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# **RESEARCH ARTICLE**

# Thermal, Physical, Chemical, and Mechanical Properties of Cellulose Acetate From Cigarette Filters

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### ABSTRACT

Cigarette filters, primarily composed of cellulose acetate (CA) fibers, pose a significant environmental concern due to their persistence and potential toxicity. This study aimed to comprehensively characterize the physicochemical and thermomechanical properties of CA fibers from unsmoked and smoked cigarette filters. Fourier-transform infrared spectroscopy (FTIR) analysis revealed distinct spectral changes in smoked filters, indicating smoke residue deposition. The higher degree of substitution (DS) observed in filter fibers relative to pure CA powder suggests reduced biodegradability and potential for long-term environmental persistence. Morphological analysis using optical and scanning electron microscopy confirmed the trilobal fiber structure of CA. Thermogravimetric analysis (TGA) demonstrated similar decomposition behavior for all samples, with moisture retention and volatiles in filter fibers. Differential scanning calorimetry (DSC) revealed the effects of additives and smoking on the thermal transitions of CA. Dynamic mechanical analysis (DMA) indicated comparable thermomechanical behavior between unsmoked and smoked filters. The storage moduli were fitted into a modified stiffness-temperature model, evidencing changes in the bond strength distribution as a function of smoking condition. This research provides a comprehensive framework for understanding the impact of the smoking process on the properties and environmental behavior of CA filter fibers.

### 1 | Introduction

With the constantly increasing global production of plastics, the boundaries between mechanical and environmental sciences must coalesce to resolve the grand challenges of macro- and microplastic pollution that adversely affect ecosystems. The separation between these fields of study manifests due to the dichotomy between their respective foci. The environmental sciences pursue mitigation approaches to lessen the detrimental impact of improperly and inadequately disposed resilient materials in landfills and waterways, emphasizing chemical decomposition, trace elements, and the interaction between human-made materials and the surrounding environment. Alternatively, mechanical sciences amplify the properties and performance of materials to withstand deployment in extreme conditions, increasing resiliency and negatively affecting the environment. In other words, while engineers are optimizing the mechanical and structural integrity of materials, environmental scientists are trying to devise approaches to break them down safely at the end of life. The long-term objective of this research is to blur the transdisciplinary boundaries between these fields of study by systematically investigating the process–structure–property

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interrelationship of cellulose acetate (CA) due to its prominence in a broad range of applications.

Previous research on CA has primarily focused on characterizing its physicochemical and thermomechanical properties as a function of composition and manufacturing technique [1–6]. On the one hand, the focus on the physicochemical attributes stems from the pursuit of a fundamental understanding of the processstructure relationship, where spectroscopic techniques, for example, Fourier transform infrared (FTIR) spectroscopy, reveal the molecular structures and the degree of substitution (DS) and acetylation [7]. Recent literature reported FTIR spectral peaks associated with CA, including the effect of additives (such as plasticizers and molecular modifiers) and manufacturing approaches (e.g., solvent casting) [3, 6], which assist in the identification and classification of stability, resiliency, and endurance [4, 7–9]. On the other hand, thermomechanical properties are imperative for defining the optimal processing conditions and developing products that meet rigorous design requirements. The thermomechanical properties are at the intersection of the process-structure-property nexus, entailing the transition points (glass transition and melting temperatures), the pyrolysis (degradation temperatures and residual mass), and the thermodynamics of phase transitions, affecting the mechanical and geometric stability within the operating range and the proper processing conditions [10]. CA is generally classified as a thermoplastic biopolymer, where the mechanical properties of this class of material are sensitive to temperature, strain rate, and environmental conditions [10]. The mechanical properties encompass the viscoelastic storage and loss moduli, commonly characterized as a function of temperature and frequency to assist in product design and analyses. A summary of the state of the art of the viscoelastic behavior of CA is presented in the forthcoming section. However, these characterizations were limited to specific formulations that are locally synthesized, and the study of CA in physical products (specifically cigarette filters) still needs to be investigated. Cigarette filters are the most littered item in the world, with more than 4 trillion filters littered annually, constituting 30%–40% of littered objects [11, 12]. Therefore, studying CA from cigarette filters as a common pollutant is the primary motivation for this research.

The focus on matter-nature interactions necessitates exploring the synergistic relationship between the DS based on the molecular structure of CA, the thermal decomposition and transitions as a function of form and processing conditions, and the thermomechanical properties for design functionality. First, the DS measures the average number of substituent acetyl groups per cellulose monomer in the CA backbone. The DS is a direct function of the acetyl percentage, increasing with higher substitution percentages. Previous research has confirmed that an increase in DS correlates with higher environmental persistence upon disposal, as the increase in acetyl groups inhibits the natural hydrolysis of the cellulose backbone [13-15]. The DS of manufactured CA ranges between ~1.8 and 3, with the majority at 2.5 [15]. CA DS positively correlates with elongation percentage, indicating that the acetyl groups improve mechanical endurance, whereas it has negative correlations with glass transition temperature, yield stress, and tensile strength [13]. Consequently, the change in DS of CA in cigarette filters during manufacturing is crucial for understanding the degradation

behavior. Wilkinson et al. recently reported higher DS for CA fibers extracted from unsmoked cigarettes than the neat counterpart, leading to an imperative research question about the effect of smoking conditions on the DS of CA filters [16]. The importance of this investigation stems from the fundamental process–structure–property interrelationship between smoking conditions, carbonization, tobacco contamination, and thermal annealing of the CA fibers within cigarette filters.

