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SILOXANE-PHOSPHONATE FINISHES ON CELLULOSE: THERMAL CHARACTERIZATION AND FLAMMABILITY DATA

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Abstract

There are many characteristics inherent to cotton fibers that make them desirable for use in industrial and consumer products. However, other traits constrain cotton utilization, especially when combustibility is an issue. Existing research suggests that phosphorous-based flame-retardants promote the formation of a protective char layer that minimizes the fuel available for flame propagation. In addition to improving processability and a number of mechanical properties, siloxanes have been shown to enhance flame retardant performance in conjunction with conventional flame retardant agents. In this study, new siloxane-phosphonate monomers applied to cotton fabric were characterized for thermal stability using thermogravimetric analysis (TGA). Flammability testing using the Oxygen Index (OI) apparatus was used to elucidate TGA results.

Introduction

Cotton fibers have many characteristics that make them desirable for use in a wide range of applications. However, other traits are detrimental and limit or prohibit cotton's use, especially when combustibility is an issue. While cotton and cotton-containing fabrics constitute a large segment of the apparel and home furnishings markets, stringent guidelines exist for consumer protection in applications such as children's sleepwear, protective apparel, carpets, and mattress components. These restrictions limit cottons appeal and use in these products (16 CFR 1630-1; 16 CFR 1615-6; 16 CFR 1632). By minimizing flammability, cotton can meet these guidelines and realize a greater market share.

A large body of scientific work exists concerning flame retardant agents and cellulose. For most end uses, an ideal flame retardant agent for cellulose should retard or arrest flaming and/or smoldering, be stable and durable, and have no damaging physiological effects or negative impact on aesthetic or mechanical properties. Phosphorous containing compounds have repeatedly been shown to act as effective flame retarding agents when applied to substrates with high oxygen content such as cellulose. It has been suggested that phosphorous-based flame-retardants promote the formation of a protective char layer that minimizes the fuel available for propagation of a flame (Howell et al., 1999). In addition to improving processability and some mechanical properties, siloxanes have been shown to enhance performance in conjunction with conventional flame retardant agents (Nelson et al., 1998). The use of a siloxane-phosphonate material may show improved flame retardant behavior over conventional techniques.

Thermogravimetric analysis (TGA) is used commonly to describe decomposition patterns, material stability, and effects of additives on a material's thermal performance (Khanna 1996). Nakanishi, et al. have extensively examined the use of TGA for characterizing flame retardance of cellulosic fibers. Clear correlations have been shown between the thermal degradation onset point (TDOP), percent char residue, and results of Limiting Oxygen Index (LOI), when evaluating material flammability. In general, phosphorous-based flame retardant agents that perform well in LOI tests when applied to cellulosic materials have a lower TDOP and greater percent char residue (Nakanishi et al., 1998).

Oxygen Index (OI) is a standard flammability test for materials that provides a way to characterize the burning behavior and combustibility of a material. The test identifies the percentage of oxygen in the atmosphere required to maintain "candle-like burning behavior (ASTM 2000)." While a useful industry standard, LOI provides little quantitative data that can be helpful in designing future experiments and treatment options. The use of TDOP and char residue produced by thermogravimetric analysis helps to quantify improvements and can produce incremental advancements in procedure and new material development.

In this study, new siloxane-phosphonate monomers were applied to cotton fabric and characterized using TGA and LOI in order to gain information about their possible use as flame retardant finishes on cotton textiles.

Experimental

Materials

Syntheses of $(CH_3O)_2CH_3Si(CH_2)_3P{=}O(OCH_2CH_3)_2$, monomer **A**, and $(CH_3O)_3Si(CH_2)_3P{=}O(OCH_2CH_3)_2$, monomer **B**, (Figure 1) were prepared as previously reported (Gallagher 2000; Gallagher 2003a; Gallagher 2003b). All other reagents were obtained from Aldrich and used as received. Cotton twill fabric was obtained from Test Fabrics, Incorporated and used as received.

Characterization
Thermal analyses were performed with TA Instruments model 2950 thermogravimetric analyzer (TGA) under a purge of N_2 at a heating rate of 10 °C/minute. Oxygen Index was performed using a Dynisco Oxygen Index Chamber.

Fabric Treatment
The fabrics were weighed after oven drying to obtain initial weights and then immersed in the formulations until saturated. Once removed from the baths, the fabrics were allowed to lay flat under ambient conditions to permit polymerization and reaction with the cellulose before being returned to the oven to cure. Once removed from the oven, the fabrics were weighed and then washed in a conventional washing machine using the "cold" setting and dried in a conventional dryer. Upon removal from the dryer, the samples were weighed to determine percent add on of the formulation.

Results and Discussion

Several formulations were created for comparison of TGA and LOI of the monomer polymerized on fabric (see Table 1). Standards for each of these series underwent identical treatments without addition of the monomer.

Table 1. Sample Formulations.

