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〈Research Paper〉

# Flame-retardant Coating of Cotton Fabric via UV curing of DMEP

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**Abstract**— A new UV-curable coating was carried out to impart the flame-retardant property to cotton fabric using Bis[2-(methacryloyloxy)ehtyl]phosphate(DMEP) and 2-hydroxy-2-methyl-1-phenyl-propan-1-one(HMPP) as a UV-curable monomer and a photoinitiator, respectively. The cotton fabrics were applied with various amounts of DMEP and HMPP via padding and UV irradiation, and the optimal concentrations of DMEP and HMPP in the formulation were 40%(w/w) and 7%omp respectively. A limiteed oxygen index(LOI) up to 28.9 was obtained for the UV-cured fabric, which may occur through a condensed phase mechanism as verified by the increased residue number with increased application level. The characterization of the UV-cured coating was made by IR analysis, thermo-gravimetric analysis, LOI test, and scanning electron microscopy.

**Keywords:** *cotton, flame retardant coating, UV curing, DMEP, HMPP, LOI*

## 1. Introduction

Self-extinguishing property can be imparted to flammable textiles by incorporating various flame retardant materials based on phosphorous, nitrogen, halogens, borates, metal hydroxides and other hydrated inorganic additives[1)].

Mechanisms in flame retardancy are often explained by condensed (solid) phase or gas-phase mechanism[2)].

Active retardants such as organo phosphorous compounds alter the pyrolytic process of substrate in such a way that the amount of flammable gases produced is minimized and accordingly the amount of char formation is increased. In the gas-phase mechanism, active halogen-based compounds function as inhibitors that capture flame-propagating species, resulting in decrease in the heat returning to the substrate. Halogen-free flame retardants such as phosphorous or nitrogen based compounds have been increasingly important in commercial flame retardants for textiles because the absence of toxic gas generation during combustion process, such as dioxin and halogen acid, as well as low smoke evolution. Most of flame retardants were applied to textiles via thermal curing of water based formulations of the phosphorous or halogen compounds. Surface coatings based on photopolymerization and photocrosslinking reactions have been significantly applied for the production of high functional textiles including durable press finish of cotton[3)], shrink-proofing of wool fiber[4)], environmentally friendly low salt dyeing for cotton[5)], union dyeing for wool and cotton blend fabrics[6)] and preferential water-repellent finish to PET knit[7)], etc.

The UV curing has been widely used in several industrial applications such as graphics, inks, adhesives, and coating for paper, plastics, metals and glass surfaces. The popularity of the new technology is due to its distinct advantages of low temperature curing, fast polymerization rate, in-line production and low energy requirement as well as omission of volatile organic solvents in the formulation. UV curing has been introduced to impart flame-resistance to fibers and polymers

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using UV-curable flame retardants such as poly(bisphenol A acryloxyethyl phosphate)[8], methacrylated phenolic melamine[9], hyperbranched polyurethane acrylates[10], hyperbranched polyphosphate acrylate[11], acrylated benzenephosphonates[12], dimethyl(2-acryloxyethyl)phosphonate and oligomeric vinyl phosphonate[13], etc.

Plasma grafting of acrylate monomers containing both phosphorous and nitrogen such as diethyl (acryloyloxyethyl) phosphoramidate and acryloyl-1,3-bis(diethylphophoramidate) have been also studied[14,15]. And flame retardant coating on cotton has been reported in the radiation grafting of 2,3-diepoxypropyl methacrylate under $^{60}$Co source and successive reaction with ethylenediamine and orthophosphorous solution[16]. This study is to investigate the feasibility of DMEP as a flame retardant coating of cotton fabric via UV curing.

## 2. Materials and methods

### 2.1 Fabrics and UV-curable formulation

Scoured and bleached cotton and PET fabric were used with a size of 18.0㎝ × 12.5㎝. Bis [2-(methacryloyloxy)ethyl] phosphate (DMEP) and 2-hydroxy-2-methyl-1-phenyl-propan-1-one (HMMP) were obtained from Sigma-Aldrich and used as a phosphorous-containing monomer and photoinitiator, respectively(Scheme 1).

