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ORIGINAL PAPER

Spectroscopic Analysis of Cotton Treated with Neutralized Maleinized Soybean Oil

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Abstract Water-soluble vegetable oil derivatives were synthesized and investigated as biobased reagents for cellulosic textiles. Maleinized soybean oil (MSO), having an acid value of 156 mg KOH/g, was neutralized with ammonium hydroxide to render it water soluble. Infrared spectroscopy indicated the formation of ester linkages during the cure of MSO treated textiles. Therefore, the formation of anhydride and amide intermediates upon heating ammonia neutralized MSO were investigated. Construction of the cyclic anhydride was observed as a pathway to esterification; however, amidation was not observed among this ammonia neutralized MSO. Neutralization of MSO with ethanolamine and triethylamine yielded secondary and tertiary amides but not esters at 160 °C.

Keywords Vegetable oil macromonomer · Maleinized soybean oil · Cotton · Esterification · Ammonia · Amine · Amidation · Succinic anhydride · Neutralized

Introduction

Polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid (BTCA) and citric acid (CA) have been identified as potential non-formaldehyde-based alternatives to 1,2-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) for finishing cotton fabrics [1–5]. BTCA exhibits wrinkle resistance similar to DMDHEU, but is more expensive [2, 3]. CA has been promoted as a renewable alternative to both DMDHEU and BTCA; unfortunately, CA treated fabrics are comparatively less resistant to wrinkling [2]. Wrinkle resistance has been attributed to the reagent's crosslinking efficiency and molecular architecture. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has proved useful in quantifying crosslinker retention and determining the esterification mechanisms between polycarboxylic acid crosslinkers and cellulose hydroxyls [1, 2, 4, 5]. DRIFTS analysis indicated that crosslinking among di-, tri-, and tetracarboxylic acids resulted from the formation of reactive 5 or 6 member cyclic anhydrides [4, 5]. Durable press reagents of aqueous ammonia neutralized, maleinized soybean oil were investigated in Johnson et al. [6]. Soybean oil is an inexpensive, renewable resource, whose triglycerides can be modified with maleic anhydride to create a flexible crosslinker. This concept of the 'flexible crosslinker' was discussed in Chen [7].

The esterification of cotton cellulose upon treatment with neutralized maleinized soybean oil (NMSO) was investigated in this study via FTIR. The reactivity of anhydrides and amide intermediates for the esterification of cellulose was of interest. Amidation of MSO anhydrides via excess ammonia is believed to result in amic acid functional triglycerides. This study has revisited the concept of amic acid modification of cellulose (since Cuculo [8]) to explore this viable reaction mechanism. Likewise, MSO reactions with and without aqueous ammonia or amine neutralization were determined from IR spectra.

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Experimental Procedures

Synthesis of Maleinized Soybean Oil

Five hundred grams (0.56 mol) of soybean oil (Alnor Oil Company, Inc., Valley Stream, NY, USA) and 83.5 mg of 2-mercaptobenzothiazole (Fluka & Riedel-de Haën, St. Louis, MO, USA) were charged into a 1,000-mL, three-neck flask equipped with condenser, stirrer, and nitrogen inlet. The reactants were heated to 100 °C and purged with nitrogen for 1 h to remove the oxygen existing in the system. 111.8 g (1.12 mol) maleic anhydride (Acros Organics, Morris Plains, NJ, USA) was added to the solution, and the temperature was increased to 215 °C and maintained for 2.5 h to yield MSO (Fig. 1) with an acid value of 155.57 mg KOH/g.

Finish Preparation

Aqueous MSO was prepared by blending 53 g of MSO with 47 g of ammonium hydroxide (29% assay, Fisher Scientific) and diluted with deionized water to prepare a 6.8 wt% MSO solution. MSO (6.8 wt%) was neutralized with ethanolamine and triethylamine (3 wt%, Acros Organics, Morris Plains, NJ, USA) in place of ammonia to study the effect of different neutralizing agents. Amine neutralized solutions were dissolved in tetrahydrofuran (THF) and 10 wt% water.

