SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CA17107

STSM title: "Flame-Retardant Cotton Fabric via Surface-Initiated PhotoATRP of Dimethyl(methacryloyloxymethyl) Phosphonate"

STSM start and end date: 01/04/2021 to 30/04/2021

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PURPOSE OF THE STSM:

Cotton, as a natural textile fiber, has numerous advantages, such as biodegradability, breathability, softness, and comfort. It is widely used in garments, bedding, curtains and carpets, etc. However, it easily combusts at as low as a 18% of Limiting Oxygen Index (LOI) value. Therefore, the development of flame-retardant substrates is gaining a great concern.

The aim of this STSM-proposal is to prepare a flame-retardant cotton fabric via PhotoATRP technique. PhotoATRP is an eco-friendly technique and provides surface modifications with controlled polymer molecular weights and using a small amount of catalyst. Such technique has an affirmative output on the final product properties and its reproducibility. The proposed flame-retardant cotton fabric will be prepared via surface-initiated PhotoATRP grafting of dimethyl(methacryloyloxymethyl) phosphonate (MACP1) monomer from the fabric surface. N, Br and Si elements will be also introduced to the fabric to have more efficient properties (Synergistic effects).

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The proposed flame-retardant cotton fabric was prepared via many steps. The first one was conducting a reaction between a cotton fabric and (3-aminopropyl) triethoxysilane (APTES). This reaction was done in toluene at 110 C for 7 hours. Then, the fabric was washed and dried to be reacted with α-bromoisobutyryl bromide (BIBB). This reaction is to anchor the initiator groups, *necessary for grafting, onto the fabric. Then the fabric was washed and dried to be grafted with MAPC1 monomer using PhotoATRP method. The polymerization was conducted in DMF for 24 hours. In this step different monomer concentrations were studied giving different weight gain. Some of grafted fabrics were additionally treated with melamine and chitosan solutions to add more nitrogen content onto the fabric. The modified fabrics were tested by FTIR, XPS and their flammability was evaluated with horizontal and vertical flame testes.*

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The chemical modifications of the cotton fabric were achieved. All these modifications have been confirmed by ATR-FTIR and XPS.

ATR-FTIR Spectra

The FTIR spectra of pure cotton (Cell-OH), Cotton modified with APTES (Cell-Si), Cotton macroinitiator (Cell-Si-Br) and grafted cotton (Cell-Si-g-PMAPC1) with two different weight gain 15%, and 65% are shown in Fig. 1. The broad band in (Cell-OH) at 3420 cm^{-1} is attributed to hydroxyl groups and the absorption band at 2900 is characteristic of C-H linkages. The weak bands at 1059 and 1025 cm^{-1} are attributed to skeletal vibrations involving C-O stretching. Other peaks at 1160 cm cm^{-1}, 1100 cm^{-1} and 894 cm^{-1}, attributable to asymmetric bridge C-O-C stretching and C-H deformation, respectively, are characteristic of amorphous cellulose. In Cell-Si, the amine N–H deformation vibration at 1580 cm^{-1} confirmed the presence of the APTES on the cotton fibers surface. The band of Si–O–Si vibration mode at 1075 cm^{-1} is blurred in the spectrum of Cell-Si due to the cellulose fingerprint in the 1150–900 cm^{-1} spectral region. A new peak at 1740 cm^{-1} appeared in cell-Si-Br, which can be assigned to carbonyl group, indicating the 2-bomoisobutyrates had successfully been immobilized on the surfaces of the cellulose fabric. The same peak appeared also in the grafted fabrics which are assigned to the ester group. The absorption peaks at 1255 cm^{-1} is assigned to -P=O. However, the peaks at 1050, and 958 cm^{-1} which are assigned to the vibrations of -P=O, P-C-O, and P-O-CH_3 in the grafted fabric were blurred.

