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Durable Press Finish of Cotton via Dual Curing Using UV Light and Heat

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Abstract: Continuous photografting/crosslinking of polyethyleneglycol dimethacrylate oligomers onto cotton using a water-soluble benzophenone photoinitiator was investigated. Photografting increased with increasing irradiation dose, oligomer concentration and photoinitiator concentration. Maximum grafting efficiency of DM 400 and 600 were 83% and 79%, respectively. The photografting increased the wrinkle resistance of cotton implying surface crosslinking of cotton. Both surface crosslinking and bulk crosslinking of cotton were accomplished via dual curing of a mixed formulation containing both a thermally curable component (BTCA/SHP) and a UV-curable component. The wrinkle resistance of the crosslinked cotton was found to be higher when cured by thermal curing after UV curing rather than by UV curing after thermal curing due to the facile post-polymerization of the UV active component. The presence of crosslinks in the dually crosslinked cotton was verified with FT-IR and thermogravimetric analysis.

Keywords: Dual curing, Photografting, Crosslinking, UV curing, Wrinkle resistance

Introduction

Polycarboxylic acids, such as butanetetracaboxylic acid (BTCA) and citric acid, have been studied as durable-press finishing agents which could eliminate the formaldehyde release of the crosslinked cotton with conventional dimethyloldihydroxyethylene urea (DMDHEU)[1]. Among the formaldehyde-free polycarboxylic acids, BTCA with sodium hypophosphite has been widely known for its superior performances such as excellent durable press apppearance, high fabric strength retention, and durability to repeated laundering[2]. However the strength deterioration of the crosslinked cottons, particularly abrasion resistance, has not been fully solved in the reactant crosslinker finishing [3,4]. Various methods have been tried in the textile science community to overcome such deficiencies in the crosslinked cotton including wet-fixation[5], polymerization-crosslinking [6-8]. The processes shared a common principle in that they encouraged the polymer deposition and/or the formation of long, flexible crosslinks rather than simple and short crosslinks within cotton cellulose. A new polymerization-crosslinking treatment was reported to imparte excellent strength retention properties such as improved abrasion resistance of crosslinked cotton even comparable to untreated cotton[9]. The study involved the polymerization/crosslinking of itaconic acid and maleic acid using potassium persulfate and sodium hypophosphite as a polymerization initiator and an esterification catalyst respectively.

Photografting of various monomers and oligomers has been studied for modifying the properties of various substrates such as synthetic and natural polymers[10,11]. Cationic photopolymerization of a polysiloxane diepoxide via UV curing technique has been reported to impart both crease resistance and excellent abrasion resistance retention to crosslinked cotton with DMDHEU[12]. This study intends to investigate the crosslinking of cotton via dual curing of a mixed formulation, which is cured by both UV light and heat as energy sources. The formulation was composed of photocurable and thermally curable systems: the photocurable system contains a bifunctional photocurable prepolymer and a photoinitiator, while the thermally curable system consists of a tetrafunctional BTCA as a formaldehyde-free crosslinker and sodium hypophosphite as a thermal catalyst. The photocurable formulation can induce photo-polymerization and photocrosslinking at the same time, possibly contributing to enhanced wrinkle resistance and strength retention of the crosslinked cotton.

Experimental

Materials

Bleached plain weave cotton fabric (109 g/m^2) was used throughout this study. UV active polyethyleneglycol dimethacrylate 400 (DM 400) and 600 (DM 600) were purchased from Aldrich and their approximate molecular weights were 536 and 875, respectively. 4-benzoyl(benzyl) trimethylammonium chloride (BTC, Aldrich) was used as a photoinitiator. 1,2,3,4-butanetetracarboxylic acid (BTCA) and sodium hypophosphite monohydrate (SHP) were obtained from Aldrich and Duksan Chemical Co., respectively. Polyethyleneglycol 400 (PEG 400) and 600 (PEG 600) from Junsei Chemical Co. were used as ingredients in the thermal curing of BTCA. All chemicals were used as received.