Cotton fabrics were also treated with 3.6 wt% soybean oil dissolved in hexanes and 10 wt% MSO dissolved in THF (both solvents were obtained from Fisher Scientific, Pittsburgh, PA, USA). Cotton fabrics treated with 5 wt% maleamic acid (Aldrich, St. Louis, MO, USA), were dried at 50 °C for 30 min, cured at 150 °C for 6 min, and rinsed with ammonium hydroxide for 4 min.

FTIR Spectroscopy

All IR spectrometer scans were collected at 128 scans and a resolution of 4 cm^{-1}. Molecular functionalities were identified from FTIR spectra of NMSO collected on a sodium chloride disc. The spectra of aqueous ammonium hydroxide neutralized MSO was collected using the diamond tip probe of ReactIR™ 4000 (Mettler Toledo) against a water background. Thin film and solution spectra were normalized to C–H stretching at 2,926 cm^{-1} [9].

Reaction mechanisms were characterized via DRIFTS using a Digilab FTIR spectrometer in conjunction with a BioRad diffuse reflectance attachment. Samples were prepared by filling the depth of the sample holder with smooth stacked layers of treated fabric. Potassium bromide was employed as the background for IR scans. Spectral data were normalized to the C–H bending peak at 1,319 cm^{-1} [2, 4, 5] with a common baseline.

Results and Discussion

Soybean Oil and MSO Reference Spectra

Cotton fabrics, treated with soybean oil (3.6 wt% in hexane) and MSO (10 wt% in THF), were dried under ambient conditions, warmed to 80 °C, and cured at 160 °C. Cured MSO treated cotton had been rinsed with potassium hydroxide and ammonium hydroxide prior to DRIFTS analysis. The DRIFTS spectra of the treated cotton fabrics and cellulose subtraction spectra are shown in Fig. 2i, ii. The FTIR spectra display the triglyceride ester carbonyl at 1,744 cm^{-1} [9], and the asymmetric and symmetric stretches of cyclic anhydride functionalities at 1,786 and 1,861 cm^{-1} [4, 5, 9, 12]. Free acid carbonyls of MSO are

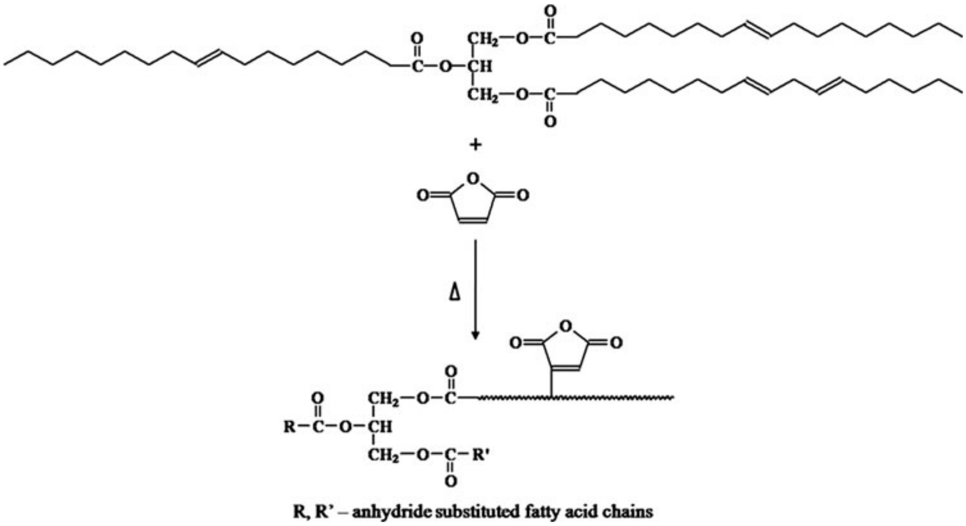
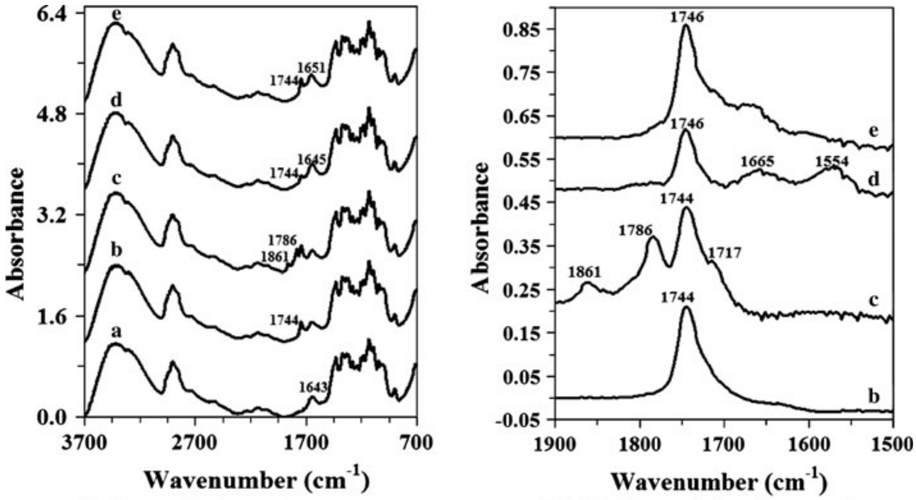


