



Preparation of fluoro derivative of cellulose acetate with (1,1,1,3,3,3)-hexafluoro-2-propanol by Mitsunobu reaction and its characterization

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ABSTRACT

Novel ethers of cellulose acetate with (1,1,1,3,3,3)-hexafluoro-2-propanol (HFP) were prepared at an ambient condition using the Mitsunobu reaction. Reaction time was varied from 27 h to 93 h to identify the effect of the amount of fluorination. Based on energy dispersive X-ray spectroscopy analysis, the degree of substitution of HFP on the cellulose acetate was found to be 0.24 for 93 h and 0.13 for 27 h reaction time. Infrared analysis confirmed the etherification of cellulose acetate with HFP.

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1. Introduction

Cellulose is biosynthesized by plants, bacteria, algae and fungi, which is the most abundant and widespread biopolymer. Although cellulose has been traditionally used in large quantities in paper making and cotton textiles, it is an important renewable resource for the development of environment friendly, biocompatible and diverse functional materials. The cellulose chain has three –OH groups in each repeating unit. Therefore, diverse cellulose derivatives can be synthesized and currently utilized in diverse application fields including optical films (Fan, Liu, Lu, & Liu, 2009), controlled release systems in pharmaceuticals (Shalaby, Ikada, Langer, & Williams, 1993), composites (Liu, Zhang, Zhou, & Wu, 2008) and biodegradable plastics (Sun et al., 2010).

Chemical modification of polysaccharides such as cellulose has become a hot research topic which is stimulating a rich variety of studies and approaches. However, relatively little work on fluorinated derivatives has been reported. The most effective treatments append fluorinated moieties through chemical or physical means, which induce both hydrophobic and lipophobic properties to the ensuing low-energy surfaces. Additionally, the presence of these moieties tends to impart a high thermal sta-

bility, reduce the chemical and biological fragility and enhance interactions with various gases. Therefore the chemical modification of cellulose fibers with fluorinated reagents represents a promising strategy for the development of innovative functional biopolymer materials for numerous potential applications. To date, only a few studies dealing with this topic have been published, namely, trifluoroacetylation (Cunha, Freire, Silvestre, Neto, & Gandini, 2006; Yuan, Nishiyama, & Kuga, 2005), homogeneous modification with tri- and difluoroethoxy acetic acid (Glasser, Becker, & Todd, 2000; Sealey, Frazier, Samaranayake, & Glasser, 2000), surface modification with perfluorinated oligo(ethylene oxide) (Fabbri, Champon, Castellano, Belgacem, & Gandini, 2004), plasma treatment with carbon tetrafluoride (Sahin, Manolache, Young, & Denes, 2002) and fluorotrimethylsilane (Navarro et al., 2003). Surface graft-copolymerization with glycidyl methacrylate followed by coupling with pentadecafluorooctanoyl chloride (Nystrom, Lindqvist, Ostmark, Hult, & Malmstrom, 2006) and surface modification with pentafluorobenzoyl chloride (Cunha et al., 2007) have been investigated.

In the present investigation, we report the fluoro derivative of cellulose acetate (CA) by a simple etherification reaction with hexafluoro-2-propanol. Generally etherification of cellulose has been reported in harsh condition like high basic condition and elevated temperature, but, for the first time, we report the etherification of cellulose acetate under an ambient condition using the Mitsunobu reaction. The fluorinated products were analyzed by

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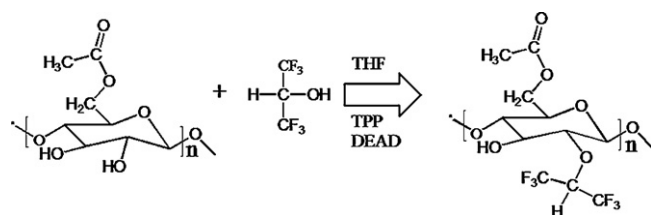


Fig. 1. Schematic view of the fluorination reaction with CA and TPP.

Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and thermogravimetric analysis (TGA). Using these techniques the fluorinated CA was compared with pure CA.

2. Materials and methods

2.1. Materials

Cellulose acetate (molecular weight=30,000, acetyl content 39.8 wt.%), tetrahydrofuran (THF), triphenylphosphine (TPP), (1,1,1,3,3,3)-hexafluoro-2-propanol (HFP), diethylazodicarboxylate (DEAD) were obtained from Aldrich, Tennessee, USA, and used without further purification.

