

Conversion of Waste Cigarette Filter into Recycled Cellulose Acetate: An Industrial Feedstock

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Abstract

One of the largest contributors to waste are cigarette filters, which contribute an estimated 4.5 trillion tons of waste into the environment every year. This study proposes a plausible waste conversion protocol for the preparation of cellulose acetate from cigarette filters, an essential industrial feedstock. The collected cigarette filters were decolourised and deodorised with bleaching and surface acting agents, respectively. Cellulose obtained was converted to cellulose acetate by acetylation in the presence of acetic acid, acetic anhydride, and sulphuric acid. Further, spectroscopic methods (FT-IR and NMR) were used to confirm the synthesis of cellulose acetate, while the thermogravimetric analysis, scanning electron microscope (SEM), and X-ray diffractogram (XRD) were used to determine the thermal stability, crystalline size, and morphology of the materials, respectively. The high percentage yields of both cellulose and acetylated cellulose are indicative of the high conversion rate or recovery rate of cellulose and cellulose acetate. The XRD analysis was used to determine the size of the particles, crystallinity, and amorphous nature of the cellulose and cellulose acetate. A reduction in the average crystalline size was observed using the Scherer equation alongside the XRD data. The spectrum of cellulose showed the occurrence of a broad absorption band at around 3450 cm⁻¹ corresponding to an-OH stretching vibration, indicating a moisture peak due to interaction between the cellulose hydroxyl group and water, while the C-H vibrations at 2950 cm⁻¹ are due to alkyl groups. The appearance of several new absorption peaks was observed in the spectrum of cellulose acetate; at 1752 cm⁻¹ and 1232 cm⁻¹ represent the stretching vibrations of the C=O and C-O of the acetate, respectively. The ¹³C NMR of cellulose acetate shows the presence of ten carbon atoms. The peaks at 173.84–172.08 ppm indicated the presence of quaternary carbon atoms in the acetate. The signals at 102.55 and 94.61 ppm are the (1₄) carbon linkage of D-glucose units, while the signals at 80.08–69.57 ppm are the oxymethine carbon atoms. These results have established the possibility of obtaining a good yield of acetate from cigarette filters as a route to reducing the amount of cigarette waste generated.

Keywords: cellulose, cellulose acetate, cigarette, waste, interconversion, sustainability

Introduction

According to the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal of 1989,

Art. 2(1), "'Wastes' are substance or objects, which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law". The growing amount of waste produced in modern society

has a huge impact on the environment. Waste Cigarette filter is one of the most common and non-biodegrade form of litter worldwide with an estimated 5.6 trillion filter generated worldwide in 2002 and nine trillion are projected for 2025. Global environmental burden of cigarette litter could be greatly exacerbated in the coming years unless there is a change in the manner in which global populations dispose-off cigarette filters. Due to the ubiquitous nature and magnitude of cigarette filters discharged into the environment. Research has shown that cigarette butts contribute to storm drain trash that eventually ends up in rivers and oceans (Novotny et al., 2009). Cigarette filters are made of a mixture of cellulose derivatives that can persist in the environment for generations, which leach out toxic chemicals into the environment through cigarette particulate matter (Slaughter, 2011). Cellulose can be easily converted into cellulose acetate (Figure

1) (a compound with a high processability and biodegradable potential) widely known for its numerous applications in membrane separation processes, production of matrices for controlled drug release, protection of optical films, among other applications (Cheng, Dowd, Selling, & Biswas, 2010; Ribeiro et al., 2016)

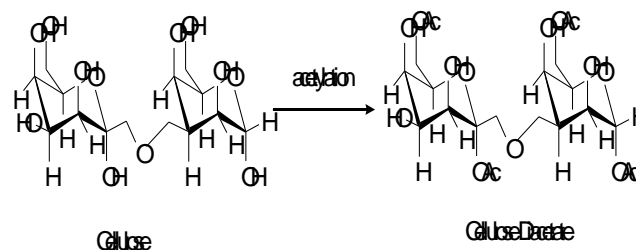


Figure 1: Acetylation of cellulose to cellulose acetate.

This study aimed to propose a plausible waste conversion protocol for the preparation of cellulose acetate from waste cigarette filters; an essential industrial feedstock.

