

Synthesis and performance of flame retardant additives based on cyclodiphosph(V)azane of sulfaguanidine, 1,3-di-[*N*]-2-pyrimidinylsulfanilamide]-2, 2, 2.4, 4, 4-hexachlorocyclodiphosph(V)azane and 1,3-di-[*N*]-2-pyrimidinylsulfanilamide]-2, 4-di[aminoacetic acid]-2, 4-dichlorocyclodiphosph(V)azane incorporated into polyurethane varnish

H. Abd El-Wahab^a, M. Abd El-Fattah^{b,*}, N. Abd El-Khalik^c, Carmen M. Sharaby^c

^a Chemistry Department, Faculty of Science, Al Azhar University, Cairo, Egypt

^b Production Department, Egyptian Petroleum Research Institute (EPRI), Cairo, Egypt

^c Chemistry Department, Faculty of Science(Girls), Al Azhar University, Cairo, Egypt

ARTICLE INFO

Article history:

Received 5 January 2012

Accepted 20 February 2012

Available online 3 April 2012

Keywords:

Flame retardant coatings

Fire retardant coatings

Flame retardant additives

Cyclodiphosph(V)azane

Polyurethane paint

ABSTRACT

Cyclodiphosphazenes and their polymeric products are some of the oldest and best known class of nitrogen and phosphorus containing compounds. In recent years there has been considerable interest in the phosphazene-based family of materials due to the wide range of thermal and chemical stabilities associated with them. In addition, these materials are capable of imparting flame-retardant properties when incorporated into polymers and their composites. Flame retardants can be incorporated into polymeric materials either as additives or as reactive materials. Additive type flame retardants are widely used by means of blending them with a specific polymeric material. In this particular research, cyclodiphosph(V)azane of sulfaguanidine, 1, 3-di-[*N*]-2-pyrimidinylsulfanilamide]-2, 2, 2.4, 4, 4-hexachlorocyclodiphosph(V)azane and 1, 3-di-[*N*]-2-pyrimidinylsulfanilamide]-2, 4-di[aminoacetic acid]-2, 4-dichlorocyclodiphosph(V)azane were synthesized for use as flame retardant additives with polyurethane varnish. These additives are physically incorporated into the polyurethane varnish formula. Experimental coatings were manufactured on a laboratory scale and applied by brush on wood and steel panels. The fire retardant ability of each coating type was characterized using the limiting oxygen index (LOI) test. The mechanical properties of these flame retardants were also examined to evaluate the drawbacks of the additives. Results of the LOI indicated that coating with these compounds containing chlorine, nitrogen and phosphorus exhibit a very good retardant effect, when blended with polyurethane varnish. Cyclodiphosph(V)azane of 1,3-di-[*N*]-2-pyrimidinylsulfanilamide]-2, 2, 2.4, 4, 4-hexachlorocyclodiphosph(V)azane showed the best flame retardant and mechanical properties of the additives investigated.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Flame retardants are incorporated into polymers to achieve a required fire resistance. Flame retardants act either in the vapor phase, or the condensed phase, through a chemical and/or physical mechanism that allows interference with the combustion process during heating, pyrolysis, ignition or flame spread [1–6]. Lu and Hamerton provide an excellent summary of common types of

flame retardants and their fire suppressing mechanisms [7]. Flame retardants may be incorporated into polymeric materials either as additives or as reactive materials. Additive-type flame retardants, which are widely used, are generally incorporated into polymers by physical means. This obviously provides the most economical and expeditious way of promoting flame retardancy for commercial polymers. The objective of adding a flame retardant to a polymer is to increase the resistance of the material to ignition, and to reduce the flame spread. Thus, instead of the flame growing it self extinguishes. The resultant products are still combustible, and the use of the flame retardant is to minimize, not eliminate, the fire risk associated with the use of a polymer in a specific application [8]. In recent years there has been considerable interest in the

* Corresponding author. Tel.: +20 1006425240; fax: +20 222747433.