Thermogravimetric behavior (pyrolysis) is foundational for studying the degradation and decomposition of CA, including the discernment of the degradation temperature and decomposition residuals. The former informs the maximum operating and manufacturing temperatures and indicates thermal degradation after disposal. The degradation temperatures of neat and plasticized CAs have been reported a priori, ranging between 360°C and 372°C and achieving complete thermal decomposition within 300°C-400°C [1, 3-6, 17]. With a specific focus on CA fibers extracted from unsmoked cigarette filters, Wilkinson et al. reported a degradation temperature of 370°C compared to 376°C for neat CA powder used as a control [16]. Furthermore, performing the thermogravimetric analysis (TGA) at different heating rates yields the activation energy [18]. The activation energy also depends on the morphology and processing conditions, resulting in a broad variance in the reported values. For example, the activation energy of neat CA varies between 80-152 and 94–222 kJ mol<sup>-1</sup> for plasticized CA as a function of plasticizing agents [4, 19, 20]. Plasticized and processed CA fibers from unsmoked cigarette filters have an activation energy of 184 kJ mol<sup>-1</sup> [16]. However, the calculation of the thermal endurance has not yet been reported for the CA formulation predominantly used in the manufacturing of cigarette filters, which can readily be resolved from the activation energy using ASTM E1877-21 [21]. Pursuing a complete dataset of the thermal performance of CA fibers from unsmoked and smoked cigarette filters is a contributing motivation for this research.

The dynamic mechanical properties of CA are also responsible for its endurance as a function of environmental and operating conditions during manufacturing and after disposal. The dynamic mechanical properties include the storage modulus (a measure of material stiffness) and loss modulus (an indicator of material damping) as a function of temperature and frequency [10]. When measured as a function of temperature, the dynamic properties of polymers, in general, exhibit a pronounced transition from a brittle, glass-like phase to a rubbery, more malleable behavior, separated by the glass transition temperature  $(T_g)$ . Below  $T_g$ , the material stiffness dominates the overall mechanical response, transitioning to a dampening-dominated behavior above  $T_{g}$  [10]. While the dynamic mechanical method of determining  $T_{g}$  is reliable, calorimetric approaches are more accurate [22, 23]. Reported  $T_{a}$ for neat CA ranges from 192°C to 202°C and ~55°C to 175°C for the plasticized counterparts [20, 24-26]. We previously found  $T_{\sigma} = 176^{\circ}$ C for unsmoked cigarette filters and  $T_{\sigma} = 171^{\circ}$ C for CA powder [16]. In the glassy regime, the storage and loss moduli of neat and plasticized CA range between ~1.3-5 GPa and ~125-225 MPa, respectively [25-27]. In addition to the composition, the manufacturing process also plays a crucial role in the ultimate mechanical properties. For example, the yield strength of CA varies as a function of the processing method, reporting ~25-85, 14.2-29.4, and 26.5-57.0 MPa for solvent casting, twin-screw extrusion, and injection molding, respectively [13, 28, 29]. However, the dynamic mechanical properties of CA fibers from cigarette filters are absent from the open literature; hence, the focus of the research leading to this report.

This research aims to assess the thermomechanical and physicochemical properties of CA fibers extracted from unsmoked and smoked cigarette filters, elucidating changes in material properties associated with the smoking condition (unsmoked vs. smoked). The novelty of this research hinges on the systemization of the testing protocols and centralization of CA fibers properties as a function of realistic manufacturing and use conditions. In this study, the physicochemical properties of smoked and unsmoked cigarette filter fibers were characterized using FTIR spectroscopy, allowing for the calculation of the DS [7]. TGA was used to identify the decomposition temperature, calculate the activation energy, and extrapolate the thermal endurance of the filters. The primary thermal transitions of these materials were measured using differential scanning calorimetry (DSC), including the glass transition and melting temperatures, along with the latent heat. Dynamic mechanical analysis (DMA) ascertained the storage and loss moduli as a function of temperature and frequency. The outcomes of this comprehensive experimental effort are the first of their kind in pursuing the process-structure-property interrelationship of unsmoked and smoked cigarette filters to the best of our knowledge. Hence, this study fills the gap in the literature on the thermal, physical, chemical, and mechanical properties of a pervasive pollutant, creating a foundation for future investigations of the environmental impacts of disposed cigarette filters. The imperativeness of studying the properties, persistence, and degradation of smoked cigarette filters stems from their potential ecological effects on waterways and wildlife while guiding future research in devising novel approaches to mitigate such adversity through recycling or reuse.

### 2 | Materials and Methods

### 2.1 | Sample Preparation

Cigarette filters comprise CA fibers tightly tangled and wrapped together to form a cylinder (plug), which is, in turn, glued to the cigarette rod (as shown in the anatomy of a typical cigarette rod in Figure 1). The filter fibers consist primarily of CA and chemical additives to facilitate the manufacturing process, including plasticizers (triacetin ca. 10wt% and polyethylene glycol 200 up to 8 wt%), titanium dioxide, aluminum oxide, and sodium chloride (<1wt% combined), as antibacterial, flammability, and thermal stabilizing agents [30, 31]. After smoking, the filter may be contaminated with additional chemicals due to carbonization, tobacco contamination, and organic residue from the smoker [32, 33].

