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KERATIN POLYMER HAVING IMPROVED THERMAL PROPERTIES

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Abstract

In this paper, wool keratin polymers having significantly improved thermal properties through the chemical modifications with P, N and Cl synergic effects are reported. The changes of chemical compositions of the keratin polymers before and after the treatment were characterised by using Fourier Transform Infra-Red (FTIR), ³¹P Nuclear Magnetic Resonance (³¹P-NMR) and Energy-Dispersive X-ray (EDX) techniques. Their thermal properties were examined through Thermo Gravimetric Analysis (TGA) and Differential scanning Calorimetry (DSC). The treated keratin polymers have shown much less mass losses and greater char residues than that of untreated keratin polymer during the pyrolysis process in TGA. The treated keratin polymers are envisaged to have advantages of improved flame retardant properties.

Key words: wool keratin, thermal properties, flame retardant

1. Introduction

Wool is natural flame retardant material due to relatively high nitrogen (16%) and sulphur (3-4%) contents, high ignition temperature (570-600°C), low heat of combustion (27kJ/g) and relatively high limited oxygen index (LOI) (25-28%)¹, it burns slowly without melting and dripping, and it self-extinguishes when heat source is removed². However, flame still can propagate in wool once ignition has occurred³, which restricts their specific applications in protective clothing although wool fibres have unique moisture management properties.

Many of traditional flame retardants for wool fibres were based on halogen compounds, such as halo-organic acid anhydrides⁴, bis(beta-chloroethyl) vinyl phosphonate (VP)⁵, tris(2,3-dibromopropyl) phosphate⁶, they either react with wool fibres or form cross-linked structures on the fibre surfaces. These compounds influence the pyrolysis reaction, prevent the formation of flammable volatiles, and promote the formation of char and thus act as flame retardant for wool. However, in comparison with the limited flame retardant effects of those chlorinated flame retardant agents, some of chlorinated flame retardants including short chain chlorinated paraffin flame retardants are toxic and carcinogenic and have been legally banned, also quite a few of the chlorinated flame retardants have been restricted as they could produce highly toxic and corrosive gases with great amount of smoke in combustion⁷, and some bromine-containing flame retardants have potential to form dioxins and furans under either severe thermal stress or in combustion⁸.

Commercial flame retardant processes Proban[®] and Pyrovatex[®] for cellulosic fibres have also been applied to wool^{9, 10, 11, 12}. Proban[®] process applied a condensation of tetrakis(hydroxymethyl) phosphonium chloride (THPC), urea and melamine resin on wool fabric, followed by curing and oxidation. While Pyrovatex[®] process employed methylol dimethoxyphosphonopropionamide (Pyrovatex CP) melamine resin. However, not only these treatment processes involve the use of carcinogenic compound formaldehyde but also formaldehyde is released from these chemical treated wool fabrics¹³.

Currently, Zirpro[®] process based on the exhaustion of anionic complexes such as hexafluorozirconates (ZrF_6^{2-}) and hexafluorotitanates (TiF_6^{2-}) onto positively charged sites in wool under acidic conditions is still in use today^{14, 15, 16}. The LOI of the Zirpro wool was in a range of 30-35%. However, the presence of zirconium and fluorine ions in the effluent discharges could cause environmental issues.

Other flame retardant agents including inorganic compounds (e.g., ammonium polyphosphate, melamine phosphates¹⁷), cyclic polyol phosphoryl chloride^{18, 19}, sol of metal oxide²⁰ (e.g. MnO_2), and alendronate or pamidronate²¹ were also reported for the treatment of wool fibres, but a great amount of cyclic polyol phosphoryl chloride discharged to effluent causes environmental issues, the sol of metal oxide treatment was not durable and alendronate and pamidronate treatment only showed a slight increase (1-2%) of LOI in treated wool fibres. Therefore, alternative technical routes to improve the flame retardant properties of wool materials are desirable.

Keratin polymer extracted from wool fibres have highly similar chemical composition to wool fibres^{22, 23} and can be regenerated and made into film membrane²⁴, this suggests that regenerated keratin polymer film membrane could have the same excellent moisture management properties as wool fibres have, which has potential to be used for many functional clothing including protective clothing. In this research, a modified wool keratin polymer having significantly improved thermal properties through a chemical modification having P, N and Cl synergic effects is reported.

2 Modification of keratin polymer

In this research, keratin polymer of 12000~48000 Daltons extracted from 64s merino wool fibre and purified was chemically modified using a flame retardant agent A, having P and N synergic effect under different conditions as shown in Table 1. The process was described as below:

2g of the flame retardant agent A and 50ml THF were dissolved with stirring in a round bottom flask (250ml) fitted in oil bath. 2g of the keratin polymer was added into the flask with (or without) catalyst Triethylamine and the solution was refluxed (72-74°C) for a period of time (24 hours or 48 hours) with the use of water condenser on the round bottom flask. The resultant keratin polymer modified with flame retardant agent A was washed with 50ml THF twice to remove the excess chemicals and then washed thoroughly with distilled water to remove any residue of THF and dried at 40°C for 8 hours ready for use.

Table 1: Chemical modification of wool keratin polymer under different conditions

Samples	Keratin polymer (g)	Agent A (g)	Ttriethylamine (ml)	THF (ml)	Time duration (h)
Sample 0	untreated keratin				
Sample 1	2	2	0	50	24
Sample 2			10	50	24
Sample 3			20	50	24
Sample 4			20	50	48

3. Characterisation of resultant keratin polymers

The changes in chemical compositions of the keratin polymers before and after the chemical treatments were characterised using Fourier Transform Infra-Red (FTIR) spectroscopy, gel-phase ^{31}P Nuclear Magnetic Resonance spectroscopy (gel-phase ^{31}P -NMR) and Energy-Dispersive X-ray spectroscopy (EDX). The thermal properties of the treated keratin polymers were examined using Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) techniques.