E-mail address: eprimaf68@yahoo.com (M.A. El-Fattah).

phosphazene-based family of materials because they not only have a wide range of thermal and chemical stabilities, but can also provide improved thermal and flame-retardant properties to polymers and their composites [9–11]. Cyclotriphosphazene, as a ring compound consisting of alternating phosphorus and nitrogen atoms with two substituents attached to the phosphorus atoms, exhibits unusual thermal properties such as flame retardancy and self-extinguish ability. Many studies of flame retardants have focused attention on these particular two atoms. The flame retardants reported in a number of papers have these hetero-atoms [12–16]. Cyclotriphosphazene has several advantages as a flame retardant functional oligomer. Firstly, the flexible synthetic methodology can be developed for preparation of cyclotriphosphazene-based copolymers with various substituents. Secondly, thermal and non-flammable properties of the cyclotriphosphazene moieties can be conferred to the resulting polymers, especially of low molecular weights [17–20]. Therefore, when cyclotriphosphazenes are incorporated into the network of thermoset polymers, they can increase the thermal properties and flame retardancy of the polymers because of phosphorus and nitrogen flame retardant synergy. The reason for this is that the thermal decomposition of the phosphazene-based polymers is an endothermic process, and phosphate, metaphosphate and polyphosphate generated in the thermal decomposition form a non-volatile protective film on the surface of the polymer. This protective film isolates the polymer from the air, and the non-flammable gases released such as CO₂, NH₃ and N₂ cut off the supply of oxygen, achieving the aim of synergistic flame retardancy [21,22]. The phosphazene based polymers have more effective flame retardancy than other flame retardants, making them a new focus for study [23,24]. For this particular research work we use a new additive flame retardant based on cyclodiphosph(V)azane of types (I–III), which were physically added to the polyurethane varnish, to make it flame retardant. The limiting oxygen index (LOI) test was used to assess the flame retardancy properties of the additives. The physical and mechanical resistances were also studied to evaluate any drawbacks associated with the additives.

2. Experimental

2.1. Materials

All the chemicals used during the project were sourced either locally, or from international companies.

2.2. Methods and techniques

The hexachlorodiphosph(V)azane was prepared using the methods of Chapmann et al. [25] and Zhnurova and Kirzanov [26]. Their complexes were prepared and characterized by the co-author Sharaby [27,28].

2.2.1. Synthesis of cyclodiphosph(V)azane of sulfaguanidine (compound I)

Sulfaguanidine [*N*]-amidinosulfanilamide] (0.1 mol, 28.60 g) in dry benzene (100 ml) was added drop-wise, using a dropping funnel, to phosphorus pentachloride (0.1 mol, 20.90 g) in dry benzene (200 ml) at 15 °C. The reaction mixture was heated under reflux for 3 h, utilizing anhydrous conditions, and continuously stirred via the hot plate magnetic stirrer (the experiment was carried out in a well-ventilated area due to the carcinogenic nature of benzene). The reaction mixture was cooled to room temperature and the solids formed filtered and washed several times with dry benzene and dry diethyl ether. The 1,3-di-*[N*]-amidinosulfanilamide]-2,

Table 1
Polyurethane varnish composition.

Component	wt%
Refined sunflower oil	33.42
Glycerol	0.039
Litharge (lead oxide catalyst)	0.03
Pentaerythritol	4.61
Turpentine	47.30
Barium octoate drier	0.26
Toluene diisocyanate	11.37
Mixed drier	2.11
UV absorber	0.26
Anti skinning agent	0.32
Fire retardant additives	0.3–1.3

Viscosity: G-1 (Gardner), color: 3 (Gardner), solid content: 53 ± 2%.

2,2,4,4,4-hexachlorocyclodiphosph(V)azane was obtained as solid crystals.

