

Performance of Flame Retardant Wool Fabric Grafted with Vinyl Phosphate

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ABSTRACT

In this paper, a flame retardant dimethyl-2-(methacryloyloxyethyl) phosphate (DMMEP) was applied to wool fabrics by the graft copolymerization technique initiated with potassium persulfate (KPS) in water media. FTIR and SEM testing were used to explore the grafting evidence on the fiber surface, the SEM results show chemical deposition on the wool fiber surface and the scales could not be seen clearly. FTIR testing exhibited IR absorption of DMMEP on the wool fiber. Thermal gravimetric analysis, differential thermal analysis (DTA), and char residue morphology SEM observation show the decomposition mode of wool fabrics and infer the possible flame retardant mechanism. The phosphorus based flame retardant DMMEP was prone to promote more nonflammable char during combustion, and increased add-on of DMMEP produced increased fabric char. With a DMMEP add-on increase from 50% to 100% on the weight of wool fabric, the treated wool fabric demonstrated high flame retardancy with an LOI above 35% which means it can not be ignited with a candle like fire, and could pass the vertical flammability test. DMMEP treatment slightly affected whiteness and moisture regain, but yielded a relatively large decrease in permeability and tensile strength, which should be explored further in later research.

Keywords: Wool, graft copolymerization, flame retardant, performance, DMMEP

INTRODUCTION

Wool is a natural protein fiber and is widely used in apparel, interior textiles, and industrial applications for its outstanding comfort and aesthetic qualities [1], especially in thermal protective clothing for people working in hazardous occupations such as oil handling, furnace attendance, and firefighting.

Wool has some natural flame retardancy and high ignition temperature (500~600°C) due to its high nitrogen content (16%) [2]. Further treatment with flame retardants should be applied to meet the flame retardancy requirements for products such as domestic furnishings, public transportation and protective clothing [3].

The “Zipro” wool flame retardant treatment published during the 1970’s and 1980’s [4 – 7] was based on the exhaustion of negatively charged zirconium or titanium salts under acid conditions, to enable bonding with positively charged wool. And 3% deposition of flame retardants could endow wool fiber flame retardancy without negative effects on wool’s natural properties like handle, and moisture regain; and the treatments could endure washing and dry cleaning. A.R. Horrocks demonstrated intumescent agents like tetrakis-hydroxymethyl phosphonium condensates (THPC), N-methylol dimethyl phosphonopropionamide derivatives (MDPA) applied onto wool fabric and worked by forming yielded a high thermal resistance insulation char layer and enhanced flame retardancy [8-10]. Very recently, Sun treated wool with SiO₂ and SiO₂-Al₂O₃ sol, respectively. The Si-Al oxide increased the stability of wool and prolonged the thermal degradation of wool fiber, restrained the generation of combustible gas and oxidation of char, and effectively inhibited the discharge of smoke and toxic gas [11]. THPC, MDPA had a potential formaldehyde release problem, and other treatments were all based on inorganic compounds.

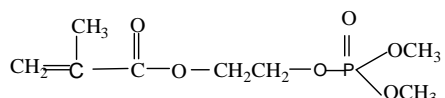
In this paper, a new organophosphorus compound dimethyl methacryloyloxyethyl phosphate (DMMEP) was applied onto wool fabric by the graft method initiated by potassium persulfate. Graft evidence from FTIR was used to explore the thermal

decomposition mode and possible flame retardancy mechanism.

EXPERIMENTAL

Materials and Reagents

Scoured wool fabrics (plain woven, 188 g/m²) were purchased from Jiangsu Sunlight Group, Flame retardant dimethyl-2-(methacryloyloxyethyl) phosphate (DMMEP, seen as scheme 1) was synthesized as previously reported [12]. Other chemicals were commercial reagent grade.



SCHEME 1. Structure of DMMEP.