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Dual Curing and Thermal Curing

All fabrics were impregnated by padding through the liquor trough to give an approximately 80-90% wet pickup with an aqueous formulation. The padded samples were not dried before curing. Two types of dual curing were performed by combining thermal curing and UV curing in different sequences: UV-T and T-UV indicate the curing sequence of thermal curing after UV curing and vice versa, respectively. For the UV curing step, the amount of photoinitiator within the formulation was 3% o.w.p. (on the weight of UV active prepolymer concentration) unless stated otherwise. The padded fabrics were cured using a laboratory UV curing machine (F-450, Fusion Co.) having a D bulb (120 W/cm). A standard cure time of 4×4 passes (4 passes on each side of the fabric) was used at the conveyer speed of 4.6 m/min (1.26 J/pass/cm^2) unless stated otherwise. In the thermal curing step, the padded fabric was mounted on a pin frame and cured at 180°C for 3 minutes in a stenter without drying. For heat-only treatment of BTCA/SHP, cotton fabric was padded with an aqueous formulation consisting of various amounts of BTCA and 0.3 mole ratio of SHP with respect to BTCA with or without PEG addition, then the fabrics were dried at 80°C for 3 minutes and cured at 180°C for 3 minutes. The cured fabrics were washed with water and dried at room temperature.

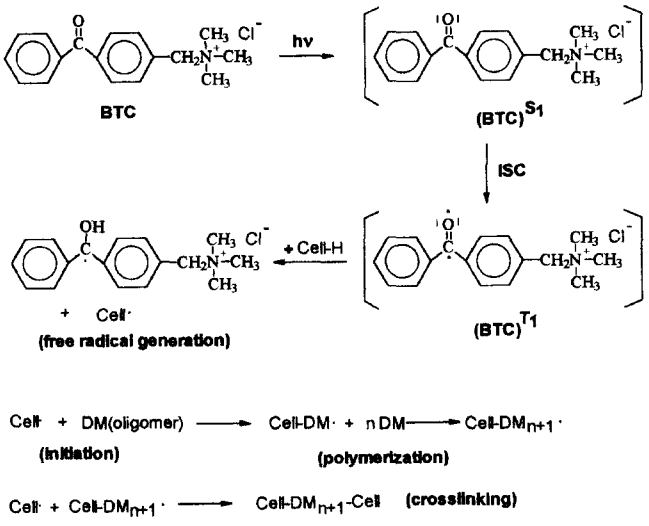
Analysis of Untreated and Crosslinked Cotton Fabrics

Add-on and % grafting were determined gravimetrically by measuring the weight increase of treated fabric after washing and drying under vacuum. Grafting efficiency was calculated from the percentage of the reacted with respect to the amount of applied UV active oligomers. Laundering was done according to AATCC 124-1989 followed by tumble drying. The standard methods used to evaluate performance properties of the treated fabric were as the following: conditioned crease recovery angle by AATCC 66-1984, breaking force and elongation by ASTM D 5035-90 (strip force), Elmendorf tear resistance by ASTM D 1424-83, Stoll flex abrasion resistance by ASTM D 3885-92, and durable press rating by AATCC 124-1989. Wet crease recovery angle was measured according to the methods of AATCC 66-1984 except that the samples were immersed in distilled water at least 20 minutes and excess water on the fabric was blotted with filter paper before testing. The influence of treatment on fabric handle before and after crosslinking was assessed with Kawabata Evaluation System for Fabric (KES-F). FT-IR spectra were obtained with a FT-IR spectrophotometer (MIDAC) using potassium bromide pellet technique. A Seiko SSC/5200 thermal analyser was used to perform thermogravimetric (TG) and differential thermogravimetric (DTG) analysis. A sample was held at 50°C until it became constant weight and heated at 20°C/min to the final temperature. In the measurement of moisture regain, the preconditioned fabric at 20°C and 65% RH for at least 24 hrs was heated from 30°C to 100°C and kept at 100°C for 30 minutes.

Results and Discussion

Continuous Photografting of DM 400 and DM 600

The continuous photocurable system used in this study differs from batchwise liquid phase photografting systems in that there are only less than 90% o.w.f. (on the weight of fabric) of water available for dissolving oligomer and polymer, which dries up with increasing irradiation time due



Scheme 1. Mechanism of photografting and crosslinking during UV curing.

