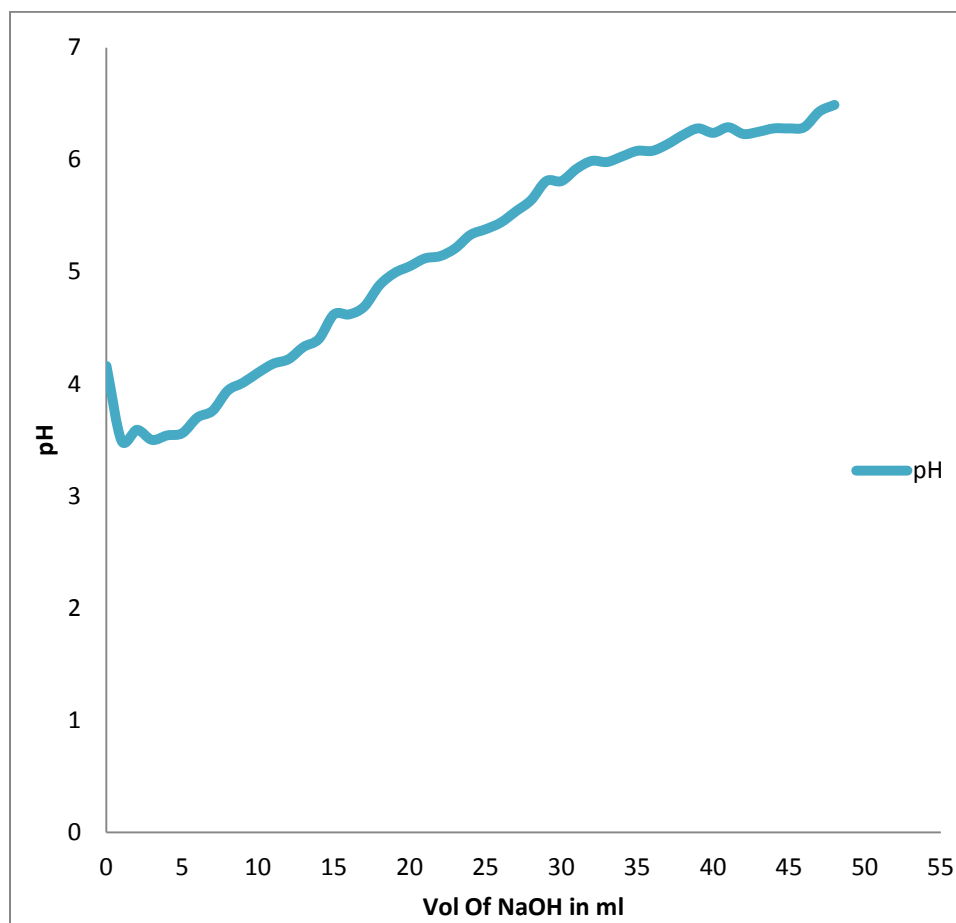


Figure 16: Titration of Phosphorylated Cellulose with NaOH

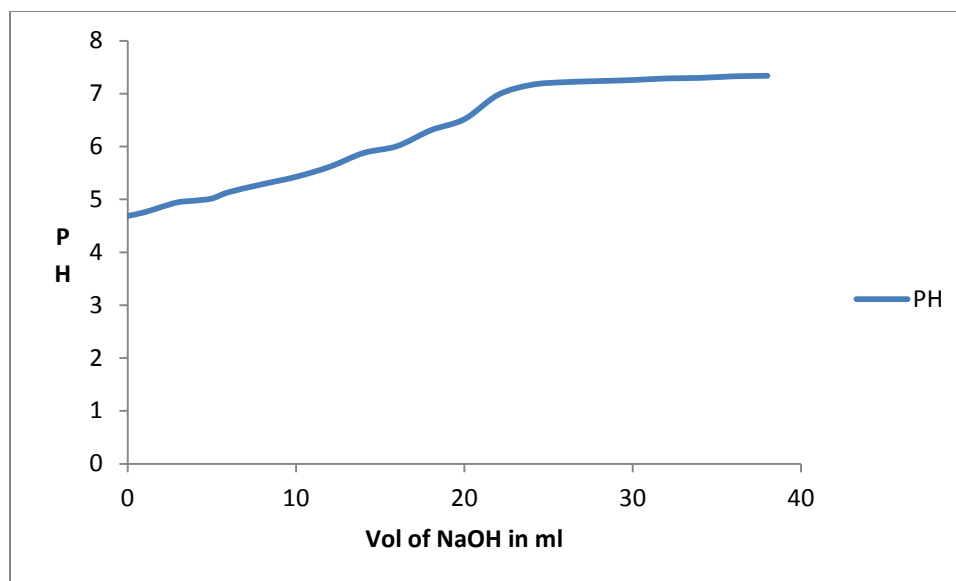


Figure 17: Titration of NFC-PO₄ Ammonia Wash with NaOH