3.1 Fourier Transform InfraRed (FTIR) spectra analysis

In order to characterise the changes of the functional groups in the modified keratin polymers, the FTIR spectra of the flame retardant agent A, untreated and treated keratin polymer were obtained on a Perkin-Elmer Spectrum BX spotlight Fourier transform infra-red (FTIR) spectroscope using KBr pellet technique in the range of 4000 to 400 cm^{-1} with 16 repetitious scans averaged for each spectrum.

3.2 ^{31}P Nuclear Magnetic Resonance (^{31}P -NMR) analysis

In order to study the changes in the chemical compositions of the keratin polymer before and after the chemical treatments, the ^{31}P -NMR spectra of untreated and treated keratin polymer (sample 3) were obtained on Bruker 500 UltrashieldTM NMR, and Formic acid-d₂ 99at.% D was used to dissolve the untreated keratin polymer as the treated keratin polymer cannot be dissolved in most of common organic and inorganic solvents. The NMR tube was packed with the treated keratin polymer, 4cm depth, and then wetted with Tetrahydrofuran-d₈ 99.6at.%D. Chemical shifts were reported in ppm on the δ scale.

3.3 Energy Dispersive X-ray (EDX) analysis

In order to examine the changes of the element compositions of the keratin polymers after chemical modification, the elemental analysis of the untreated and treated keratin polymer were performed on a Jeol JSM-6610LV scanning electron microscope coupled to an Oxford Instruments INCA X-max80 EDS microanalysis system. 20kV of the accelerating voltage, 50 of magnification and the Silicon Drift Detector were employed in the testing. The result of each sample is the average of three measurements.

3.4 Thermogravimetric Analysis (TGA)

The thermal behaviour of the treated and untreated keratin polymers were characterised by using thermal gravimetric analysis (TGA) performed in the Stanton Redcroft TGH1000 thermo-gravimetric analyser, in the range of 20 to 800°C with a heating rate of 5°Cmin⁻¹ under a constant flow of nitrogen (50cm³min⁻¹). Sample weight was in the range of 20-21mg.

In order to exclude the interference of the water regain within the samples on TGA result, samples were dried at 100°C for 3hrs to remove most of the water moisture inside the samples, and then kept in a desiccator before TGA analysis.

3.5 Differential Scanning Calorimetric analysis (DSC)

The pyrolysis process of the treated and untreated keratin polymers were also analysed using Differential Scanning Calorimetric analysis which was performed in a PerkinElmer Jade DSC machine in the range of 30 °C to 440°C with a heating rate 20°Cmin⁻¹ under a constant flow of nitrogen (30cm³min⁻¹).

4 Result and discussion

4.1 FTIR spectra

The FTIR spectra of chemical reactive groups of both untreated and treated keratin polymers are shown in Figure 1. It is worth to point out that there is a characteristic difference in the FTIR spectra between the extracted keratin polymer and the original keratin polymer in wool fibres, there appears a much strong peak at 2936 cm⁻¹, which is related to C-H bond stretching vibration, in the FTIR spectra of the extracted keratin polymer but this peak is not found in the original keratin polymer in wool fibres. Such difference is due to much of the disulfide bonds (CH₂-S-S-CH₂) in the original keratin polymer in wool fibres were cleaved in the extracted polymers, and this increases the polarity of the C-H bond²⁵. Besides this, as shown in the FTIR spectra in Figure 1, untreated keratin polymer (sample 0) has all the main absorption bands existing in original keratin in wool fibres^{26, 27, Error! Bookmark not defined.}. The peak shown near 3290cm⁻¹ is related to N-H bond stretching vibration, the peak at 1640cm⁻¹ (Amide I) is associated with C=O bond stretching vibration, the peaks at both 1540cm⁻¹ (Amide II) and 1240cm⁻¹ (Amide III) are related to both N-H bending vibration and C-N stretching vibration^{26, 27}.

However, it is interestingly found in Figure 1 that the characteristic peak at 2936cm⁻¹ in FTIR spectra of the untreated keratin polymer mentioned above is not found in the FTIR spectra of the treated keratin polymers, in particular samples 2~4; this indicates that a new crosslinking might be formed between the keratin chains during the chemical modifications. In addition, a strong peak of P-Cl bond (530cm⁻¹) is observed in the FTIR spectra of the treated keratin polymer in Figure 1. This suggests that the agent A was bonded with the keratin polymer via functional groups such as -NH₂ in keratin.

