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FACILE AND VERSATILE METHOD FOR THIN LAYER COATING OF π-CONJUGATED POLYMER ONTOCELLULOSE-BASED FIBROUS MATERIALS

Yige Han[1], Hiroki Noguchi[1], Nobuo Yamada[1], Yutaka Kuwahara[1], Makoto Takafuji[1,2], Shoji Nagaoka[2,3], Hirotaka Ihara[1,2*]

[1]Department of Applied Chemistry and Biochemistry, Kumamoto University, Kumamoto, Japan
[2]Kumamoto Institute for Photo-Electro Organics (PHOENICS), Kumamoto, Japan
[3]Materials and Regional Resources Laboratory, Kumamoto Industrial Research Institute, Kumamoto, Japan

Abstract. This paper introduces a facile preparation method for π-conjugated polymer-coated fibrous materials. The method is characterized by *insitu* polymerization of 1,5-dihydroxynaphthalene and 1,3,5-trimethyl-1,3,5-triazinane on cellulose fibers, and promotion of annelation reaction to carbon-like π-conjugated structures. The polymer content loaded onto the fibers and extension of π-conjugated structures are discussed.

Keywords: *π- conjugated polymer, thin layer, cellulose fibers, surface polymerization, black materials.*

Corresponding Authors: *Hirotaka Ihara, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan, Tel.: +81-96-342-3662,* ***e-mail:*** *ihara@kumamoto-u.ac.jp*

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1. Introduction

Amorphous carbon is highly stable physically and chemically and is valued as a functional material. The principal qualities for characterizing amorphous carbon are the sp^2/sp^3 carbon bond ratio and the degree of crystallinity of the substance. Activated carbon, as a typical example of carbon materials, can be used to adsorb harmful substances in deodorization, water quality cleaning, and other applications by employing this property (Fu & Wang, 2011; Hale et al., 2012; Nagaoka et al., 2002; Pérez-Gregorio, 2010; Rashidi & Yusup, 2017). Plant materials such as wood, bamboo, and palm kernel shells are used as the starting material of activated carbon (Aravindhan et al., 2009; Hameed et al., 2007; Ioannidou & Zabaniotou, 2007). To produce activated carbon, physical processes using high-temperature carbonization (800–950˚C) employing a gas such as steam, carbon dioxide, or air and chemical processes in which the material is heated to make it porous after treatment by a chemical reagent such as zinc chloride are used (Abe et al., 2001; Marsh & Rodríguez-Reinoso, 2006; Ozdemir et al., 2014).

This paper proposes a new process for carbon-like thin layer coating of fibrous materials such as cotton fibers and cellulose nanofibers. The authors developed this process by applying a method for producing a π-conjugated polymer by a one-pot polymerization reaction using 1,5-dihydroxynaphthalene (DHN) and 1,3,5-trimethyl-1,3,5-triazinane (TMTA) (Figure 1) (Murakami et al., 2017). In this process, by using a protic solvent such as ethanol and water, it is possible to produce spherical and monodisperse fine particles with a mean diameter ranging from submicron size to several microns (Murakami et al., 2017). When this is done in the presence of porous silica, π-conjugated polymerization proceeds on the silica pores and carbonization proceeds thereafter by heat treatment at a comparatively low temperature (Noguchi et al., 2017). In this paper, we report the production of fibrous materials covered with a carbon-like, π-conjugated polymer thin layer by the means of interfacial polymerization onto cellulose-based fibers used as a carrier material, followed by low-temperature heat treatment.

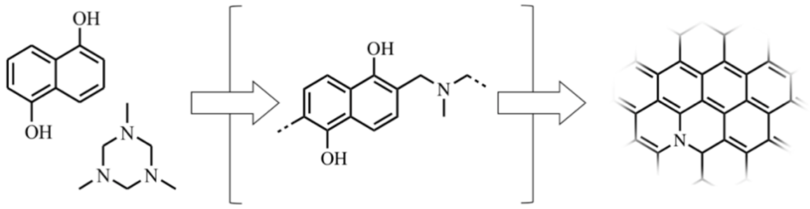

Figure 1. Plausible reaction mechanism for the addition-condensation reaction using 1,5-dihydroxynaphthalene (DHN) and 1,3,5-trimethyl-1,3,5-triazinane (TMTA).

2. Experimental

2.1. Materials

Cotton fibers (COT) and cellulose nanofibers (CNF) were obtained from Yamato Kojo Corporation and Chuetsu Pulp & Paper Co., Ltd, respectively. DHN and TMTA were purchased from Tokyo Chemical Industry Co., Ltd. and used as received without further purification.