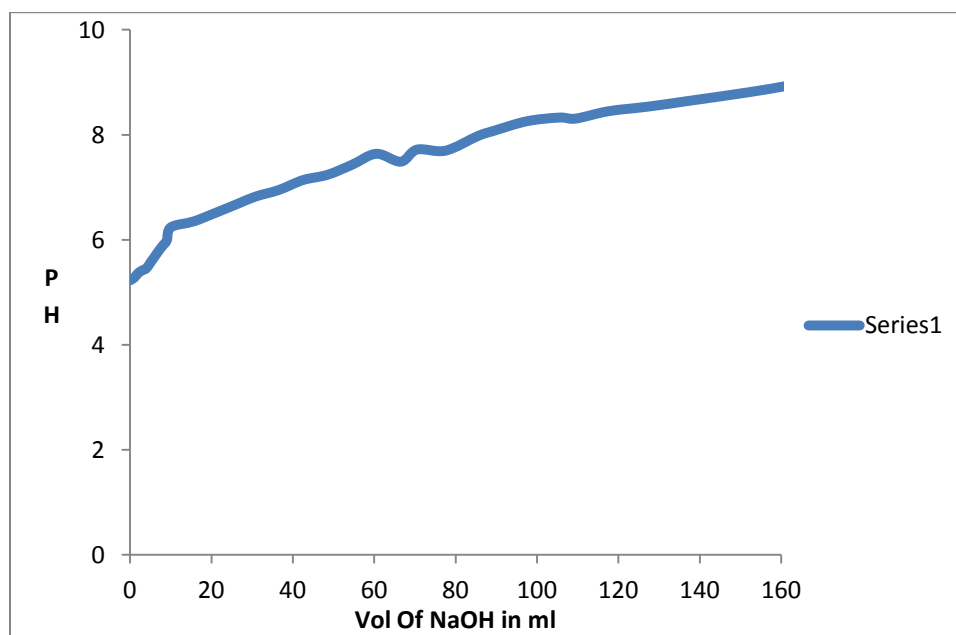


Figure 18: Titrations of NFC-PO₄Q Ammonia Wash with NaOH

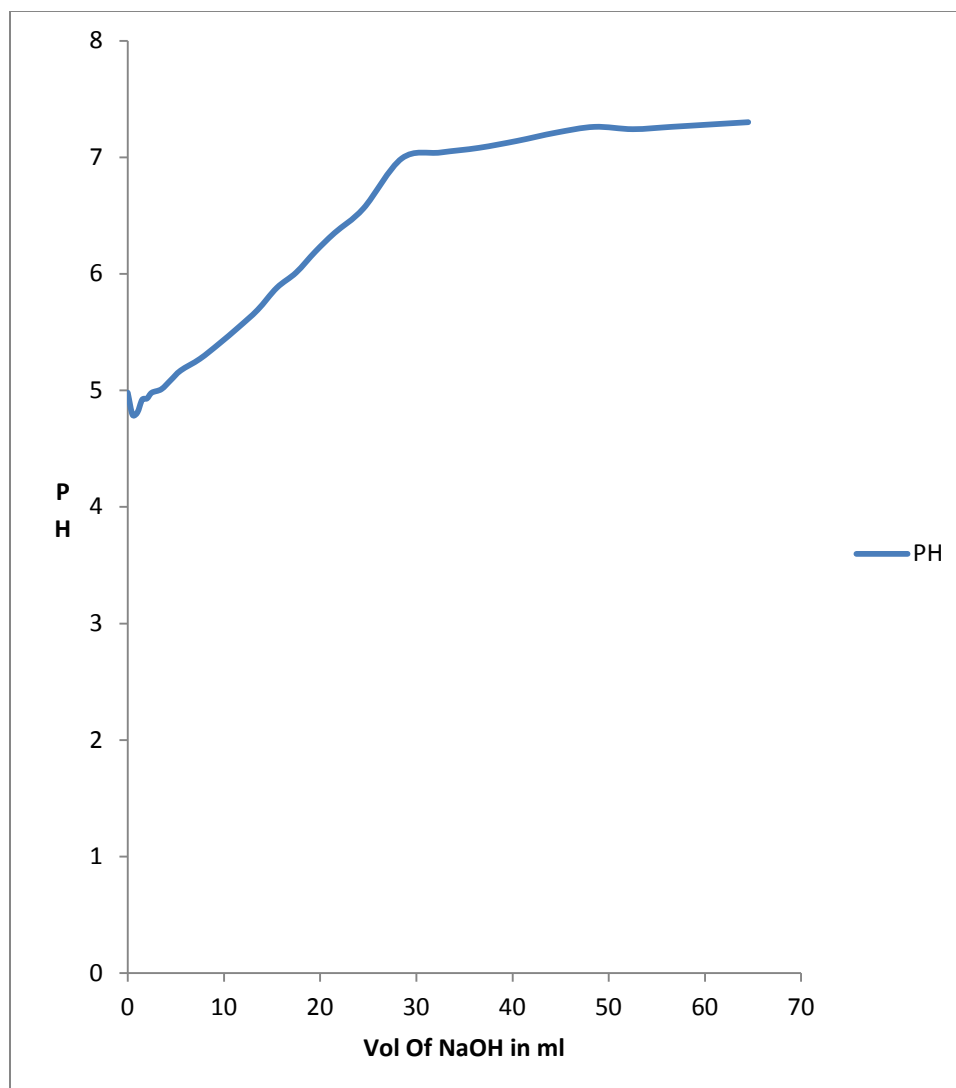


Figure 19: Titration of RHF-PO₄ Ammonia Wash with NaOH

APPENDIX B:

DYNAMIC MECHANICAL ANALYSIS

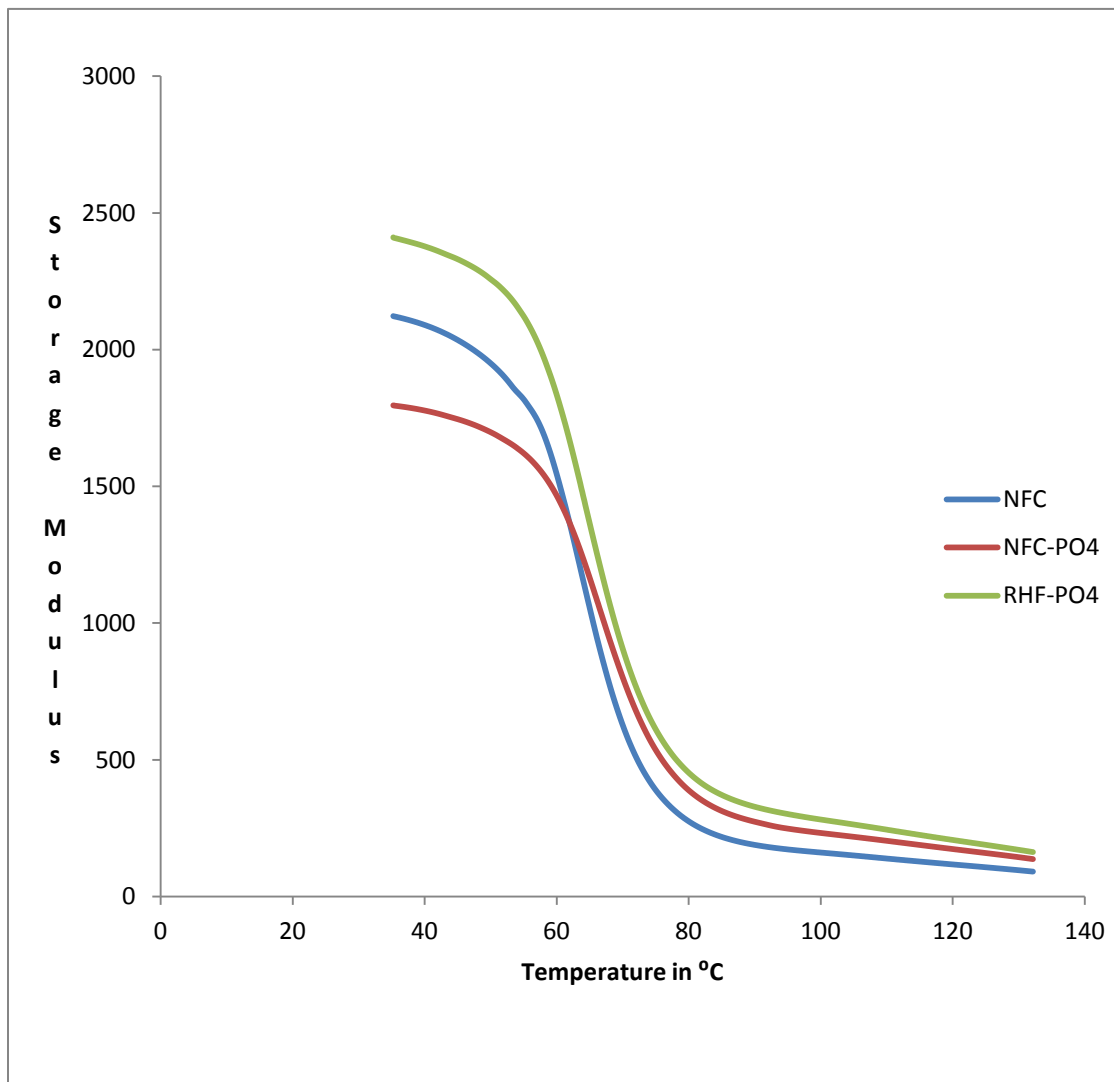


Figure 20: Storage Modulus Peaks of NFC, NFC-PO₄ and RHF-PO₄

