

Flame-Retarding Modification of Nylon 6 Textile

KANG DE YAO,^{1,*} WEIPING HAN,¹ and DECHANG HAN²

¹Department of Material Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China,

²Department of Textile Chemistry, Tianjin Institute of Textile Science and Technology, Tianjin 300160, People's Republic of China

SYNOPSIS

For the purpose of flame retardation, nylon 6 textile was first hydroxymethylated and then the methylol group containing nylon 6 textile was finished with Pyrovatex CP at 160–170°C. The limiting oxygen index (LOI) value increased from 23.6 for the original textile to 31.4 for the modified one. The mechanism of flame retardation was investigated using thermogravimetry (TGA), differential scanning calorimetry (DSC), elemental analysis, infrared spectroscopy, and X-ray diffraction. Results reveal that Pyrovatex CP plays a flame-retarding role in both the condensed and gas phases.

INTRODUCTION

From a technological viewpoint, flame-retardation studies of synthetic fibers are very interesting and challenging. As we know, most flame retardants that are effective in cellulose are not effective for nylon.¹ Therefore, novel ways to reduce the fire hazard of nylon 6 textile need to be explored further. On the basis of the polymer reaction, we modified nylon 6 textile to produce a somewhat reactive group, e.g., a methylol group, and the modified nylon 6 textile can be compounded with *N*-methylol-3-(dimethoxy)phosphonopropioamide (Pyrovatex CP) to render the textile flame-retardant.

The aim of the present work was to elucidate the mode of action of this flame-retarding modification of nylon 6 textile.

EXPERIMENTAL

Materials

Nylon 6 was an undyed textile. Formaldehyde (36%), Pyrovatex CP, and all materials used here are commercially available.

Preparation of Flame-Retarding Nylon 6 Textile

Hydroxymethylation of nylon 6 textile was carried out in a 36% formaldehyde aqueous solution at pH = 0.9–1.0 and 70–80°C for 1–2 h. The modified textile after washing with water to free it from residual formaldehyde was treated in a 10–50% Pyrovatex CP solution for 5–30 min and then the dried textile was kept at 150–180°C for a further 2–6 min to obtain the flame-retarding nylon 6 textile.

Flammability Test

The limiting oxygen index (LOI) was determined on a YG 813 oxygen index apparatus (Changzhou No. 2 Textile Machine Factory, P.R. China) in accordance with the standard procedure.²

Infrared Spectroscopy

A Shimadzu spectrometer IR-435 was used. The nylon 6 textile samples were extracted with water for 70 h in advance. Infrared spectra were examined in KBr discs.

Elemental Analysis

Phosphorus contents of samples were evaluated by a titration method. Samples were burned in an oxygen combustion flask. The resulting products were absorbed in an aqueous solution of sodium hydrox-

* To whom correspondence should be addressed.

ide. The solution with added $\text{La}(\text{NO}_3)_3$ was titrated with EDTA.

Thermogravimetry

Thermogravimetry analysis (TGA) was performed in air with a Shimadzu thermogravimetric analyzer DT-30B. Samples of about 3.2 mg were heated at a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 700°C .

Differential Scanning Calorimetry

A Perkin-Elmer Model DSC-2C differential scanning calorimeter was used. Samples of about 2.6 mg were heated at $20^\circ\text{C}/\text{min}$ from room temperature to 520°C in air.

X-Ray Diffraction

About 4.5 g of dried sample was pyrolyzed at about 550°C for 40 min and then cooled to obtain residue. X-ray diffraction spectra of residues were obtained on a Rigaku D/max-ra diffractometer with a graphite monochromator and $\text{CuK}\alpha$ target at 50 kV, $170 \mu\text{A}$.

RESULTS AND DISCUSSION

Flammability Characteristics

IR spectra of nylon 6 (N), a composite of nylon 6 with Pyrovatex CP (CP-N) and a methylol nylon

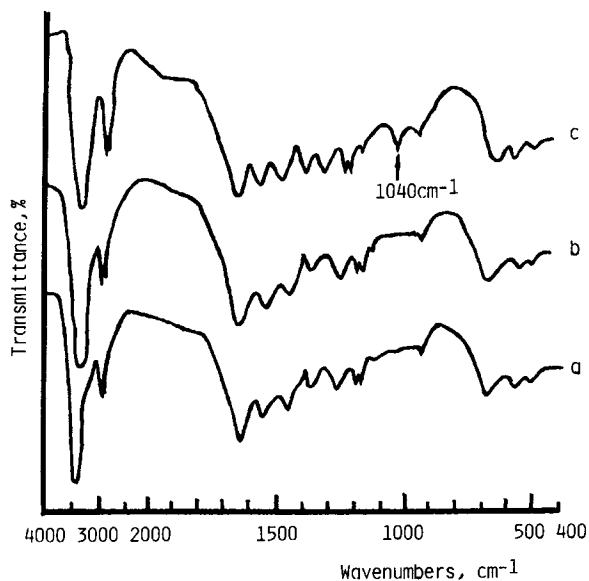


Figure 1 IR spectra of different nylon 6 textiles: (a) N; (b) CP-N; (c) CP-MN.