Preparation of Flame Retardancy Wool

The wool fabrics (2g) were immersed into a reaction mixture containing DMMEP x g, potassium persulfate (KPS) $0.01 x$ g and 60 ml deionized water in a 100 ml Erlenmeyer flask; the pH value of the solution was adjusted to 2.5. Then the flask was sealed with a rubber-stopper and put into a water bath under oscillation at 90°C for 60 min. Then the sample was rinsed with methanol followed by water, and finally dried at room temperature under vacuum to a constant weight. The weight gain was calculated from Eq. (1):

$$\text{weight gain(\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

Where W_2 and W_1 are the weight of grafted and original wool fabric respectively.

Characterization and Measurements

Infrared spectra of wool were recorded on a Nicolet 5700 FTIR instrument with KBr pellets. The surface morphology of wool and char residue after combustion was examined with a Hitachi S-4700 scanning electron microscope (SEM) at acceleration voltage of 15 kV after gold coating. Char residue was measured according to Eq. (2) as follows: pristine wool W_1 was weighed and then and put into muffin oven at 600 °C for 10 min and weighed again to determine the char W_2 ,

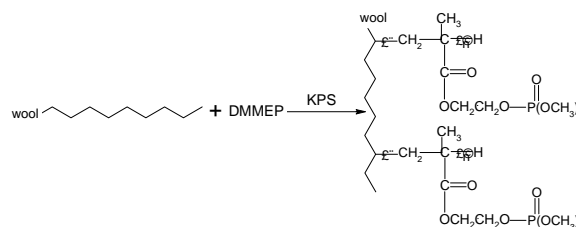
$$\text{char residue(\%)} = \frac{W_2}{W_1} \times 100 \quad (2)$$

Char residue morphology was investigated by scanning electron microscopy and the surface of char residues was sputter-coated with gold layer before examination. Thermal gravimetric analysis (TGA) and differential thermal analysis were carried out at the same time from 40°C to 600°C on a SDT Q600 TA instruments with heating rate of 10°C/min under the nitrogen atmosphere with flux 100 ml/min, and each sample was controlled to 5~7 mg in primary weight. LOI was measured according to ASTM D 2863 on a Fire Testing Technology Oxygen Index Instrument. Char length was measured according to ASTM Standard Method D6413-99. Tensile properties of grafted wool fabrics were measured. The fabric tensile strength was measured according to ASTM Standard Method D 5035-95 with an Instron 4482 tester. Samples were put into a conditioning room (at 21.1°C and 65% RH) for 24 hours before tensile testing. The whiteness of wool fabric was measured by WSD III whiteness instrument, and the result was the average of eight measurements. Moisture regain was evaluated in the standard conditions of 20°C and 65% relative humidity (RH) (ISO 2060: Determination of moisture content and moisture regain of textile-oven-drying method, 1994). Permeability of wool fabrics was tested by Digital Fabric Permeability Testing Instrument YG[B]461D according to GB/T5453-1997(eqv. ISO9237: 1995).

RESULTS AND DISCUSSION

FTIR

FTIR analysis was used to demonstrate the existing evidence of chemicals grafted on the fiber surface [13-14]. Mechanism of graft copolymerization of wool with DMMEP was free radical initiated copolymerization as in Scheme 2. Wool and DMMEP were initiated by KPS, and DMMEP was grafted onto wool by chain propagation. Figure 1 shows the FTIR spectra of pristine wool (a) and FR wool (b).



Scheme 2. Graft polymerization of wool with DMMEP.

Compared with pristine wool, curve of FR wool appeared as new IR absorption peaks at band 855cm⁻¹, 971 cm⁻¹ and 1052 cm⁻¹ which were corresponded to

the stretching vibration of P-C, P-O-C and C-O-C of PDMMEP [15] And band near 527 cm^{-1} assign to S-S bond stretching vibration where the peak intensity decreased compared with pristine wool which mainly because the deposition of DMMEP covered the wool surface. At band near 1684 cm^{-1} the peak broadened which was mainly because of the overlap of C=O stretching vibration of DMMEP and wool¹⁶. From the IR results, it is obvious seen that DEMEP was grafted onto wool fabrics.

