

# SILOXANE-FUNCTIONALIZED CELLULOSE ACETATE AS ENVIRONMENTALLY BENIGN MATERIAL FOR POTENTIAL FLAME RETARDANT APPLICATIONS

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*Received October 5, 2015*

Of late, there have been many restrictions on the usage of certain types of halogenated flame retardant materials. These restrictions have been put into place because of the release of toxic gases that are detrimental to humans and environment during combustion. Therefore, finding alternative environmentally safe flame retardant (FR) materials is imperative. Herein we report the synthesis, characterization and thermal studies of environmentally benign polysiloxane-grafted cellulose acetate materials as halogen-free flame retardant materials. These novel materials were synthesized from the cellulose acetate and characterized using nuclear magnetic resonance (NMR) and infrared (FTIR-ATR) spectroscopic techniques. Thermo-gravimetric analysis (TGA) showed that polysiloxane-grafted cellulose (PDMS-CA) has twice the char yield of control cellulose acetate at 600 °C. Furthermore, pyrolysis-combustion flow calorimetry (PCFC) showed PDMS-CA has significantly lower total heat release capacity (205.6 J/g-K) compared to the control cellulose acetate (338.0 J/g-K).

**Keywords:** cellulose acetate, cellulose functionalization, flame retardant materials, polysiloxanes

## INTRODUCTION

Brominated FR materials, namely decabromo- and penta-bromodiphenyl oxides, are well known as the most efficient and cost-effective FR materials.<sup>1-2</sup> However, in the recent past, the European Union and some of the states in the United States have banned and/or put many restrictions on the usage of brominated FR materials because of the release of toxic and potentially carcinogenic brominated furans and dioxins during combustion.<sup>3-6</sup> Therefore, finding alternative environmentally safe FR materials is imperative.

Polysiloxane grafted cellulose acetate could be a potential alternative to halogen-based FR materials. Cellulose is the most abundant polymer found in nature consisting of anhydroglucose units linked together by  $\beta$ -1,4-glycosidic bonds. In addition, cellulose is also a major component of cotton fabric, which is the most widely used

natural renewable fiber.<sup>7</sup> However, the inherent combustibility of cellulose makes cotton fabric more flame susceptible.<sup>8</sup> The addition of a flame retardant additive, which imparts flame retardancy to the fabric, is essential to reduce the flammability of cotton fabric. It is well known that the silicon containing compounds improve the flame retardant properties of polymers by forming intumescent char in the condensed phase, and exhibiting low levels of heat release.<sup>9-13</sup> Furthermore, the siloxane based copolymers are considered to be environmentally friendly for FR applications due to the generation of non-toxic byproducts, such as cyclic siloxanes and silica, upon combustion.<sup>13</sup> Thus it is anticipated to have better flame retardant properties upon combining these two materials. Herein we report the functionalization of cellulose acetate with polysiloxane, and their structural characterization,

as well as thermal and flame retardant studies of the new siloxane-functionalized cellulose using the cellulose acetate as a starting material.

## EXPERIMENTAL

### Materials

Aminopropyl-terminated polydimethylsiloxane (A12-PDMS; MW 900-1100) was purchased from Gelest Inc. Cellulose acetate, anhydrous *N,N'*-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. 2,2-dimethyl-1,3-dioxane-4,6-dione or Meldrum's acid, *N,N'*-Dicyclohexylcarbodiimide (DCC), *N*-hydroxysuccinimide (NHS) and 1,4-dioxane were purchased from Alfa Aesar and used without further purification.