The unsmoked filters used in this study were extracted from commercially available packs of Marlboro Red cigarettes. The tobacco and cigarette paper were cut from the filter at the end of the tipping paper (Figure 1), and any remaining tobacco was gently scraped from the filter. The plug wrap and tipping papers were subsequently sliced along the length of the filter, with the slice placed adjacent to the glue strip used to adhere the plug wrap to the filter, allowing for the unraveling and removal of the papers and glue around the filter. The smoked filters were obtained from Schick's laboratory at the Department of Medicine at the University of California, San Francisco. The Marlboro Red cigarette filters were smoked using a TE-10z smoking machine (Teague Enterprises) according to ISO Standard 3308:2000 [34]. The cigarettes were ignited using nickel-chromium wire for the first two puffs and were puffed 10 times before being extinguished by ejection into a basin of dry ice. The smoked cigarette weight ranged from 0.25–0.55g, with an average of 0.39g [35]. Each testing regimen used five cigarettes selected randomly from the pack. Unmodified CA powder (CAS 9004-35-7, Sigma-Aldrich) was also used as a control, with a number-averaged molecular weight of 50,000 g mol<sup>-1</sup> and a DS of 2.4–2.5 (given acetyl 39.2-40.2 wt%).

### 2.2 | FTIR Spectroscopy

The unsmoked filters, smoked filters, and CA powder were all pressed into flakes using a 12-ton hydraulic press to minimize the effect of free volume and morphological irregularities on the spectroscopic measurements. The exterior sides of the cigarette filters (unsmoked and smoked) were first sliced off using a sharp, clean blade, resulting in an oval-like crosssection. These faces were then used as the compression sides on the hydraulic press, with the cuts ensuring that no remaining traces of plug wrap, tipping paper, or glue were present on the testing face (Figure S1). Filters were held under the press for 30 min at ~9 kN. The CA powder was pressed using the same pre-processing conditions. Infrared spectra were collected using a Thermo Fischer Scientific FTIR-ATR spectrometer (Nicolet iS5 with the OMNIC software) at a resolution of 1 cm<sup>-1</sup> over a 64-scan average. Samples were scanned over 400-4000 cm<sup>-1</sup>, encompassing the fingerprint and



FIGURE 1 | Anatomy of an off-the-shelf *Marlboro Red* cigarette, denoting the primary components. [Color figure can be viewed at wileyonlinelibrary.com]

functional group regions. The relative intensities of the 1040 and  $1240 \text{ cm}^{-1}$  peaks were compared using the methods of Fei et al. to determine the DS of the samples [7]. The spectral peak at  $1040 \text{ cm}^{-1}$  corresponds to the stretching of the C–O bond in the cellulose backbone and is unchanging with respect to the DS. The  $1240 \text{ cm}^{-1}$  peak is associated with the C–O bond in the ether group of the acetyl group and is related to the DS of the CA. All samples were intentionally conditioned in an ambient environment to mimic the conditions upon disposal and promote the intensity of the  $1640 \text{ cm}^{-1}$  peak caused by H–O bending in absorbed water [7].

# 2.3 | TGA

TGA samples were extracted from the filters at the specified locations shown in Figure 2 to account for inter- and intra-filter variations at the mouth, middle, and tobacco sides. Disc sections were separated from the filter using a guided sectioning device (detailed in Figure S2) and a stainless-steel blade, ensuring consistent geometry and size. The latter is imperative for a repeatable heat transfer process. All samples were 1.6-1.9-mm-thick and weighed ca. 9-10 mg. The samples were dehydrated under N<sub>2</sub> in the furnace until the weight stabilized to suppress natural hydration and evaporation. The experimental steps are identical to Wilkinson et al. using a TA Instruments Q50 TGA, starting with heating to 50°C and holding isothermal for 2min, then ramping to 750°C at a rate of 10°C min<sup>-1</sup> [16]. The differential thermogravimetric (DTG) response was elicited by differentiating the thermograms with respect to temperature, where prominent peaks indicate the respective degradation temperatures. Five samples were tested from each location, and a multiway analysis of variance (ANOVA) was performed as a function of sample location and smoking condition. Testing of the CA powder carefully followed the testing procedure except for spreading a thin, even layer (ca. 13–14 mg) of the powder across the bottom of the TGA pan. The activation energy was measured using the methods in ASTM E1641-23 [18] by repeating the previously mentioned testing procedure at 5°C–20°Cmin<sup>-1</sup> in steps of 5°Cmin<sup>-1</sup>. Activation energy analysis weight loss was referenced to the onset of degradation in neat CA at 300°C [16], irrespective of the sample type. Finally, the thermal endurance was calculated according to ASTM E1877-21 [21] based on the activation energy and a typical TGA thermogram to estimate the persistence of the filter fibers.