2.2. Preparation of fluoro derivative of CA

In a typical reaction, CA (100 mg), TPP (720 mg), HFP (0.15 mL) and DEAD (0.42 mL) were dissolved in 15 mL of anhydrous THF. The mixture of the above solutions was stirred at an ambient temperature for 27 h (CA-HFP27) and 93 h (CA-HFP93) under nitrogen atmosphere. The reactant was poured into 150 mL of methanol. The precipitate was isolated by filtration. The un-reacted starting materials and byproducts were removed by repeated washing with methanol and water. The CA-HFP27 and CA-HFP93 were dissolved in THF and spin-coated with a spin coater at 1000 rpm. XRD patterns and FTIR spectra were recorded using a Nicolet-6700 spectrometer and wide angle X-ray diffractometer. TGA was analyzed by using STA 409 PC/NETZSCH, analyses were carried out under nitrogen and the samples were heated at a rate of 10 °C/min. Morphology and EDX of powder samples were recorded using an SEM (Hitachi S-4200).

3. Results and discussion

Fluorination of polysaccharides such as cellulose and chitin is a promising strategy for the development of innovative functional biopolymer and several applications of the fluorinated biopolymers have been reported such as fluoro-methylphenylcarbamates of cellulose as chiral stationary phase for high performance liquid chromatography (HPLC) (Yashima, Yamamoto, & Okamoto, 1995), fluorinated chitin derivative as cytotoxicity material (Chow & Khor, 2002) and fluorinated polysaccharides as anti-bacterial and anti-tumor agents (Makino, Ohmae, & Kabayashi, 2006; Kobayashi & Kondo, 1997). The Mitsunobu reaction was discovered by Oyo Mitsunobu and converts an alcohol into a variety of esters using TPP and DEAD (Mitsunobu & Yamata, 1967). Fig. 1 shows the schematic view of the Mitsunobu reaction with HFP and CA. To minimize the water content, anhydrous THF was used as a solvent and reacted in dry nitrogen condition. Fig. 2 shows the FTIR spectra of CA, CA-HFP27, and CA-HFP93. CA has sharp and strong absorption peaks at 1050, 1300, 1400, and 1730 cm^{-1} . Broad absorption peak centered at 3400 cm^{-1} shows characteristic absorption by -OH group. The HFP has sharp absorption peaks at 690, 730, 850, and 900 cm^{-1} , and broad and strong absorption peaks in between

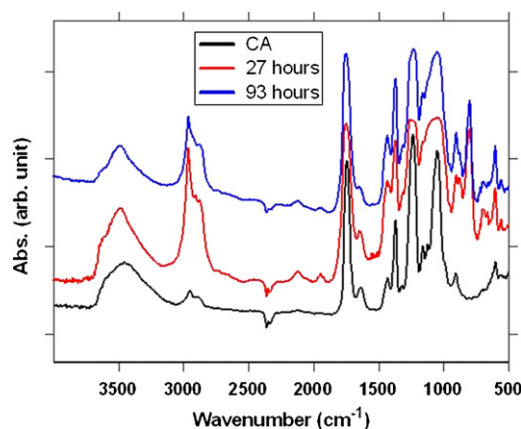


Fig. 2. FTIR spectra of pure CA, CA-HFP27, and CA-HFP93.

1100–1400 cm^{-1} and 3100–3700 cm^{-1} . Note that the absorption intensity of CA around 2800–3000 cm^{-1} representing -CH, -CH₂, and -CH₃ stretching vibrations is relatively weak. Sharp and new FTIR absorption peaks of CA-HFP27 and CA-HFP93 appeared at 600, 800, and 900 cm^{-1} . Since the ester absorption intensities (1730 cm^{-1}) of CA, CA-HFP27 and CA-HFP93 were approximately same, the absorption peak was used to normalize the absorption spectra to compare the relative absorption intensity. The absorption peaks between 1000 and 1400 cm^{-1} and 2800 and 3000 cm^{-1} are drastically increased. The absorption intensities of the CA-HFP93 at 800 cm^{-1} representing C-F bending vibration and 2800–3000 cm^{-1} became weaker than those of the CA-HFP27. It can be rationalized in that the small amount of fluorine may help stretching or bending vibrations of the CA-HFP27 due to the strong electronegativity of fluorine. However, as the amount of fluorine increased the hydrogen bond network of F-H-O and F-H-C might restrict the stretching and bending vibrations of CA-HFP93 (Edwards, 1994).

