Notes

Aryl Azide-Based Photografting of β-Cyclodextrin onto Cellulose Diacetate Fibers

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Cellulose – the most abundant natural polymer – is a biodegradable, renewable, inexpensive, and easily extractable source of raw materials for textile and paper industries.[1] Despite its several advantages, chemical modifications of cellulose need to be carried out for wider applications, such as plastics, coatings, composites, and biomaterials.[2] In general, the modifications of polymer fibers including cellulose and its derivatives have widely been used for altering/improving their physical and chemical properties.[3,4] The modification processes advance mechanical and chemical features of polymer fibers, and give them properties specified for designed applications.

The grafting methods have frequently been used for the modifications of polymer surfaces.[5] Especially, photografting has some advantages over other grafting methods, including simplicity, substrate independency to some extent, variability of chemical compositions with monomers employed and, mild reaction conditions.[6] The photografting method has been applied to polymer fibers: for example, poly(ethylene terephthalate) fibers were grafted with lactose by using photoreactive phenyl azide groups,[3a] and ultra high molecular weight polyethylene fibers with acrylamide groups by using diphenyl ketone as a photo-initiaton agent.[3b] We also demonstrated that poly(glycolic acid) fibers could be modified by the photoreaction of aryl azide groups.[3c] In this work, cellulose diacetate (CDA) fibers, a derivative of cellulose, were modified with cyclodextrins by the photografting method. The CDA fibers have mainly been used as a cigarette filter due to their properties of the absorption and removal of low levels of certain organic chemicals.[7] They also can be easily bonded with plasticizers and are stable to storage under various conditions of humidity and temperature. We envisioned that the adsorption and removal of harmful polycyclic aromatic hydrocarbons, such as benzo[a]pyrene, benzo[a]anthracene and chrysene, present in the smoke from the cigarette, could be increased by the modification of the CDA fibers with cyclodextrins.

Cyclodextrins are water-soluble cyclic oligosaccharides consisting of glucopyranose units.[8] They have a doughnut-shaped structure with variable cavity volumes and can include various guest molecules-fragrance, aromatic pollutants or drugs-into their hydrophobic cavity.[9] The chemical grafting of cyclodextrins onto CDA fibers by using epichlorohydrin as a crosslinking agent has been reported by Szejtli *et al.*, and the