Methodology

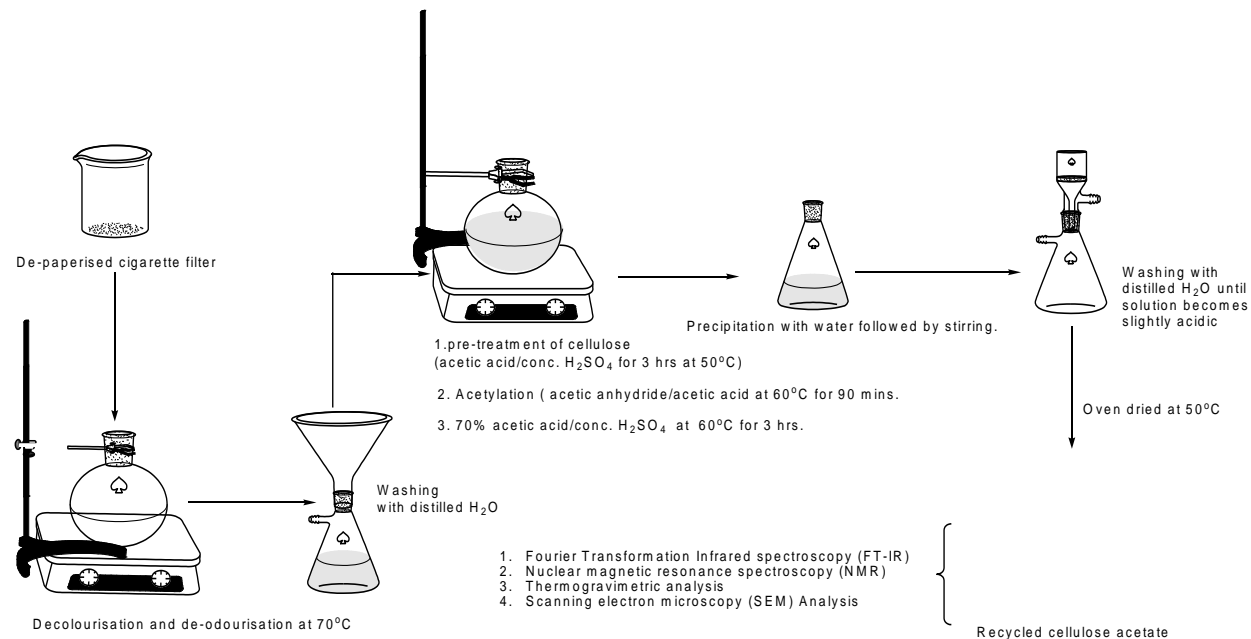


Figure 2: Flowchart for the conversion of spent cigarette filter to cellulose acetate

Results

A mixture of an alkaline bleaching and surface acting agent was selected to break down the toxic chemical mixture attached to the filter structure and to produce an odourless white pulp-like material, respectively. The

intermediate product and final product yields from the waste cigarette gave about 72.20% cellulose and 70.10% cellulose acetate, respectively; this is a high recovery yield for a recycled waste (Table 1). The elemental compositional of the recycled material were within 0.2 range of the calculated.

Table 1: Characteristics properties, % yield and elemental analysis

Samples	Melting point (°C)	Average crystallite size (nm)	% Yield	Elemental analysis		
				%C	%H	%O
Cigarette waste	*	*	198.27	*	*	*
Cellulose	439.63	105.85	143.15	45.25(45.40)	6.89(7.08)	47.86(47.52)
Cellulose acetate	305.16	52.92	138.89	48.87(49.07)	6.54 (6.36)	44.59 (44.57)

Physical property analysis of the obtained cellulose and cellulose acetate indicated a melting point of 439.63 and 305.16°C, respectively. The average crystallite size (D), calculated from Scherrer equation was 105.85 and 52.92 nm this implies the formation of nanomaterial via the acetylation process.

Figure 3 shows the infrared spectrum of cellulose and cellulose acetate. The peak at 1705 cm^{-1} , assigned to the C=O stretching vibrations typical of the structural features of cellulose acetate (Ibrahim *et al.*, 2010).

Further absorption bands from 3310 to 3038 cm^{-1} related to OH groups of cellulose and cellulose acetate. Bands at 2856 cm^{-1} are related to C-H bonds specific to cellulose acetate specific to cellulose. In addition, is the appearance of the ester carbonyl peak at 1752 cm^{-1} due to O=CO-CH₃ stretching of acetate and the CO stretching of acetyl groups at 1232 and 607 cm^{-1} . This is the strongest evidence

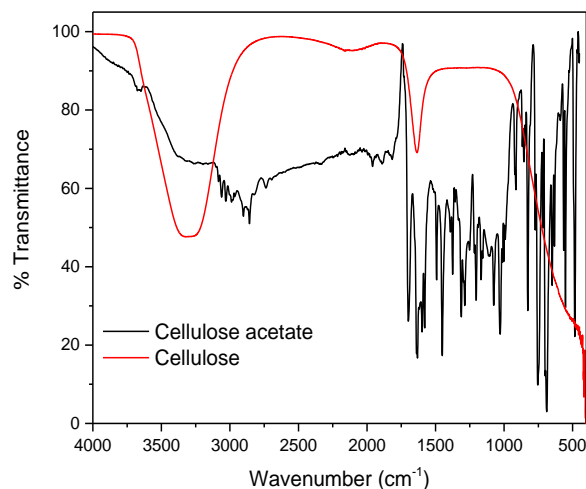


Figure 3: Functional group spectrum of cellulose and cellulose acetate

that the material has been acetylated.