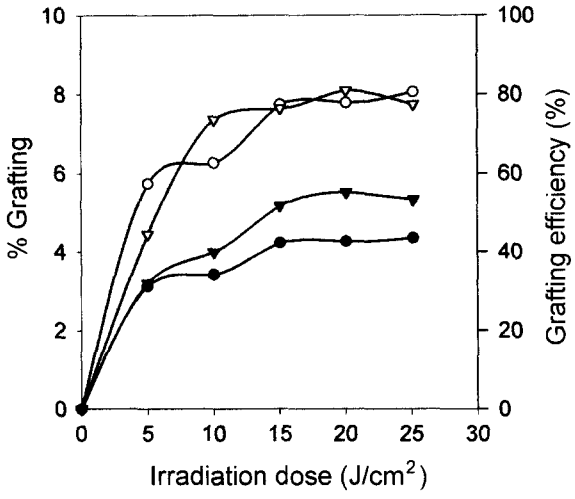


Figure 1. Effect of irradiation dose on photografting of DM 400 and 600: DM 600: % grafting, ●; grafting efficiency, ○; DM 400: % grafting, ▼; grafting efficiency, ▽. Treatment condition: DM oligomer concentration, 8% owb; photoinitiator concentration, 3% owp.

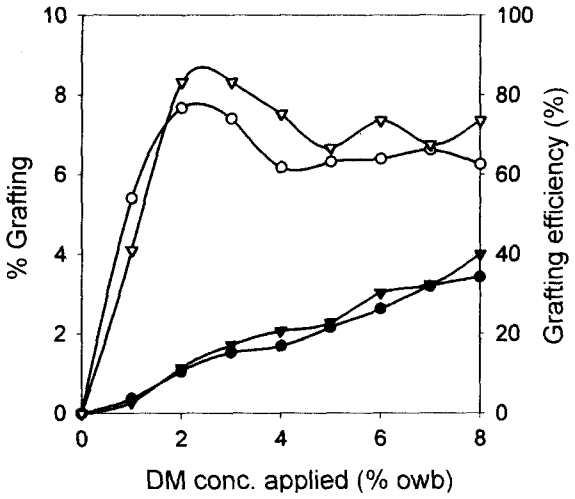


Figure 2. Effect of oligomer concentration on photografting of DM 400 and 600: Legends are the same as in Figure 1. Treatment condition: photoinitiator concentration, 3% owp; irradiation dose. 10.1 J/cm^2.

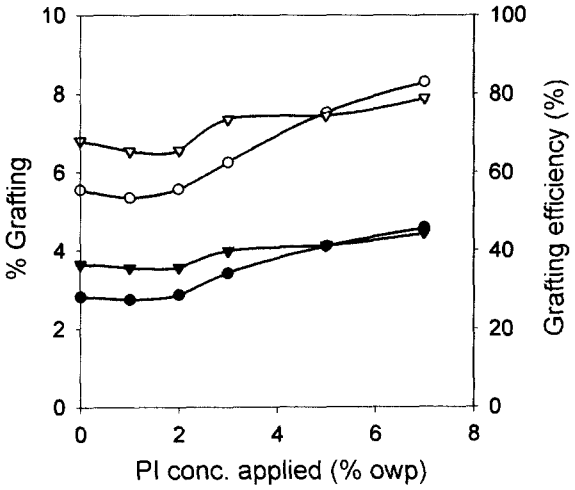


Figure 3. Effect of photoinitiator concentration on photografting of DM 400 and 600: Legends are the same as in Figure 1. Treatment condition: DM oligomer concentration, 8% owb; irradiation dose. 10.1 J/cm^2.

to the presence of infra-red emission within the spectrum of the D lamp. Photografting mechanism to be occurred during irradiation was outlined in Scheme 1. Upon UV irradiation, cellulose radicals can be generated by hydrogen abstraction of the triplet-state photoinitiator. The radicals initiate graft polymerization of DM oligomers and finally the grafted polymer chains form a polymer network.