# 2.4 | DSC

DSC testing was performed on a TA Instruments DSC25. The initial preparation of the DSC samples was identical to the steps in Section 2.3. The filter disc was then divided into two semicircular sections. One section was compressed radially and carefully placed into the DSC pan (TA Tzero aluminum pans) so that the filter fibers were aligned vertically to the bottom of the pan. The samples were then lightly tamped to ensure proper contact between the filter and the bottom of the pan. The samples (3.9–4.8 mg) were then dehydrated under N<sub>2</sub> just before sealing the lids (TA Tzero aluminum hermetic lids) with a 0.4 mm hole. The testing procedure for the DSC began with a ramp from ambient temperature to 325°C at a rate of 10°C min<sup>-1</sup> (referred to hereafter as the first heating cycle). Each sample was held isothermal at 325°C for 120s, then cooled to -50°C. The sample was again held isothermal for 60s, followed by another ramp



**FIGURE 2** | Experimental flowchart depicting sample preparation for each testing type. Sample extraction sites for TGA and DSC characterization of intra-filter variation are explicitly identified. [Color figure can be viewed at wileyonlinelibrary.com]

to 325°C (second heating cycle). The latent heat was taken as the area under the endothermic peak in the first heating cycle, as defined by the span from 190°C to 260°C. The melting and transition temperatures were identified as the local peaks of the endothermic transition within this span. The glass transition temperature ( $T_g$ ) was defined as the half-height of the endothermic transition drop from the second heating cycle with the tangent lines extending 50°C above and below the transition. Inter- and intra-filter variations were accounted for using a multiway ANOVA to determine differences between the sample extraction locations (n = 5) identified in Figure 2. The steps above were followed carefully for the CA powder (~8–9 mg) except for loading an even layer of powder directly into the pan.

### 2.5 | DMA

DMA testing was conducted using a DMA850 (TA Instruments) equipped with the fiber/film tension clamp. The previously pressed filters (~0.5-mm-thick) were cut using a rectangular punch along the fiber direction, resulting in  $5 \times 20 \text{ mm}$  samples. The samples were tested as a function of temperature using an oscillating temperature ramp from 50°C to 250°C at 3°C min<sup>-1</sup>. The storage and loss moduli were determined using a displacement oscillation of 10 µm at a rate of 0.5 Hz, with a preload of 0.25 N. Five samples of the unsmoked and smoked cigarette filters were tested. All DMA testing as a function of temperature was completed using an N<sub>2</sub> chamber purge, ensuring a nonreactive environment.

### 2.6 | Micrographic Characterization

Optical microscopy (OM) was completed using a Keyence VHX-7100 digital microscope equipped with the VHX-E lens set. Composite depth imaging was performed along different focal planes, allowing for the full depth of the fibers to be accurately captured. Scanning electron microscopy (SEM) was performed on a Quanta 450 at a high vacuum with an accelerating

voltage ranging from 1 to 10 kV and working distances spanning 8–20 mm. All SEM samples were platinum sputter coated using a Q150T (Quorum Technologies EMS) to a thickness of 6 nm. Conductive double-sided carbon tape was used to ground the samples, with extra tape placed along the filter sides to prevent the charging of individual ungrounded fibers. In addition to the unsmoked and smoked filters, the CA powder was also imaged to determine differences in geometry.

## 3 | Results and Discussion

# 3.1 | Physicochemical Properties (FTIR, OM, and SEM)

Figure 3 shows the infrared spectra of the unsmoked and smoked filters and the CA powder reference, reporting their transmittance physicochemical signatures, including the fingerprint and functional group regions. The fingerprint region is characteristic of CA, as discussed next, while the functional group region is quieter due to the relatively simple molecular structure of the CA polymer. Table 1 lists the spectral peaks and associated bond vibrations considered in this study. The presence of CA in the unsmoked and smoked filters is confirmed by the spectral peaks at 1734, 1367, 1215, and  $1031 \,\mathrm{cm}^{-1}$ , consistent with previous results in [36–39]. These spectral peaks correspond to the stretching of the C=O double bond in the carbonyl group ( $\nu_{C=0}$ ), stretching of the –OH bond in the cellulose backbone and unacetylated hydroxyl groups ( $\nu_{OH}$ ), stretching of the C–O bond in the ether group ( $\nu_{C-O}$ ), and stretching of the C–O–C bonds in the pyranose rings ( $\nu_{C-O-C}$ ), respectively. Since the above-mentioned spectral peaks are characteristic of CA, their presence in the signatures shown in Figure 3 affirms the common molecular source, irrespective of the sample type. Although triacetin is used as a plasticizer in the manufacturing of cigarette filter fibers, the identification of the corresponding characteristic spectral peaks is inhibited by the peaks either coinciding with the CA peaks (in the case of peaks at 1223, 1371, and 1744 cm<sup>-1</sup>) or being obscured by adjacent more prominent



**FIGURE 3** | FTIR spectra of CA fibers extracted from unsmoked and smoked cigarette filters compared to the spectra of unprocessed CA powder. [Color figure can be viewed at wileyonlinelibrary.com]

characteristic CA peaks (such as the peak at  $1049 \text{ cm}^{-1}$ ) [40]. Triacetin may also be responsible for the change in intensity of the 1123 and  $1160 \text{ cm}^{-1}$  peaks relative to the  $1141 \text{ cm}^{-1}$  baseline for the unsmoked filters and CA powder due to characteristic triacetin peaks at 1099 and  $1148 \text{ cm}^{-1}$  [40]. The difference between the unsmoked and smoked CA fiber spectra is minimal in the fingerprint region, with the characteristic spectral features matching. However, there is a noticeable difference in the observed peaks in the functional group region, specifically within  $2800-3000 \text{ cm}^{-1}$ . The unsmoked filter and CA powder spectra exhibit two overlapping low peaks at ~2880 and ~2940 \text{ cm}^{-1}, while the smoked cigarette filter spectra display four distinct convoluted peaks at 2852, 2871, 2922, and 2953 cm^{-1}, commonly attributed to –CH stretching and postulated to be due to tobacco smoke residue [41].