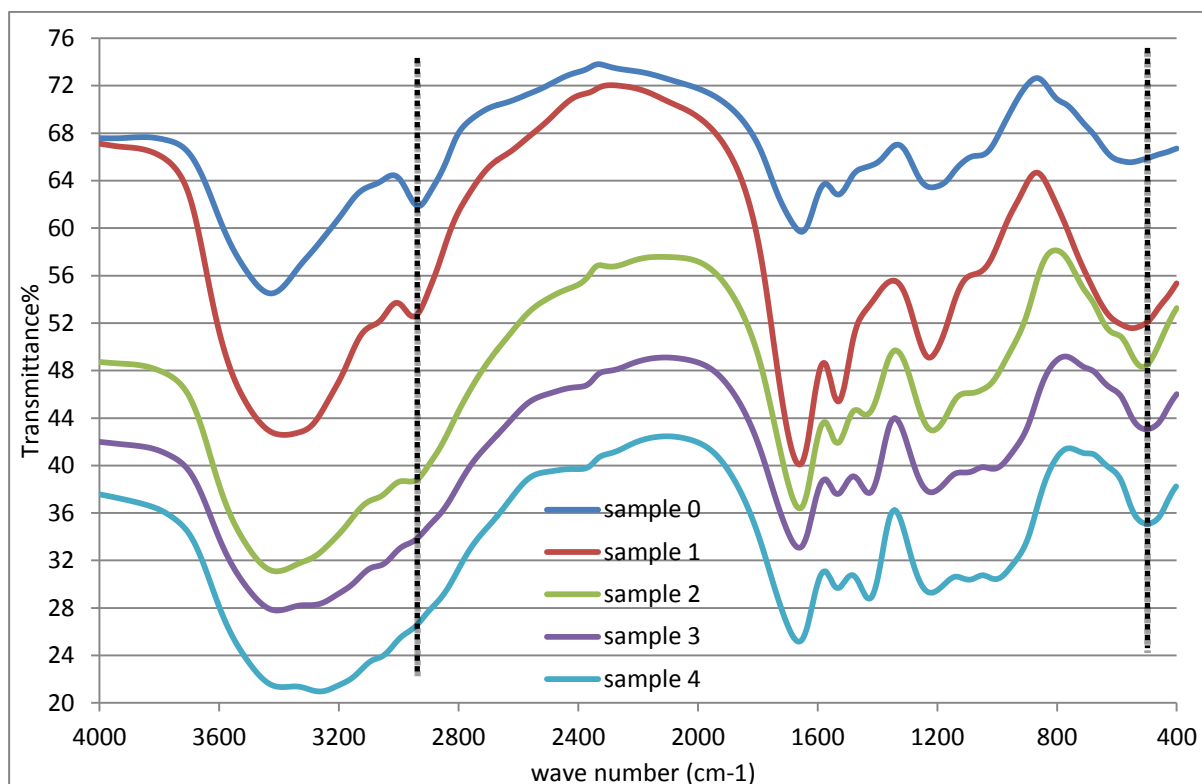


Figure 1 FTIR spectra of the untreated (sample 0) and treated keratin polymers (samples 0-4)

4.2 ^{31}P -NMR spectra

The ^{31}P -NMR spectra showing the chemical compositions of the untreated and treated keratin polymer are shown in Figure 2 and Figure 3.

It is found in Figure 2 that no peak is shown in the ^{31}P -NMR spectra of the untreated keratin polymer (see Figure 2), this indicates that while there are three peaks shown in the ^{31}P -NMR spectra of the treated keratin polymer, including two sharp peaks shown at 2.74 ppm and 1.52 ppm, and one lump peak shown at 0.06 ppm (see Figure 3). Those three peaks are associated with three different phosphorus-related chemical bonds in the chemical structure of the modified keratin polymer. It is thus suggested that there is a significant difference in chemical structure between the untreated and treated keratin polymer. As P-Cl groups were identified in FTIR in the treated keratin polymer, it might be deduced that at least one of these three peaks is due to the P-Cl groups attached on the functional groups in the keratin polymer with some new covalent bonds. In summary, it is concluded that the flame retardant agent A is chemically bonded with the keratin polymer via some new covalent bonds.

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PROCNO       1

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INSTRUM      av500mic
PROBHD       5 mm PABBO BB-
PULPROG      zgpg30
TD           65536
SOLVENT      DMSO-d6
NS           2048
DS           8
SWH           41666.668 Hz
FIDRES       0.630783 Hz
AQ           0.7844940 sec
RG           510.6
WDW           EM
SSB           0
LB           12.000 usec
TE           299.3 K
DE           0.1000000 sec
DQ1          0.0300000 sec
DQ2          0.0300000 sec
TD0          2

===== CHANNEL f1 =====
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P1           8.50 usec
PL1         0.00 dB
SFO1        202.6344000 MHz

===== CHANNEL f2 =====
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PCPD2       80.00 usec
PL2         -2.00 dB
PL12        15.26 dB
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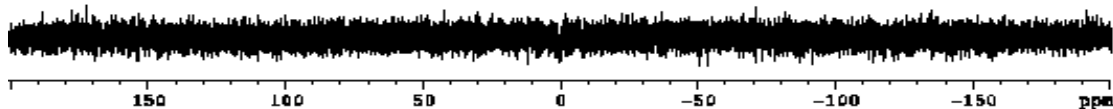