2.2.2. Synthesis of 1,3-di-*[N*]-2-pyrimidinylsulfanilamide]-2,2,4,4,4-hexachlorocyclodiphosph(V)azane (compound II)

Sulfadiazine [*N*]-2-pyrimidinylsulfanilamide] (0.1 mol, 25.0 g) in 100 ml cold dry benzene was added in small portions to a well-stirred cold solution of phosphorus pentachloride (0.1 mol, 20.90 g) in 100 ml of cold dry benzene. This was done over a 30 min period at 15 °C under dry conditions. Following completion of the reaction (HCl gas ceased to evolve), filtration and removal of all solvent under vacuum, a residue was obtained, which on crystallization yielded white crystals.

2.2.3. Synthesis of 1,3-di-*[N*]-2-pyrimidinylsulfanilamide]-2,4-di-*[aminoacetic acid]*-2,4-dichlorocyclodiphosph(V)azane (compound III)

Glycine (0.02 mol, 1.50 g) was added in small portions to a well-stirred solution of compound II (0.01 mol, 7.68 g) in 100 ml acetonitrile during a 30 min period. After the addition was completed, the reaction mixture was heated under reflux for 3 h. Following completion of the reaction (HCl gas ceased to evolve), the reaction mixture was filtered while hot, and the solid obtained was washed several times with acetonitrile and diethyl ether and then dried under vacuum to give the corresponding aminoacyclodiphosphazane derivative. The reaction yields were then determined, as were the physicochemical characteristics such as color and melting point of the three compounds.

2.3. Characterization techniques

The microanalysis for carbon, hydrogen and sulfur were undertaken at the Cairo University Microanalytical Centre. The phosphorus content was determined gravimetrically as phosphoammonium molybdate [29]. The IR spectra were recorded on a Shimadzu FT-IR spectrometer (KBr technique). ¹H NMR spectra (DMSO-d₆) were measured on a Varian Gemini 200 MHz spectrometer, using TMS as an internal standard.

2.4. Coating composition and film preparation

The coating compositions were prepared by means of incorporating cyclodiphosph(V)azane of types (I–III), in the ratio of 0.3–1.3, into polyurethane varnish. The composition of the varnish is tabulated in Table 1. The samples of different molar ratio were then applied to both steel and glass panels by means of a brush. All efforts were made to maintain a uniform film thickness of 100 ± 5 μm for evaluating the physical and mechanical properties.

2.5. Flame retardant testing method

The performance of polyurethane varnish, with incorporated additives, was evaluated in a limited oxygen index (LOI) chamber. LOI values were determined by standardized tests such as ISO 4589-1: 1996 and ASTM D: 2863-97. Test panels were prepared using a combustible material (wood specimen). It was important that the panels were free of any surface contamination, or imperfections, prior to the coating application. Hand tool cleaning (sand paper) was carefully used to treat the faces and edges of the panels. Final dry film thickness (DFT) was $100 \pm 5 \mu\text{m}$. In all cases, the film application was applied by means of brushing. Following 10 days of air drying, the panels under study were heated at $50\text{--}60^\circ\text{C}$ for 2 h to eliminate any remaining solvent.

2.6. Physical and mechanical testing of films

A variety of physical and mechanical evaluations of the painted films were carried out according to appropriate ASTM standard test methods. These included the preparation of the steel panels (ASTM Method D: 609-95), measurement of film thickness (ASTM Method D: 1005-95), the degree of gloss for individual resin coatings (ASTM 523-08), film hardness by pencil test (ASTM Method D: 3363-92a), adhesion 'cross hatch test' (ASTM Method D: 3359-95a), flexibility 'bend' test (ASTM Method D: 522-93a) and resistance to mechanical damage 'impact resistance' (ASTM Method D: 2794-93).

3. Results and discussion

In 1937 the birth of polyurethanes (PUs) occurred in Germany when Bayer laboratories explored their use as fiber-forming polymers [30]. Polyurethanes are an important class of polymers that have wide application in a number of different industrial sectors such as coatings, foams, adhesives, sealants and elastomers [31]. Polyurethane top-coats, recommended for paint systems commonly utilized for corrosion protection of steel structures, are used in highly corrosive atmospheres (C5 category) [32]. Demand for flame retardant polyurethane paints is extremely strong within the surface coatings industry. Several attempts to increase the thermal stability of polyurethanes by means of introducing thermally stable groups have been reported [33,34]. In this work we study the use of cyclodiphosph(V)azane of types (I–III) as flame retardant additives in polyurethane varnish. This has been undertaken in an attempt to improve the resulting polymer's flame retardancy, due to the fact that phosphazene is known to impart thermal stability, and flame retardant characteristics to polymer systems. This is due to the strength of the P–N bonds, which render most phosphorus–nitrogen compounds exceptionally thermal stable [35].