### Synthesis of functionalized cellulose acetate (FCA, 1)

Meldrum's acid (2.4 g, 1665.00 mmol) was added to the pre-dissolved solution of cellulose acetate (2 g, 0.066 mmol) in 1,4-dioxane solvent (100 mL). The mixture refluxed over a period of 12 h under nitrogen atmosphere. At the end of the reaction, the reaction mass was cooled down to room temperature and the solvent was removed using a rotary evaporator. The resulted crude compound was washed with diethyl ether (3 X 50 mL) to obtain pure compound **1** in a quantitative yield. *Spectroscopic data*: FTIR-ATR  $\nu_{\max}$  3481 (br), 3000-2500 (br), 1738 (vs), 1719 (vs), 1371 (m), 1220 (s), 1150 (s), 1036 (s), 888 (w), 868 (s), and 601 (m)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  5.72 (s, br, 2H), 4.93 (t, 1H), 4.75 (t, 1H), 4.52 (m, 2H), 4.42-4.21 (m, 5H), 3.89-3.72 (m, 6H), 3.47 (s, 4H), and 2.13-1.96 (s, 3H);  $^{13}\text{C-NMR}$  (500 MHz,

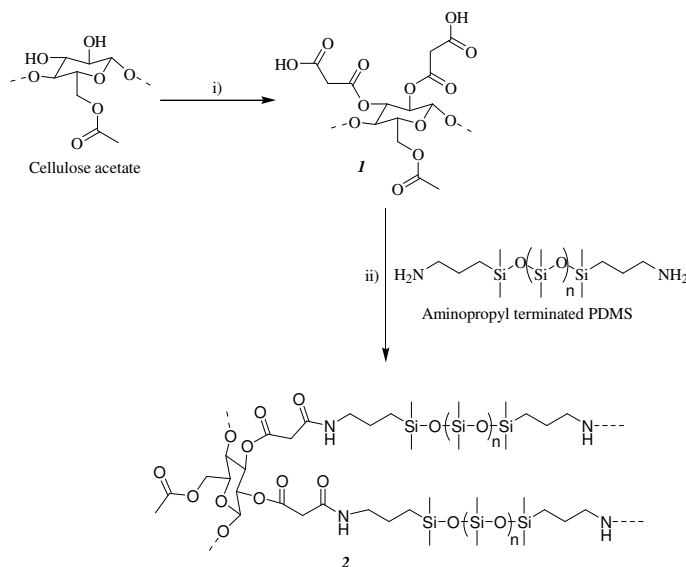
$\text{CDCl}_3$ , ppm)  $\delta$  169.25, 166.79, 166.65, 163.51, 161.22, 160.71, 160.59, 90.75, 73.43, 69.97, 68.60, 67.04, 66.94, 66.30, 66.09, 65.37, 63.59, 63.01, 62.61, 62.27, 61.26, 61.21, 60.78, 60.60, 40.84 and 40.64.

### Synthesis of PDMS grafted cellulose (PDMS-CA, 2)

Intermediate **1** (1 g, 0.0178 mmol) and NHS (0.62 g, 5.32 mmol) were dissolved in anhydrous THF under nitrogen atmosphere. After 15 min, DCC (1.1 g, 5.42 mmol) also added to this reaction mass and stirred for over a period of 12 h. Then, the white solid *N,N'*-dicyclohexylurea (DCU) was removed by filtration and A12-PDMS (5.42 mmol) was added to the resulted filtrate. This reaction mass was stirred for 12 h under nitrogen atmosphere at ambient temperature. The reaction mass was concentrated on a rotary evaporator and the resulted residue was washed with saturated sodium bicarbonate solution (1 x 30 mL). Subsequent concentration of the organic layer yielded final compound **2**. *Spectroscopic data*: FTIR-ATR  $\nu_{\max}$  3317 (w), 2960 (m), 2925 (w), 2847 (w), 1736 (s), 1653 (m), 1621 (w), 1573 (w), 1257 (vs), 1082 (vs), 1012 (vs), 863 (w), 789 (vs), 701 (w), and 653 (w)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  5.72 (s, br, 2H), 4.93 (t, 1H), 4.75 (t, 1H), 4.52 (m, 2H), 4.42-4.21 (m, 5H), 3.89-3.72 (m, 6H), 3.47 (s, 4H), 3.25 (t, 4H), and 2.13-1.96 (s, 3H), 1.56 (m, 4H), 0.55 (t, 4H) and 0.10-0.07 (100H).

### Methods of characterization

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded on a Bruker Avance Spectrospin-500 spectrometer. Attenuated total reflection Fourier transform infrared spectra (ATR-FTIR) were recorded on a Thermo Nicolet 4700 FTIR-ATR spectrometer.