Sample	Formulation
ST	---
B_{HCl} 1-4	0.01M Hydrochloric acid + monomer
B_{ac} 1-4	0.01M Acetic acid + monomer
B_{ca} 1-4	0.01M Citric acid + monomer
B_{H2O} 1-4	Water + monomer

TGA results of untreated cotton fabric and fabrics treated with **B** in solution of dilute acetic acid are shown in Figure 2. The untreated fabric (ST) has a higher TDOP and lower percent char yield which compare favorably to those found in the literature (Nakanishi et al., 1998). Fabrics treated with monomer **B** applied have lower TDOPs and much higher char yields, respectively decreasing and increasing with increased add-on. All four samples follow similar degradation curves. This trend was seen with all other formulations although preparations using monomer **A** did produce similar results, the improvements were not as notable as those measured with monomer **B**.

In Figure 3, the relationship is shown between add-on, char residue, and LOI using the B_{ac} series as an example. The untreated fabric (ST) has very little char residue and requires less oxygen to burn than the treated fabrics. A clear trend is apparent as increased add-on of monomer B in a citric acid solution produces an improved char yield as well as an increase in LOI. Most of the formulations and treatments examined followed similar behaviors. From the flammability testing, an additional observation can be made. With an increase in add-on, char integrity improved. Even the lowest add-on showed a marked increased in integrity of the tested fabric structure.

Conclusions

New siloxane-phosphonate polymers were applied to cotton fabric and characterized using TGA and LOI. In all cases, fabrics treated with formulations including monomers **A** or **B** regardless of acid used exhibited higher char yields, lower TDOP, and an increase in LOI over untreated fabrics. Ongoing work is examining other possible formulations and treatment parameters that combine additional co-reagents with monomers **A** and **B**. Future work will examine their flame retardancy, finish durability, and extended thermal characterization.

Acknowledgements

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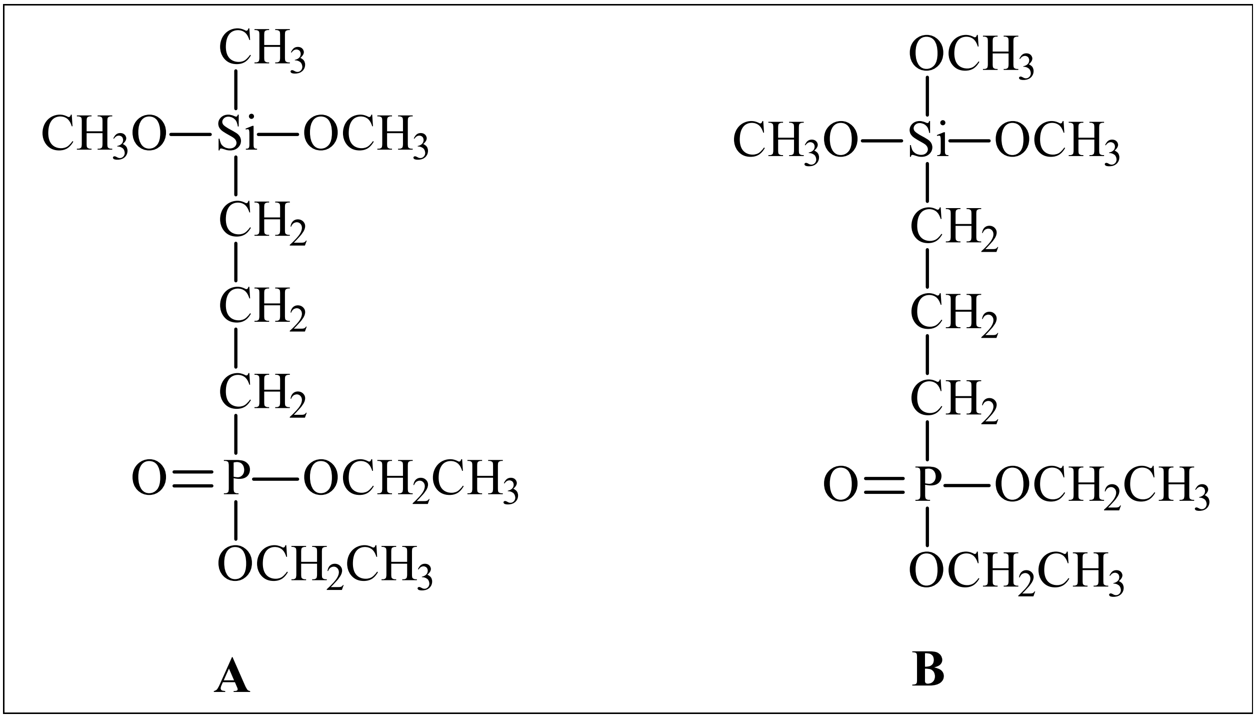

Figure 1. Structure for monomers **A** and **B**.