The FTIR spectra in Figure 3 are used in the calculation of the DS based on the absorbance intensity of the hydroxyl group [7].

$$DS = 1.8742 - 1.2541r + 1.9760r^2$$
(1)

where *r* is the ratio of the absorbance intensity of the 1213 and  $1030 \text{ cm}^{-1}$  peaks based on a baseline between 935 and 1580 cm<sup>-1</sup>.

**TABLE 1**FTIR spectral peaks of unsmoked and smoked CA fibersand pristine CA powder.

Wavenumber					
Unsmoked filter	Smoked filter	CA powder	Functional groups [ <mark>36</mark> ]		
1734	1733	1735	ν <sub>C=0</sub> in the carbonyl group		
1367	1366	1368	ν <sub>OH</sub> in the backbone and hydroxyl groups		
1214	1213	1216	$\nu_{CO}$ in the ether group		
1030	1029	1032	ν <sub>C-O-C</sub> in the pyranose ring		
900	899	901	$\nu_{as}$ in the pyranose ring or $\delta_{CH}$ out of plane		
601	601	602	$\gamma_{\rm OH}$ out of plane		

It is imperative to reiterate all materials were used as received to minimize postprocessing steps. The DS values were 2.53, 2.51, and 2.28 for the unsmoked filters, smoked filters, and reference CA powder, respectively. DS for the CA powder is slightly lower than the manufacturer specification ( $DS \approx 2.4$ –2.5), likely due to the powder morphology and light–CA interactions in the spectrometers [42]. The unsmoked and smoked filters show significantly higher degrees of substitution than the reference CA powder, attributed to the additives and manufacturing processes, indicating that DS is unphased by the smoking conditions. The increase in DS is an important benchmark, as multiple reports indicate a strong inverse correlation between DS and biodegradability [13–15], which is related to the construction of the filter and the process-structure–property interrelationship rather than a consequence of smoking.

Figure 4 shows a collage of optical micrographs of the unsmoked filters (Figure 4a), smoked filters (Figure 4b), and the reference CA powder (Figure 4c). The morphological characteristics of the CA fibers extracted from unsmoked cigarette filters have been discussed previously in a recent study by the authors, noting a density of 100s of fibers per mm<sup>2</sup> [16]. The morphology of the smoked filters mirrors the unsmoked counterparts, evidencing similar filter structure, fiber geometry and width, and external fiber plasticization. The smoked filter micrographs confirm the entanglement of the fibers and ensuing minor porosity to capture un-lodged tobacco and ash particulates (Figure 4b). Notably, the filter color appears to change from white for the unsmoked samples to yellow for the smoked filters, possibly attributed to tobacco oil released during the smoking process and the associated increase in temperature. The CA powder micrographs are shown in Figure 4c for comparison. Figure 5 displays the SEM micrographs of the unsmoked (Figure 5a) and smoked (Figure 5b) cigarette filters, demonstrating the retention of the overall geometrical and morphological properties of the CA fibers. These fibers have a trilobal cross-sectional geometry (see inset in Figure 5a) [16]. Figure 5c is a series of SEM micrographs highlighting tobacco and ash particulate entrapment due to the smoking process.

### 3.2 | Thermal Decomposition Properties (TGA)

The typical pyrolysis behaviors of the unsmoked and smoked filters and CA powder reference are depicted in Figure 6. The representative thermograms are the average of at least five separate measurements of each sample type (Figure 6a). The



**FIGURE 4** | Optical micrographs of (a) an axial view of an unsmoked cigarette filter, (b) an axial view of a smoked cigarette filter, and (c) reference pristine CA powder. [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 5** | Scanning electron (SEM) micrographs of (a) CA fibers extracted from an unsmoked cigarette filter with an inset higher magnification micrograph of the trilobal fibers, (b) CA fibers extracted from a smoked cigarette filter, and (c) tobacco and tobacco-smoked residue affixed to individual CA fibers in smoked cigarette filters.



**FIGURE 6** | (a) Pyrolysis of CA fibers extracted from the unsmoked and smoked cigarette filters and CA powder (average thermograms). (b) Differential thermogram (DTG) plot of CA fibers from unsmoked and smoked cigarette filters and CA powder (average DTGs). [Color figure can be viewed at wileyonlinelibrary.com]

representative differential gravimetry (DTG) curves are shown in Figure 6b, clarifying the separate decomposition regimes and their transitions. While the comparison between the pyrolysis of CA fibers from unsmoked cigarette filters and neat CA powder has been discussed comprehensively in Wilkinson et al. [16], a summary of the significant findings is included herein for completion. The CA powder does not exhibit degradation until the onset at ~300°C. The unsmoked and smoked filters show two initial decompositions centered around 125°C and 190°C, attributed to the release of trapped water and volatiles. The primary decomposition of samples considered herein generally agrees with the decomposition temperatures ( $T_d$ ) previously reported for CA (~372°C) [1, 5, 6, 8, 17]. The degradation temperatures