Fig. 3 shows XRD patterns of CA, CA-HFP27 and CA-HFP93. The maximum diffraction peaks of CA, CA-HFP27 and CA-HFP93 are at $2\theta = 20.27^\circ$, 20.31° and 22.61° , respectively. The maximum diffraction peak of CA-HFP27 is slightly shifted toward higher angle with respect to the pure CA, meanwhile the maximum diffraction peak of CA-HFP93 is drastically shifted toward the higher angle. This may be attributed to the presence of the hydrogen bonds with F-H-O and F-H-C, which have changed the stacking pattern of the cellulose acetate film.

TGA and differential thermogravimetry (DTG) curves of CA, CA-HFP27 and CA-HFP93 are shown in Fig. 4a and b, respectively.

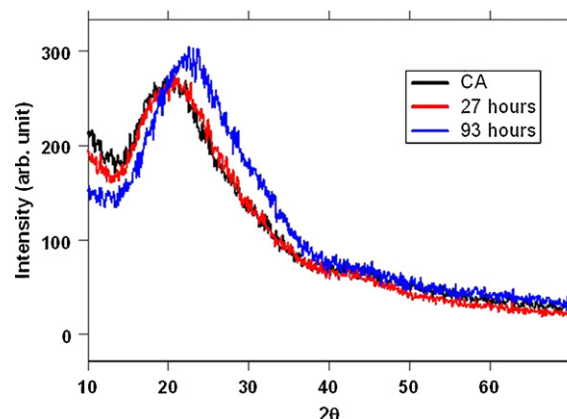


Fig. 3. XRD patterns of CA, CA-HFP27, and CA-HFP93.

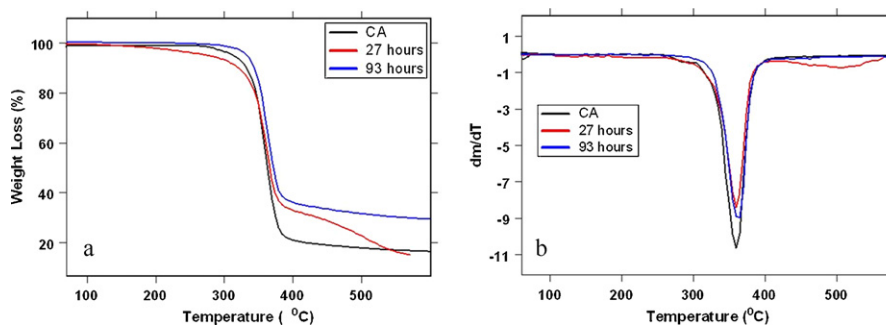


Fig. 4. (a) TGA and (b) DTG of CA, CA-HFP27, and CA-HFP93.

