Investigation of Synergistic Effects of Phosphorus, Nitrogen and Silicon in the Flame Retardancy of Cellulose-based Cotton Textiles Processed by Plasma-Induced Graft Polymerization

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Abstract: Using plasma-induced graft polymerization, the kinetics of polymerization of a silicon-containing acrylate monomer was determined. The synergistic effects of phosphorus, nitrogen and silicon in the flame retardancy of cotton textiles were subsequently investigated as a physical mixture of silicon-containing monomer and a phosphoramidate monomer containing a phosphorus-nitrogen bond.

Keywords: Flame retardants, Synergistic effects, Textiles, Silicon, Plasma Polymerization

1. Introduction

With the increasing concern of their toxicity and environmental-friendliness, a recent global ban on the use of halogenated flame retardants [1] points to an increasing demand and need to develop new classes of wash resistant and environmentally friendly flame retardants. This is especially important for cellulose-based cotton textiles, since they are mostly used in the production of clothes and fabrics for everyday use by the human population.

In this regard, it has been previously shown in the literature [2] that for natural cellulose-based cotton fabrics, flame retardancy could be conferred through the plasma-induced graft polymerization (PIGP) technique applied onto phosphoramidate monomers containing phosphorus-nitrogen bonds. In particular, one of the monomer compounds, diethyl (acryloxyethyl) phosphoramidate (DEAEPN) (Scheme 1), has shown promising potential in industrial application owing to its good flame retardancy and its relatively high phosphorus content (12.3 %) in the molecule. On the other hand, these are not the only classes of compounds being studied as potential flame retardant materials.

As their combustion products are not considered to be pollutants in fire, there have been studies on the possible use of silicon-based compounds as flame retardants [3, 4]. Recently, investigations on the synergistic effects of phosphorus, nitrogen and silicon have been reported in the literature [5] on polypropylene substrates. In view of the potential of such effects on cotton textiles, it would be of interest to investigate the possible synergistic effects using various strategies of using phosphorus, nitrogen and silicon-containing monomers to modify the surface of cellulose-based cotton textiles via the PIGP process. One of them would include using a physical mixture of flame retardant materials comprising phosphoramidate (source of phosphorus and nitrogen) and a silicon-containing acrylate monomer. Since it is commercially available and has been used mostly as additive for dental restorative materials [6] and surface coatings [7], we are interested in finding out if 3-(acryloyloxy)propyltrimethoxysilane (APTMS) (Scheme 1) would also confer flame retardant properties to cotton textiles.

Therefore, we conducted investigations on the behavior of APTMS under plasma treatment. Herein we report a study on the kinetics of polymerization of APTMS and its comparison to that of DEAEPN when it is placed under argon plasma treatment. This is then followed by a preliminary investigation of synergistic effects between phosphorus, nitrogen and silicon using APTMS as the silicon-containing monomer, and DEAEPN as the phosphorus and nitrogen – containing phosphoramidate monomer.

DEAEPN

APTMS

Scheme 1: Chemical structures of DEAEPN and APTMS

2. Experimental

General Comments

All experiments involving the synthesis of air and moisture sensitive compounds were performed using a standard Schlenk vacuum line in oven-dried flasks under argon atmosphere. Solvents such as dichloromethane, and $CDCl_3$ were purified by distillation from calcium hydride. For commercially available chemicals, acryloyl chloride (Merck, ≥ 96 %) was purified by distillation under argon, while diethyl chlorophosphate (Acros, 95 %), 2 – ethanolamine (Fluka, 99 %), 3-(acryloyloxy)propyltrimethoxysilane (APTMS) (Alfa Aesar, 95 %), ethylene glycol diacrylate (EGDA, purchased from ABCR) and phenyl-bis(acyl)phosphanoxide (BAPO, IRGACURE 819, purchased from BASF Swiss, formerly Ciba Specialty Chemicals, Switzerland) were used as purchased without further purification. Cotton textile samples (density 180 g cm^{-2}) were purchased from EMPA Test Materials Company, St Gallen, Switzerland.

NMR spectroscopy

NMR spectra were recorded on Bruker Avance 250 and 300 spectrometers.

Synthesis of DEAEPN

The synthesis of DEAEPN was performed in accordance to the protocol published in the literature [2].

Kinetics of Polymerization

The kinetics of polymerization for a given monomer was determined by liquid state ^1H NMR spectroscopy. A series of glass petri dishes were each weighed and filled with a defined amount of monomer and 5 wt% initiator (Irgacure 819) as a solution in dichloromethane. The solvent was slowly evaporated under ambient conditions while the sample was protected from sources of light. After which, each of the samples underwent its respective plasma treatment for 0, 2, 5, 10, 15, 20 minutes. The kinetics of polymerization was monitored by ^1H NMR in DMSO for APTMS and $CDCl_3$ for DEAEPN. The characteristic integral of the double bond of monomer was then compared to that of the polymer.