Figure 4(a) is the thermogram of cellulose acetate which illustrates a three-stage decomposition. The first stage at 266-300°C

with a mass loss of 38.86% (4.06 mg) represent the lost of the majority of the hydroxyl group and second stage (434-467°C) mass loss of 16.17% (1.69 mg) of decomposition represent the acetate groups.

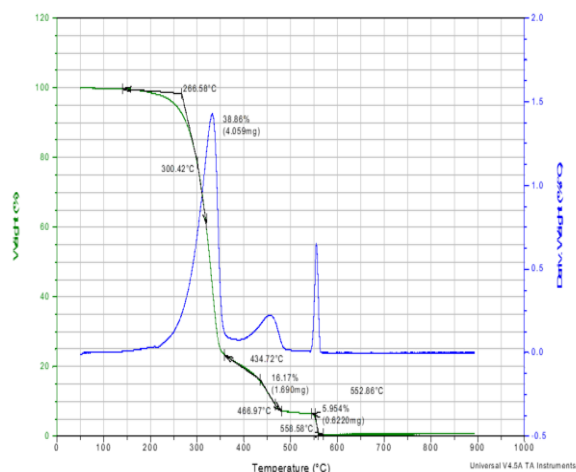


Figure.4 (a): Thermogram of cellulose acetate

A mass of 5.954% (0.622 mg) is evolved at a temperature of 553°C causing the thermal cleavage of the glyosidic bond leaving the carbon as a residue. The thermal response of cellulose (Figure 3(b)), three stages of decomposition was also observed. The first

derivative plot with a mass loss of 41.16% (4.235 mg) at a temperature range of 267-303°C is attributed to the hydroxyl group since

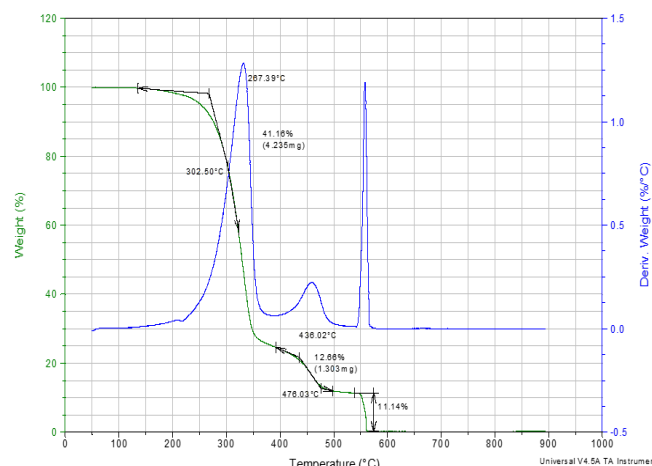


Figure.4 (b): Thermogram of cellulose

it constitutes the majority of the compound. It appears that the cellulose further decomposes with a percentage mass of 12.66 (1.30 mg) between 436-476°C. At around 580°C, a mass loss of 11.41% is observed and this can probably be due cleavage of the glyosidic bond leaving carbon as a residue.

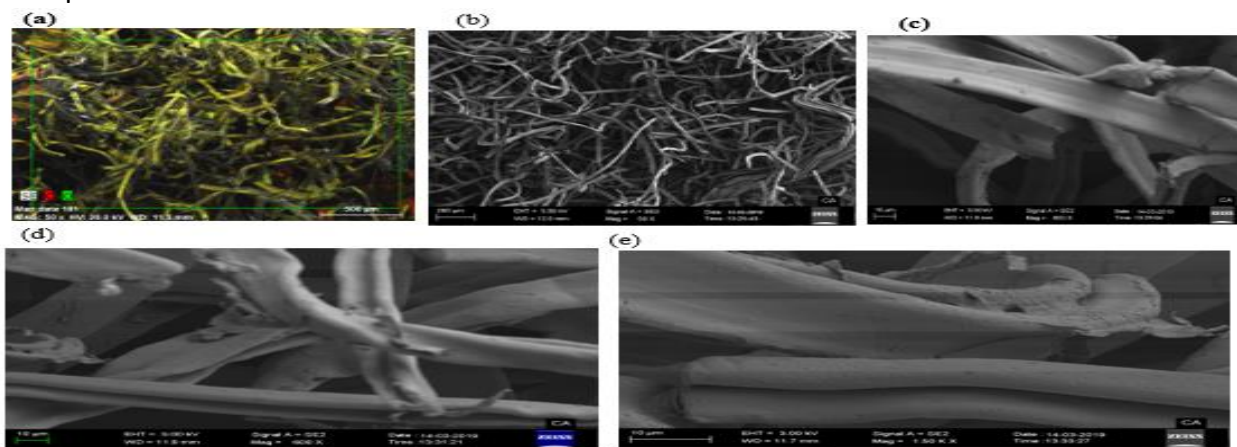


Figure 5: Micrographs of cellulose diacetate taken in SE mode at a magnification various magnification

occur due to the presence of the sulfuric acid catalyst (Figure 5(b-e)). These processes

modify the morphology of the material, which become more disorganized and undergo a defibrillation process.