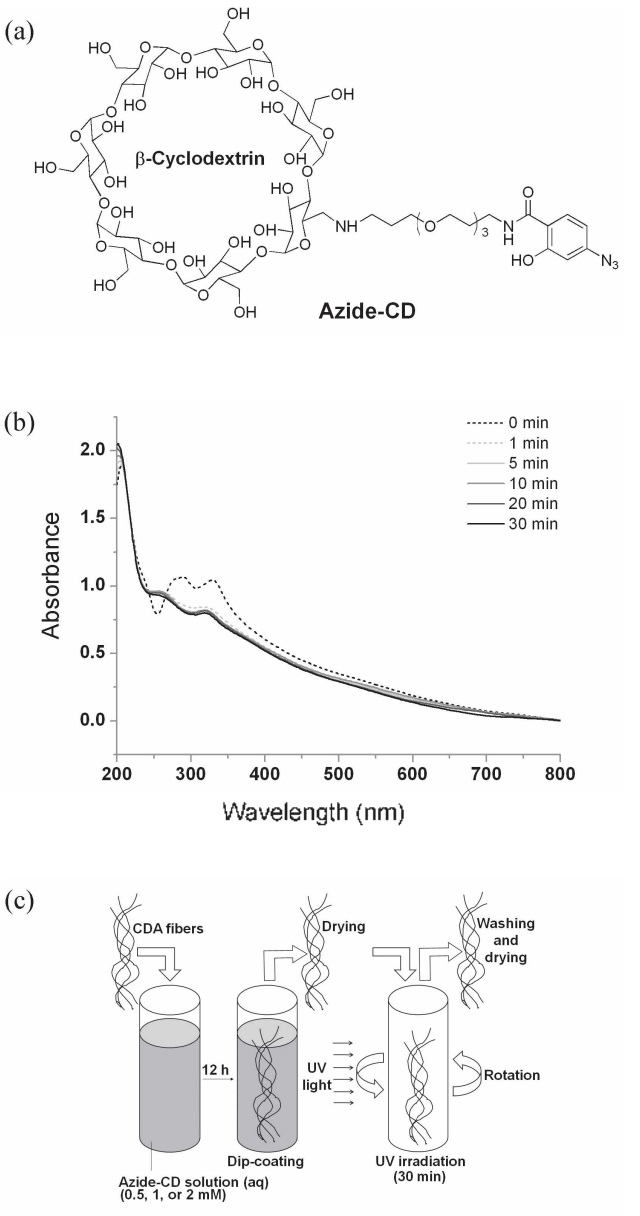

Figure 1. (a) Structure of Azide-CD, (b) UV spectra of the Azide-CD solution (C = 0.4 mM) before and after UV irradiation, (c) Procedure for photografting Azide-CD onto CDA fibers.

inclusion ability of the cyclodextrin-modified CDA for components in the cigarette smoke was demonstrated.[10] However, their approach was found to be difficult to follow primarily due to the insolubility of CDA in most organic solvents. CDA fibers were partially soluble in acetonitrile but the solubility was not sufficient for solution-phase reaction. Therefore we, as an alternative, developed a photografting method for modifying CDA fibers with cyclodextrins.

N-(6,9,12-Trioxa-azapentadecan-15-yl)-4-azido-2-hydroxybenzamido-β-cyclodextrin (Azide-CD), containing both aryl azide and β-cyclodextrin moieties, was used in this study (Figure 1a). Upon UV irradiation, aryl azide is converted into the highly reactive aryl nitrene, which is known to undergo a multitude of reactions, such as insertion into C-H, N-H, and O-H bonds, addition to olefins, proton-abstraction reactions, ring expansion, and ring contraction reactions. We thought that the β-cyclodextrin moiety could be photochemically fixed onto CDA through insertion reactions, which yield covalent bonds with the hydrocarbons of the CDA surface. The UV absorption characteristics of Azide-CD were first investigated with a 0.4 mM aqueous solution before and after UV irradiation (Figure 1b). Without irradiation, the UV absorption peak of Azide-CD was observed at 288 nm with a shoulder at 329 nm, characteristic of the photoreactive aryl azide group. The absorption peak was found to disappear within 1 min of the exposure to 254 nm UV light, indicating the photolysis of the aryl azide and the photosensitivity of Azide-CD. Based on the spectra, we concluded that photografting reaction would be completed essentially within 1 min, but the irradiation time was set to be 30 min in order to react sufficiently and equally with the whole of CDA fibers, having a 3-dimensional structure. Figure 1c shows the reaction procedure employed in this study (For the detailed experimental procedure, refer to the Experimental Section). The concentration of Azide-CD was 0.5, 1, or 2 mM. The Azide-CD-grafted CDA fibers were still insoluble in most organic solvents after the reaction.

The FT-IR spectra confirmed the successful photografting of Azide-CD onto CDA fibers (Figure 2). The IR spectrum of the intact CDA fibers exhibited the characteristic bands at 3500 (O-H stretching), 2950 and 2890 (C-H stretching), 1750 (C=O stretching), 1640 (medium O-H bending of adsorbed water), 1440 (CH_2 bending), 1380 (CH_3 bending), 1240 (C-O stretching), and 902 cm^{-1} (symmetric in-phase ring stretching). Especially, the absorption bands at 1160 (antisymmetric stretching of the C-O-C bridges) and 1050 cm^{-1} (skeletal vibration involving the C-O stretching) were characteristics of the saccharide structure. The IR spectrum of the Azide-CD-coated CDA fibers, after the dip-coating, showed the characteristic peak of azide ($-N_3$) stretching at 2120 cm^{-1}.[11] After photografting, we observed the disappearance of the azide peak, implying that Azide-CD was covalently bonded onto the CDA fibers via the conversion of the aryl azide group to the highly reactive nitrene by UV irradiation. We also observed additional peaks at 3500-3100 (N-H stretching), 1680-1630 (amide C=O stretching), 1600 and 1470 (aromatic C=C stretching), near 1600 (amide N-H bending), and 1350-1000 cm^{-1} (amine C-N stretching).