Figures 1, 2, and 3 show dependence of % grafting and grafting efficiency of grafted cotton on irradiation time, oligomer concentration, and photoinitiator concentration, respectively. The effect of irradiation dose on the photografting of oligomers was shown in Figure 1. Approximately 80% of

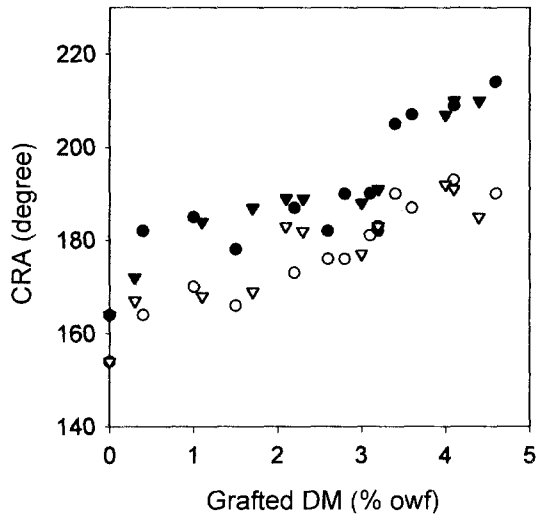


Figure 4. Effect of grafted oligomer on crease recovery angle (CRA): DM 600: dry CRA, ●; wet CRA, ○; DM 400: dry CRA, ▼; wet CRA, ▽.

grafting efficiency was readily achieved with prolonged irradiation. The grafting efficiencies of both oligomers were similar, whereas slightly higher % grafting was obtained with DM 400 oligomer than DM 600. This may be due to higher density of methacrylate groups of DM 400 than that of DM 600 at the same application level.

The % grafting of DM 400 and DM 600 increased with increasing application level (Figure 2). It was observed that grafting efficiency reached an optimal point around 2 to 3% o.w.b. (on the weight of bath) since the optical density of the padded formulation increased with increasing UV active prepolymer concentration. The increase in optical density of the formulation may result in preventing the UV light reaching the interface between the fiber surface and the formulation, thus yielding more pronounced homopolymer formation to be rinsed off during washing. The effect of photoinitiator concentration on the % grafting and grafting efficiency was shown in Figure 3. With increasing photoinitiator concentration both values increased accordingly. However it was found that the oligomers can be grafted even without a photoinitiator because irradiated cellulose molecules with 340 nm or shorter wavelength are able to generate polymeric radicals and hence they can initiate photografting without a photoinitiator[13].

Durable Press Performance of Crosslinked Cotton Via Dual Curing Technique

The effect of photografting on the wrinkle recovery of treated fabric was shown in Figure 4. Both dry and wet crease recovery angles (CRAs) gradually increased with increasing amount of grafted oligomers: the increment of both recovery angles reached up to ca. 50 degree. Different chain lengths of the DM 400 and 600 had little effect on the

recovery angle. However the improved CRA was not sufficient for wrinkle resistant finish of cotton fabric because polymer networks/crosslinks by photografting could locate largely in the surface region due to limited penetration of UV light.

Therefore we employed BTCA, a formaldehyde-free crosslinker, as a component for bulk-crosslinking of cotton in the dual curing system. Although the crosslinker has been known for excellent performance, photografting of DM may enhance overall performance including mechanical strength retention and durable press rating. Either heat-only or UV-only treatment of the mixed formulation, consisting of the thermally-curable BTCA/SHP component and the UV curable DM/BTC component, did not produce significant improvement in wrinkle resistance because the crosslinking reaction of each component was limited due to the presence of the other component. The influence of dual curing

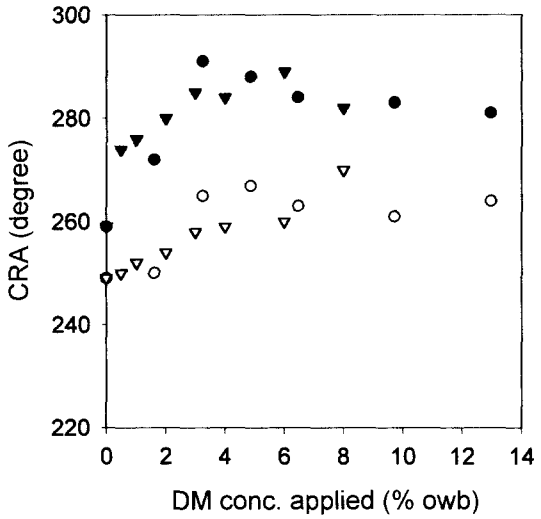


Figure 5. Effect of oligomer concentration on dry and wet CRA in UV-T dual curing: DM 600: dry CRA, ●; wet CRA, ○; DM 400: dry CRA, ▼; wet CRA, ▽; BTCA concentration, 4.7% owb.