Figure 2 ^{31}P -NMR spectra of the untreated keratin polymer

Name Junyu
Room No Design
Sample Sample 5

```

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EXPNO        10
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INSTRUM      av500mic
PROBHD       5 mm PABBO BB-
PULPROG      zgpg30
TD           65536
SOLVENT      DMSO-d6
NS           2048
DS           8
SWH           41666.668 Hz
FIDRES       0.630783 Hz
AQ           0.7844940 sec
RG           510.6
WDW           EM
SSB           0
LB           12.000 usec
TE           299.3 K
DE           0.1000000 sec
DQ1          0.0300000 sec
DQ2          0.0300000 sec
TD0          2

===== CHANNEL f1 =====
NUC1         31P
P1           8.50 usec
PL1         0.00 dB
SFO1        202.6344000 MHz

===== CHANNEL f2 =====
CPDPRG2     wa1t16
NUC2         1H
PCPD2       80.00 usec
PL2         -2.00 dB
PL12        15.26 dB
SFO2        500.1325023 MHz
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SSB         0
LB          3.00 Hz
GB          0
PC          1.40

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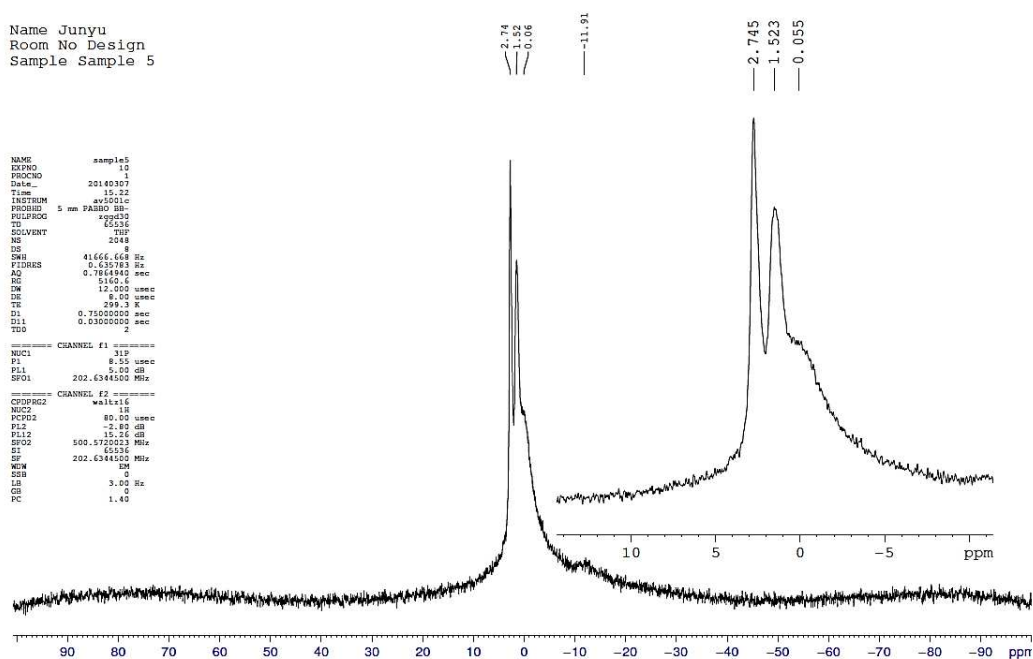


Figure 3 ^{31}P -NMR spectra of the treated keratin polymer

4.3 Elemental analysis

The elemental analysis of the treated keratin polymer was examined using EDX technique as shown in

Table 2. There are no P and Cl elements detected in the untreated keratin polymer, while there are a significant amount of both P (up to 12.6%) and Cl (up to 6.8%) appeared in the treated keratin polymer. The detected Cl in the treated keratin polymer may be explained that P-Cl groups in agent A were not reacted with the keratin polymer completely. It is also found that there are massive increases of the element N (range from 16.7% to 22.2%) in treated keratin polymer in comparison with untreated keratin (11.2%), and this means that the treated keratin polymer contains as much 1.5 ~ 2.0 times of element N as in untreated keratin polymer. These findings further prove that the flame retardant agent A has a P-N synergic flame retardant effect when bonded with keratin polymers.

While the compositions of the elements of the keratin polymers obtained from the EDX measurement on different samples were very useful for comparison purposes, the further research is needed for the quantification of the amount of the Cl, P and N introduced into the entire sample of the treated keratin polymer, because the elemental analysis performed using EDX technique is only limited to the sample surfaces. In this research, the level of element P in the keratin polymers is an indication of the content of the flame retardant agent A introduced into the treated wool keratin.

Based on both the phosphorus levels shown in