are 370.1°C±0.8°C, 363.9°C±0.9°C, and 375.8°C±0.9°C for unsmoked filters, smoked filters, and CA powder, respectively. The difference between  $T_d$  of unsmoked and smoked filter fibers is possibly due to the tobacco and ash particulates or the chemical changes within the filter fibers (as evidenced in the FTIR spectra). On the other hand, the distinct pyrolysis of the fibers and the powder is attributed to (1) differences in morphology and (2) processing and manufacturing steps. Finally, ANOVA using a 95% confidence interval confirms a significant statistical difference in the thermal degradation behavior between unsmoked/smoked filters and between filters/CA powder, which affects the decomposition response upon disposal, as discussed in the forthcoming section. Figure 7 shows the insensitivity of the degradation behavior to sample extraction location (Figure 2) in unsmoked and smoked cigarette filters through the respective thermograms and DTGs. The positional degradation temperatures (n = 5 per position) for the unsmoked filters are  $369.7^{\circ}C \pm 1.1^{\circ}C$ ,  $370.3^{\circ}C \pm 0.4^{\circ}C$ , and  $370.4^{\circ}C \pm 0.2^{\circ}C$  for the mouth, middle, and tobacco sides, respectively, while they are  $363.6^{\circ}C \pm 0.7^{\circ}C$ ,  $364.4^{\circ}C \pm 1.1^{\circ}C$ , and  $363.5^{\circ}C \pm 0.5^{\circ}C$  for the samples extracted from smoked filters [16]. The assertion of the positional insensitivity is further ascertained by ANOVA, returning a *p* value of 0.20 for all filter samples considered herein, irrespective of the smoking condition. Additionally, a *p* value of 0.32 is reported when considering only the samples from smoked filters, confirming no statistical difference.

The pyrolysis also allows for the calculation of the activation energy of thermal degradation using decomposition kinetics, following the Flynn-Wall-Ozawa method as prescribed by ASTM E1641-23 [18, 43, 44]. Figure 8 shows the logarithm of the heating rate as a function of the inverse of the constant conversion temperatures, with best-fit lines overlaid. The calculated activation energies are  $184.3 \pm 7.6 \text{ kJ mol}^{-1}$  for the unsmoked cigarette filters,  $186.4 \pm 6.4 \text{ kJ mol}^{-1}$  for the smoked cigarette filters,  $186.4 \pm 6.4 \text{ kJ mol}^{-1}$  for the Smoked cigarette filters, and  $185.0 \pm 9.9 \text{ kJ mol}^{-1}$  for the CA powder. The similar values between the filters and the CA powder confirm the convergence of the Flynn–Wall–Ozawa method on the calculation of the activation energy of CA. The activation energy results further indicate that smoking conditions play a negligible role in activation energy. The comparable activation energies also support the sole decomposition of CA, irrespective of the sample type, since water and volatiles escaped at lower temperatures.

The thermal endurance is calculated based on the activation energies discussed above and the pyrolysis at a chosen conversion level using ASTM E1877-21 [21]. The thermal endurance curves of the unsmoked and smoked filters and CA powder nearly coincide with a slight offset along the temperature axis due to the difference in primary decomposition temperature. Figure 9 plots the thermal endurance as a function of the



**FIGURE 7** | (a) Pyrolysis and (b) differential thermogravimetry (DTG) plot of unsmoked (dotted lines) and smoked (solid lines) CA fibers around the primary decomposition peak (~365°C–370°C) as a function of extraction site (e.g., mouth, middle, and tobacco sides). [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 8** | Arrhenius plot of the natural log of the heating rate vs. inverse temperature at constant conversions for (a) unsmoked CA filter fibers and (b) smoked CA filter fibers. [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 9** | Thermal endurance plot of degradation time as a function of the reciprocal of environmental temperature for all sample types considered in this research. [Color figure can be viewed at wileyonlinelibrary.com]

sample type and environmental temperature, which is used to forecast the persistence of CA in the environment upon disposal while only considering degradation stemming from thermal decomposition. At an anticipated environmental temperature of 15°C, the respective thermal endurances are 11.8, 13.1, and 19.1 trillion years. In practice, the filters will degrade on much shorter time scales due to other degradation processes such as hydrolysis and photodegradation [15].

### 3.3 | Thermal Transitions (DSC)

Initial DSC heating cycles are sensitive to primary transitions, specifically when melting. The average DSC thermographs (n=5)from the first heating cycle of the unsmoked filters, smoked filters, and reference CA powder are shown in Figure 10. The average specific heat of fusion ( $\Delta H_{\rm m}$ ) was calculated by integration of the thermographs between 190°C and 260°C, resulting in  $\Delta H_{\rm m} = 7.9 \pm 1.2$ ,  $8.2\pm0.8$ , and  $15.0\pm0.3$  J/g<sup>-1</sup> for the unsmoked filter fibers, smoked filter fibers, and reference CA powder, respectively. These values are within the range of reported values  $(3-59 \text{ Jg}^{-1})$  [26, 45–47]. The agreement of the specific heat of fusion between the unsmoked and smoked filters indicates the common molecular source, crystallinity, and DS [27, 47]. However, the dichotomy in the specific enthalpies of the CA fibers compared to the reference CA powder is due to the presence of plasticizers in the filters [48, 49]. The distinct molecular structure of the samples is also related to changes in the melting behavior. Finally, the slight differences in heat flux and melting behavior between smoking conditions are likely due to the presence of the tobacco and ash remains identified in Section 3.1.