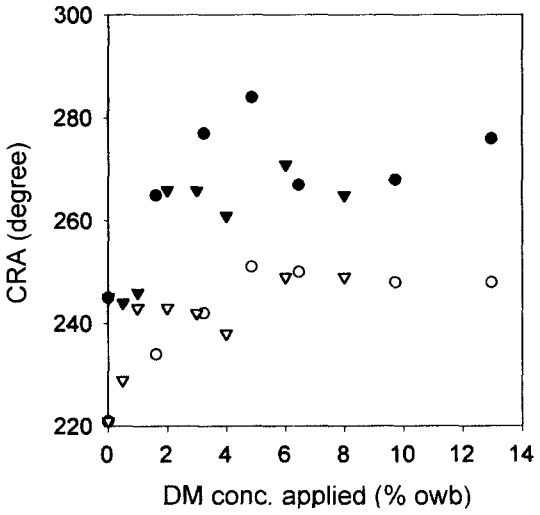


Figure 6. Effect of oligomer concentration on dry and wet CRA in T-UV dual curing: Legends are the same as in Figure 5.

Table 1. Durable press performance of crosslinked cotton

Treatment	Add-on (% owf)	CRA		WI	Tensile		AR	TS		%R	DP rating
		Dry	Wet		BS	%E		W	F		
Untreated	0	164	154	60	100	100	100	100	100	100	1.2
BTCA	3.9[a]	263	237	57	58	78	14	54	50	91	3.3
	5.5[a]	295	261	57	52	75	9	46	41	73	3.5
	6.9[a]	304	264	57	46	70	7	42	41	70	3.5
	8.5[a]	311	281	53	45	67	6	40	33	66	3.7
BTCA/PEG 600	5.6[b]	269	254	57	58	79	12	-	52	-	-
BTCA/DM 600	6.0[c]	291	265	52	60	82	16	56	60	87	3.3
	7.0[c]	288	267	48	59	79	14	52	54	87	3.4
	7.8[c]	284	263	47	64	80	13	52	50	84	3.4
	5.5[d]	263	256	44	65	82	17	47	50	87	3.4
	7.9[e]	301	266	47	51	54	5	53	-	-	-
BTCA/PEG 400	5.6[b]	279	254	57	57	72	13	-	51	-	3.4
BTCA/DM 400	4.7[c]	280	254	51	65	83	14	53	53	-	3.3
	5.2[c]	285	258	51	61	81	14	54	54	-	3.5
	5.8[c]	284	259	52	60	80	16	53	56	-	3.5
	8.2[d]	302	264	50	57	57	6	52	-	-	-

BS, %E, TS, AR, %R denote retention of breaking strength, percent elongation, tearing strength, stoll flex abrasion, moisture regain, respectively; CRA: crease recovery angle; WI: whiteness index.

Treatment condition: thermal cure, [a]BTCA of 4.7, 7, 9, 11% owb; [b]BTCA, 4.7% owb; dual cure(UV-T), [c]BTCA, 4.7% owb; [d]BTCA, 4.7% owb with 7% owp of BTC, [e]BTCA, 7% owb.

sequence on the wrinkle recovery of padded cotton fabric with the dually curable formulation was given in Figures 5 and 6. It was observed that dual curing of mixed formulation produced better crease recovery than both single treatments such as UV curing or thermal curing and more importantly thermal curing after UV curing (UV-T) gave higher recovery angles than the reverse sequence (T-UV). This may be caused by the fact that dark post-polymerization, polymerization of UV curable component after UV radiation, was encouraged additionally by the heat provided from the following thermal curing step because post-polymerization is entirely a thermal process[14]. However the sequence of UV curing after thermal curing could not aid the post-polymerization of DM oligomers. Also it was found that there were optimal concentrations of DM 400 or 600 in achieving best resiliency of the treated. Excessive crosslinking of DM oligomers may deter crosslinking of BTCA in UV-T dual curing and vice versa in the case of T-UV dual curing.