Fig. 1 Synthesis of MSO



(i) Normalized spectra overlay.

(ii) Cellulose subtraction spectra.

Fig. 2 DRIFTS **i** normalized spectra and **ii** cellulose subtraction spectra of *a* untreated cotton, *b* soybean oil treated cotton and *c* MSO impregnated cotton fabric heated to 80 °C for 6 min and cured at 160 °C for 4 min, *d* cured MSO treated cotton 'c' rinsed with potassium hydroxide, *e* cured MSO treated cotton ''c' rinsed with ammonium hydroxide

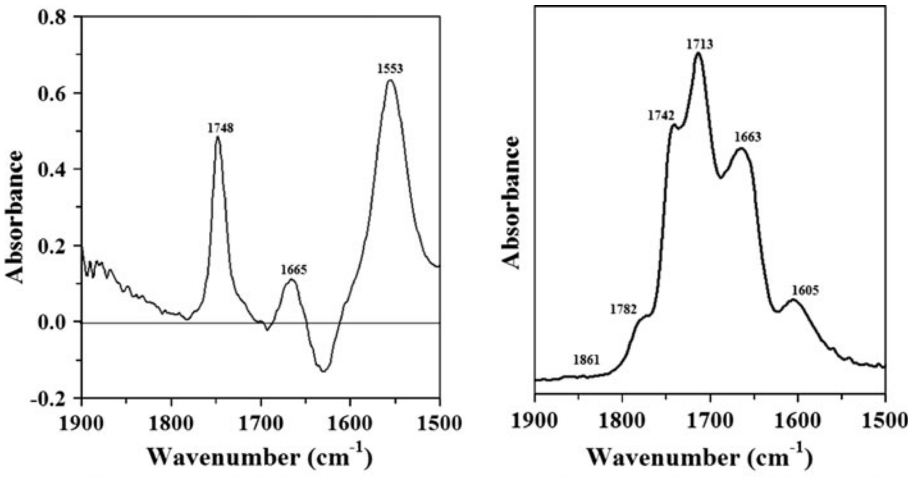
noted by the 1,717 cm^{-1} peak (Fig. 2iic) and are attributed to ring opening of some anhydride moieties [4, 5, 9].