The diffractogram (Figure 6) produced unique diffraction patterns; suggesting different substitution groups.

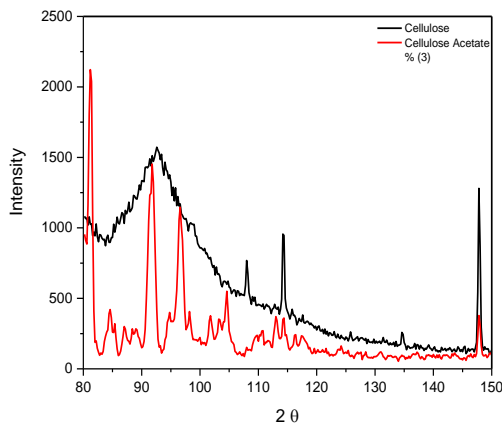


Figure 6: Diffractogram of cellulose and cellulose acetate

A smaller nano-semicrystalline size (52.92 nm) was observed on analysis of the acetylated. Derivative indicating a homogeneous crystal composition compared to the amorphous broader peaks of the cellulose. Acetylation of cellulose caused a increase in the peak intensity as well as a significant change in crystallite sizes compared to the hydroxy derivative.

^1H NMR (400 MHz, acetone) ^1H NMR (400 MHz, DMSO- d_6) δ 6.18 (d, $J = 8.3$ Hz, 1H), 5.87 (ddd, $J = 8.3, 6.9, 3.7$ Hz, 1H), 5.16 – 5.05 (m, 3H), 4.95 (d, $J = 9.7$ Hz, 1H), 4.70 (q, $J = 7.0$ Hz, 1H), 4.62 – 4.31 (m, 5H), 4.22 (q, $J = 7.0$ Hz, 1H), 3.71 (d, $J = 7.9$ Hz, 6H), 3.60 (s, 6H), 2.92 (td, $J = 7.0, 2.5$ Hz, 1H), 2.80 – 2.67 (m, 4H), 2.57 (td, $J = 7.0, 3.8$ Hz, 1H). ^{13}C NMR (100 MHz, acetone) δ 173.84, 172.81, 172.26, 172.08, 102.55, 94.61,

80.08, 74.50, 71.33, 70.42, 69.95, 69.64, 51.98, 51.97, 51.85, 51.82, 50.79, 38.42, 38.04.

A new peak at (δ 173.84, 172.81, 172.26, 172.08 ppm) indicating the formation of new bond between oxygen atom of (-OH) group of glucopyranose ring of cellulose after the acetylation of the molecule. Four methoxy carbon (69.95, 51.98, 51.82 and 94.61 ppm) bearing the -OH groups of glucopyranose ring of cellulose where present confirming the formation of a diacetate. The glyosidic carbons at 1,6 positions resonates at 102.55 and 80.08 ppm. Appearance of 5.87 (ddd, $J = 8.3, 6.9, 3.7$ Hz, 1H), 5.16 – 5.05 (m, 3H) representing the -OH protons. The presence of a peak in the methoxy region (38.42 and 38.04 ppm) with considerable intensity confirms the structure of cellulose diacetate.

Conclusions

De-odouration and de-colourisation of the waste cigarette filter is an essential step to maximize the cellulose acetate product. The properties of the cellulosic material allow for easy chemical conversion into cellulose and cellulose acetate. A high yield of the acetylated product was obtained an indication of high economic viability of the process. The acetylated cellulose was found to be soluble in acetone and insoluble in mixture of chloroform and methanol (9:1v/v). These findings confirm the presence of cellulose diacetate. The NMR spectrum of the cellulose diacetate consisted of two obvious adsorption regions. The first region belongs to the substituted acetyl groups and the second region corresponds to hydroxyl group of the glucopyranose units.

The thermal stability of the cellulose acetate is improved as shown by the decrease in weight loss % at (around 500°C) (5.96%) and a slight

decrease in the value of initial decomposition temperature (T_0) (266–300°C) as compared to that of cellulose (267–303°C), where the total weight loss % reached 41.16%. The decrease in the thermal stability of the modified sample is mainly attributed to the acetylation process. Acetylation causes the formation of nano-semicrystalline polymer for production of matrices for controlled drug release.

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