The effect of the photografting on surface morphologies of CDA fibers was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Figure 3 shows the SEM micrographs of the CDA fibers UV-grafted with different concentrations of Azide-CD. The SEM micrographs showed that the surface of the Azide-CD-grafted CDA fibers was heterogeneous, containing lump- and protuberance-like small fragments, compared with the relatively clean surface of the intact CDA fibers. The protuberances became bigger and the surface of the CDA fibers became more irregular as the concentration of Azide-CD increased from 0.5 to 2 mM. Any kind of physical damages on the fiber, however, was not

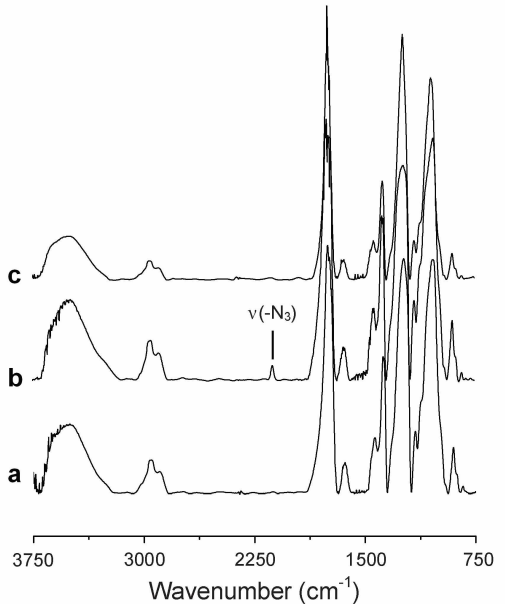

Figure 2. FT-IR spectra of (a) intact CDA fibers, (b) Azide-CD-coated CDA fibers after immersion in the 2-mM aqueous solution of Azide-CD, and (c) Azide-CD-grafted CDA fibers after UV irradiation.

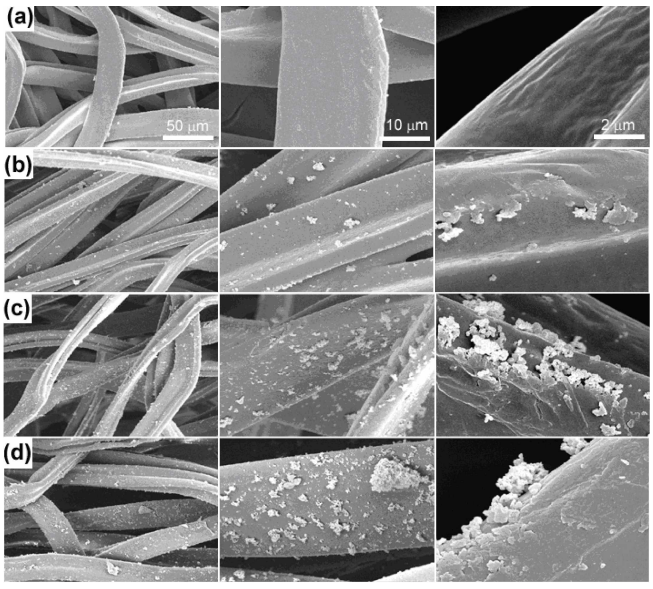

Figure 3. SEM micrographs of the CDA fibers photografted with different concentrations of Azide-CD: (a) 0 mM (intact), (b) 0.5 mM, (c) 1 mM, and (d) 2 mM.

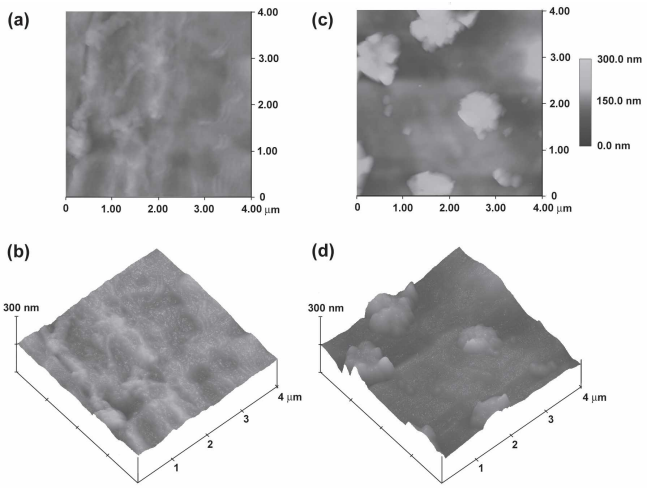

Figure 4. AFM micrographs of CDA fibers: (a,b) intact CDA fibers and (c,d) Azide-CD-grafted CDA fibers with the 2 mM aqueous solution of Azide-CD.