Alkaline rinses convert the anhydrides to their carboxylate salts and facilitate the distinction between carbonyls of the cellulose ester and free acids [5]. The subtraction spectra of MSO treated cotton rinsed with potassium hydroxide (Fig. 2iid) shows a distinct peak for carboxylate anions at 1,554 cm^{-1} [5]. Ammonium carboxylate functionalities also assist in the removal of unreacted MSO. The subtraction spectra of MSO revealed a reduction in the triglyceride ester peak at 1,746 cm^{-1}, which is indicative of MSO content after rinsing in Fig. 2iid. The spectra of cured MSO/THF treated fabrics did not reveal absorbance peaks/shoulders indicative of esterification with cellulose.

Water retained by cotton displayed a bending absorbance peak at 1,643 cm^{-1} (Fig. 2i) [10, 11]. Removal of the absorbed water is very difficult, such that elevated temperature leads to hydrolytic degradation of cellulose rather than desorption [10]. Alkali rinsing shifted the water bending peak to a higher frequency; this behavior is due to water interactions with potassium ions [11]. A broad peak at 1,665 cm^{-1} (Fig. 2iid) represented potassium ions in interaction with absorbed water.

Ammonium Hydroxide Neutralized MSO Reactions

A spectrum of aqueous MSO was analyzed to elucidate peaks after incorporation of the base. NMSO was prepared with an excess of ammonia (10 mol of ammonia to 1 mol of anhydride). The ionization of ammonium hydroxide NMSO was observed in real time via in situ IR spectroscopy using a ReactIR™ spectrometer (Fig. 3i). The strong absorbance peak at 1,553 cm^{-1} without accompanying peaks indicative of cyclic anhydrides (~1,788 and 1,861 cm^{-1}, Fig. 2ic, iic)



(i) Aqueous NMSO solution.

(ii) NMSO dried at 50 °C for 30 minutes and cured at 160 °C for 6 minutes.

Fig. 3 NMSO solutions **i** ReactIR spectra of aqueous ammonia hydroxide NMSO **ii** Ammonium hydroxide NMSO dried at 50 °C for 30 min and cured at 160 °C for 6 min and carboxylic acids (~1,716 cm^{-1}) confirmed ionization into its ammonium salts [4, 5, 9, 12]. The 1,665 cm^{-1} peak, which is similarly observed in subtraction spectra (Fig. 2iid) of KOH rinsed MSO treated fabric, represented alkaline moisture interacting with the MSO.

NMSO was dried in an aluminum weighing dish for 30 min at 50 °C and subsequently cured for 6 min at 160 °C. The resulting film was transferred to a sodium chloride plate for IR analysis. The spectrum, Fig. 3ii, indicated the presence of alkaline moisture by the absorbance peak at 1,665 cm^{-1} and ammonium ions by the peak at 1,605 cm^{-1}. Other peak determinations from cured NMSO include the triglyceride ester (1,742 cm^{-1}), carboxylic acid (1,713 cm^{-1}), and cyclic anhydride (1,782 and 1,861 cm^{-1}) [4, 5, 9, 12].

Cellulose subtraction spectra of aqueous ammonia NMSO immersed fabrics (Fig. 4) displayed triglyceride ester absorbance at 1,744 cm^{-1}. Alkaline moisture (1,668 cm^{-1}) and carboxylate acids (1,557 cm^{-1}) that were observed among MSO at 80 °C (Fig. 4a) were no longer observed at 160 °C (Fig. 4b). The removal of ammonium salts was further confirmed by the disappearance of absorbance around 1,605 cm^{-1}, which intersects with carboxylate absorbance (Fig. 4a). Acid carbonyl groups absorb at 1,717 cm^{-1}. Upon rinsing with ammonium hydroxide, some of the anhydrides were hydrolyzed to ammonium carboxylate salts; the mild absorbance at 1,557 cm^{-1}. The broad shoulder alongside the triglyceride ester peak (seen in Fig. 4c but not in MSO/THF treated cotton in Fig. 2iid,) has been attributed to ester linkages between MSO and cellulose. Yang et al. [5] recorded ester absorbance in the range of 1,714–1,732 cm^{-1} from cotton fabrics heat-treated with succinic anhydride at 100 °C. Dehydration of MSO ammonium salts releases ammonia and water to form anhydrides. Figure 5i shows the reaction mechanism between cellulose and ammonia neutralized MSO which yields one acid moiety per ester carbonyl.