Figure 7 shows the effect of PEG 400 and 600 addition in the BTCA/SHP system which was cured by heat only. The PEGs can react with BTCA and become a part of network structure because they contain two hydroxyl groups at both ends of each molecule. As expected, enhanced CRA were obtained with both PEGs but the obtained CRA level was lower than the previous dual-cured samples, particularly with UV-T sequence, because some of carboxylic groups in BTCA molecules were unable to crosslink cotton due to the esterification of BTCA with PEGs.

Durable press performance of dual-cured fabrics was summarized in Table 1. In general the mechanical strengths of dual-cured cotton, particularly abrasion resistance, were slightly higher than those of fabric crosslinked with BTCA alone irrespective of the kinds of the DM oligomers. The improvement in mechanical strengths of dual cured fabric was comparable to the thermal cured samples containing small amount of PEG 400 or 600 as an additive, implying that flexible polyether chains within crosslinks beneficially affected the mechanical strength of crosslinked cotton. Also the improvement was coupled with higher crease recovery increase in the dually cured samples than in the thermally cured cotton with BTCA/PEGs. Additional crosslinking of DM oligomers by dual curing significantly increased the wet recovery of cured sample without sacrificing its mechanical strength compared to thermal curing of BTCA alone. Also the moisture regain of dual-cured cotton was substantially higher than that of thermally crosslinked cotton with BTCA at similar resiliency. The handle of the treated fabric was similar to the BTCA-crosslinked fabric at similar application level as shown by bending and shear properties as well as stiffness values in Table 2.

Analysis of Untreated and Crosslinked Cotton

The crosslinking between cotton cellulose and DM or

Table 2. KES-F analysis of untreated and treated cotton fabrics

Treatment	Bending		Shear		Koshi
	B	2HB	G	2HG5	(stiffness)
Untreated	0.063	0.059	1.28	5.54	6.4
BTCA(3.9%)[a)]	0.066	0.050	2.09	7.71	7.6
BTCA(5.5%)[b)]	0.074	0.056	2.05	7.27	7.6
BTCA[a)]+DM400(5.8%)	0.077	0.061	2.15	7.24	7.7
BTCA[a)]+PEG400(5.6%)	0.065	0.063	1.92	7.48	7.2

Values in parenthesis denotes add-on(% owf), [a), b)]treated with 4.7% owb and 7% owb of BTCA, respectively.

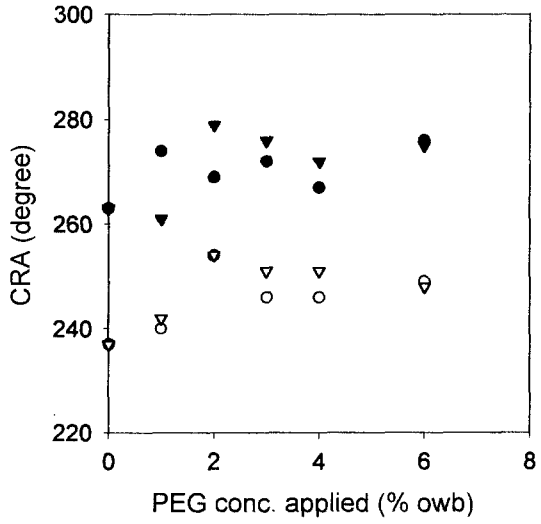


Figure 7. Effect of oligomer concentration on dry and wet CRA in thermal curing: PEG 600: dry CRA, ●; wet CRA, ○; PEG 400: dry CRA, ▼; wet CRA, ▽; BTCA concentration, 4.7% owb.