Preparation of cotton textiles under a standard atmosphere

Before each experiment, these textiles were cut into dimensions of 50 mm x 100 mm, and placed under a standard atmosphere (Humidity 65 ± 2 %) containing a saturated aqueous solution of NH_4NO_3. Each sample was placed for at least 24 h prior to further experimentations.

Impregnation of cotton textiles with flame retardant monomer

For the preparation of the flame retardant solution, a mixture of monomers (a total of 20 % on the weight of the textile fabric), together with EGDA as a cross-linking agent (10 % on the weight of the monomers) and BAPO (5 % on the weight of the monomers) as the photoinitiator, was dissolved in ethanol to make a solution-to-substrate ratio of 1.3 to 1 (1.3 mL solution to 1 g of substrate). The conditioned textiles were weighed and placed on a glass petri dish. The solution was then spread onto the cotton textile sample dropwise using a syringe in a defined order. After complete evaporation of the solvent, the samples were weighed again to determine the uptake. The uptake of the monomers is calculated by

$$\%\ \text{Uptake} = \frac{w_f - w_o}{w_o} \times 100\%,$$

where w_f is the final weight of the fabric after impregnation of monomers, and w_o is the weight of the virgin fabric before modification, and

$$\%\ E = \%\ \text{Uptake} \times \frac{M_r(E)}{M_r(M)}$$

where E = P, N or Si, $M_r(E)$ is the atomic weight of the element, and $M_r(M)$ is the molecular weight of the corresponding monomer.

Plasma Induced Graft Polymerization on Cotton Textiles

The microwave plasma was generated by Europlasma DC300PC system. It includes a microwave generator of 2.46 GHz with a tunable power ranging from 0 to 600 W, generating the argon glow discharge; a 27-litre aluminum-based vacuum chamber, in which the PIGP process takes place; and a pumping system comprising a primary pump (E2M28 PFPE, *Edwards*). The gas flow was regulated by unit mass flow controllers.

In a typical PIGP process, the monomer-impregnated cotton textile sample, placed on a petri dish, was transferred into a plasma chamber and treated for 20 minutes (F_{Ar} = 125 sccm; RF = 100 W; P_{base} = 40 Pa).

Limiting Oxygen Index (LOI) Measurement

The LOI measurements on treated cotton fabrics were performed in accordance to ISO 4589-2 using an Oxygen Index Test Apparatus (*Fire Instrumentation Research Equipment Ltd*) with a digital readout of oxygen concentration to an uncertainty of ± 0.1%. For the measurement of LOI, the modified cotton textile sample was mounted on a sample holder, and the flame (Propane, Shell Gas) was directed from the top onto the textile to begin the burning process. The LOI value is defined as the percentage of oxygen in a nitrogen/oxygen mixture required to sustain the burning of a substrate of length 80 mm in 3 minutes.

3. Results and Discussion

Kinetics of Polymerization

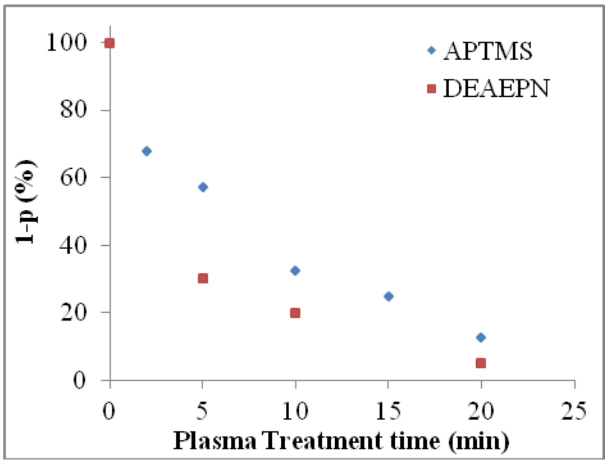

Figure 1 The extent of polymerization of the respective monomers with varying plasma treatment time.

Figure 1 shows how the polymerization of each monomer APTMS and DEAEPN progresses with increasing duration of plasma treatment. Here, APTMS is observed to undergo polymerization upon plasma treatment. 90 % of conversion is reached with 20 minutes of treatment. In comparison to the rate of polymerization of DEAEPN, however, APTMS appears to polymerize at a slower rate. This could be attributed to the possibility of chain transfer reactions, rendering more cross-linked polymer chains, hence the more gel-like appearance as observed during the experiment.