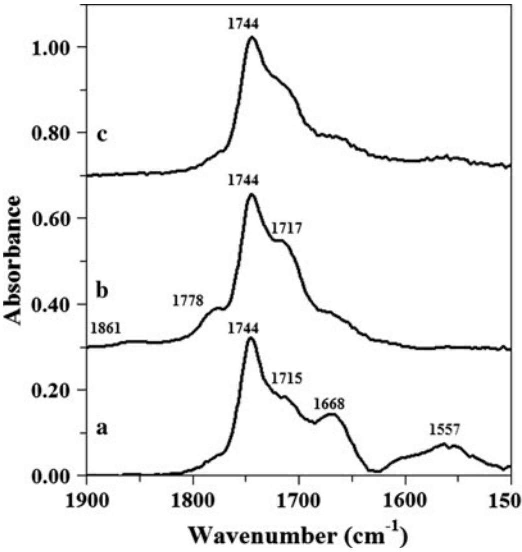


Fig. 4 Cellulose subtraction spectra of ammonium hydroxide neutralized MSO treated fabric *a* dried at 80 °C for 6 min; *b* dried at 80 °C for 6 min and cured at 160 °C for 4 min; *c* dried at 80 °C for 6 min, cured at 160 °C for 4 min, and rinsed with ammonium hydroxide for 4 min

Ammonia is believed to enable esterification that is not feasible with treatment of un-neutralized MSO dissolved in THF (Fig. 4iid). Yang et al. [13, 14] observed that macromonomers are unable to penetrate the microstructure of cellulose as well as small molecules. However, Ford et al. [15] observed that NMSO (156 mg KOH/g) penetrated the amorphous domains of cellulose by the study of X-ray diffraction. Ammonia neutralization enhanced the accessibility of reaction sites upon curing [15], and anhydrides are given the opportunity to react with cellulose hydroxyl groups. Ekman et al. [16] reported the use of liquid ammonia to increase the accessibility of cellulose hydroxyls groups for reaction with the reagent.

The subtraction spectrum of aqueous ammonia rinsed MSO/THF treated fabric (Fig. 2iie) showed absorbance between the characteristic absorbance peaks for carboxylic acids (1,718 cm^{-1}) and alkaline water (1,672 cm^{-1}), which is attributed to the synthesis of amides. The amidation reaction between cyclic anhydrides and ammonia is described by Smith and March [17]. Further evidence of amide formation from IR analysis is shown in the spectra of maleamic acid treated cotton (Fig. 6) and cotton treated with amine NMSO (Fig. 7i). The plausible mechanism of cellulose esterification from amides, formed as byproducts of MSO in the presence of heat and ammonia, was studied with maleamic acid, which has amide and carboxylic acid functionalities, as the model compound.

Although IR analysis was not employed, Cuculo observed cellulose modification with amic acids via titration of free carboxylic acids [8]. Acid carbonyl absorbance was not observed upon drying maleamic acid treated fabric at 50 °C for 30 min (Fig. 6ia, iia) due to salt formation with primary amide functionalities [17]. Amide carboxylate acids are denoted by absorbance at 1,557 cm^{-1} (Fig. 6ia, iia). Proton transfer from carbonyl acids to amide functionalities produces protonated amides [18], which absorb at 1,699 cm^{-1} in Fig. 6ia, iia. Maleamic acid treated fabric that was cured at 150 °C for 6 min exhibited a 1,722 cm^{-1} peak, which is composed of esters and carboxylic acids (Fig. 6ib, iib). After alkaline rinsing, free acids were converted to ammonium salts (Fig. 6ic, iic) and unreacted maleamic acid was removed. Esters were distinguished at 1,721 cm^{-1} (Fig. 6iic). The reaction mechanism of maleamic acid treated fabrics, based on IR spectra presented in Fig. 6, is shown in Fig. 5ii.