Scheme 1: Reagents and reaction conditions; i) Meldrum's acid, dioxane, reflux, 12 h;  
ii) (a) *N*-hydroxysuccinimide (NHS), *N,N'*-Dicyclohexylcarbodiimide (DCC), tetrahydrofuran, r.t., 12 h;  
(b) Aminopropyl-terminated polydimethylsiloxane, tetrahydrofuran, r.t., 12 h

Thermal decomposition was studied under nitrogen using a TA Instrument 2050 thermogravimetric analyzer (TGA) at the heating rate of 20 °C/min.

Flammability properties, such as total heat release (THR) and heat release capacity (HRC), were measured using a pyrolysis-combustion flow calorimeter (PCFC) or micro-scale combustion calorimetry (MCC) using a FAA micro-calorimeter from FTT Ltd.<sup>12,14</sup> A thermogravimetric analyzer coupled to a Fourier transform infrared spectrometer, TGA-FTIR, was used to analyze the evolved gaseous products during the thermal degradation process.<sup>14-15</sup>

## RESULTS AND DISCUSSION

Since cellulose has very poor solubility in common organic solvents, we used cellulose acetate as a starting material for the functionalization. The subsequent functionalization produced an intermediate **1**, which was then grafted onto polysiloxane, as shown in the synthetic Scheme 1. Intermediate **1** was synthesized by heating 2,2-dimethyl-1,3-dioxane-4,6-dione (also known as Meldrum's acid), which is a very reactive electrophile to react alcohols,<sup>16-17</sup> with cellulose acetate at 100 °C for 24 h under nitrogen atmosphere to produce **1** in a nearly quantitative yield (>95%). Then, the grafting of aminopropyl terminated polydimethylsiloxane on to intermediate **1** was carried using the coupling reaction in the presence of *N*-hydroxysuccinamide (NHS) and *N,N'*-dicyclohexyl carbodiimide (DCC) in THF at ambient temperature over a period of 24 h, which afforded the final compound **2**.

Intermediate **1** and product **2** were characterized structurally by using various spectroscopic techniques.

The successful nucleophilic addition reaction followed by the ring opening of Meldrum's acid to the formation of compound **1** was clearly observed in its <sup>1</sup>H, <sup>13</sup>C NMR (Figs. 1 and 2), and also in its FTIR spectra (Fig. 3). The characteristic chemical shift values of malonyl  $\alpha$ -protons (4H) appeared at  $\delta$  3.48, and of malonyl  $\alpha$ -carbon at  $\delta$  40.64. The <sup>13</sup>C NMR spectrum showed acid carbonyl carbon peaks at  $\delta$  161.12-160.59. In addition, IR absorption at 1700 cm<sup>-1</sup> and a broad peak ranging from 3000-2500 cm<sup>-1</sup> further confirms the presence of newly formed acid groups. Similarly, the final product **2**, graft copolymer of cellulose acetate-siloxane, was also verified by its <sup>1</sup>H NMR and IR spectra. The presence of the Si-CH<sub>3</sub> protons at  $\delta$  0.00, and  $\alpha$ -protons attached to newly formed amide N-attached methylene protons at  $\delta$  3.23 and the