### 2.2 Impregnation and UV irradiation

Aqueous formulations of DMEP and HMMP were impregnated to the fabrics and squeezed to padding ratios of 90±2% using a laboratory mangle where HMMP concentration was applied on the weight of the monomer concentration (w/w%) in the formulation. The impregnated fabrics were dried at 80°C for 3 minutes and UV irradiation was performed on both fabric sides with a medium pressure mercury lamp (80W/cm) and the UV energy was adjustedby extending irradiation time with changing conveyer speed. The spectral irradiance (Fig. 1) and UV energy of the UV lamp were measured using a spectroradiometer (International light) and a Powerpuck (EIT) respectively. Also add on (A%) and add on efficiency (AE%) was determined gravimetrically based on vacuum dried weight.

$$A\ (\%) = (W_3-W_1)\ /\ (W_1)$$

$$AE\ (\%) = (W_3-W_1)\ /\ (W_2-W_1)$$

where, $W_1$, $W_2$ and $W_3$ are weights before and after irradiation and weight after water-rinsing respectively.

### 2.3 Whiteness index and limited oxygen index (LOI) measurement

CIE whiteness index was calculated from reflectance measured by a colorimeter (Coloreye 3100, Macbeth) and LOI were measured with an oxygen index combustibility tester (Yasuda Seiki Seisakusho, Japan) according to ISO 4589:2000 (Determination of burning behavior by oxygen index). Spectral UV absorbances of DMEP and HMMP were measured using a UV/Vis spectrophotometer (Agilent Technologies).

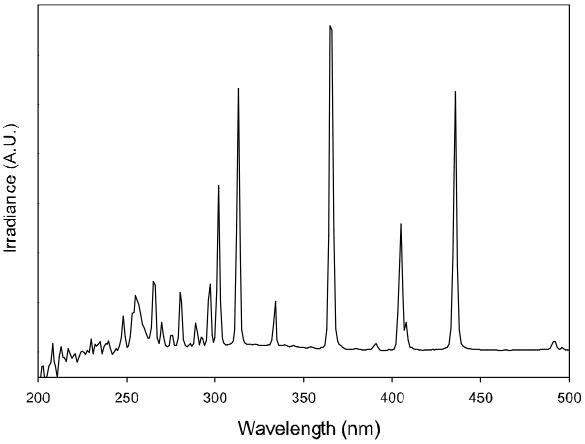
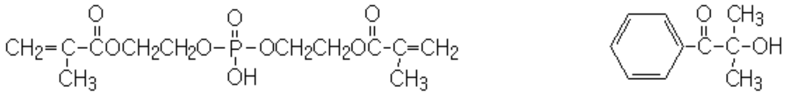


Fig. 1. Spectral irradiance of a UV irradiator used in this study.


$CH_2{=}C(CH_3){-}C({=}O){-}OCH_2CH_2O{-}P({=}O)(OH){-}OCH_2CH_2O{-}C({=}O){-}C(CH_3){=}CH_2$

(a) (b)

Scheme 1. Molecular structures of finishing agents: (a) DMEP, (b) HMMP.

## 2.4 FT-IR and FE-SEM analysis

FT-IR spectrometer (300E, JASCO) was used to observe the change in the molecular structure of the coated fabrics using both KBr pellet and ATR method. The subtracted ATR spectra were obtained by subtracting the absorbance of the untreated spectrum from that of the irradiated. IR spectra of the thermally degraded products in coated cotton at different themperature were obtained using KBr pellet method during pyrolysis. Also Scanning electron microscopy (FE-SEM, JEOL 6500F) was used to characterize the surface microstructure of the coated fabric surfaces.

## 2.5 Thermo-gravimetric analysis

Thermal behavior of the photopolymerized fabric was observed to evaluate flame retardancy using a thermogravimetric analyzer (TGA Q500) at a heating rate of 20℃/min under nitrogen gas atmosphere. Residue number($N_r$) was calculated from the following equation:

$$N_r = (R_f/F)/R_u$$

where, $R_f$ and $R_u$ represent the weight percentages of the residual carbonaceous char of the UV-coated cotton fabric and the untreated after pyrolytic decomposition respectively and F is the weight fraction of the fabric in the treated fabric.

# 3. Results and Discussions

## 3.1 Effect of coating conditions on add-on and add-on efficiency

UV light of 80W/cm intensity was irradiated on both sides of the coated cotton fabrics which were previously padded with the aqueous formulation of both HMMP and DMEP and subsequently dried. Effect of monomer and photoinitiator concentration on add-on and add-on efficiency of the UV-coated cotton fabrics were shown in Table 1. At the same PI concentration to the monomer, add-on increased with the monomer concentration but add-on efficiency showed a maximum at the 30% DMEP application level.

The photoinitiator (PI) concentration has more profound effect on the curing compared with the monomer and PI concentration increase from 0% to 7% remarkably increased from 4.7% add-on to 19.2% at the 30% DMEP application level.