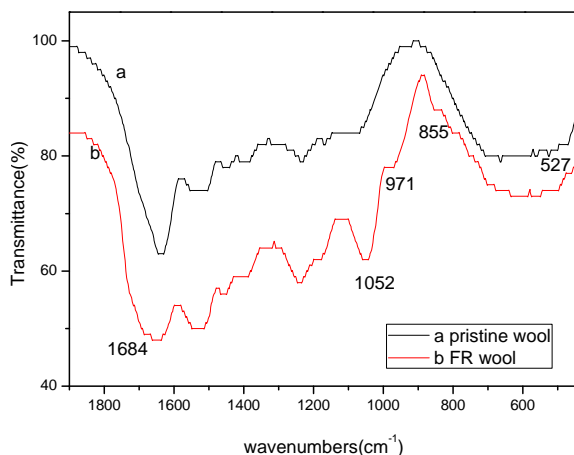


FIGURE 1. FTIR spectra of pristine wool (a) and FR wool ((b, weight gain 22.3%).

Surface and Char Morphology (SEM)

SEM was utilized to determine the effect of DMMEP on the wool fiber surface and the char morphology after combustion (Figure 2). Figure 2 shows that the surface of pristine wool fiber (a) was smooth with evident scales while the surface of FR wool fiber was rough and the scale was not so clear (b), which shows that there was chemical deposition on the fiber surface.

Figure 2(c) shows that the char of pristine wool was intumescent, porous, soft and fragile, which means pristine wool produced more gas during combustion, while the char morphology of Figure 2(d) was rigid, flat, and nonporous. This evidence indicates that FR wool has a tendency to form more nonflammable char than flammable gas during combustion.

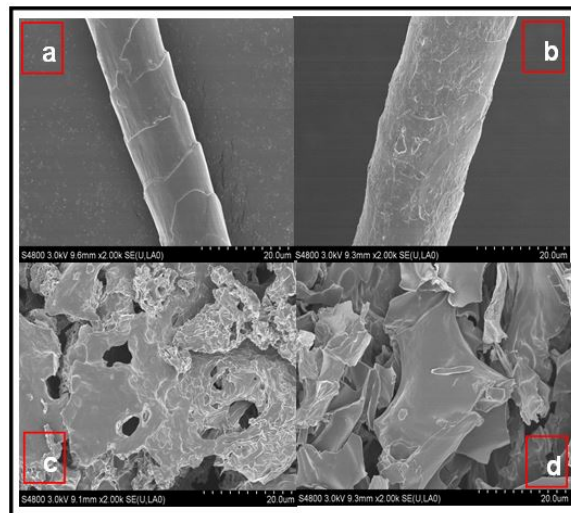


FIGURE 2. Surface and char morphology of pristine wool (a, c for surface) and FR wool ((b, d for char, weight gain 22.3%).

TG And DTA

Thermogravimetric (TG) analysis is one of the most effective tools to evaluate the thermal stability and thermal decomposition behavior of materials. Figure 3 showed the TG and DTG curves of pristine wool (a) and FR wool (b, weight gain 22.3%). From DTG curves it could be got the weight loss stages and maximum decomposition temperature. Differential thermal analysis (DTA) curves could give the information that if the wool was exothermic or endothermic during thermal decomposition. All the thermal analysis data collected from Figure 3 and Figure 4 are listed in Table 1.

The thermogravimetric curves for pristine wool showed four mass loss stages. The first stage was at 76°C with weight loss 7%, which is the loss of regain water. The second stage was at 246°C with weight loss 12%, which was the initial decomposition of wool [17-18]. The third stage was at 307°C with weight loss 38%. This stage was responsible for the major weight loss. The last weight loss stage was at 400°C with weight loss 21%. While the FR wool showed three mass loss stages, that is, absorbed water loss 7% at 76°C , initial decomposition at 235°C with weight loss 9% and major weight loss 52% at 337°C . The DTA results were better in accordance with the TG data which showed four endothermic peaks for pristine wool and three endothermic peaks for FR

wool. The residual char at 600°C of FR wool increased to 32% compared with 22% of pristine wool. The initial decomposition temperature of FR wool shifted to a lower level by 11°C, and in the major mass loss stage, weight of FR wool reduced much more than pristine wool. This was mainly because of the adding of phosphorus flame retardant DMMEP promote non-flammable char formation during being heated.