The synthesis of amide functionalities in situ is feasible, as observed from MSO treated cotton, which had been

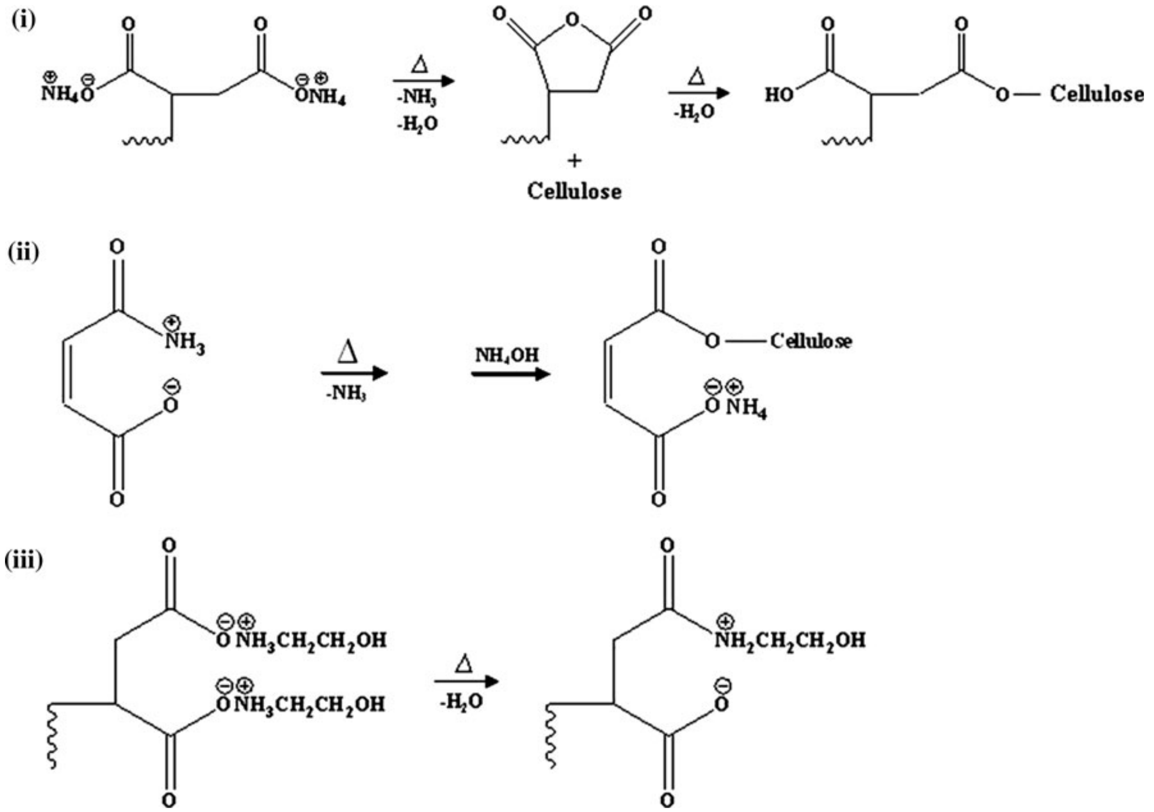
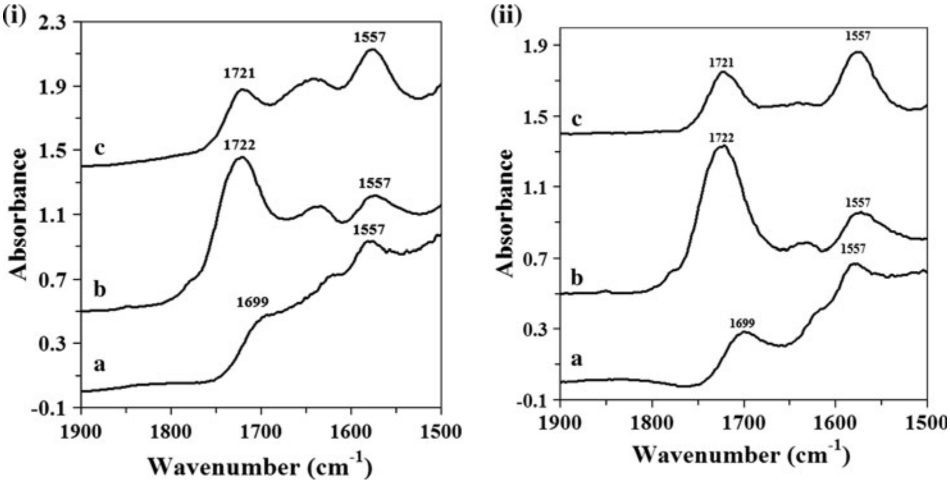