However add-on efficiency showed a maximum at 7% PI concentration. The significant influence of PI demonstrated the importance of enough free radicals generation to overcome atmospheric oxygen inhibition. However excessive free radicals activated termination reaction rather than propagation reaction during photopolymerization. Effect of UV energy on the add-on and add on efficiency was investigated at the optimal DMEP and HMMP concentrations (Table 2). UV irradiation larger than a UV energy of 0.8J/cm$^2$ did not produce higher add-on and add-on efficiency because higher UV energy may promote the photodegradation of the coated cotton fabrics as well as photopolymerization of DMEP.

**Table 1.** Add-on and add-on efficiency of UV-cured cotton fabrics

| DMEP (%) | HMMP (%owm) | A (%) | AE (%) | Whiteness index |
|---|---|---|---|---|
| 0 | 0 | | | 125 |
| 10 | 7 | 6.5 | 53.0 | 96 |
| 20 | 7 | 9.4 | 64.2 | 93 |
| 30 | 0 | 4.7 | 17.1 | 95 |
| | 1 | 10.8 | 42.6 | 98 |
| | 3 | 13.8 | 52.8 | 94 |
| | 5 | 14.3 | 54.6 | 92 |
| | 7 | 18.9 | 70.5 | 92 |
| | 9 | 19.2 | 67.4 | 92 |
| 40 | 7 | 21.9 | 69.0 | 89 |
| 50 | 7 | 41.5 | 80.5 | 88 |

**Table 2.** Effects of UV energy on add-on and add-on efficiency

| UV energy (J/㎠) | A(%) | AE(%) | Whiteness Index |
|---|---|---|---|
| 1.6 | 21.8 | 74.7 | 92 |
| 1.9 | 22.4 | 75.6 | 91 |
| 2.3 | 19.8 | 73.9 | 91 |
| 3.2 | 18.9 | 74.1 | 90 |
| 5.0 | 20.5 | 75.3 | 78 |
| 10.3 | 17.1 | 68.8 | 74 |

## 3.2 FT-IR and SEM analysis of UV-coated cotton fabrics

The UV-coated DMEP on cotton was characterized by FT-IR analysis. Fig. 2 shows FT-IR spectra of the pristine and photopolymerized DMEP alone. P=O and P-O-C stretching vibrations of the acid phosphate were observed at 1250 cm$^{-1}$ and 1030cm$^{-1}$ respectively, while C=O, C-C-O and O-C-C stretching of dimethacrylates located at 1720, 1174 and 1070 cm$^{-1}$ which were shifted to 1730, 1169 and 1060 cm$^{-1}$ after photopolymerization[16]. Also the ethylenic unsaturation band of the DMEP located at 1640 cm$^{-1}$ disappeared. The subtracted spectrum of UV-coated cotton fabric in Fig. 3 indicated the presence of the polymerized DMEP on the cotton which is similar to the photopolymerized DMEP spectrum.

The change of molecular structure of the coated cotton during pyrolysis was estimated by obtaining IR spectra of the thermally degraded products of the coated cotton at different temperatures (Fig. 4). Above 200°C, thermal decomposition of the polymerized DMEP occurred as indicated by the diminished absorbance of the ester linkage. The decomposition of UV-coated cotton was more noticeable in the degraded products at 300 °C or more. New bands at 1630 and 1710 cm$^{-1}$ were ascribed to C=C and C=O stretching of pyrolyzed carbonaceous char due increased conjugation. And the additional peaks located at 1004 and 900 cm$^{-1}$ may be resulted from asymmetric and symmetric stretching of P-O-P linkage of phosphate carbon complex and the vibration at 1090 cm$^{-1}$ was attributed to $PO_2/PO_3$ stretching vibration due to increased oxidation at the elevated temperature.

Highly conjugated carbon adduct containing phosphorous seemed to be formed during pyrolysis.

The change of microscopic structure in the UV-cured fabrics were shown in Fig. 5. Compared with untreated cotton, the polymerized DMEP was apparently coated on the fibers and no significant interfiber bonds were observed.

However most of the cured DMEP may exist in the amorphous region of the cotton fiber considering the significant increase in the flame reatardancy of the UV-cured fabrics.