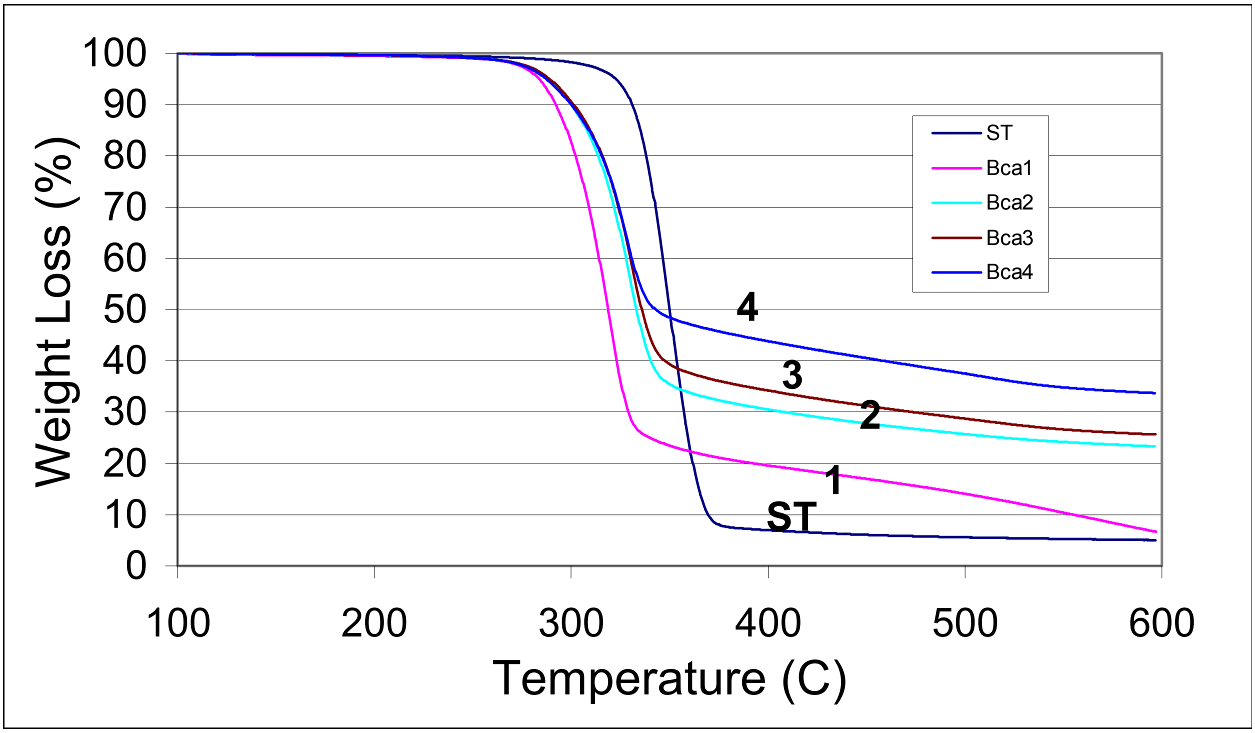

Figure 2. TGA results for B_{ca}.

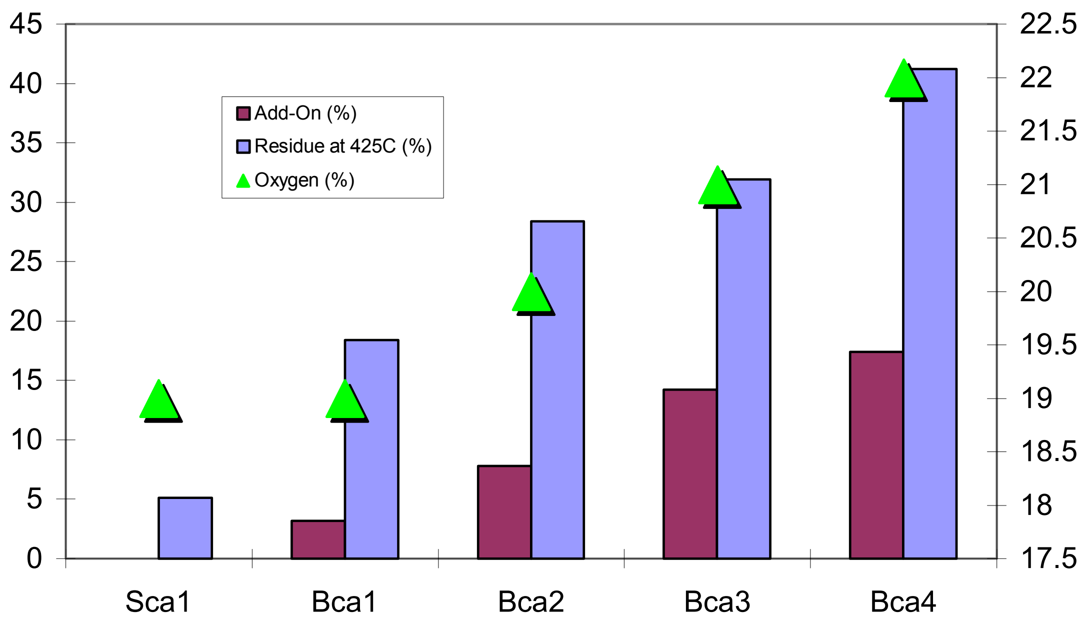

Figure 3. Add-On, Percent Residue, and Oxygen Index for B_{ca} samples.