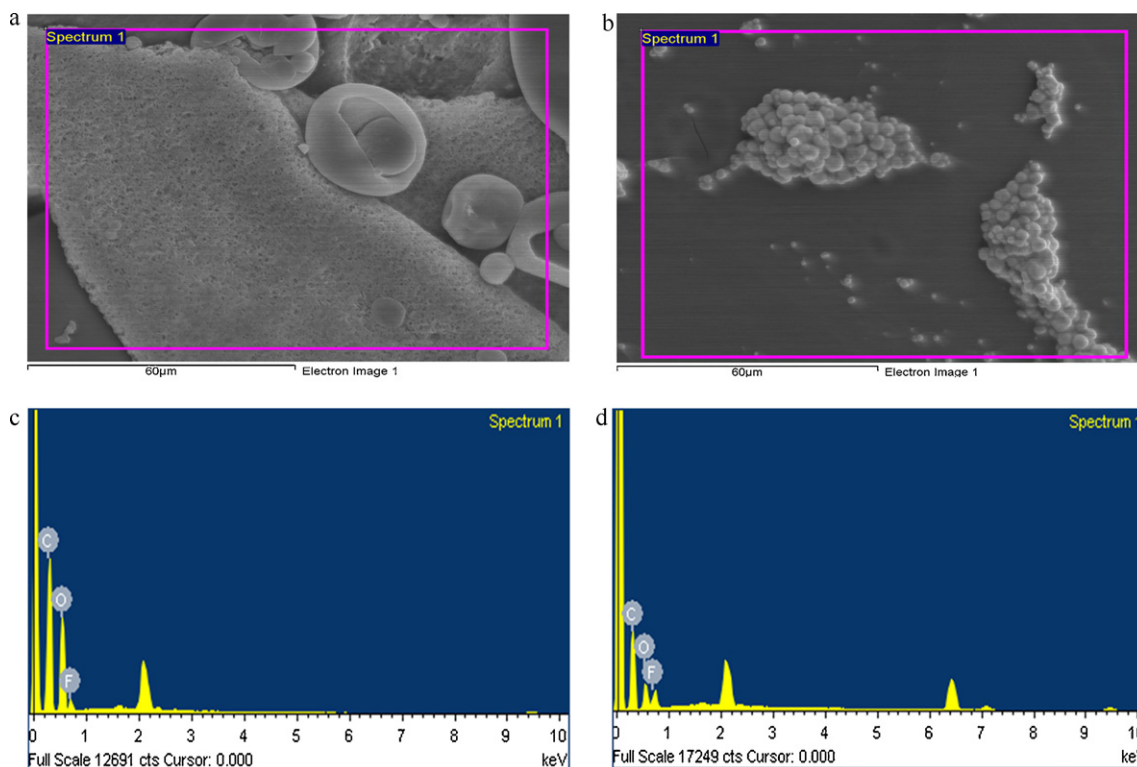


Fig. 5. (a) SEM image of CA-HFP27, (b) SEM image of CA-HFP93, (c) EDX pattern of CA-HFP27, and (d) EDX pattern of CA-HFP93.

Chatterjee proposed three steps of the CA decomposition processes (Chatterjee & Conrad, 1968). In the first step, the absorbed water or the volatile matter evaporates from room temperature to 330 °C. In the second step, the main CA chains degrade from 330 to 450 °C. In the third step, the degraded products carbonize to ash from 450 °C. The pristine CA slowly decomposes at 260 °C and starts to drastically decompose at 320 °C. There is no second decomposition peak as shown in Fig. 2b. The peaks of DTG curves are 359.2, 359.0 and 364.2 °C for CA, CA-HFP27 and CA-HFP93, respectively. The CA-HFP27 shows earlier decomposition compared with the pure CA. It could be due to the disturbance of the intra- or intermolecular hydrogen bonds. As the reaction time increased, more HFP might be attached to the CA chain and formed strong intra- and intermolecular hydrogen bonds due to a strong electronegativity of the fluorine. Therefore, CA-HFP93 shows higher thermal stability than the pure CA and CA-HFP27. Moreover, the residuals of CA, CA-HFA27 and CA-HFP93 were approximately 15, 12 and 30%. Large amount of residual mass of CA-HFP93 could be attributed to carbon mass from the etherification reaction. CA-HFP27 shows second decomposition peak at approximately 500 °C. These results show

that CA-HFP27 has intermediate physical and chemical properties between the pure CA and CA-HFP93.

Surface morphology of the samples was characterized by SEM analysis (Fig. 5) and the fluorine content in the samples was analyzed by EDX. The pure CA has a porous morphology whereas hexafluoro propyl pendent has a smooth morphology. EDX result shows that CA-HFP27 and CA-HFP93 have fluorine contents of 9.2 and 16.7 wt.%, respectively. From the EDX results, degree of substitution was found to be 0.24 and 0.13 for CA-HFP93 and CA-HFP27, respectively.

4. Conclusions

Mitsunobu reaction was employed to attach HFP molecules to CA with the varied reaction time from 27 h to 93 h. FTIR result clearly indicated the existence of HFP in the polymer after purification. However, it is difficult to quantitatively compare due to the abnormal behavior of hydrogen bonds between F and H. The maximum XRD peak slightly shifted toward higher angle for CA-HFP27 compared with the pure CA, meanwhile the maximum XRD

peak of CA-HFP93 noticeably shifted up. The thermal stability of CA-HFP93 is higher than both of the pure CA and CA-HFP27. EDX result shows that CA-HFP27 and CA-HFP93 have fluorine contents of 9.2 and 16.7 wt.%, respectively.

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