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A novel approach for grafting of β-cyclodextrin onto wool via laccase/TEMPO oxidation

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ABSTRACT

This study demonstrated a new enzymatic methodology to graft β-cyclodextrin onto wool.

The primary hydroxyl groups in β-cyclodextrin were oxidized to aldehyde groups using laccase/2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), which reacted with the amino groups of wool to form Schiff bases. The effects of treatment conditions (treatment temperature, laccase dosage, TEMPO dosage, treatment time) on the aldehyde and carboxyl contents in β-cyclodextrin were studied. FTIR spectrum of oxidized β-cyclodextrin showed the presence of aldehyde and carboxyl groups. Results of MALDI-TOF mass spectroscopy confirmed the coupling of β-cyclodextrin to tyrosine, which was used as a model compound for wool. ATR-FTIR spectroscopy of the grafted wool confirmed the presence of β-cyclodextrin in grafted wool and the formation of a Schiff base between β-cyclodextrin and wool.

1. Introduction

Cyclodextrins are cyclic, non-reducing oligosaccharides. The three types of cyclodextrins are α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin, which contain six, seven, and eight monosaccharide moieties, respectively (Ibrahim & El-Zairy, 2009; Voncina & Le Marechal, 2005). Among them, β-cyclodextrin is the most attractive commercially available one, because of its simple synthesis, availability, and low cost (Dong et al., 2014). The outer side of the cyclodextrin molecule is hydrophilic, whereas the central cavity is hydrophobic, which can entrap a wide variety of small molecules to improve the chemical stability, absorption and bioavailability and also control their release (Dong et al., 2014; Rajendiran & Siva, 2014). Cyclodextrins have been applied in pharmaceuticals (Ijaz et al., 2015), cosmetics (Centini et al., 2007), environmental protection (Singh, Sharma, & Banerjee, 2002), food industry (Astray, Gonzalez-Barreiro, Mejuto, Rial-Otero, & Simal-Gándara, 2009), textiles (Cireli & Yurdakul, 2006), and other industries (Del Valle, 2004).

The applications of cyclodextrins and their derivatives in the textile field appeared in the early 1980s (El Ghoul et al., 2010). Textile fabrics grafted with cyclodextrins can be functionally modified and used for release of fragrance (Wang & Chen, 2005), adsorption of odor (Buschmann, Denter, Knittel, & Schollmeyer, 1998), UV protection (Ibrahim & El-Zairy, 2009; Ibrahim, El-Zairy, Abdalla, & Khalil, 2013; Ibrahim, Khalil, & Eid, 2015), anti-microbial (Hebeish, El-Shafei, Sharaf, & Zaghloul, 2014; Haji, Khajeh Mehrizi, & Akbarpour, 2015; Racu, Cogeanu, Diaconescu, & Grigoriu, 2012). Cyclodextrins can be covalently grafted onto textile fibers through reactive derivatives of cyclodextrins (e.g. monochlorotriazinyl-β-CD, dihydroxypropyl-ethlyhexylglycidyl-β-CD), or by using suitable crosslinking agents (Dehabadi, Buschmann, & Gutmann, 2014).

The primary OH groups in polysaccharides can be oxidized by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)/NaBr/NaOCl into their corresponding aldehyde and carboxyl groups (Delattre et al., 2009). Recently, research has shown that NaBr/NaOCl can be replaced by laccase in TEMPO-mediated oxidation of polysaccharides (Marzorati, Danieli, Haltrich, & Riva, 2005).

Laccase (EC.1.10.3.2.) can catalyze the formation of reactive radicals from phenols, aromatic or aliphatic amines by one electron oxidation. More diverse substrates such as alcohols, sugars, or aromatic methyl groups can be oxidized by laccase/chemical mediator system (Riva, 2006). Jaušovec et al. used laccase as the biocatalyst and TEMPO as the mediator to obtain highly reactive C_6-aldehyde groups in cellulose (Jaušovec, Vogrinčič, & Kokol, 2015). Xu et al. reported that aldehyde and carboxyl groups could be introduced in softwood-derived cellulosic fibers by oxidation using laccase/TEMPO (Xu, Song, Qian, & Shen, 2013). In our previous work, the primary OH groups, present in cotton fibers were oxidized by laccase/TEMPO to introduce aldehyde groups, which were then reacted with amino groups of octadecylamine to form

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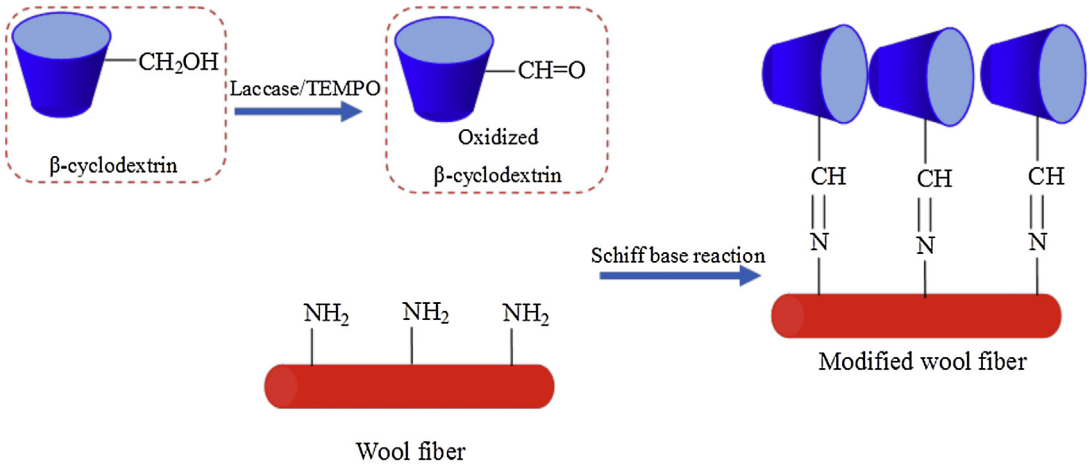

Fig. 1. Schematic illustration of the grafting reaction between β-cyclodextrin and wool fiber.