absence of primary amine N-attached methylene protons of precursor aminopropyl siloxane at  $\delta$  2.63 clearly indicated the formation of final compound **2**. Furthermore, the IR spectrum of **2** also exhibits strong absorption bands at 1650 and 1080 cm<sup>-1</sup> corresponding to the amide C=O, and Si-O-Si stretching, respectively. Thermal stability studies of these materials were investigated using thermogravimetric analysis (TGA) under nitrogen atmosphere. Intermediate **1** showed an interesting degradation pattern as seen in Figure 4, where onset degradation temperature of the **1** is much lower (120 to 150 °C) than that of the starting material cellulose acetate (340 °C). This first step weight loss in TGA at 120 °C is mainly because of occurring of facile decarboxylation in **1**. The presence of monoester malonic acid group in **1** facilitates the facile decarboxylation due to the formation of a six membered transition state. A similar phenomenon is well known in  $\beta$ -keto acids, where stable enolate ion intermediate is the driving force for the easy decarboxylation.<sup>18-19</sup> Moreover, we corroborated the facile decarboxylation by using TGA-FTIR, thermogravimetric analysis coupled to Fourier transform infrared spectroscopy,<sup>14-15</sup> by which the FTIR spectra of the evolved carbon dioxide can be monitored during thermal analysis. Gram-Schmidt chromatograms (Figs. 5 and 6) represent the total absorption of the evolved carbon dioxide during TGA analysis as a function of time. Figure 6 shows a very clear facile decarboxylation in **1** around 150 °C in addition to carbon dioxide evolution at its degradation temperature (340 °C). In contrast to this, the starting material cellulose acetate did not show facile decarboxylation (Fig. 5), but it showed carbon dioxide evolution only at its degradation temperature (340 °C). The onset degradation temperature of polysiloxane-grafted cellulose is 200 °C, which is higher than that of precursor **1** (120 °C), and lower than that of cellulose acetate (340 °C). This intermediate degradation temperature indicates the grafting of siloxane onto the cellulose acetate backbone through the conversion of acid groups of **1** into amides of final compound **2**. Moreover, this final product showed a better thermal stability by forming 22% char at 600 °C, compared to that of cellulose acetate, which showed only 11% char yield.

The flammability characteristics of siloxane grafted cellulose and its precursors were studied using pyrolysis/combustion flow calorimetry (PCFC) (Fig. 7 and Table 1). The observed total

heat release (total HR) values of **1** and **2** are 11.3 and 18.1 kJ/g, respectively. The low total HR value for **1** can be attributed to the generation of a significant amount of carbon dioxide during the

pyrolysis process of **1** through decarboxylation, which is mentioned earlier.

Table 1  
Thermal and flammability properties of CA, FCA and PDMS-CA

Compound	HR capacity sum (J/g-K)	Total HR (kJ/g)	Char yield at 600 °C (TGA) (%)
CA	338.0	11.3	11
FCA	195.7	11.2	5
PDMS-CA	205.6	18.1	22

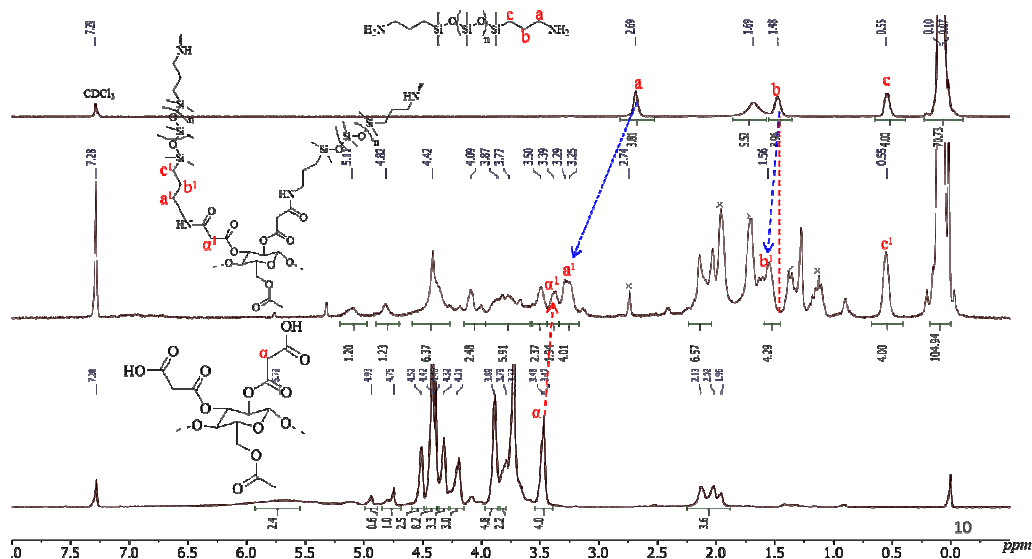


Figure 1:  $^1\text{H}$  NMR spectra of functionalized cellulose acetate (bottom), aminopropyl terminated polydimethylsiloxane grafted cellulose (middle), and aminopropyl terminated PDMS, in  $\text{CDCl}_3$