Table 2 and the chemical treatment conditions shown in Table 1, it is found that the reactions between the agent A and the wool keratin polymers were affected by the amount of catalyst added and the reaction duration time. With the aid of the catalyst employed, the phosphorus level in sample 2 is about as much as 4.4 times of that in sample 1 without catalyst. With the increase of the amount of the catalyst from 5 to 10 ml per gram of keratin, the phosphorus level increases from 6.0% in sample 2 to 9.6% in sample 3; with the increase of the reaction time duration from 24 hours to 48 hours, the phosphorus level increases from 9.6% to 12.6% in comparison of samples 3 and 4.

Table 2 Elemental analysis of the untreated and treated keratin polymer

Samples	C (%)	O (%)	N (%)	P (%)	S (%)	Cl (%)
Sample 0 (untreated)	53.9	28.0	11.2	0.0	5.1	0.0
Sample 1	49.1	28.5	16.7	1.4	3.0	1.3
Sample 2	35.7	29.3	22.2	6.0	2.2	3.8
Sample 3	32.9	28.9	19.7	9.6	2.0	6.0
Sample 4	27.8	28.9	21.3	12.6	1.6	6.8

4.4 Thermal degradation analysis (TGA)

The TG curves of both untreated and treated keratin polymer samples are shown in Figure 4, and the mass losses and char residues in TG Analysis is shown in Table 3. As shown in Figure 4, there were two regions of major mass losses above 200°C for both of the untreated and treated keratin polymer. The first mass loss process occurred between 200°C and 350°C, and the second mass loss process occurred between 350°C and 800°C. Interestingly, it is noticed that the mass losses of the treated keratin polymers are much less than that of the untreated keratin polymer in the degradation process (see Table 3), while the char residues of the treated keratin polymers are much greater than that of the untreated keratin polymer. The

mass losses of the treated keratin polymer (39.4% in average) was less than that of untreated wool keratin polymer (49.7%) in the temperature range of 200 to 350°C, and the char residue of the treated keratin polymer (average 37.4%) was much more than that of untreated wool keratin polymer (22.8%) at 800°C. In comparison with TGA result of Zirpro wool²⁸, which is the wool treated with 9.74% zirconium oxychloride, 9.6% of citric acid and 6.3% of formic acid at 95°C for 45mins, it is found in Table 4 that the mass losses of these treated keratin polymer (40.97% in average) was less than that of the Zirpro wool (46.05%) at the temperature range between 212°C and 374°C, which is about 11% of decrease of the mass losses in Zirpro wool. It is also noticed that the char residues of the treated keratin polymer (42.03% in average) was significantly greater than that of the Zirpro wool (32.02%) at 600°C, which is about 31% of increase of the char residues in Zirpro wool.

It was demonstrated that the pyrolytic region of the keratin polymer occurring from 200°C to 350°C involved the release of a number of volatile compounds such as H₂S, CO₂, H₂O and HCN²⁹, because of the destruction of disulfide linkages, followed by the thermal pyrolysis of the chain linkages, peptide bridges and some other lateral chains, which finally led to backbone degradation of the keratin polymer³⁰. The second pyrolytic region of the keratin polymer over 350°C was an exothermic reaction that the char oxidation reactions dominate²⁹. Therefore, there must be much less carbon chain linkage in the treated