2.2. Polymerization on cotton fibers

COT (1.3 g) was immersed in 200 mL of ethanol, and 80.1 mg (2.5 mM) of DHN and 64.6 mg (2.5 mM) of TMTA were added to it. The liquid was heated to 75 ˚C and maintained at this temperature for 24 h. The cotton was filtered out with a glass filter, thoroughly washed with ethanol, and dried under decreased pressure at room temperature to obtain polymer-coated cotton fibers (*p*-COT). The *p*-COT was heat-treated for 12 h at 300˚C in a nitrogen atmosphere to produce black materials (*cp*-COT). Polymer-coated CNF was produced by a similar procedure.

2.3. Measurements

The materials were analyzed by optical microscopy (OM), scanning (SEM) and transmission (TEM) electron microscopies, thermogravimetric (TG) analysis, ζ potential measurement, and UV-visible, infrared (IR), Raman and fluorescent spectroscopies. The OM, SEM and TEM employed were a D22 (Olympus Corp., Tokyo, Japan), a Hitachi SU-8000 (Hitachi-High Tech Corp., Tokyo, Japan) and a JEM-1400 plus Transmission Electron Microscope (JEOL, Tokyo, Japan), respectively. TG analysis was carried out both in air and in nitrogen atmosphere in the temperature range of 100–1000˚C using an SII Exstar 6000 TG/DTA 6300 thermobalance (SII, Chiba, Japan). A Micro Corder JM10 Analyzer (J-Science Lab Co., Ltd., Kyoto, Japan) was employed for elemental analysis. UV-3600 plus (Shimadzu Corp., Kyoto, Japan), FT/IR-4100 (JASCO Corp., Tokyo, Japan), NRS-5100 (JASCO Corp., Tokyo, Japan), and Quantaurus-Tau (Hamamatsu Photonics K.K., Shizuoka, Japan) were employed to measure the UV-visible, IR, Raman and fluorescent spectra, respectively. Zetasizer nano ZS (Malvern Instruments Ltd., Worcestershire, UK) was employed to measure ζ potential of DHN-TMTA polymer.

3. Results and discussion

3.1. Polymerization on cotton fibers

Bare COT was immersed in ethanol that contained DHN and TMTA, and heated at 75˚C. The colorless mixture turned pale yellow and finally dark green during the reaction. Optical microscopy confirmed that the cotton fibers were brown colored. On the other hand, although the liquid had a brownish-red color, it was not possible to confirm any other solid component such as fine particles by optical microscopy; thus, it appears that a soluble polymer was produced as a by-product. Figure 2 shows the optical micrographs of the cotton fibers after collection by filtration and successive washing with ethanol. The color of COT finally changed to reddish dark brown. The obtained cotton is abbreviated as *p*-COT.

For the SEM images of COT and *p*-COT, there is no significant difference between the surfaces of COT and *p*-COT. However, Figure 2 shows that the transparency of the fibers decreased with polymerization, and the surface blackening is observed by heat treatment at 300 ˚C. These results indicate that the color is due to a thin-layer component obtained from the polymerization of DHN and TMTA on cotton fibers.

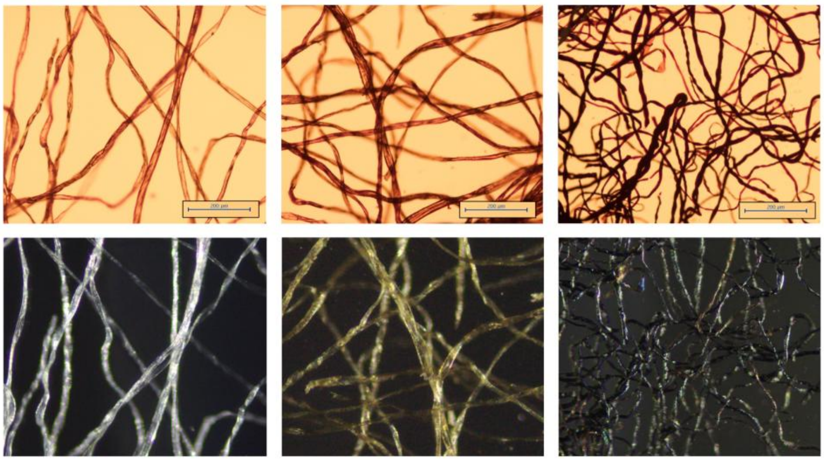
COT *p*-COT-24h *cp*-COT

Figure 2. Optical micrographs of polymer-coated cottons (*p*-COT) and blackened cotton fibers (*cp*-COT). *p*-COT-24h was prepared by polymerization with COT for 24 h at 75 ˚C. *cp*-COT was obtained after heat treatment of *p*-COT-24h for 12 h at 300˚C under N_2 atmosphere. The photographs above and below were taken by transmitted and side lights, respectively. The scale bars indicate 200 μm.