Table I LOI and Phosphorus Content of Nylon 6 Textiles

Value	Sample	
	CP-N	CP-MN
LOI	23.6	31.4
P (wt %)	0	2.92

6 compound with Pyrovatex CP (CP-MN) are shown in Figure 1. In comparison with N and also with CP-N, only the sample of CP-MN has an absorption band at 1040 cm^{-1} , which is due to phosphonate ester.³ The results indicate that only the MN can combine with Pyrovatex CP:

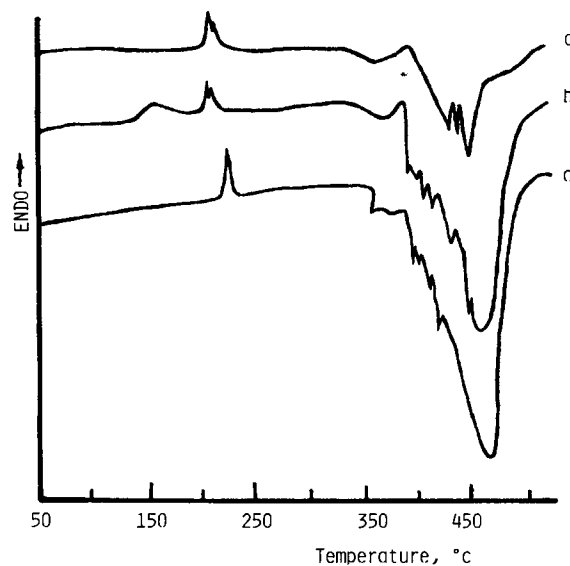
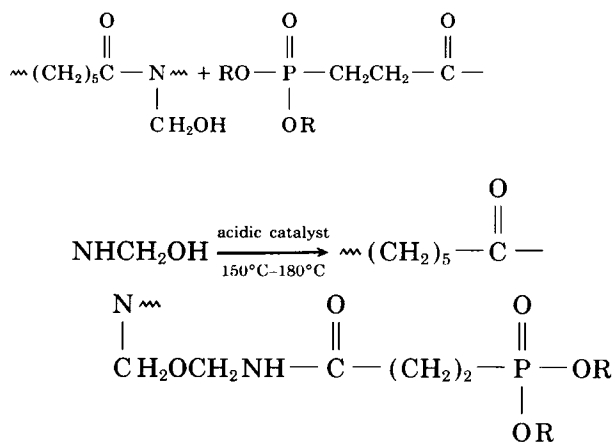


Figure 2 The influence of flame-retarding modification on DSC thermogram of nylon 6. (a) N; (b) MN; (c) CP-MN.

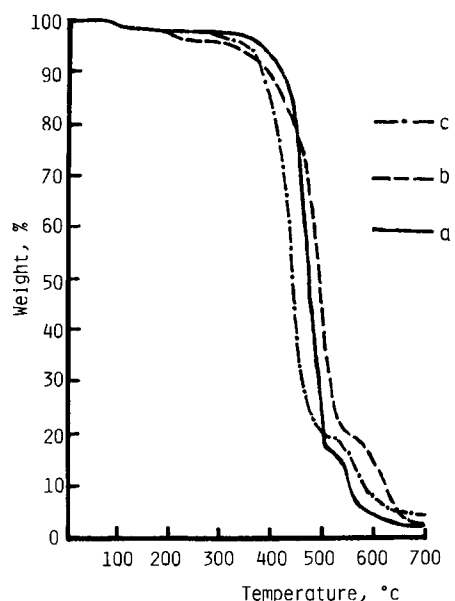
Table II Melting Characteristics of Nylon 6 Crystalline

Value	Sample		
	N	MN	CP-MN
Melting peak	Single	Double	Double
Melting point (°C)	223	204	203
Melting enthalpy (kJ/kg)	76.24	62.47	63.56
Peak width, (°C)	13	21	24

Table III Thermal Oxidation of Different Nylon 6 Textile from DSC Thermogram

Value	Sample		
	N	MN	CP-MN
Initial pyrolysis temperature (°C)	345	324	329
Enthalpy (kJ/kg)	-1031.8	-1022.2	-320.9
T_{\max} of peak (°C)	459	450	434