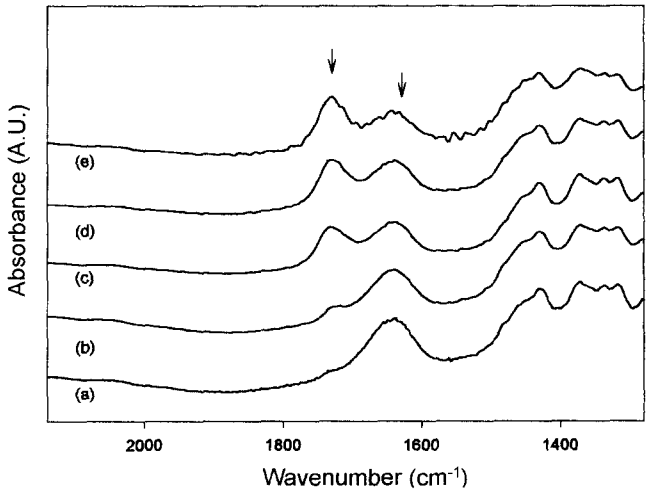


Figure 8. FT-IR spectra of untreated and crosslinked cotton: (a) untreated cotton, (b) photografted cotton with DM 600, (c) thermal-cured cotton with BTCA, (d) dual-cured cotton with BTCA and DM 600, (e) thermal-cured cotton with BTCA and PEG 600.

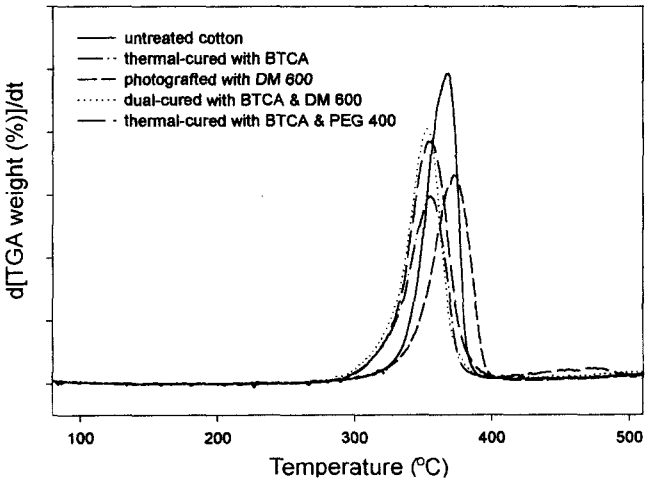


Figure 9. Differential thermogravimetric curves of untreated and crosslinked cotton.

BTCA was investigated by FT-IR spectroscopy as shown in Figure 8. Carbonyl stretchin g peak at 1728 cm^{-1} appeared in the photografted cotton with DM 600 via UV curing, probably originating from the ester groups in grafted methacrylate groups of the oligomer. The peak at 1635 cm^{-1} looks to be related with the curing because of the intensity change but it was assigned to the absorbed water within cotton[15]. Also no peak related with unreacted double bond was found. BTCA treated cotton displayed intense carbonyl stretching at the same wavenumber due to the esterification between BTCA and cellulose[16]. The dual cured fabric showed stronger carbonyl stretching compared to BTCA-crosslinked cotton. In addition even stronger carbonyl peak was found in the case of PEG/BTCA system, probably resulting from additional esterification between BTCA and PEG as well as between BTCA and cellulose.

Thermogravimetric (TG) analysis of untreated and treated cotton fabric including the derivative of weight loss (DTG) were carried out and shown in Figure 9. It has been known that durable-press reactants impart higher thermal stability to crosslinked cotton such as higher % residues and lower maximum rates of weight loss due to effective crosslinks compared to the untreated cotton[17,18]. The dual cured cotton as well as the thermally cured with BTCA alone followed the trend, while photografted cotton and BTCA treated fabric with PEG had lower percent residue at the end of heating program. All treated samples showed lower maximum rates of weight loss compared to the untreated one but peak temperatures were slightly different possibly representing their unique crosslink structures.

Conclusion

The continuous photografting of DM oligomers onto cotton with high grafting efficiency of ca. 80% was achieved by padding with the omission of additional drying step and subsequent curing of a formulation of oligomers and photoinitiator by UV light. Photografting increased progressively with increasing irradiation dose, oligomer and photoinitiator concentration. The photgrafting improved the wrinkle resistance of cotton. Dual curing of a mixed formulation consisting of photocurable and thermally curable components by UV and heat was beneficial to improve mechanical strength retention of crosslinked cotton compared to thermal curing of BTCA only or BTCA/PEG systems. UV-T sequence in the dual curing produced higher crease recovery than T-UV sequence possibly due to the post-polymerization of UV active oligomers. The higher resiliency of the dually crosslinked cotton did not cause severe handle impairment compared with BTCA-crosslinked cotton at the same application level. FT-IR and thermal analysis verified the presence of effective crosslinks in the dual-cured cotton fabric.

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