keratin polymers being thermally pyrolysed, which leads to the much less mass losses and higher char residues in the degradation process. The reason could be associated with the P, N and Cl synergic effect occurred. It is deduced that N promotes the phosphorylation of keratin polymer, and therefore inhibits the release of volatiles during the pyrolysis process of keratin polymer, in addition, P-Cl containing compound e.g. phosphorus halides might form and act as free-radical combustion inhibitors to retard the combustion of the treated keratin polymer. However, the chlorinated structure might have potential to release harmful gases during combustion, and the research to identify the needs to include chloride element in the compounds and the possibility to remove it from treated wool are ongoing.

In summary, it is thus concluded that the designed chemical modification of the keratin polymer in this research has inhibited the formation of flammable volatiles, and has enhanced the formation of char during the pyrolysis of the keratin polymer. Because enhanced char formation over 500°C is synonymous with improved flame retardant performance³¹, it is envisaged that the treated wool keratin polymer will have much improved flame retardant properties.

Table 3 Mass loss in the temperature range of 200 ~350°C and char residue at 800°C of the untreated (sample 0) and treated wool keratin polymer (samples 1-4)

Sample	Mass losses in the range of 200 to 350°C (%)	Mass losses in the range of 212 to 374°C (%)	Char residue at 600°C (%)	Char residue at 800°C (%)
Sample 0 (untreated)	49.7	52.96	28.0	22.8
Sample 1	41.8	41.14	39.3	34.2
Sample 2	40.1	39.37	41.1	36.0
Sample 3	39.0	41.13	42.8	38.4
Sample 4	36.5	38.64	44.9	41.1
Average of	39.4	41.0	42.0	37.4

samples 1~4				
Zirpro wool ²⁸	/	46.1	32.0	/

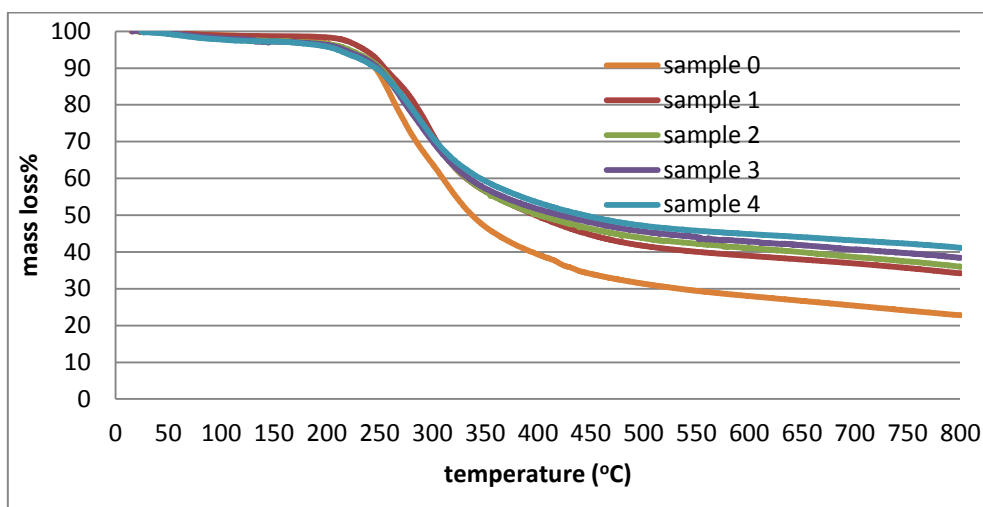


Figure 4 TG curves of untreated (sample 0) and treated keratin polymer (samples 1-4)

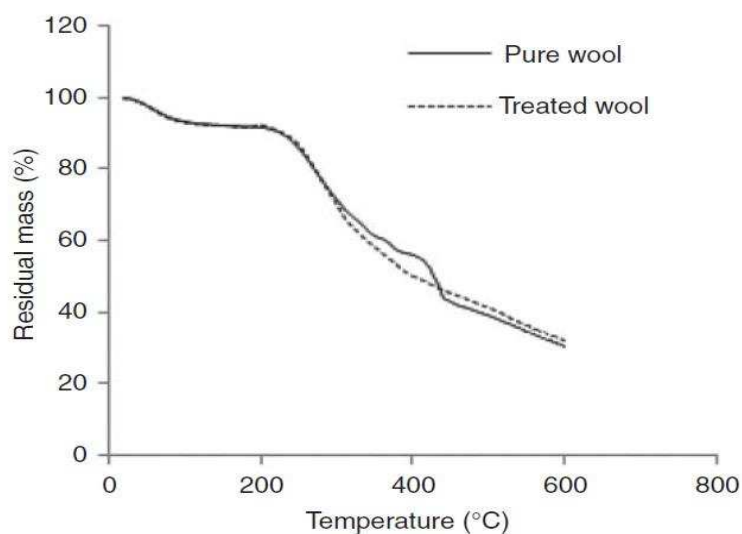


Figure 5 TG curve of Zirpro wool treated with 9.74% zirconium oxychloride, 9.6% citric acid, 6.3% formic acid at 95°C for 45min, figure from ²⁸

4.5 Differential scanning calorimetric analysis

The thermal properties of the treated keratin polymer were also analysed by using DSC technique. The DSC curves of the untreated and treated keratin polymer are presented in Figure 6Figure 10. It is observed that there is clearly an exothermic peak occurring between 220°C and 260°C in the DSC curves of the treated keratin polymer, particularly in the samples 2 to 3. Such exothermic peak has never been found in the DSC curve for untreated keratin polymer (see Figure 6). In contrast, there is a small endothermic peak in the same range of temperature in the DSC curve of untreated keratin polymer (see Figure 6). It is thus concluded

that the exothermic peak occurring between 220°C and 260°C indicates the influence of the chemical modification on the thermal pyrolysis of the keratin polymer, and that this exothermic peak represents the energy consumed to break the new bonds formed in the untreated keratin polymer.