Although the mechanism of polymerization using DHN and TMTA remains unclear, it is thought that polymerization proceeds through the intermediate (Murakami et al., 2017) shown in brackets in Figure 1. When the polymerization was carried out without any carrier, the product was insoluble in ethanol and other good solvents such as chloroform, dimethylformamide (DMF), and tetrahydrofuran, and there was hardly any swelling; this suggests the simultaneous occurrence of high-density cross linking.

The color of the cotton fibers darkened as the reaction progressed. This indicates that the π-conjugated system extends through annelation of the resulting polymer as well as by progressive polymerization. It should be noted that in the absence of cotton fibers, the sp^2/sp^3 carbon ratio of the product was 1.09.

This can also be confirmed from the fact that introduction of the polymer into cotton increased the content of nitrogen, as determined by elemental analysis (Table 1). The source of nitrogen component is attributed to TMTA. However, because annelation can be expected to be accompanied by elimination of nitrogen, the quantity of polymer introduced cannot be calculated from the elemental analysis data.

Table 1. Elemental analysis results of bare cotton and treated cottons

From bare COT				From *p*-COT-24h			
	C (%)	N (%)	C/N		C (%)	N (%)	C/N
COT	41.80	0.26	191.2	*p*-COT-24h	42.96	0.43	99.9
c-COT	75.63	0.36	210.1	*cp*-COT	73.87	0.67	110.3

Figure 3 shows the TG profiles of bare COT and *p*-COT obtained after 24 h-reaction. COT showed two-step decompositions observed at temperatures around 320–360˚C and 360–480˚C in air although the DHN-TMTA polymer without cotton exhibited a higher decomposition temperature (350–550˚C), as indicated by the broken lines in Figure 3. This indicates that the cotton component as the core remained even after the polymerization process, and the produced polymer is immobilized as a thin layer on the cotton surface.

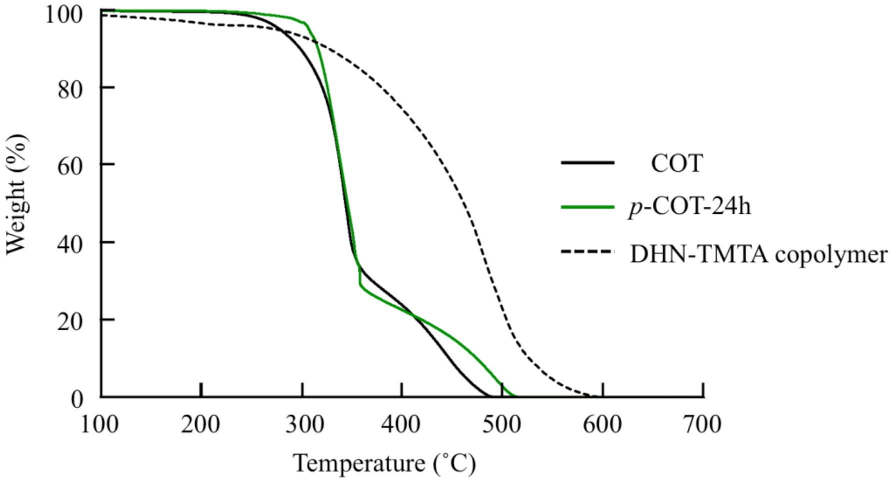

Figure 3. Thermogravimetric profiles of COT and *p*-COT-24h, which was prepared by polymerization for 24 h at 75 ˚C, and DHN-TMA polymer prepared without cotton. Measurement condition: heating rate, 10˚C min^{-1} in air.

3.2. Estimated structures of thin-layer component

IR spectroscopy showed no distinct difference between COT and *p*-COT, while the absorption band around 3300 cm^{-1}, which can be attributed to an OH group, increased slightly. According to the ζ-potential measurement, we observed a negative property for the DHN-TMTA polymer, which indicates that the surface charge of the polymer is reflected by a phenoxy moiety as a part of DHN.