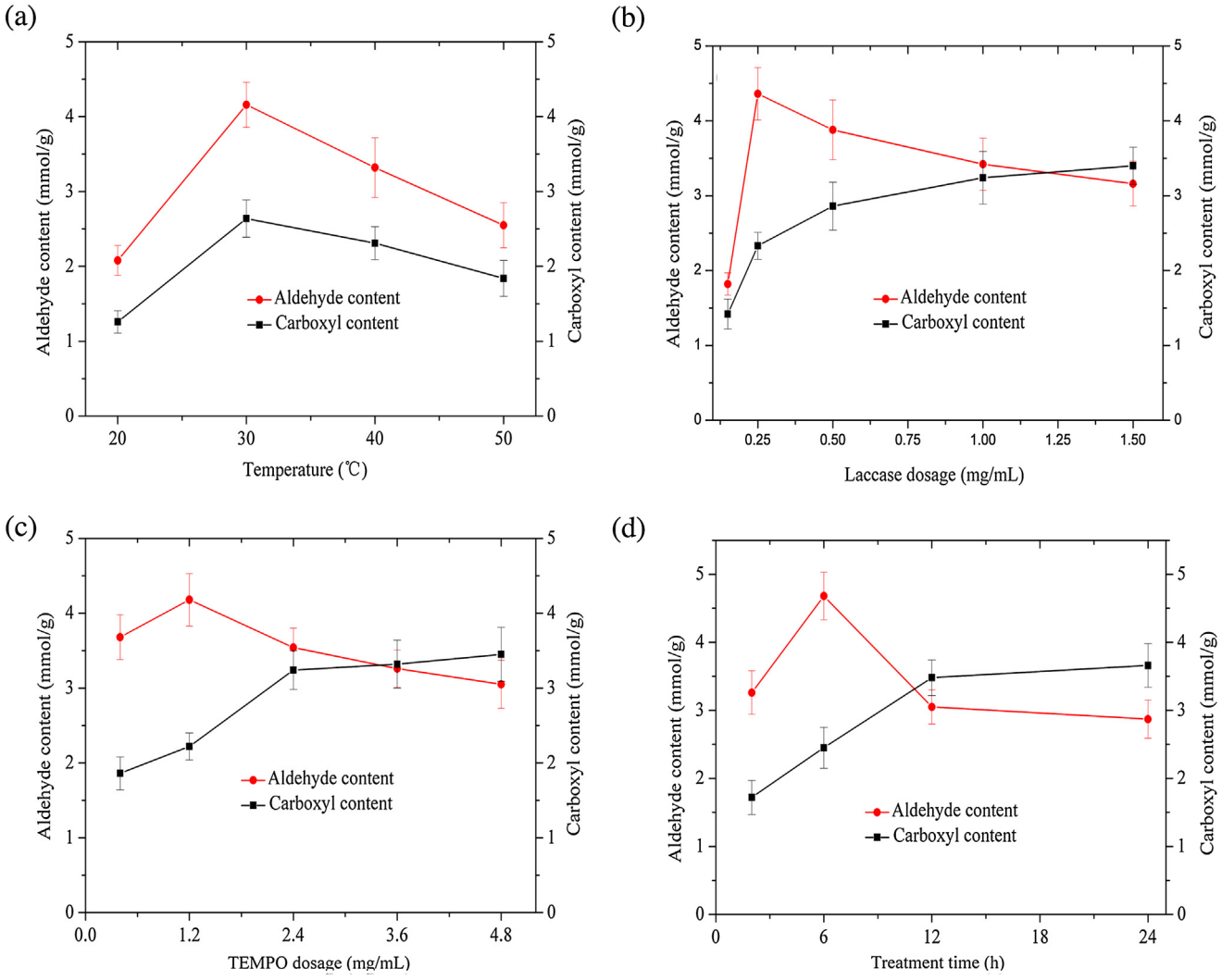

Fig. 2. Effects of treatment conditions on aldehyde and carboxyl contents of oxidized β-cyclodextrin: (a) treatment temperature, (b) laccase dosage, (c) TEMPO dosage, (d) treatment time.

Schiff bases. Hydrophobic cotton fabrics were prepared by grafting hydrophobic octadecylamine onto the surfaces of cotton fibers using laccase/TEMPO (Yu et al., 2016).

In the present work, a novel approach to grafting of β-cyclodextrin onto woolen fibers has been reported. To the best of our knowledge, for the first time, primary OHs of β-cyclodextrin were oxidized by laccase/TEMPO to obtain aldehyde and carboxyl