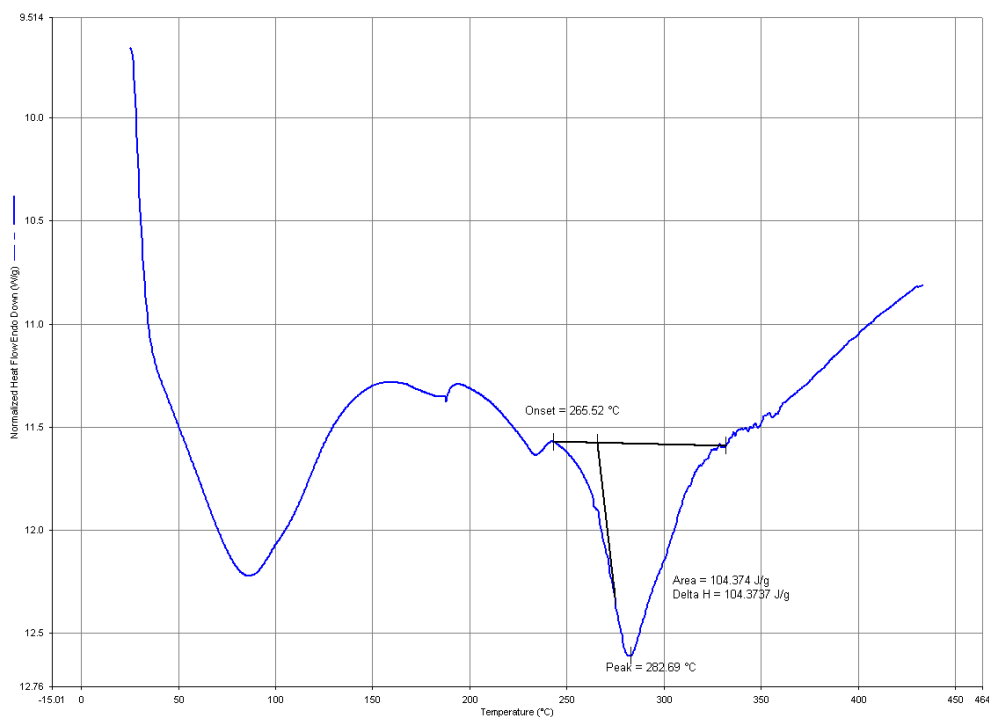


Figure 6 DSC curve of the untreated keratin polymer (sample 0)

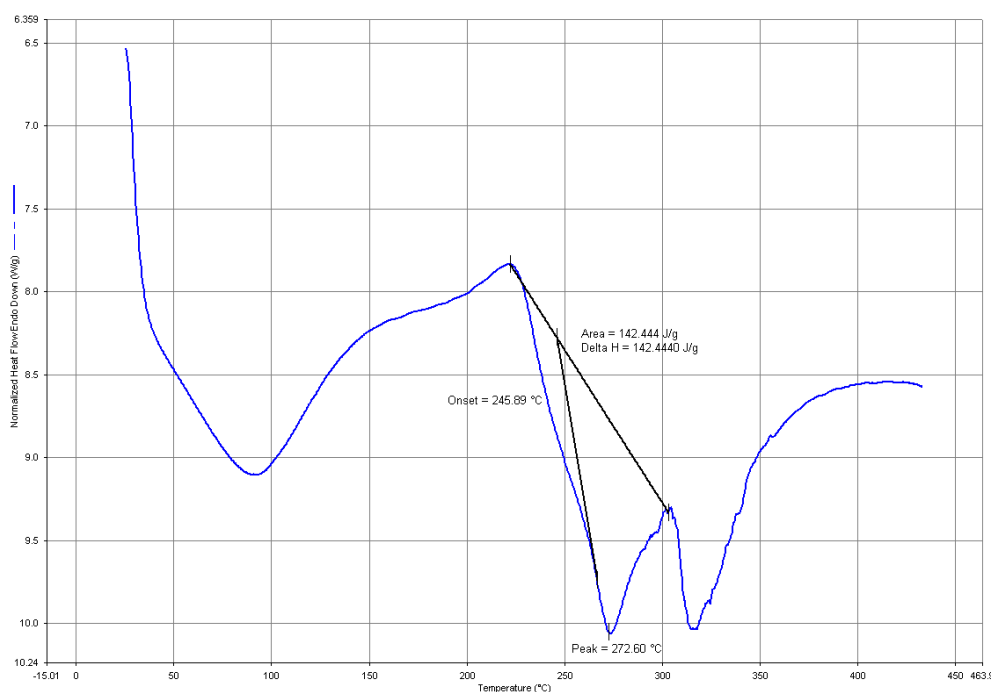


Figure 7 DSC curve of the treated keratin polymer (sample 1)

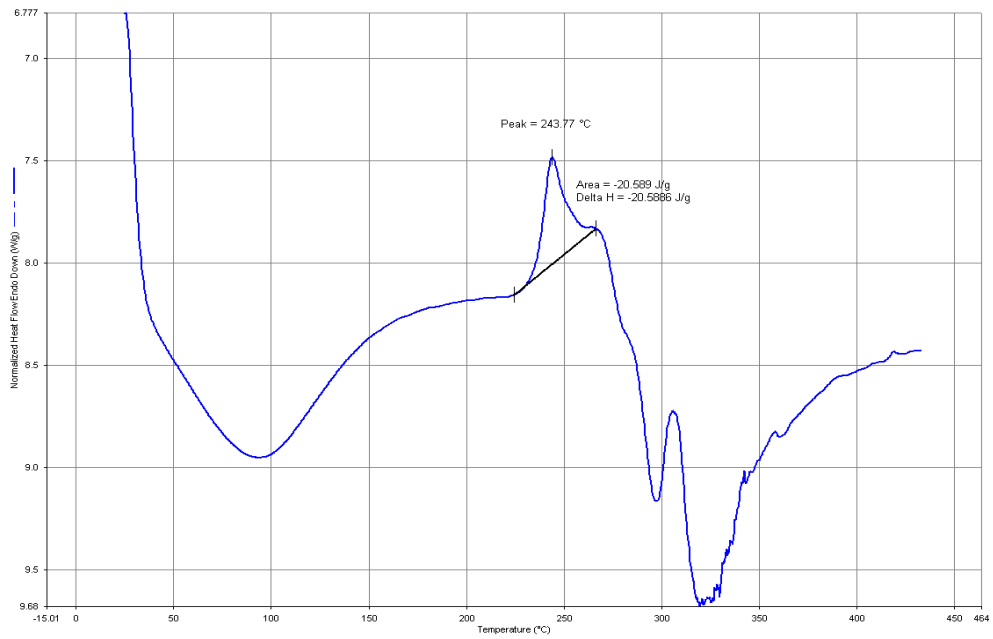


Figure 8 DSC curve of the treated keratin polymer (sample 2)

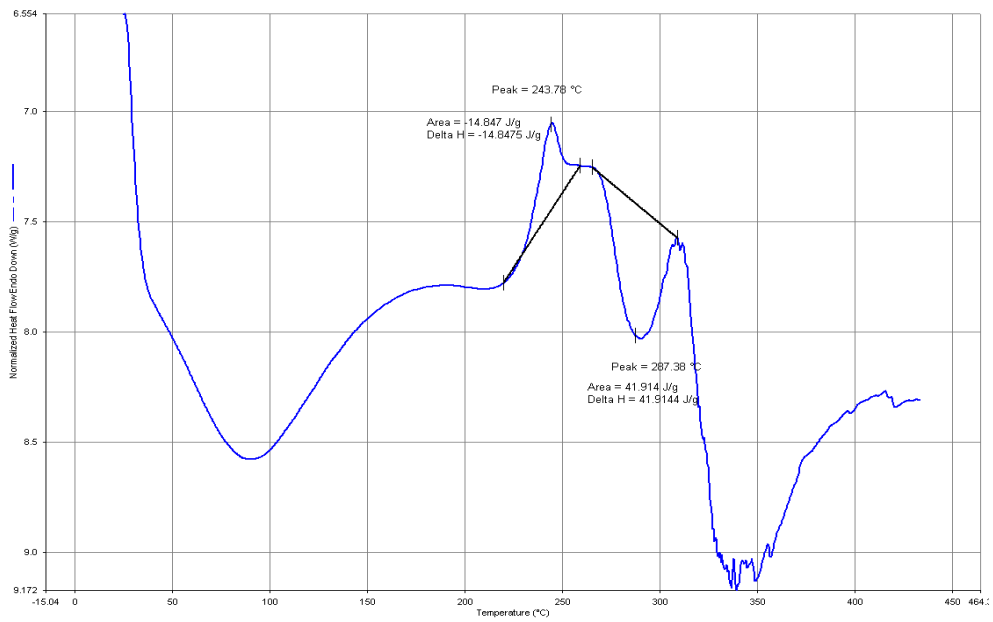


Figure 9 DSC curve of the treated keratin polymer (sample 3)

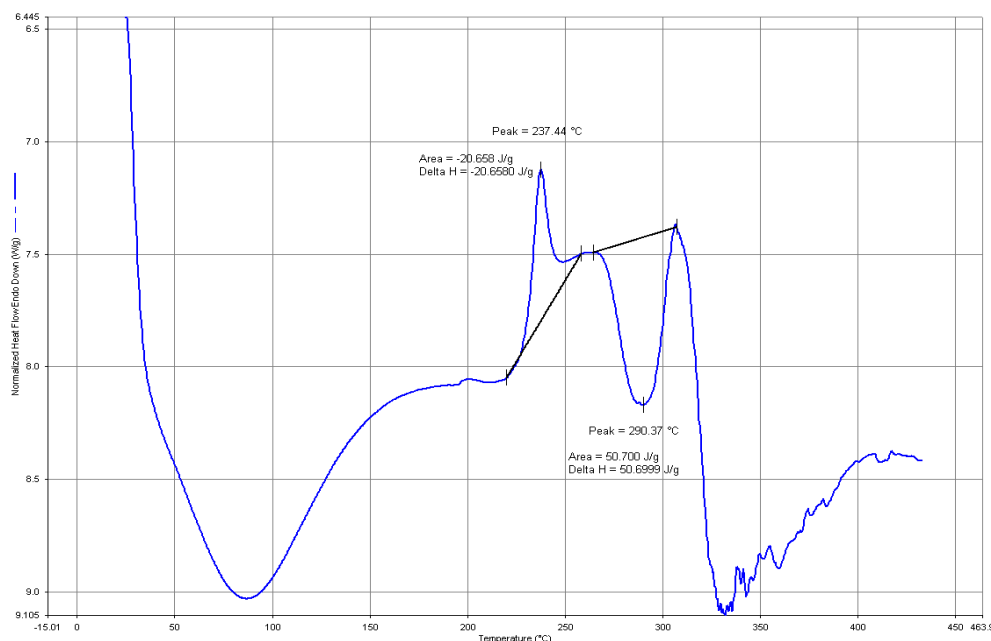


Figure 10 DSC curve of the treated keratin polymer (sample 4)

Conclusions

The thermal properties of keratin polymer chemically modified using a flame retardant agent having N-P synergic effect is significantly improved. The changes of both active groups and key elements of the keratin polymer before and after the chemical treatment are characterised, and the FTIR and ^{31}P -NMR analysis indicated that the P and Cl elements are bonded with the wool keratin polymer successfully. It is found that the treated keratin polymer has significant less mass losses and much greater char residues than that of untreated keratin polymer during their pyrolysis processes. It is believed that an exothermic peak occurring between 220°C and 260°C in DSC analysis is associated with the influence of the flame retardant agent treatment on the thermal pyrolysis of the treated keratin polymer. This treated keratin polymer is envisaged to have improved flame retardant properties and such treatment process could also be used in the treatment of wool fibres, yarns and fabrics.

References

- ¹ L. Benisek. *Zirpro Wool Textiles*. Fire and Materials. 1984,8 (4) , p183-195.
- ² N. A. G. Johnson and I. M. Russell. *Advances in wool technology*. Woodhead publishing limited, Cambridge England, 2009, p165-167.
- ³ I. K. Walker, W. J. Harrison, A. G. Read. Ignition of Wool in Air. Part I: Ignition Temperatures of Dry Wool, *New Zealand J. Sci.* 1969, 10, p32-51.
- ⁴ R. E. Whitfield, M. Friedman. Chemical Modification of Wool with Chlorendic Anhydride and Related Halo-organic Acid Anhydrides, *Textile Chemist and Colorist*. 1973,5, p76-78.
- ⁵ M. Friedman, S. Tillin. Flame-Resistant Wool. *Textile Research Journal*, 1970, 40, p1045-1047.
- ⁶ S. Tillin, C. E. Pardo, W. Fong, M. Friedman. Flameproof and Shrinkproof Wool, *Textile Research Journal*. 1972,42, p135-136.
- ⁷ A. R. Horrocks. *Handbook of Technical Textiles*, Woodhead publishing limited, Cambridge England, 2000, p264-291.

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- ⁸ DA de Wit., An overview of brominated flame retardants in the environment. *Chemosphere*. 2002. 46(5), p583-624.
- ⁹ L. O. Bajpai, C. S. Whewell, J. M. Woodhouse. Action of Tetrakis(hydroxymethyl)phosphonium Chloride on Wool. *Nature* 1960 (187), p602-603
- ¹⁰ M. J. Williams. THPC-Treated Wool: Amino Acid Analysis. *Textile Chemist and Colorist*. 1970,p41-44.
- ¹¹ G. G. Crawshaw, P. A. Duffield, P. N. Mehta. Flammability and Flam proofing of Wool Fabrics, *J. Appl. Polymer Sci. (Appl. Polym. Symp. No.18)* 1971,p1183-1197.