Figure 4a shows the UV-visible reflectance spectra of *p*-COT. Through the polymerization process, the transmissivity decreased remarkably in the wide range of the measured wavelength. In addition, fluorescent spectroscopy provided furthermore information. As shown in Fig. 4b, an emission around 530 nm is observed in the fluorescent spectra of *p*-COT although no similar fluorescence is observed in the spectrum of COT. On the other hand, a similar emission was observed in the spectrum of DHN-TMTA polymer without cotton. As shown in Fig. 4c, this emission intensity increased in the early stage of reaction but decreased in the last stage. These results indicate that the dark-colored component in *p*-COT was produced via a low-molecular intermediate exhibiting fluorescence and extension of π-conjugated structures by an annelation reaction, and is insolubilized by a cross-linking reaction.

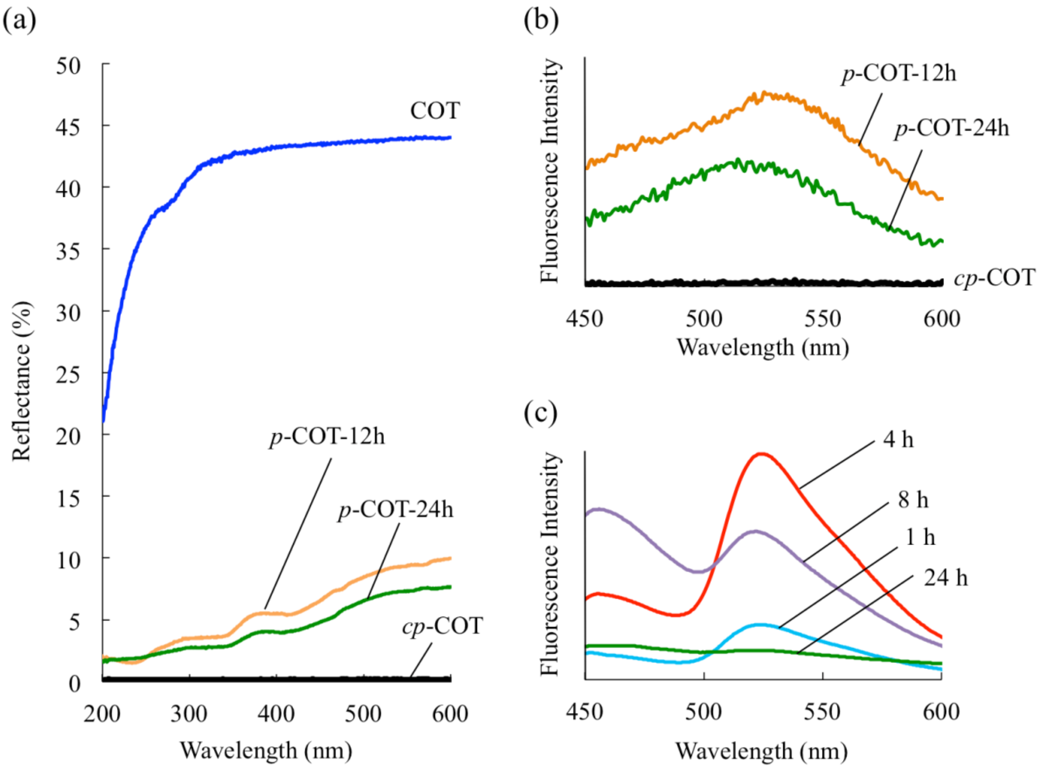

Figure 4.(a) UV-visible reflectance spectra of COT and *p*-COT. Fluorescent spectra of (b) *p*-COT and (c) DHN-TMTA polymer without cotton excited at 405 and 400 nm, respectively. The fluorescent spectra of the DHN-TMTA polymer were monitored on the reaction of a mixture of DHN (1 mM) and TMTA (1 mM) in ethanol without cotton.

3.3. Promotion of annelation

In general, carbonization of polymer materials can be promoted by high-temperature heat treatment under a nitrogen atmosphere. In this study, the heat treatment for carbonization was carried out at a relatively low temperature. As shown in Fig. 5b, slight color change was observed after heat treatment at 200˚C; however, complete blackening was confirmed at 300 ˚C as shown in Figure 2 (right) and Figure 5c. Since the decomposition temperature range is very similar to that of bare cotton as shown in the TG profile (Figure 3), it is concluded that the blackening, which corresponds to carbonization, occurs in the DHN-TMTA polymer component. Such a low-temperature carbonization can be emphasized as a distinct advantage because a low-temperature annelation can be preceded by elimination of nitrogen atoms in this method, while the general mechanism is based on dehydrogenation at higher temperatures.