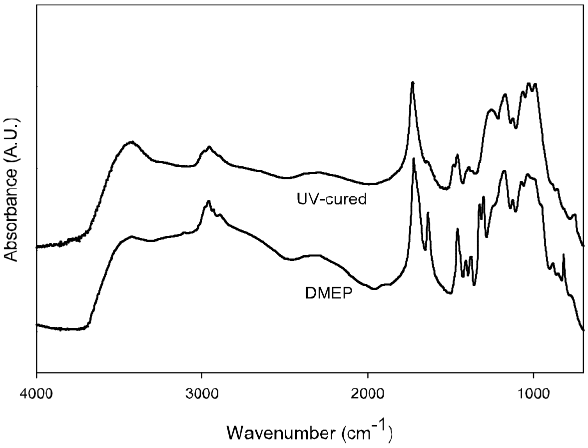


**Fig. 2.** Infrared spectra of uncured and UV-cured DMEP.

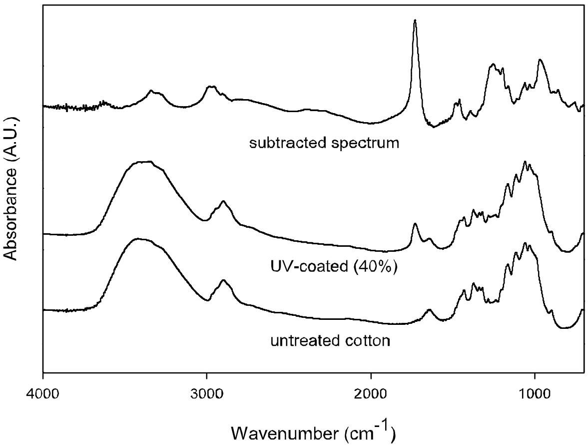


**Fig. 3.** Infrared spectra of uncured and UV-cured cotton fabrics.

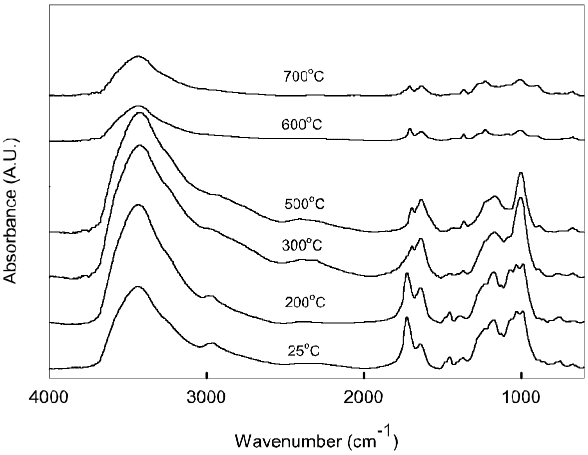
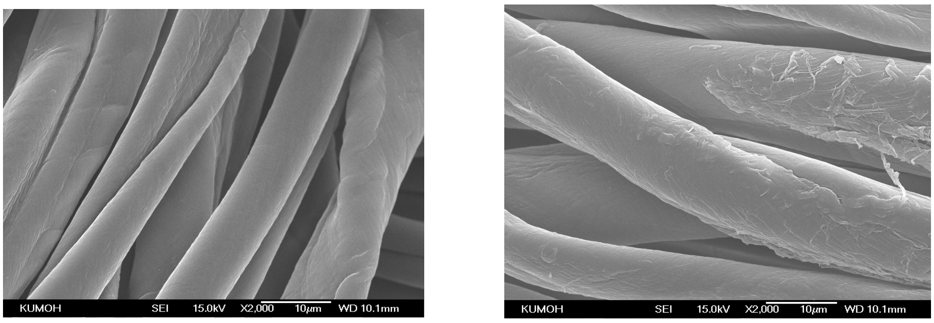


**Fig. 4.** IR spectra of thermally degraded products of UV-cured cotton.



(a) (b)

**Fig. 5.** SEM photographs of cotton fabrics: (a) untreated, (b) UV coated with 20% DMEP.

## 3.3 Flame retardancy of UV-coated cotton fabrics

TGA and DTG curves of the UV-cured cotton fabrics were given in the Fig. 6 and 7 respectively and the TGA data were summarized in Table 3.

The coated cotton showed significant difference in thermal degradation behavior. With increasing DMEP concentration, the maximum decomposition temperature was lowered from 395 °C to 260 °C and the residual char amount increased from 8.9% up to 32.7% as well as the apparently lowered maximum decomposition rate. The phosphorous in the DMEP may facilitate the catalytic dehydration and crosslinking of the cellulosic materials during the pyrolysis according to a condensed phase mechanism. The LOI values of the UV-cured samples were evaluated and presented in Table 4. Remarkable improvement of flame retardancy was observed as high as a LOI of 28.9 compared with the pristinecotton fabric with a LOI of 18.4. Also residue number increased proportionally with increasing application level of DMEP upto 40%, which representing high efficiency of the coated DMEP in generating higher incombustible materials during pyrolysis.