Application of APTMS as a flame retardant and the investigation of its synergistic effect with DEAEPN

In order to investigate the effectiveness of APTMS as a flame retardant, as well as the possibility of synergistic effects present when used as a physical mixture with DEAEPN, we have impregnated the respective monomers at different feed ratios. After the subsequent plasma treatment via PIGP process, we measured the corresponding LOI values of the processed cotton textile. The details are summarized in Table 1:

Feed (wt% mixture)		Uptake (%)	Elements (%)			LOI
DEAEPN	APTMS		P	N	Si	
100	0	16.6	2.1	0.93	0	24.5
74.0	26.0	16.4	1.5	0.68	0.51	23.5
65.1	34.9	20.9	1.7	0.76	0.87	23.0
47.6	52.3	13.5	0.79	0.36	0.85	20.5
31.0	69.0	18.2	0.69	0.31	1.5	20.0
22.8	77.2	15.9	0.45	0.21	1.5	19.5
0	100	17.2	0	0	2.1	19.0
49.6*	50.3*	10.8 (P) 9.74 (Si)	1.3	0.60	1.2	22.0
Virgin Cotton Textile						18.5

Table 1: The effect of mixing APTMS and DEAEPN on the LOI value of cotton textile. The percentages are expressed as the weight percent of the cotton textile. (*In this sample, the cotton textile was first treated with APTMS, followed by DEAEPN.) The percentages of the respective elements were calculated based on the assumption that the monomers DEAEPN and APTMS have similar rates of uptake.

From Table 1 it could be observed that in the presence of only APTMS, there is no significant increase in LOI value, as compared to that of virgin cotton textile of the same density. However, when the cotton textile is treated with only DEAEPN, and at same loading of phosphorus as with silicon, LOI value differed significantly by 5.5 percentage points. This suggests that the presence of APTMS does not confer or confers only little flame retardant properties on the cotton textiles.

When these 2 monomers are present as a physical mixture, the LOI values appear to depend more on the amount of phosphorus than on the amount of silicon impregnated onto the cotton textile. This again suggests that APTMS has little or no flame retardant effect on the cotton textile. A possible reason for this could be the cleavage of Si–O bonds which generates methanol species. Subsequently, methanol contributes to the fuel for burning.

Furthermore, in a subsequent treatment when the cotton textile was first treated by APTMS, then successively by DEAEPN, there was a significant increase in the LOI value. This indicates that successive addition and treatment of the monomers confer an encapsulating effect of DEAEPN on the APTMS-functionalized cotton textile. This could in turn inhibit the formation or release of volatile species from the APTMS polymer that would aid the cotton textile burning process.

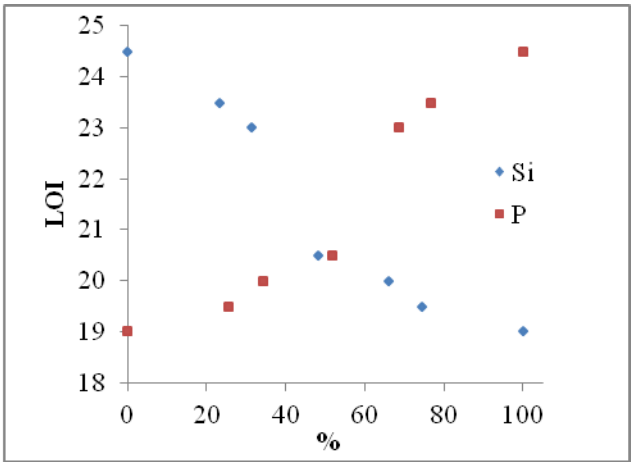

Figure 2: The relationship of LOI values with respect to the relative percentages of phosphorus and silicon.

Figure 2 shows how the LOI values are dependent on the relative amounts of phosphorus and silicon in the mixture of monomers added onto the textile. In general, LOI values are found to increase with an increase of phosphorus relative to silicon. This indicates a trend, supporting the aforementioned observation that the LOI depends only on the amount of phosphorus added onto the textile, and the presence of silicon does not contribute significantly towards the increase or decrease of the LOI values. From here we could infer that there are no synergistic effects of phosphorus, nitrogen and silicon on the flame retardant properties on cotton textiles when they are originated from a physical mixture of DEAEPN and APTMS.

Conclusions

In summary, we have shown that with argon plasma treatment, it is possible to polymerize a silicon-based acrylate monomer, in this case APTMS. However, APTMS is found to confer little or no flame retardant properties on cotton textiles. When introduced as a physical mixture with DEAEPN, the presence of Si–O bonds in APTMS does not contribute towards any synergistic effects with phosphorus and nitrogen in DEAEPN on the flame retardancy of cotton textiles.

Using a different approach, however, the possible synergistic effect can be observed when silicon is incorporated in the same molecule with phosphorus and nitrogen via covalent bonding (P–N–Si bonds). Further works are currently underway in the investigation of this synergistic effect on flame retardant properties between these three elements. As APTMS contains Si–O bonds, it would be worthwhile instead to investigate the effect of a monomer containing Si–C bonds, such as $SiMe_3$ groups, which are relatively more stable.

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