3.1. Synthesis of cyclodiphosph(V)azane of types (I–III)

In the present investigation cyclodiphosph(V)azane of types (I–III) were prepared in the hope that they might demonstrate enhanced flame retardancy properties. The chemical structures of the prepared cyclodiphosph(V)azane of types (I–III) are represented in Scheme 1. In this series all types were prepared and purified as illustrated in the experimental section. Elemental analysis, reaction yield and physical properties such as melting point and product color, were measured and listed in Table 2. The good agreement between the experimental and theoretical values of the C, H, N, S and P levels reveals that the methods of synthesis and purification of the products were performed successfully.

Table 2
Physico-chemical properties of cyclodiphosph(V)azane of types (I–III).

Characteristics	Compound I	Compound II	Compound III
Melting point ($^\circ\text{C}$)	180 ± 2	162	210
Yield (%)	73	80.5	60
Color	White	White	White
Elemental analysis			
C %			
Calc.	24.05	31.15	37.17
Found	24.30	31.62	36.95
H %			
Calc.	2.31	2.09	3.05
Found	2.45	2.48	2.86
N %			
Calc.	16.03	14.53	18.06
Found	15.81	14.42	18.36
S %			
Calc.	9.17	8.32	8.27
Found	9.35	8.40	8.07
P %			
Calc.	8.86	8.03	7.99
Found	8.55	7.87	8.15

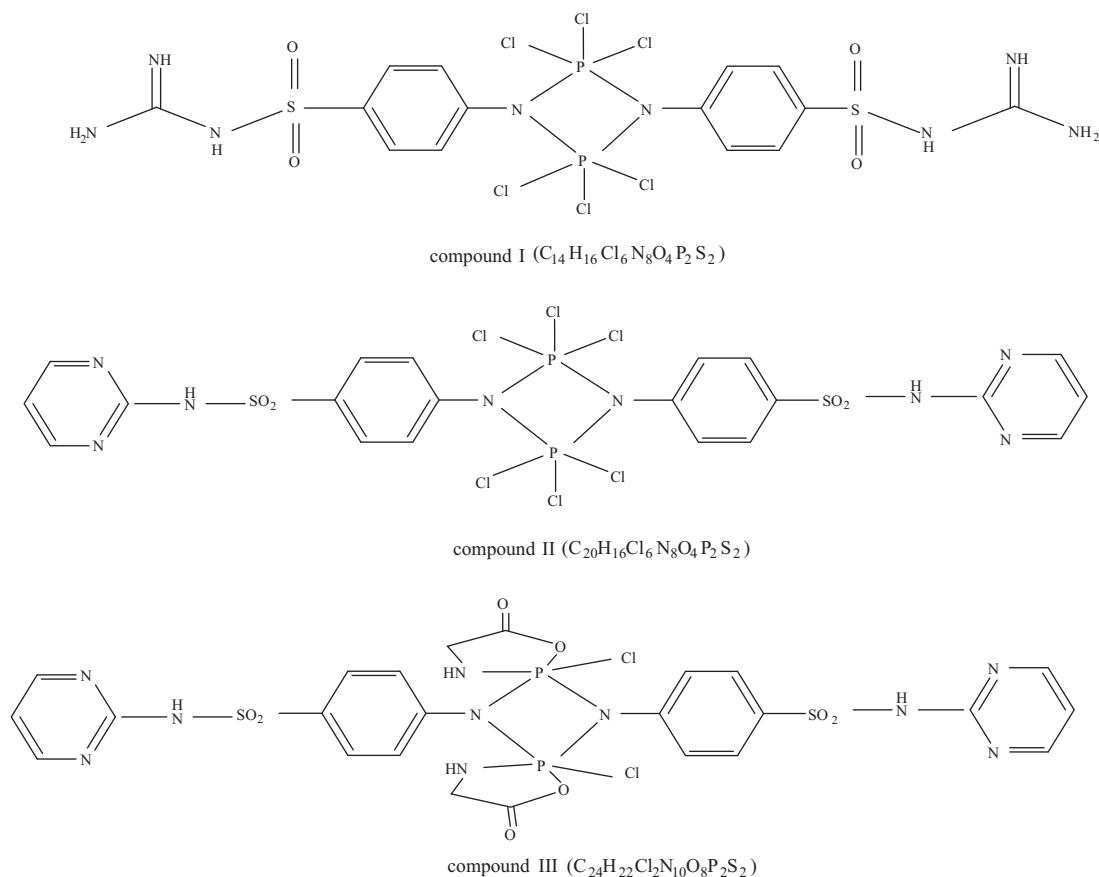
3.2. Spectral analysis of cyclodiphosph(V)azane of types (I–III)