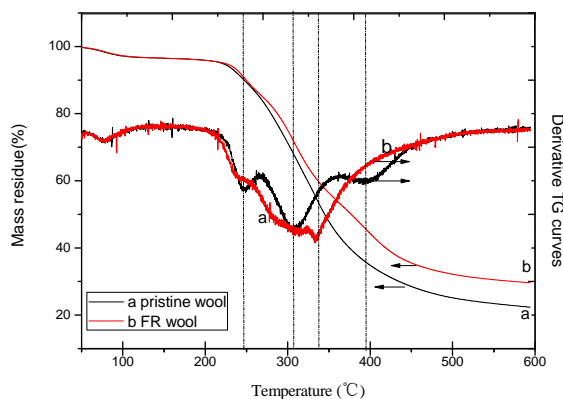


FIGURE 3. TG curves of pristine wool (a, c for surface) and FR wool ((b, d for char, weight gain 22.3%).

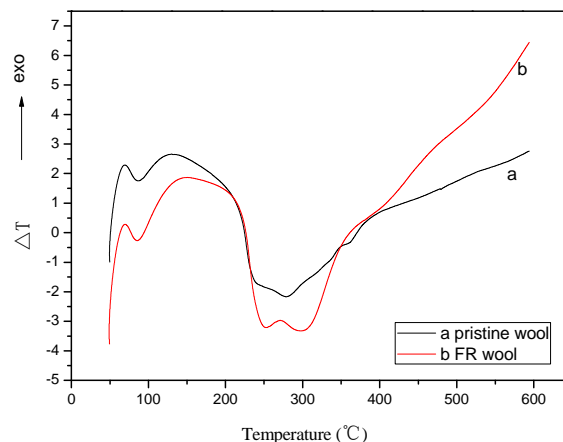


FIGURE 4. DTA curves of pristine wool (a, c for surface) and FR wool ((b, d for char, weight gain 22.3%).

Flame Retardancy Property

The flame retardancy characteristics of pristine wool and FR wool are listed in *Table II*. When increasing add on of DMMEP, the weight gain increased accordingly. The LOI increased with the increased DMMEP add on; above 100% DMMEP add on, the LOI did not increased further, which gave us the suggested DMMEP add on with not more than 100% on the weight of wool in case of

TABLE I. Thermal analysis data collected from *Figure 3* and *Figure 4*.

| Samples | Mass loss stages from TG curves | Char residue at 600°C/% | Peak assignment on DTA curve |
|---------------|---------------------------------|-------------------------|------------------------------|
| Pristine wool | 76 °C, 7% | 22 | 84 °C |
| | 246°C(T _i), 12% | | 242 °C |
| | 307°C(T _{max}), 38% | | 277°C |
| | 400°C, 21% | | 362°C |
| | | | Endo |
| FR wool | 76°C,7% | 32 | 84°C |
| | 235°C(T _i), 9% | | 249 °C |
| | 337 °C(T _{max}), 52% | | 302 °C |

waste. Fabrics are self-extinguishing with an LOI greater than 28% [19] and intrinsically non-flammable with an LOI greater than 35% [20]. Pristine wool itself can be self-extinguish when ignited with a candle like fire and adding 20%-100%

DMMEP, wool fabrics became nonflammable and could pass the vertical flammability test [21]. With the increasing weight gain, wool was prone to produce more char residue when combustion which further verified the dehydration and char formation mechanism of DMMEP flame retardant.