observed in the micrographs. The SEM micrographs at a higher magnification implied that a layer of Azide-CD was formed on the surface of the CDA fibers. The AFM analyses were also used to study the morphological changes before and after photografting (Figure 4). The AFM micrographs revealed a distinguished difference between the modified and unmodified CDA fibers. The UV-grafted CDA fibers had a relatively smooth area that was differentiated from the inherent fibrillar structure of the intact CDA fibers. The lump of the grafted Azide-CD was also verified, in agreement with the SEM micrographs. We thought that the observed lumps/protuberances might have resulted from the formation of the polymeric multilayers of Azide-CD. The heterogeneity increased with the Azide-CD concentrations in solution, perhaps because the amount of highly reactive nitrene intermediates increased as the amount of Azide-CD increased. The high reactivity of nitrenes disadvantageously led to a moderate grafting yield: the grafting yield of the CDA fibers with 2 mM Azide-CD was calculated to be about 13% (grafting yield = (dry weight of grafted fibers – dry weight of original fibers)/(dry weight of original fibers) × 100). Due to the high reactivity of nitrenes, various by-products could be formed, such as primary amines, diazo compounds, or oxidation products like nitro and nitroso. The grafting yield for lower concentrations of Azide-CD (0.5 and 1 mM) was practically difficult to quantify, because of the small weight difference of the fibers before and after grafting.

In order to further confirm the grafting of β-cyclodextrin, host-guest complexes were formed with Coumarin 6 as a model guest molecule, because Coumarin 6 was known to bind strongly with β-cyclodextrin and yield fluorescent structures.[12] Inclusion complexes of Coumarin 6 and the Azide-CD-grafted CDA fibers were studied by fluorescence spectroscopy (Figure 5). The fluorescence maximum of Coumarin 6 itself was observed at 505 nm in ethanol. After immersion of the Azide-CD-grafted CDA fibers in the Coumarin 6 solution for 12 h, the resulting fibers were subsequently immersed in ethanol for 2 h to exclude the non-specific adsorption of Coumarin 6 onto the fibers. As a control, the intact CDA

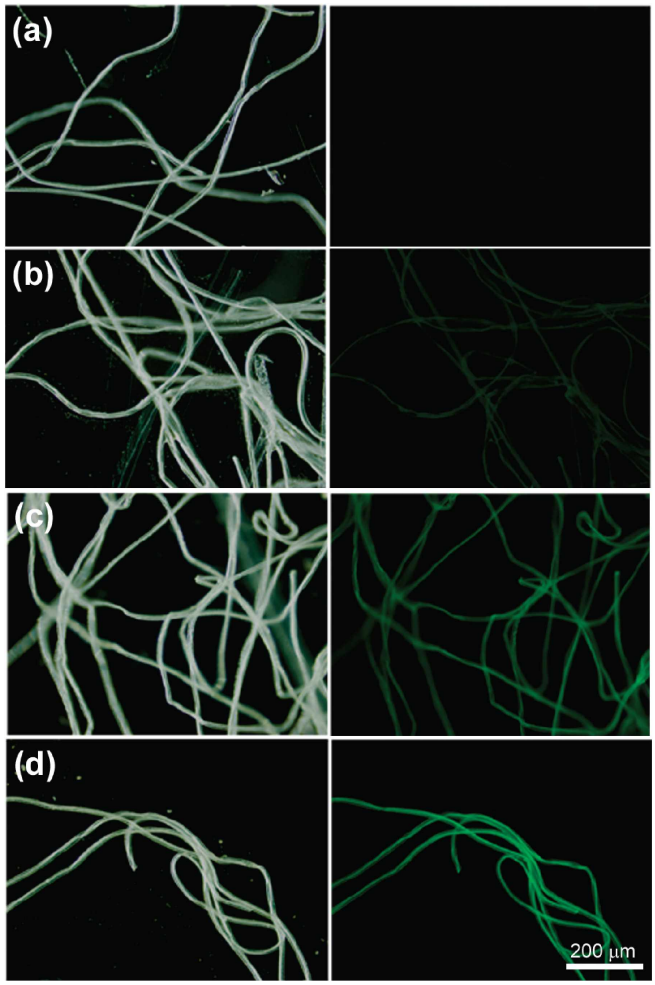

Figure 5. Optical (left) and fluorescence micrographs (right) of the CDA fibers photografted with different concentrations of Azide-CD: (a) 0 mM (intact), (b) 0.5 mM, (c) 1 mM, and (d) 2 mM.

fibers were also treated with the same procedure, confirming that the washing process removed the non-specifically adsorbed Coumarin 6 from the fibers (Figure 5a). Figure 5b-d shows that the fluorescence intensity gradually increased with the amount of grafted Azide-CD. These observations were in accordance with the SEM and AFM characterizations, indicating that the grafting amount of Azide-CD increased as the concentration of Azide-CD in solution increased.