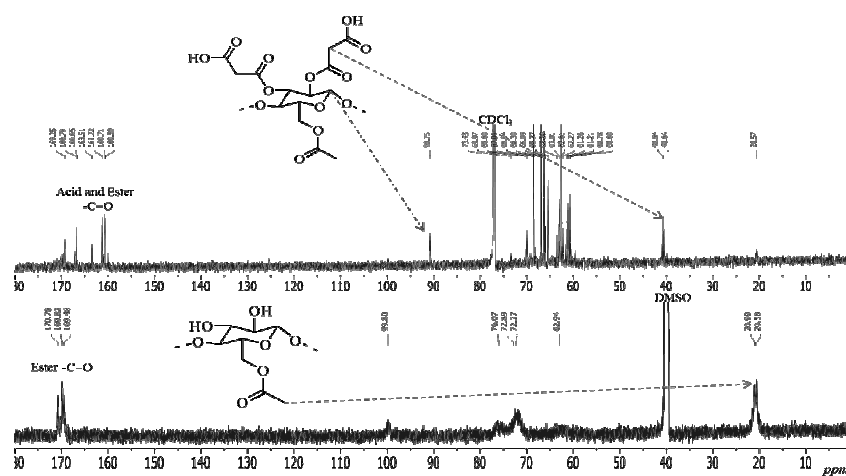


Figure 2:  $^{13}\text{C}$  NMR spectra of cellulose acetate (bottom, in  $\text{DMSO-d}_6$ ), and functionalized cellulose acetate (top, in  $\text{CDCl}_3$ )

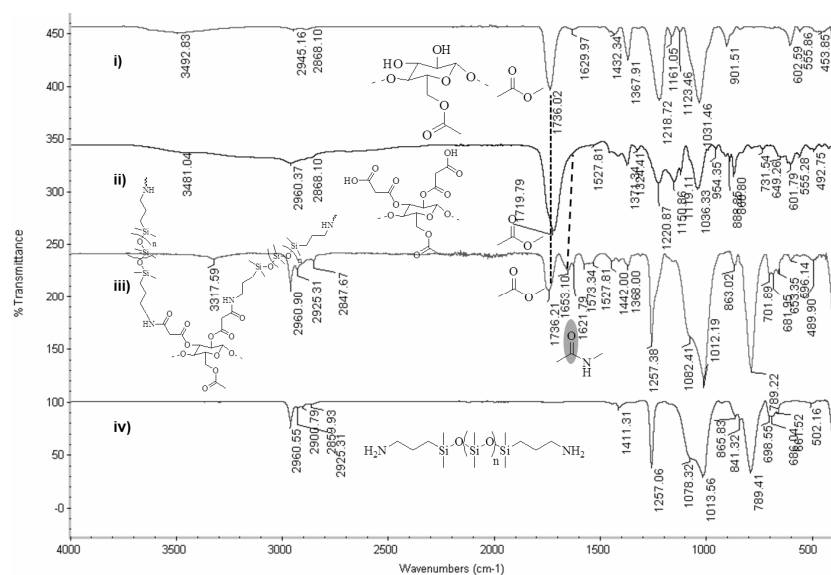


Figure 3: FTIR-ATR spectra of (i) cellulose acetate, (ii) functionalized cellulose acetate, (iii) aminopropyl terminated polydimethylsiloxane grafted cellulose acetate, and (iv) aminopropyl-terminated polydimethylsiloxane

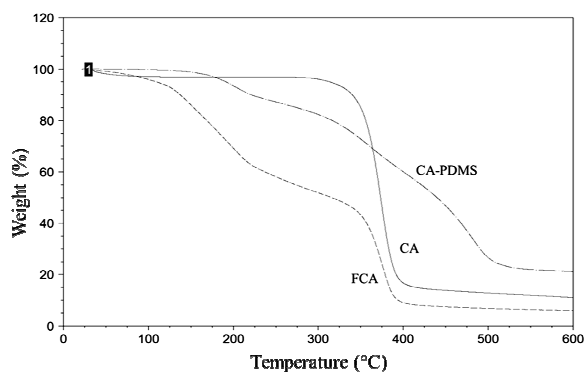


Figure 4: Thermogravimetric analysis (TGA) curves of cellulose acetate (CA), functionalized cellulose acetate (FCA), aminopropyl terminated polydimethylsiloxane grafted cellulose acetate (PDMS-CA) under  $N_2$  atmosphere at the heating rate of 20 °C/min