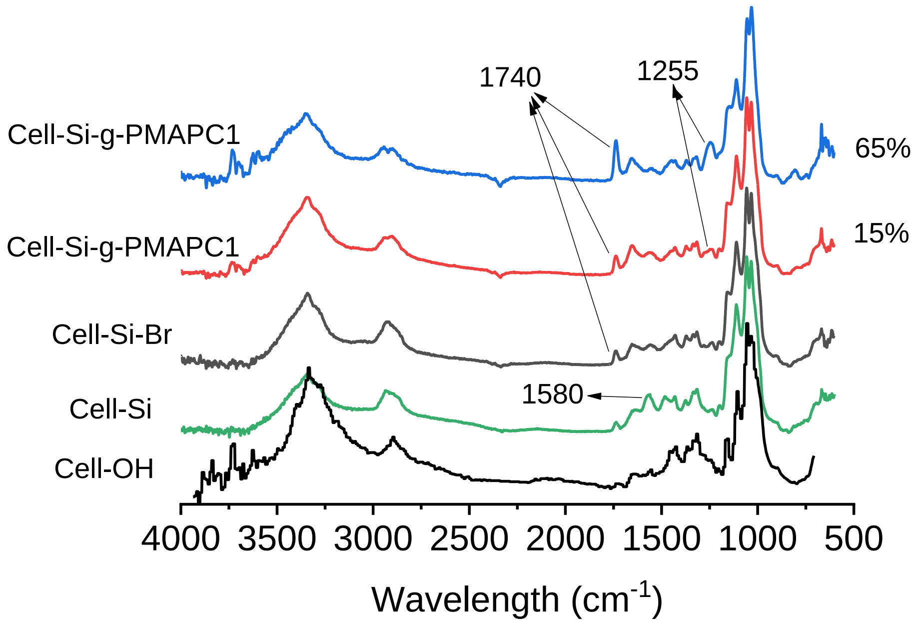

Fig.1 FTIR spectra of the modified cotton fabric.

XPS Spectra

The XPS wide-scan spectra of pure cotton (Cell-OH), Cotton macroinitiator (Cell-Si-Br) and grafted cotton (Cell-Si-g-PMAPC1) with a weight gain 22% are shown in (Fig. 2a). To further confirm the covalent grafting of cell-g-PMAPC1, C1s high-resolution XPS spectra of the grafted cotton fabric is analyzed (Fig. 2b). The pristine cotton fabric is mainly composed of the elements C and O. A signal peak of Br (between 70 and 74 eV) appeared on cell-Br confirming that BIBB was immobilized on the cotton fabric. Phosphorus (between 130 and 134 eV) could be found on the cell-g-PMAPC1, and this confirm the grafting of MAPC1 monomer. The overlapping curves of the C1s peak of the grafted fabric can be fitted by four subpeaks, which indicates the bonding states of carbon as in Fig.2b. Appearance of the peaks of ester groups at 285 eV (O-C=O) further confirm that MAPC1 monomer was grafted on the cotton surface.

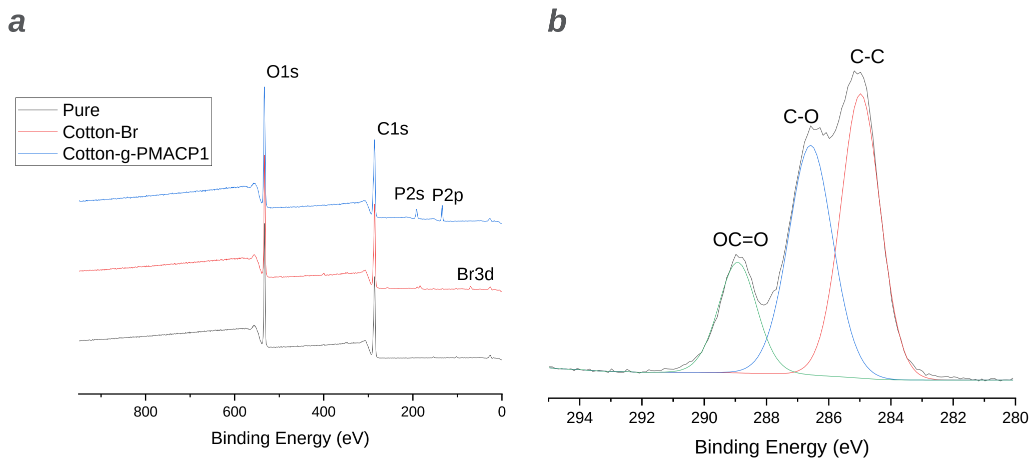

Fig. 2 XPS spectra of modified cotton fabric.

Flammability properties:

The grafted cotton fabric with different weight gain was tested by horizontal and vertical flame test. In horizontal flame testing as according to ASTM D6413, samples are clamped of two matching rectangular frames and held horizontally, then they were ignited for 12 s by a propane gas burner. The time required for the lower of the flame front to travel across the specified length is measured. The residual weight and the char length are also measured. The results are shown in table 2, and in Fig.3. It was observed from these results that with increasing the weight gain of phosphorus expressed by weight gain onto the cotton fabric, the flammability was decreased comparing to the pure cotton fabric.

1- Horizontal Flame test

Table 2.

Sample	Weight Gain (%)	Residual weight (%)	Char Length (cm)	Flame Spread Rate (mm/sec)	After Flame time (Sec)	Self-extinguishing
Pure	0	0	No	2.1	36	No
GZ18	15	48.2	8	2.19	24.5	No
GZ15	53	98.9	1	0.83	No ignition	Yes

Pure Cotton	Cell-g-PMAPC1-15%	Cell-g-PMAPC1-53%

Fig. 3 Flammability properties of modified fabric (VFT).

FUTURE COLLABORATIONS (if applicable)

As a next step for that work which could be for future cooperation, the obtained flame-retardant fabric will be additionally modified to provide multifunctional cotton fabrics that has antimicrobial activities as well. The prepared flame-retardant fabric will be further grafted with a tertiary amine containing monomer. Then it will be quaternized by some alkyl halide to introduce positive chare onto the fabric. We have already tested some samples for that and we will continue in such cooperation.