In summary, the cellulose diacetate fibers were successfully grafted with β-cyclodextrin by the photografting method, and the grafting density was varied by the concentration of Azide-CD in solution. The inclusion ability of the grafted cyclodextrin for the Coumarin 6 dye was confirmed by fluorescence spectroscopy, which showed that the fluorescence intensity gradually increased with the amount of grafted Azide-CD.

Photografting has widely been used for introducing special functions onto the polymeric surfaces for achieving specific interactions with other functional groups or species as well as improving the properties of polymer surfaces, such as adhesion, biocompatibility, hydrophilicity, antistatic property, *etc*. We believe that polymer fibers modified with cyclodextrins (α-, β, or γ-cyclodextrins) could be applicable to the formation of

filters with improved performance for capturing various organic molecules, such as fragrance, hydrophobic pollutants, or other aromatic compounds. In addition, the approach demonstrated in this note could be useful for biomedical applications, such as biomedical textiles, blood filters, or encapsulation of drugs.

Experimental Section

Materials. CDA fibers were kindly provided by KT&G (Korea). *N*-(6,9,12-Trioxa-azapentadecan-15-yl)-4-azido-2-hydroxybenzaido-β-cyclodextrin (Azide-CD) was purchased from COS Biotech, Inc., Korea. Coumarin 6 (dye content: 99+%, Aldrich) was used as received. Ultrapure water (18.3 MΩ·cm) from the Human Ultrapure System (Human Corp., Korea) was used. All the solvents were purchased from Merck.

Preparation of Azide-CD-Grafted CDA Fibers. The degree of acetyl substitution of the CDA fibers was approximately 2.5, and its width was about 26 μm. The fiber samples were soaked in an aqueous solution of Azide-CD (2 mL) with various concentrations (0.5, 1, and 2 mM) in the dark for 12 h. The Azide-CD-coated samples were taken out from the solution and dried in air for 12 h. The samples were then put into a quartz tube, and UV light (254 nm) was irradiated for 30 min. The tube was rotated slowly to obtain homogeneous irradiation. After UV grafting, the fiber samples were completely washed with water several times to remove the non-grafted Azide-CD and then dried in air for 12 h.

Complexation Ability Test of the Grafted Cyclodextrins. The solution of Coumarin 6 was prepared by dessolving Coumarin 6 in 2-mL ethanol (final concentration: 5 mM). The Azide-CD-grafted CDA fibers (0.01 g) were immersed in the Coumarin 6 solution under continuous shaking at room temperature for 12 h. The fibers were taken out from the solution and then immersed in ethanol for 2 h for washing. The complexation of β-cyclodextrin for Coumarin 6 was investigated by fluorescence spectroscopy.

Instrumentation. Irradiation was performed with a Rayonet Photochemical Mini-Reactor (Model RMR-600, Southern New England Ultraviolet Company). UV-Visible spectroscopic measurement was performed with a UV-2550 spectrophotometer (Shimadzu). Transmission Fourier transform infrared spectroscopy was performed by means of a Thermo Nicolet Nexus FT-IR spectrophotometer, taking 32 scans for each sample with a resolution of 4 cm^{-1}. Field-emission scanning electron microscopy (FE-SEM) micrographs were obtained with Philips XL30SFEG that was equipped with a thermally assisted field emission gun. The fibers were laid down on aluminum stubs using a conductive adhesive tape and sputter-coated with gold prior to measurements. Atomic force microscopy (AFM) micrographs were acquired with the tapping mode with a Nanoscope IIIa multimode scanning probe microscope (Veeco, USA) with tapping-mode etched silicon probes (TESP). Fluorescence images were acquired on an IX 71 fluorescence microscope (Olympus, Japan).

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