- ¹² M. E. Hall, S. Shah. The reaction of wool with N-Hydroxymethyl phosphonopropionamide. *Polymer degradation and stability*. 1991 (33), p207-212.
- ¹³ A.R. Horrocks. *Handbook of Technical Textiles*. Woodhead publishing limited. Cambridge England.(2000).p246-247
- ¹⁴ L. Benisek. Textile finishing. US patent 3857757(1974); 4160051(1979); 3857727 (1974)
- ¹⁵ M. Forouharshad. Flame retardant wool using zirconium oxychloride in various acidic media optimized by RSM. *Thermochimica Acta*, 2011(516), p29-34.
- ¹⁶ M. Forouharshad. Preparation of flame retardant wool using zirconium acetate optimized by CCD. *Thermochimica Acta*, 2011 (520), p134-138.
- ¹⁷ G. Camino, L. Costa. *Reviews in Inorganic Chemistry*.1986; 8, 69-100
- ¹⁸ Z. Sheng. A. R. Horrocks. Flame-retardant polymeric materials. UK patent: 2352447-A (2000)
- ¹⁹ S. Zhang, A. R. Horrocks. Substantive intumescent flame retardants for fuctional fibrous polymers. *Journal of Materials Science*. 2003, 38, p2195-2198.
- ²⁰ G. Chen. Method for flame-retardant checking wool or wool-containing textile, China patent: CN101255653. 2008
- ²¹ Q. Wang. Method for improving wool fire-retardancy with biological enzyme, China patent: CN101509193. 2009
- ²² H. Xu, J. Shi, A. Zhou, K. Yan. Keratin extraction from wool and its film forming property. *Journal of Textile Research*. 2012,33(6), p41-47
- ²³ A. Aluigi, M. Zoccola , C. Vineis , C. Tonin, F. Ferrero , M. Canetti. Study on the structure and properties of wool keratin regenerated from formic acid. *International Journal of Biological Macromolecules*. 2007, 41,p266–273
- ²⁴ K. Katoh, M. Shibayama, T. Tanabe, and K. Yamauchi, “Preparation and physicochemical properties of compression-molded keratin films,” *Biomaterials*. 2004,vol. 25, no. 12, pp. 2265–2272.
- ²⁵ L. P. Chen, W. D. Dong. Analysis on wool fibre and its film by FTIR. *Journal of Donghua University*. Vol32, 4, 2006, p105-109.
- ²⁶ J.T. Pelton. *Spectroscopic Methods for Analysis of Protein Secondary Structure*. Analytical Biochemistry, 2000. 277, p167-176.
- ²⁷ W. Gallagher. FTIR Analysis of ProteinStructure.http://download.bioon.com.cn/view/upload/201110/10233820_7954.pdf
- ²⁸ M. Forouharshad, M. Montazer, M. Bameni Moghadam and O. Saligheh. Flame Retardancy of Wool Fabric with Zirconium Oxychloride Optimized by Central Composite Design. *Journal of Fire Sciences* 2010, 28, p561-572.
- ²⁹ P.J. Davies, A.R. Horrocks, M. Miraftab. Scanning electron microscopic studies of wool/intumescent char formation, *Polymer International*, 2000, 49(10), p1125–1132.
- ³⁰ J. S. Crighton, L. Trezl and I. Rusznak. A study of significant properties of aldehyde modified keratin fibres. *Proceedings of the 6th Quinquennial International Wool Textile Research Conference*. Pretoria, 1980,V2, p339.
- ³¹ B.K. Kandola, S. Horrocks, A.R. Horrocks. Evidence of interaction in flame retardant fibre-intumescent combinations by thermal analytical techniques. *Thermochimica Acta*, 1997, 294(1), p113-125.