As shown in Figure 10, the prominent melting peak in the CA powder thermograph widens and splits into two primary peaks. The lower temperature peak ( $205.9^{\circ}C \pm 3.8^{\circ}C$  for unsmoked filters and  $206.4^{\circ}C \pm 4.0^{\circ}C$  for smoked filters) is attributed to plasticizer-rich portions of the filters and appears in 11 of 15 unsmoked samples and 12 of 15 smoked samples. This lower temperature is also thought to be associated with thermal relaxations. The higher temperature peak ( $232.0^{\circ}C \pm 4.1^{\circ}C$  for unsmoked filters and  $233.6^{\circ}C \pm 3.5^{\circ}C$  for smoked filters) appeared



**FIGURE 10** | Average DSC thermographs of the first heat of unsmoked CA filter fibers, smoked CA filter fibers, and reference CA powder. [Color figure can be viewed at wileyonlinelibrary.com]

in 10 of 15 unsmoked samples and 6 of 15 smoked samples. Due to the coincidence between the second peak and the melting point of the pristine CA powder ( $233.4^{\circ}C \pm 0.1^{\circ}C$ ), the former is ascribed to the melting transition of the CA fibers extracted from smoked and unsmoked cigarette filters. The CA powder melting temperature is confirmed by close agreement with the literature [28, 47].

The average second heat cycle thermographs for the unsmoked filters, smoked filters, and CA powder are shown in Figure 11, centered around the glass transition temperature  $(T_{\sigma} - 50^{\circ}\text{C} < T_{\sigma} < T_{\sigma} + 50^{\circ}\text{C})$ . The second heating cycle was used to nullify the effects of the thermal history of the samples due to manufacturing processes, transport conditions, and processing steps. The endothermic drop associated with  $T_{\rm q}$  in the thermographs suggests an amorphous macromolecular structure for all three sample types [50]. The difference in  $T_{a}$  between the filters and the CA powder is attributed to sample morphologies and changes in surface-to-volume ratio [16], illustrating the process-structure-property interrelationship. The average glass transition temperatures for the unsmoked filters, smoked filters, and CA powder were calculated as 176.3°C ± 0.7°C, 177.0°C ± 0.8°C, and 170.8°C ± 1.7°C, respectively, agreeing with previously reported values of 105°C-210°C [1, 5, 13, 20, 28]. Intersample ANOVA analysis indicated a statistically significant difference in  $T_{\rm g}$  based on the source (p < 0.02 for all permutations). Sample morphology, material source, DS, and plasticizer type and content were previously identified as impacting  $T_g$  [5, 13, 28]. Similarly, the sample extraction position also played a role in the variance observed in the glass transition temperature values within each filter. The positional  $T_{\sigma}$  for unsmoked filters is 176.4°C±0.7°C, 175.7°C±0.5°C, and 176.7°C±0.6°C, for the mouth, middle, and to bacco sides, and the respective  $T_{g}$  for the smoked filters is  $177.6^{\circ}C \pm 1.0^{\circ}C$ ,  $176.6^{\circ}C \pm 0.5^{\circ}C$ , and 177.0°C  $\pm$  0.2°C. The ANOVA analyses based on  $T_{\sigma}$  calculated from intra-filter samples are sensitive to the size of the dataset. The collective ANOVA results considering the smoking condition, intra-filter position, and sample weight are summarized in Table 2, evidencing the statistical dependence based on these parameters.



**FIGURE 11** | (a) Typical DSC thermographs truncated around the glass transition during the second heating cycle. (b) The effect of the extraction site on the glass transition of fibers extracted from unsmoked and smoked filters. [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 2** | ANOVA p values for multiple datasets and parameters.The number of replicates for the position is defined for each samplegroup. [Color table can be viewed at wileyonlinelibrary.com]

Sample group	Position (n=5)	Sample type	Weight	
Unsmoked filters $(n=15)$	0.121		0.235	
Smoked filters $(n=15)$	0.127	—	0.328	
CA powder $(n=5)$	_	_	0.131	
All filters $(n=30)$	0.036	0.016	0.918	
All samples $(n=35)$	_	< 0.001	_	

### 3.4 | Viscoelastic Properties (DMA)

The dynamic mechanical responses of unsmoked and smoked cigarette filter fibers as a function of temperature are shown in Figure 12. The DMA responses depict the storage (E') and loss (E'') moduli and the ratio between the moduli (loss to storage),  $tan(\delta)$ . The storage modulus is a quantification of the material stiffness, while the loss modulus is a representation of energy dissipated as heat [51, 52]. The storage moduli of the unsmoked filters decreased from 265 to 161 MPa in the glassy regime (taken herein to be 50°C-160°C, also denoted in Figure 12), while the respective E' for the smoked filters descended from 269 to 158 MPa within the same regime. The indifference in the storage moduli as a function of the smoking condition is attributed to the commonality of the base material, that is, CA fibers. However, the loss moduli values are more distinct within the glassy regime, ranging from 31 to 36 MPa and 41 to 43 MPa for the unsmoked and smoked filter fibers, respectively. The difference in the loss moduli as a function of the smoking condition is possibly associated with the evaporation of the plasticizing volatiles, as discussed in the thermogravimetric results, leading to an increase in the inter-fiber friction that is a known source of damping [52]. At the outset of the glassy regime, the glass transition is taken

