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Stimuli-responsive cellulose modified by epoxy-functionalized polymer nanoparticles with photochromic and solvatochromic properties

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ABSTRACT

Photoresponsive papers are among the fast and simple tools for detection of polarity by solvatochromic and photochromic behaviors upon UV irradiation. Here, a new, green and facile modification strategy was employed to prepare novel stimuli-responsive cellulose materials containing spiropyran by mixing microcrystalline cellulose (MCC), as a model compound, with epoxy-functionalized photochromic latex. FTIR analysis, thermal and thermo-mechanical properties were used to confirm the microstructral properties. Crystallographic analysis revealed a decrease in crystallinity of cellulose matrix and approved the incorporation of photochromic copolymer. Then stimuli-responsive papers were prepared by using pulp paper as the cellulosic matrix and their smart characteristics were studied under UV irradiation while dried or immersed into some polar and non-polar solvents. Different color changes were observed and investigated by solid-state UV–vis spectroscopy. These significant results were attributed to the efficient chemical modification and confirmed by SEM, EDX and nitrogen mapping analyses.

1. Introduction

Spiropyran as a classic photochromic compound has received much attention because of its superior physical, chemical, photochromic and reversible properties in recent decade (Crano & Guglielmetti, 1999; Crano, 2002; Klajn, 2014). The photochromism phenomenon and some of the related properties of spiropyrans were firstly investigated by Fischer and Hirschberg in 1952 (Crano & Guglielmetti, 1999; Crano, 2002). They observed the color changes of diluted solution of spiropyran while exposed to UV irradiation (less than 450 nm) and its return to colorless form under visible light (above 500 nm). Physical and chemical properties of spiropyran such as photochromism and solvatochromism characteristic can be reversibly switched "on" and "off" through isomerization reaction between spiro-form (SP, closed ring) and merocyanine-form (MC, open ring) under UV irradiation and visible light, respectively (Xia et al., 2014; Zhu et al., 2007; Zhu et al., 2006). However, SP-form have some characteristics such as three dimensional structure (Shiraishi et al., 2014; Wojtyk, Kazmaier, & Buncel, 2001), inert and colorless nature (Chen et al., 2015; Darwish et al., 2012), while the colored MC-form have the planar and zwitterionic structure with a large dipole moment. Recent studies have revealed that the response of spiropyran photochromic molecules to external stimuli such as heat (thermochromic) (Shiraishi, Miyamoto, & Hirai, 2009), UV/Vis light (Shiraishi et al., 2014; Wojtyk et al., 2001), polarity (causing solvatochromism) (Florea, McKeon, Diamond, & Benito-Lopez, 2013; Schenderlein, Voss, Stark, & Biesalski, 2013; Tian & Tian, 2014b), moisture (hydrochromic) (Sheng et al., 2014) and mechanical force (mechanochromic) (Gossweiler et al., 2015; Peterson, Larsen, Ganter, Storti, & Boydston, 2014) strongly depends on the interactions of spiropyran with the adjacent environment, as well as other factors such as molecular packing, charge, and orientation (Achilleos & Vamvakaki, 2010; Wan, Zheng, Shen, Yang, & Yin, 2014).

Incorporation of photochromic compounds into the polymer matrix would occur through doping (Sun et al., 2013; Sun, Hou, He, Liu, & Ni, 2014) or chemical bonding (Cayre, Chagneux, & Biggs, 2011; Keyvan Rad, Mahdavian, Salehi-Mobarakeh, & Abdollahi, 2016; Liao et al., 2015; Wu, Zou, Hu, & Liu, 2009). Physical linkages lead to a decrease in photostability, photochromic properties, coloration efficiency and reversibility. On the other hand, fabrication of stimuli-responsive polymer particles via copolymerization of the photochromic monomer derivatives through emulsion (Keyvan Rad et al., 2016; Zhu et al., 2007) and miniemulsion (Chen, Zeng, Wu, Su, & Tong, 2009; Tian, Wu, & Li, 2009) polymerization

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Table 1
Preparation of the photochromic cellulose samples.[a]

Photochromic copolymer content[b] (wt%)	MCC (g)	Water (mL)	PL (mL)	Sample
20	4	10	10	PC-20
25	3	10	10	PC-25
30	2.35	10	10	PC-30
40	1.5	10	10	PC-40

[a] Amount of photochromic copolymer in each sample is 1 g.
[b] Relative to the total amount of photochromic copolymer and MCC.

are among the most promising techniques. The presence of a photochromic dye beside the cellulose matrix can induce the preparation of stimuli-responsive papers with potential application in different fields such as stimuli-responsive papers (Sun et al., 2013, 2014), smart inkjet printing (Tian et al., 2009), photo-sensitive textile (Feczkó, Samu, Wenzel, Neral, & Voncina, 2013), security documents (W. Tian & Tian, 2014b), sensors and authentication systems (Sheng et al., 2014). Exploitation of polymeric carriers for transformation of photochromic dyes inside the cellulose matrix is an effective factor for improving life-time of the photochromic dye (Abdollahi, Mahdavian, & Salehi-Mobarakeh, 2015; Sun et al., 2013, 2014), omitting negative-photochromism phenomenon (Tian & Tian, 2014a,b), and increase in fatigue resistance of the dye (Crano, 2002; Klajn, 2014).