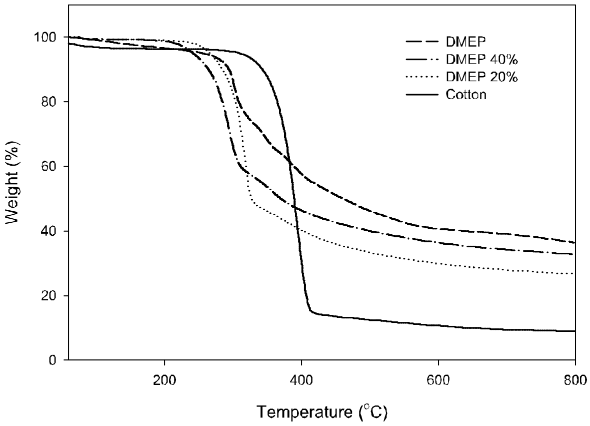


**Fig. 6.** TGA thermodiagrams of untreated and UV-cured fabrics.

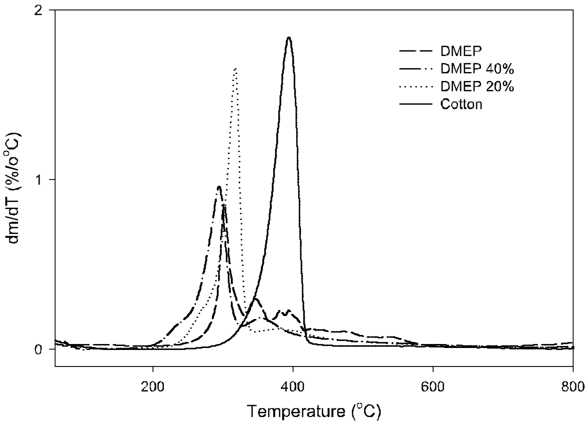


**Fig. 7.** Differential TGA thermodiagrams of untreated and UV-cured fabrics.

**Table 3.** TGA data of untreated and UV-coated cotton

| DMEP (%) | First thermal decomposition | | | Second thermal decomposition | | |
|---|---|---|---|---|---|---|
| | Range (℃) | DTGA peak (℃) | Mass loss (%) | Range (℃) | Mass loss (%) | Char yield at 800°C (%) |
| 0 | 261~422 | 395 | 81.9 | | | 8.9 |
| 10 | 210~335 | 309 | 53.9 | 335~474 | 12.1 | 20.7 |
| 20 | 199~333 | 310 | 51.9 | 333~444 | 11.2 | 26.7 |
| 30 | 188~324 | 296 | 45.7 | 324~433 | 12.8 | 29.6 |
| 40 | 174~316 | 285 | 41.7 | 316~424 | 13.7 | 32.7 |
| 50 | 162~297 | 260 | 29.4 | 296~386 | 14.4 | 24.2 |
| 100 | 218~323 | 294 | 23.0 | 323~357 | 8.3 | 36.4 |

Table 4. Residue numbers and LOI values of UV-coated cotton

| DMEP (%) | $R_f$ (%) | F | $N_r$ | LOI |
|---|---|---|---|---|
| 0 | | 1.000 | 1.00 | 18.4 |
| 10 | 20.7 | 0.935 | 2.49 | 21.5 |
| 20 | 26.7 | 0.906 | 3.31 | 21.5 |
| 30 | 29.6 | 0.811 | 4.10 | 25.4 |
| 40 | 32.7 | 0.781 | 4.70 | 25.4 |
| 50 | 24.2 | 0.585 | 4.65 | 28.9 |
| 100 | 36.4 | 0.000 | | 29.8 |

$R_u$ = 8.9%

## 4. Conclusions

UV-curable coating of DMEP and HMPP on cotton fabrics was carried out to improve flame retardant property of cotton fabric.

The cotton fabrics were treated with various amounts of DMEP and HMPP via a padding process and drying followed by UV irradiation treatment. The optimal monomer and photoinitiator concentrations in the formulation were 40% and 7%omp respectively. Higher than a UV energy of 0.8J/cm$^2$ did not produce higher add-on and add-on efficiency due to the concomitant photo-degradation effect of the UV light.

Thermal degradation behavior of the UV cured cotton followed a condensed phase mechanism as indicated by the lowered maximum decomposition temperature, the increased residual char amount as well as the apparently lowered decomposition rate with increasing DMEP concentration. Highly flame retardant property up to a LOI of 28.9 was achieved by the UV curing.

## Acknowledgrment

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