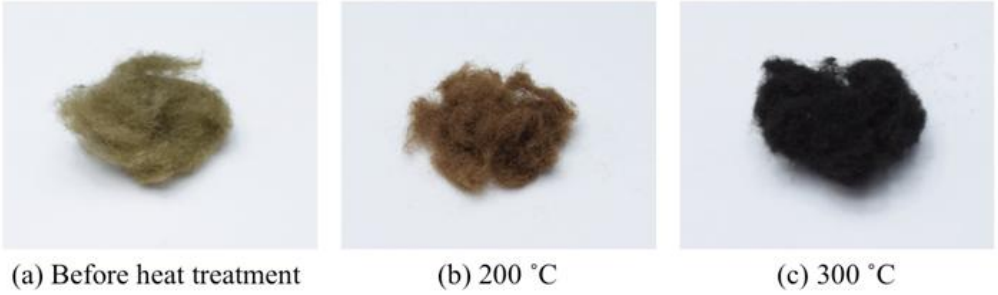

Figure 5. Effect of heat treatment of polymer-coated cottons. The samples (b) and (c) were prepared by heat treatment for 12h at 200 ˚C and 300 ˚C, respectively, under N_2 atmosphere.

3.4. Application to CNF

CNF have become the focus of attention due to their outstanding characteristics such as high strength and an elastic modulus, low thermal expansion similar to that of an inorganic glass, high barrier property to oxygen and other gases as well as lightness (Aulin et al., 2012; Fujisawa et al., 2017; Liu et al., 2011; Modal, 2017; Wu et al., 2012). However, if CNF is blended and hybridized with bulk polymers, its low compatibility becomes a problem; thus, surface modification of CNF is important (Isogai et al., 2011; Missoum et al., 2013). In this study, our method was applied for surface modification of CNF.

The surface polymerization was carried out using a CNF-containing aqueous suspension. When the suspension was diluted with ethanol and then mixed with DHN and TMTA, the color of the mixed suspension changed from white to dark green upon heating at 75˚C. However, the collected substances were almost white although the filtrates were colored. TEM observation indicated that the filtrates contained nano-sized particles, which were produced by DHN and TMTA polymer. Therefore, we modified the solvent system.

As shown in Figure 6a, when the solvent was replaced with a DMF-water mixture, dark-brown substances were obtained after filtration and successive washing with ethanol and water. Figs.6b and 6c show the TEM images of the resultant substances, which evidence that the original fibrous morphology of CNF is completely maintained.

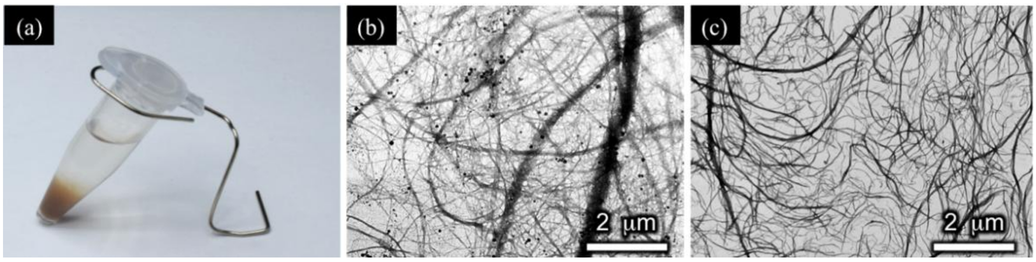

Figure 6.(a) Photograph of the centrifuged sample of polymer-coated CNF-containing suspension, and TEM images of polymer-coated CNF (b) before and (c) after successive washing.

4. Conclusion

In this study, we established a new process for producing π-conjugated polymer-coated fibrous materials. In this process, functional modification of cotton fibers used as a core material was performed by coating them via interfacial polymerization of 1,5-dihydroxynaphthalene and 1,3,5-trimethyl-1,3,5-triazinane, and by promotion of carbonization with annelation. The advantages of this process are that the polymer coating can be carried out easily by one-pot polymerization and carbonization can be promoted at a lower temperature compared to that obtained with conventional processes. In addition, the versatility of the present method was realized by using cellulose nano fibers as a core material and adjusting the solvent system. Further characterization and application of the surface-modified cellulose nano fibers will be described in future studies.

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