To increase photostability, lifetime, fatigue resistance and photochromic efficiency of chromophores in polar media (like cellulose), polymer particles could be preferably linked covalently to the matrix through specific processes (Sun et al., 2013, 2014). Functionalization of photochromic copolymers is a successful strategy to immobilize them onto other substrates through chemical bonding (Abdollahi et al., 2015). Glycidyl methacrylate (GMA), which bears an epoxy functional group, is a good candidate for preparation of such reactive polymeric particles and their involvement in stimuli-responsive cellulosic papers through a simple substitution-nucleation or ring-opening reaction.

Sun et al. (2013, 2014) has recently reported the preparation of photochromic papers by using latex particles and cellulose nanocrystals (CNC) as the carrier for spiroxazine dye. In both studies, spiroxazine was incorporated into the carrier by doping and subsequent impregnation of the paper with these carriers. Hence, they showed a developed photostability, fatigue resistance, photochromic properties and lifetime of the spiroxazine in the cellulosic matrix in comparison with simple impregnation with spiroxazine solutions. Introducing a carboxylic derivative of spiropyran to cellulose through esterification reaction between hydroxyl groups of cellulose and carboxylic moieties of spiropyran was investigated by Tian et al. (W. Tian & Tian, 2014b). It could be concluded from several reports that utilization of appropriate polymer carriers to immobilize spiropyran into cellulose matrix would prevent negative photochromism phenomenon (Crano & Guglielmetti, 1999; Tian & Tian, 2014a,b), irreversible color changes (Abdollahi et al., 2015; Sun et al., 2013, 2014) and also decrease in photochromic behavior in addition to the increase in fluorescence efficiency. The irreversible photochromic responses are attributed to the stabilization of colored form of spiropyran (MC intermediate) through formation of hydrogen bonding between MC zwitterion and highly polar medium of cellulose (Tian & Tian, 2014a). Therefore, polymer carriers can play an influential role in the final properties of stimuli-responsive materials.

In this paper and in continuum to our recent study (Abdollahi et al., 2015), we report a simple and green strategy for preparation of new stimuli-responsive cellulosic papers through chemical modification of cellulose. Photochromic epoxy-functionalized latex (PL) particles were prepared through semi-continuous emulsion polymerization with narrow size distribution and particle size below 100 nm. The obtained PL copolymer was treated with microcrystalline cellulose (MCC) via ring-opening reaction. MCC was chosen primarily as a model compound to follow the reaction and performing optimizations before employing general-purpose cellulose fibers. The result of affecting parameters for conducting this reaction were investigated by FTIR spectroscopy, crystallography, thermal and thermo-mechanical analyses. Then, stimuli-responsive paper pulps were fabricated. After full characterization, photochromic and solvatochromic properties were studied in dry and wet conditions in some different polar and non-polar solvents. To the best of our knowledge, this is the first report on preparation of such novel stimuli-responsive cellulosic paper, which specifically points out the chemical modification of cellulose by PL particles without observing any negative photochromism. This may open up a research area and introduce new cellulosic materials for chemical detectors, optical switches and authentication systems.

2. Experimental

2.1. Materials

2,3,3-trimethylindolenin, glycidyl methacrylate (GMA), microcrystalline cellulose (MCC; 20 μm) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich. High quality filter paper (MUNKTELL-Grade: 391, Lot No: 09-158, made in Bärenstein, Germany) was used here. All of the solvents and 2-hydroxy-5-nitrobenzaldehyde, methyl methacrylate (MMA), potassium persulfate (KPS), sodium hydrogencarbonate ($NaHCO_3$), triethylamine, Triton X-100, 2-bromoethanol and acryloyl chloride were supplied by Merck Chemical Co. All chemicals were used without further purification. Deionized (DI) water was used in all recipes.

2.2. Synthesis of epoxy- functionalized photochromic particles

The photochromic latex (PL here and PL-10-D in reference #32) containing spiropyran dye (3 wt% relative to the total acrylic monomers) and epoxy functional groups from GMA (10% wt relative to the total amount of monomers) were prepared by semi-continuous emulsion polymerization according to our recent published work (Abdollahi et al., 2015). $NaHCO_3$, as the buffer, set pH of the obtained latex to 8–9. Size of the latex particles were in the range of 80–90 nm and had a narrow size distribution (PDI: 1.25) (Abdollahi et al., 2015). In addition, the solid content was about 10% wt and this was confirmed by the gravimetric method (supporting information).

2.3. Preparation of the photochromic cellulose samples

In order to prepare photochromic cellulose based on spiropyran (PC-series), the aforementioned PL copolymer and microcrystalline cellulose were mixed with magnetic stirrer according to the given values in Table 1 at room temperature (25 °C) for 5 h. The obtained dispersions were dried either at room temperature or at 80 °C. The