Fig. 5 MSO reactions: **i** Ammonia neutralized MSO reactions, **ii** maleamic acid mechanism of cellulose modification, **iii** idealized amide condensation reaction from carboxylate salt

Fig. 6 Cellulose **i** normalized spectra and **ii** subtraction spectra of 5 wt% maleamic acid *a* dried at 50 °C for 30 min; *b* dried at 50 °C for 30 min and cured at 160 °C for 6 min; *c* dried at 50 °C for 30 min, cured at 160 °C for 6 min, and alkaline rinsed



rinsed with ammonia (Fig. 2iie). However, no indication of amide functionalities was observed from the spectrum of ammonium hydroxide NMSO treated fabrics (Fig. 4).

Amine Neutralized MSO

The mechanism of in-situ amide formation was further elucidated with DRIFTS subtraction spectra of MSO neutralized with ethanolamine and triethylamine (Fig. 7i, ii). At 80 °C, free acid moieties formed in fabrics treated with amine neutralized MSO were completely converted to carboxylate anions (Fig. 7ia, iia). Furthermore, alkaline water (absorbance around 1,645 $\mathrm{cm^{-1}}$) is retained by MSO neutralized with ethanolamine (absorbance ~1,650 $\mathrm{cm^{-1}}$, Fig. 7ia) rather than triethylamine (Fig. 7iia).

The molecular architecture of the neutralizing amine influences the amide pyrolysis temperature. Hee and Sutherland studied the pyrolysis of various amine salts of

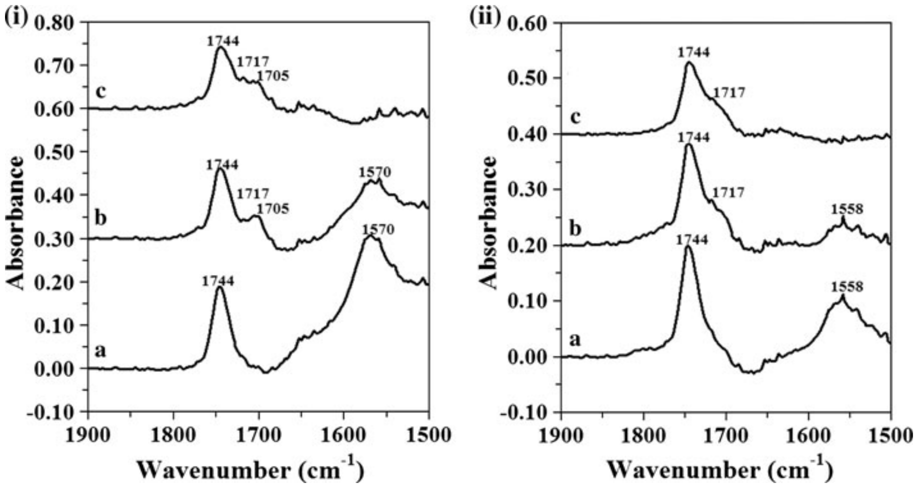


Fig. 7 Cellulose subtraction spectra of MSO neutralized with **i** ethanolamine and **ii** triethylamine: *a* dried at 80 °C for 6 min; *b* dried at 80 °C for 6 min and cured at 160 °C for 4 min; *c* dried at 80 °C for 6 min, cured at 160 °C for 4 min, and rinsed with ammonium hydroxide for 4 min