Elemental analysis data (cf. Table I) support this observation. The phosphorus content is zero for CP—N, whereas P% for CP—MN is 2.92%. The flame-retarding modification raises the LOI of N to 31.4 from 23.6, while tear strength drops only 9% and the textile obtained has the advantage of durability without influence on its feel. A phosphorus

**Figure 3** Thermogravimetry curves of various nylon 6 textiles: (a) N; (b) MN; (c) CP-MN.**Table IV Phosphorus Content of Pyrolysis Residue of CP-MN**

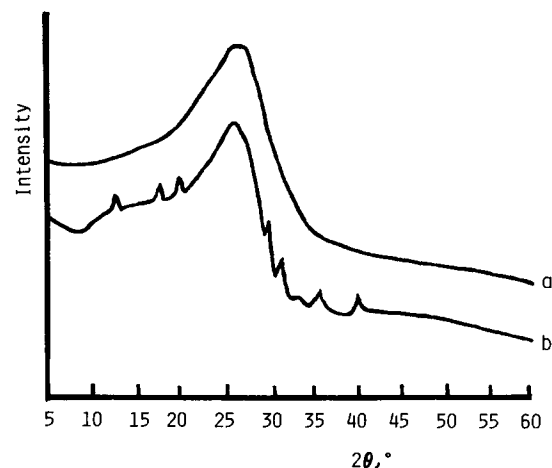
Value	Sample	
	Original Textile	Pyrolysis Residue
Weight (g)	4.4932	0.2781
P (wt %)	2.73	5.11
P (g)	0.1227	0.0142
Phosphorus in residue	11.6% (wt/wt)	
Phosphorus in gas	88.4% (wt/wt)	

content of ca. 3 wt % is enough to result in flame retardation in the CP—MN/N—P synergetic system.

Thermal Behavior Studies

The melt characteristics of crystalline obtained by DSC (Fig. 2) are listed in Table II. Data reveal that the complex melt peaks of MN and CP—MN are attributed to the heterogeneity of polymeric reactions, e.g., hydroxymethylation and compounding with Pyrovatex CP. The modification is carried out only in the amorphous regions and in the surface layer of the crystalline regions. Mixing MN with the N matrix leads to a reduction in melting point and enthalpy and enlargement in the melting region, whereas an increase in the melting enthalpy of CP—MN is due to an enhancement in the interaction between macromolecules.

Data in Table III demonstrate that CP—MN results in a decrease in thermal oxidation enthalpy. The corresponding thermogravimetric curves of N

**Figure 4** X-ray diffraction curves of pyrolysis residue of (a) N (b) CP-N.

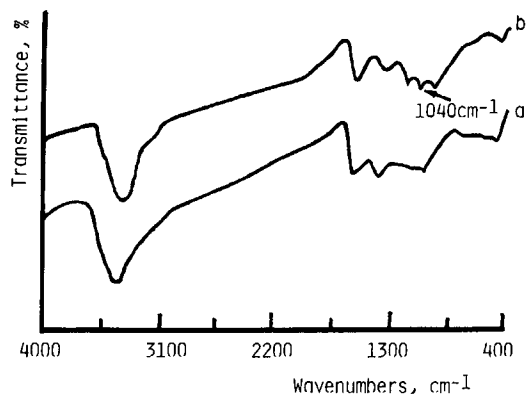


Figure 5 IR spectra of pyrolysis residue of (a) N and (b) CP-N.

and CP—MN in Figure 3 show that the lower the enthalpy, the larger is the pyrolysis residue at 700°C, i.e., 1.4 wt % for N and 3.5 wt % for CP—MN. The phosphorous content analysis data (cf. Table IV) shows that most of the phosphorus exhausts in the gas phase.

X-Ray Diffraction

Results from X-ray diffraction (Fig. 4) show that the pyrolysis residue of N is a typical amorphous carbon, whereas that of CP—MN contains a small amount of crystalline phosphorous containing polymer in addition to a matrix of amorphous carbon.

There is a 1040 cm^{-1} absorption peak due to the —P—O—C group only in the IR spectrum of the pyrolysis residue of CP—MN (cf. Fig. 5), which supports the data from X-ray diffraction.

CONCLUSION

Flame-retarding modification of nylon 6 textile through hydroxymethylation and then compounding with Pyrovatex CP can raise the LOI value of the textile. The modification results in a decrease in thermal oxidation enthalpy and an increase in the amount of pyrolysis residue. A change in phosphorus content reveals that the flame-retarding modification plays a role in both the gas and condensed phases.

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Received June 3, 1991

Accepted October 1, 1991