TABLE II. The flame retardancy property of pristine and FR wool fabrics.

| DMMEP Concentration /% | Weight Gain /% | LOI /% | Char Length /mm | Char Residue /% |
|------------------------|----------------|--------|-----------------|-----------------|
| 0 | 0 | 28.2 | 50 | 3.56 |
| 20 | 7.1 | 34.1 | 35 | 8.9 |
| 50 | 17.5 | 35.3 | 30 | 11.3 |
| 80 | 18.6 | 35.5 | 35 | 17.9 |
| 100 | 22.3 | 37.5 | 40 | 24.3 |
| 150 | 25.1 | 37.5 | 35 | 24.7 |

Whiteness, Comfort Ability and Tensile Behavior

Figure 5 showed whiteness index, moisture regain and permeability of wool fabrics.

After grafting, the whiteness index slightly decreased, which means the flame retardant treatment had no negative effect on the wool's appearance. But moisture regains and permeability dropped by 20% and 21.4% respectively. But the fabric did not feel uncomfortable when wearing because the moisture regain of FR wool fabric still had the higher level with 8.8% compared to cotton fabrics with 7%.

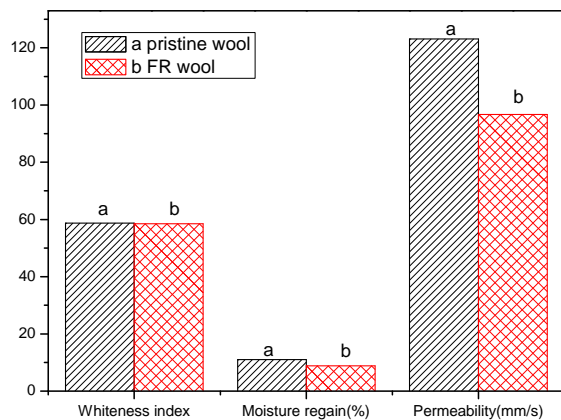


FIGURE 5. Whiteness index, moisture regain and permeability of pristine (a) and FR (b, weight gain22.3%) wool fabrics.

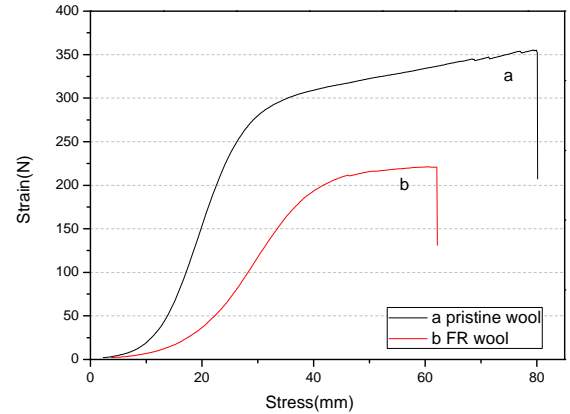


FIGURE 6. Tensile behavior of pristine (a) and FR (b, weight gain22.3%) wool fabrics.

Figure 6 showed tensile curve of pristine (a) and FR (b) wool fabrics. One can see that FR wool had a loss of tensile strength and elongation at break compared with pristine wool fabric, which is mainly because the DMMEP deposition on the wool fiber surface weakened the Hydrogen bond and Van de Waals force between wool fibers. The tensile strength dropped by 35% which could affect apparel performance; the elongation at break dropped by 14% which could be accepted. Further research should be done regarding how to control the tensile strength loss.

Conclusions and Future Work

A water soluble flame retardant monomer dimethyl-2-(methacryloyloxyethyl)phosphate (DMMEP), initiated by potassium persulfate (KPS), was successfully applied onto wool fabric. Adding 50~100% DMMEP on the weight of wool fabric yielded grafted wool fabric which exhibited good flame retardancy with an LOI above 35% and could pass the vertical flammability test. FR wool changed the thermal decomposition mode while being heated and was prone to produce more nonflammable solid char under combustion. FR wool had a slight drop of moisture regain and permeability, but had no evident effect on wearing comfort. But grafted wool tensile strength dropped and needs to be improved.

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