2,4-dichlorophenoxyacetic (2,4-D) acid and observed that the dehydration of amine salts is impeded by longer chain lengths of the substituted amine [19]. The dimethyl amine salt of 2,4-D acid was more stable than the 2,4-D salts of primary amines such as methyl amine and *n*-butyl amine [19, 20]. Carboxylate salts from ethanolamine and triethylamine are expected to be more stable than those of ammonia; indeed, salts from substituted amines were observed in greater quantities at 80 and 160 °C (Fig. 7ia, ib, iia, iib) than ammonium salts (Fig. 4a, b).

Upon curing, MSO neutralized with ethanolamine at 160 °C for 4 min exhibited an additional peak at 1,705 cm^{-1} (C=O stretching peak) between the ester carbonyl peak (1,717 cm^{-1}) and carboxylate acids (1,570 cm^{-1}) (Fig. 7ib). The 1,570 cm^{-1} carboxylic acid peak decreased upon curing as the 1,705 cm^{-1} peak formed (Fig. 7ia, ib). This transition is attributed to secondary amides generated from dehydrated carboxylate salts of ethanolamine. A scheme of this reaction mechanism is shown in Fig. 5iii. The high frequency absorbance observed for the secondary amide resulted from protonation [18] in Fig. 7ib, ic. Spinner's investigation of proton addition to the basic nitrogen showed that the primary amide absorbance of acetamide increased from 1,684–1,718 cm^{-1} [18].

The subtraction spectra of MSO neutralized with triethylamine (Fig. 6ii) did not display a carbonyl peak between the carboxylic acid carbonyl peak (1,717 cm^{-1}) and carboxylate acids (1,570 cm^{-1}) at either 80 or 160 °C (Fig. 6iia, iib), because the trialkyl substitution characteristic of triethylamine, does not facilitate the condensation reaction for amide formation [18, 20]. Unlike aqueous ammonia (Fig. 4b), the spectra of MSO neutralized with ethanolamine and triethylamine did not exhibit anhydride formation at 160 °C. Shoulders implying esterification were not observed along the 1,744 cm^{-1} peak among spectra of cured and ammonium hydroxide rinsed samples of amine NMSO (Fig. 7ic, iic). Therefore, reactive anhydrides or primary amides are necessary intermediates for esterification.

Free carboxylic acids remained (1,717 cm^{-1}) even upon ammonium hydroxide rinsing (Fig. 7ic, iic) of amine NMSO. The inability to convert acids to carboxylate salts of ammonium suggests these functionalities have been shielded by hydrophobic branches of the vegetable oil triglycerides.

Conclusion

Carboxylated soybean oil derivatives were investigated as crosslinking reagents capable of esterifying cotton fabrics. IR spectroscopy was used to determine cellulose esterification mechanisms with MSO. Subtraction spectra enabled dissemination of (inter/intra)molecular reactions and functionalities. Ammonia neutralization rendered the soybean oil derivatives water-soluble without the use of organic cosolvents. Furthermore, no esterification was observed in the absence of ammonium hydroxide, during cure i.e. fabrics treated with MSO dissolved in THF. Esterification was implied by peak broadening along the triglyceride ester. Amidation was only observed among ethanolamine NMSO functionalities and an ammonium hydroxide rinse of MSO anhydrides. Esterification via the primary amides of maleamic acids was observed, but not through the secondary amide that was formed in situ (between succinic acid functional MSO and ethanolamine).

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