to be the peak of the  $tan(\delta)$  curve, calculated as 199.1°C for unsmoked filters and 196.8°C for smoked filters. The decrease in  $T_{a}$  after smoking supports the conclusions found in Section 3.3. While the glass transition is reported higher than room temperature, it indicates a phase transition during smoking is possible since the tobacco burning temperature ranges between 470°C and 812°C, influencing the thermal and mechanical properties of the CA fibers within the filter [53]. Such effects on the structure of the fibers transpire in the DMA results above 220°C, as shown in Figure S3, reflected as pronounced perturbations in the moduli. This indicates mechanical yielding or ultimate failure of the individual fibers, evidenced in the micrographs in Figure 12c. The collective results from the DMA testing provide an opportunity to assess the load-bearing capacity of individual CA fibers. It is worth reiterating that the DMA testing was done at a constant strain of 0.1% while the oscillating stress evolved to accommodate the changes in the mechanical properties. Since the accompanying micrographic analysis suggests the crosssectional area of an individual CA fiber  $\approx 400 \,\mu m^2$  and the packing factor is ~65%, the number of fibers in a DMA sample is ca. 4000. Therefore, an individual fiber supports ~0.17 mN, leading to a ~420 MPa modulus. A detailed discussion of this mechanicsbased calculation is included in the Supporting Information.

Figure 12 also includes the fitted E' based on the modified Mahieux–Reifsnider model using Equation (2) [54, 55].

$$E(T) = \sum_{i=1}^{n} \left( E_i - E_{i+1} \right) e^{\left( - \left( \frac{T}{T_i} \right)^{m_i} \right)} + E_T$$
(2)

 $E_i$  components represent the storage moduli at each plateau before a thermal transition, and  $E_T$  represents the storage modulus after the final transition.  $T_i$  are the thermal transition temperatures, and  $m_i$  are the corresponding Weibull coefficients [54, 55]. The latter is ascribed to the bond breakage statistics at the corresponding transition, associated with the degree of restriction in molecular mobility [54]. Table 3 lists the fitting parameters of the modified stiffness-temperature model. The Weibull coefficients are an important outcome of the curve fitting, elucidating



**FIGURE 12** | Typical DMA thermograph with overlaid Mahieux–Reifsnider model of (a) unsmoked and (b) smoked cigarette filter fibers. (E', E", and the Mahieux–Reifsnider model fitting have been adjusted for fiber packing factor.) (c) contains optical micrographs of fiber failures and fusing after DMA testing. [Color figure can be viewed at wileyonlinelibrary.com]

 TABLE 3 |
 Mahieux-Reifsnider model fitting parameters for the packing factor adjusted storage modulus of unsmoked and smoked cigarette filter fibers.

Smoking condition	$E_1$ (MPa)	$T_1$ (°C)	$m_1$	<i>E</i> <sub>2</sub> (MPa)	<i>T</i> <sub>2</sub> (°C)	<i>m</i> <sub>2</sub>	$E_T$ (MPa)	<i>R</i> <sub>2</sub>
Unsmoked filters	420.7	134.2	3.118	240.4	186.7	16.465	3.41	0.9998
Smoked filters	438.3	125.8	2.762	242.1	184.9	16.003	3.77	0.9999

the bond relaxation processes [54, 55]. The  $m_i$  values reported in Table 3 point to the amorphous nature of CA due to the lack of molecular motion restrictions [55]. The slight difference in the Weibull coefficients as a function of the smoking condition is consistent with the mechanistic conclusions discussed in the preceding paragraph.

## 4 | Conclusion

This study comprehensively characterized the physicochemical and thermomechanical properties of unsmoked and smoked CA filter fibers derived from *Marlboro Red* cigarettes. FTIR spectroscopic analysis confirmed the common material source of the CA in all samples while revealing distinct spectral changes in smoked filters due to smoke residue. The higher DS observed in unsmoked and smoked filter fibers compared to neat CA powder suggests their potential for environmental persistence. Pyrolysis studies demonstrated that the filters release volatiles at low temperatures and undergo primary decomposition like neat CA powder. Thermal endurance calculations, spanning trillions of years, underscore the long-term environmental persistence of processed and plasticized CA. Due to the presence of plasticizers, the enthalpies of unsmoked and smoked filters were lower than those of neat CA powder. DMA revealed variations in the thermomechanical spectra of the different CA samples, providing insights into their structural and mechanical properties. The storage moduli were fitted in a modified stiffness-temperature model, providing Weibull coefficients of bond association of CA. This research represents the first comprehensive characterization of smoked cigarette filter fibers, shedding light on their behavior upon disposal and highlighting the need for further investigations into their environmental impact. The findings underscore the importance of developing sustainable alternatives to CA-based cigarette filters to mitigate their potential negative consequences for ecosystems.

#### **Author Contributions**

**Eric Wilkinson:** data curation (lead), formal analysis (equal), methodology (equal), validation (lead), visualization (lead), writing – original draft (equal), writing – review and editing (equal). **Eunha Hoh:** conceptualization (lead), funding acquisition (lead), methodology (supporting), project administration (lead), resources (lead), writing – review and editing (supporting). **Margaret Stack:** methodology (supporting), resources (equal), writing – review and editing (supporting). **Natalie Mladenov:** conceptualization (equal), funding acquisition (supporting), methodology (supporting), resources (supporting), writing – review and editing (supporting). **George Youssef:** conceptualization (equal), data curation (equal), formal analysis (equal), funding acquisition (supporting), methodology (lead), supervision (equal), validation (equal), visualization (equal), writing – original draft (equal), writing – review and editing (equal).

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### **Conflicts of Interest**

The authors declare no conflicts of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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### **Supporting Information**

Additional supporting information can be found online in the Supporting Information section.