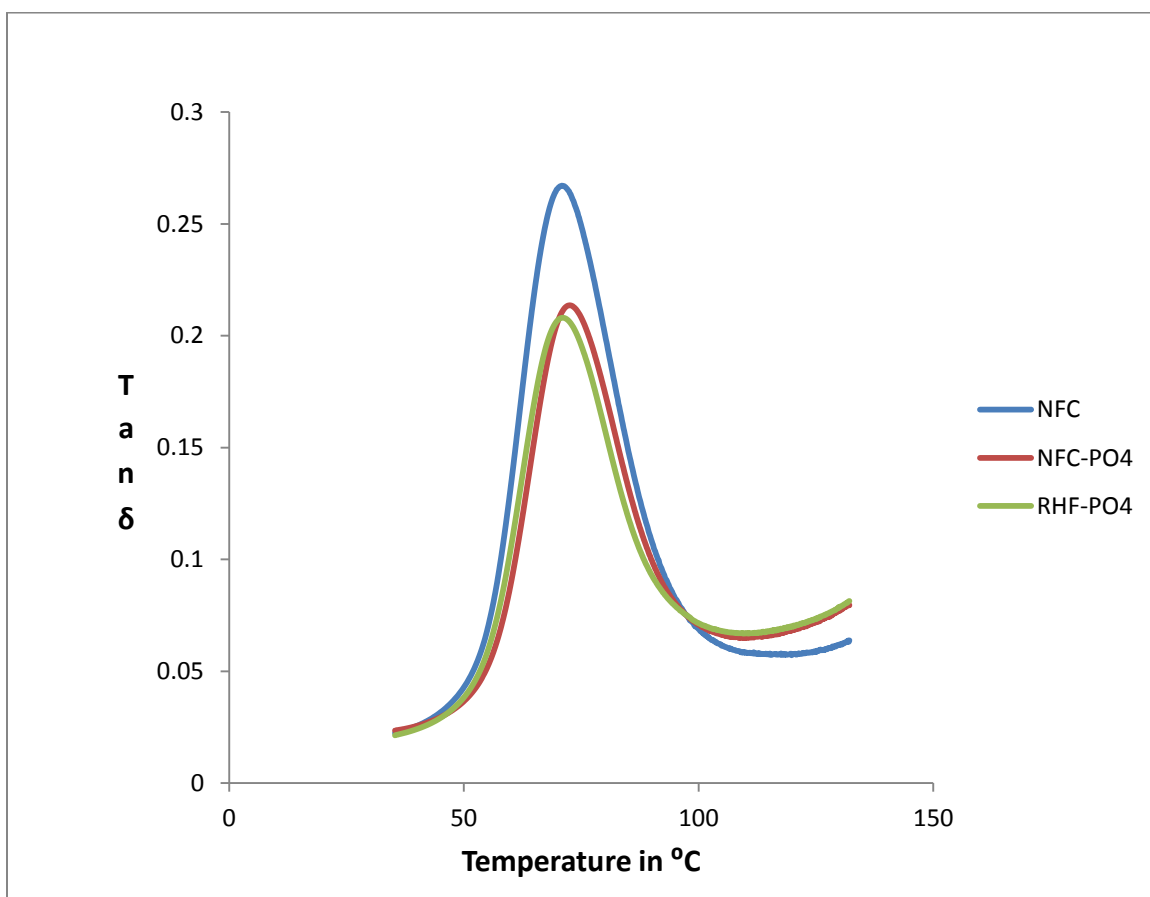


Figure 21: Tanδ Peaks of NFC, NFC-PO₄ and RHF-PO₄

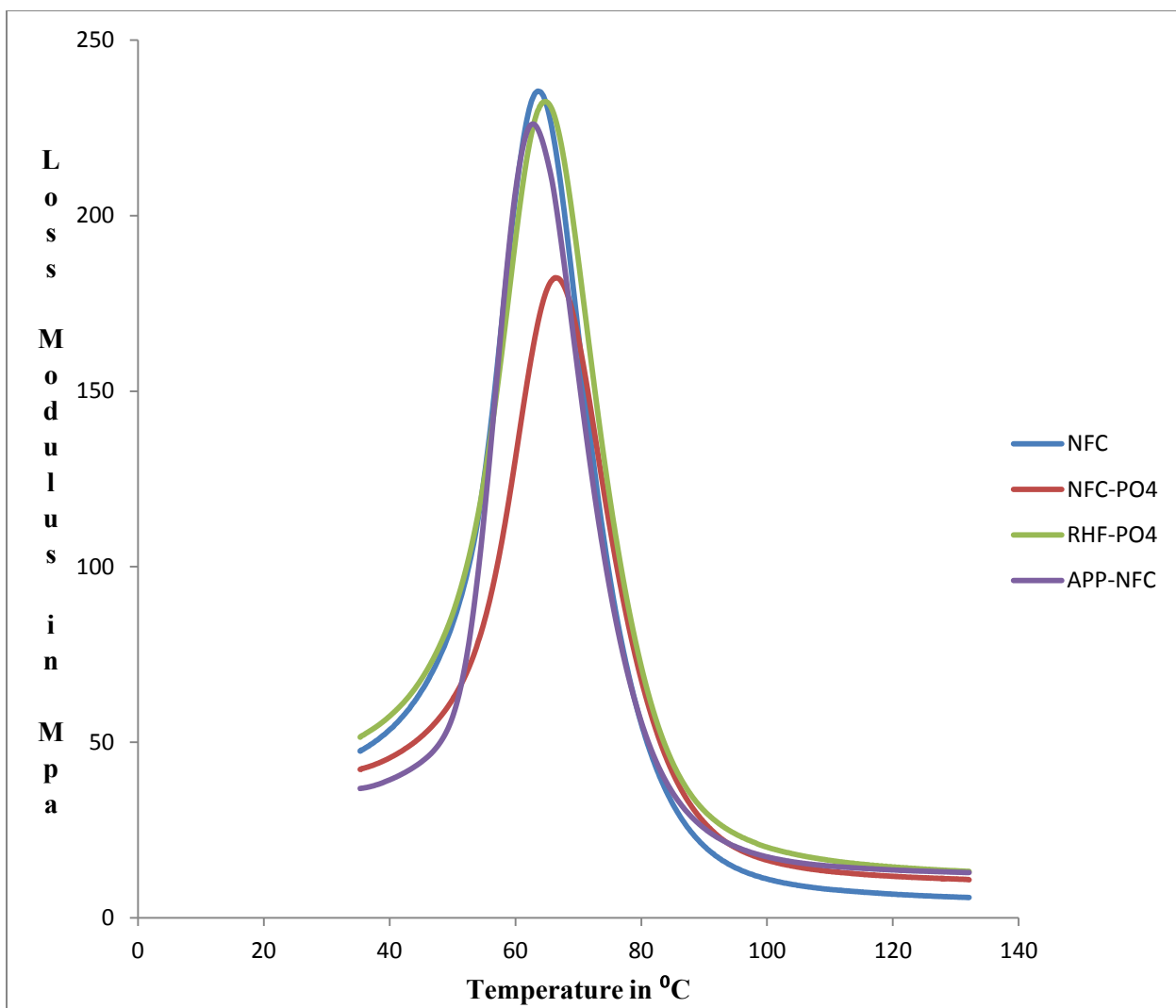


Figure 22: Loss Modulus of NFC, NFC-PO₄ and RHF-PO₄

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