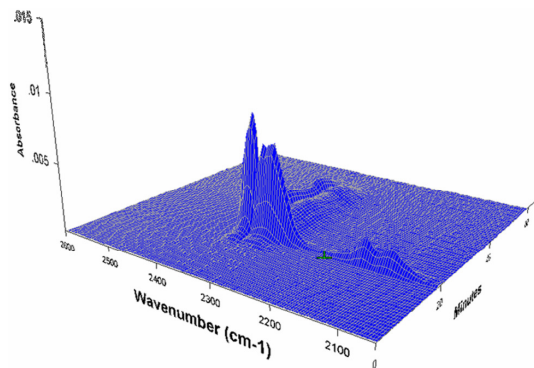


Figure 5: GRAMS/3D graph of cellulose acetate (CA) under  $N_2$  atmosphere at the heating rate of 20 °C/min

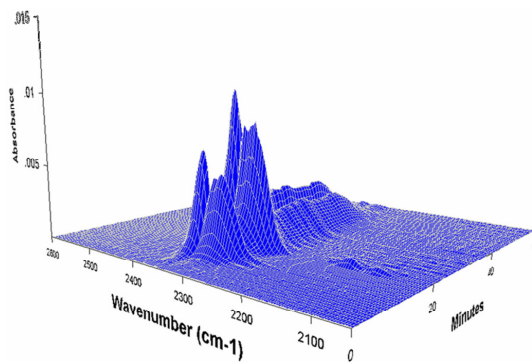


Figure 6: GRAMS/3D graph of functionalized cellulose acetate (FCA) under  $N_2$  atmosphere at the heating rate of 20 °C/min

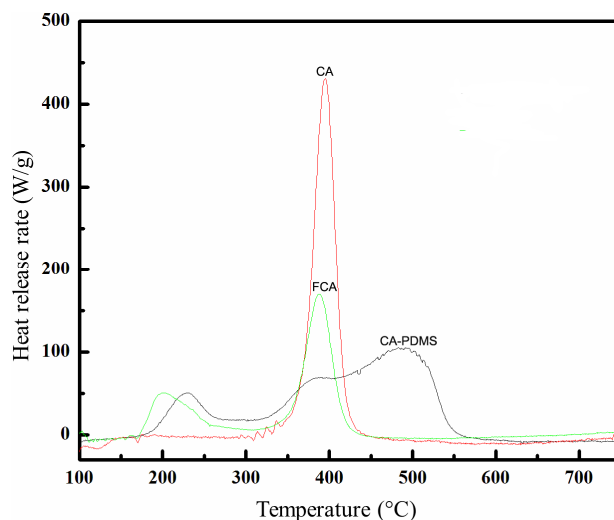


Figure 7: Heat release rate as a function of temperature, measured with a pyrolysis combustion flow calorimeter (PCFC), for cellulose acetate (CA), functionalized cellulose acetate (FCA), aminopropyl terminated polydimethylsiloxane grafted cellulose (PDMS-CA)

## CONCLUSION

Polysiloxane grafted cellulose acetate was successfully synthesized by employing mild reaction conditions and characterized using various techniques. TGA and PCFC results showed that functionalized cellulose materials have thermal and flame retardant properties that are superior to the control cellulose acetate. Better thermal stability, high char yield and less heat release capacity can make the polysiloxane grafted cellulose acetate a potential candidate as an environmentally safe flame retardant material for FR textile applications.

**ACKNOWLEDGEMENTS:** The authors, S. T. and J. K., are grateful to US Army Natick Soldier Research Development and Engineering Center (NSRDEC) for the financial support.

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