The co-author Sharaby [27,28], showed in detail the IR and ^1H NMR spectra for these compounds and their complexes. The IR characteristic bands and characteristic proton signals are summarized in Tables 3 and 4 respectively.

3.3. Evaluation of film properties

3.3.1. Evaluation of cyclodiphosph(V)azane of types (I–III) as flame retardant additives incorporated into a polyurethane varnish

Flame retardant properties of the polyurethane varnish blended with cyclodiphosph(V)azane of types (I–III) were evaluated by means of the limiting oxygen index (LOI) test. The LOI is defined as the minimum concentration of oxygen, expressed as a percentage that will support combustion of a polymer. It is measured by passing a mixture of oxygen and nitrogen over a burning specimen, and reducing the oxygen level until a critical level is reached [36]. A high oxygen concentration requirement indicates better flame retardancy of the specimen. This method is suitable as a semi-qualitative indicator of the effectiveness of the flame retardant during the research and development phase of the work. This is due to the fact that the equipment is relatively inexpensive and the size of the test sample required is small. Cyclophosphazenes, and their polymeric products, are of the oldest and best known class of nitrogen–phosphor compounds. In recent years, as has previously been mentioned, there has been renewed interest in the phosphazene-based family of materials not just because of their wide range of thermal and chemical stabilities, but also because of the potential for the improvement of the flame retardant properties of polymers and their composites. It is clear that the incorporation of cyclodiphosph(V)azane of types (I–III), physically added into polyurethane varnish in the ratios mentioned in the experimental section, results in excellent flame retardancy when compared alongside a blank polyurethane sample. The results obtained from the LOI test are shown in Table 5 and Figs. 1–3. It can be observed that the LOI value of polyurethane varnish without an additive compound is 18 and the maximum LOI with additive compounds is 37. Normal atmospheric air (i.e. the air that we breathe in) is approximately 21% oxygen, so a material with an LOI of less than 21% would burn easily in air. In comparison, a material with a LOI value of greater than 21% but less than 28% would be considered to be 'slow burning'. However, a self-extinguishing material is one that would stop burning after



Scheme 1. Chemical structure of cyclodiphosph(V)azane of types (I–III).

Table 3
IR Spectra ($4000\text{--}400\text{ cm}^{-1}$) of cyclodiphosph(V)azane of types (I–III).

Compound	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{SO}_2)$ (asym)	$\nu(\text{SO}_2)$ (sym)	$\nu(\text{P}=\text{N})$	$\nu(\text{P}=\text{Cl})$	$\nu(\text{P}=\text{NH})$	$\nu(\text{C}=\text{O})$
I	3160 br	1610 m	1310 sh	1032 sh	1162 sh	456s	–	–
II	3368 br	1618 sh	1348 s	1084 m	1156 sh	570 sh	–	–
III	3375 br	1618 sh	1342 sh	1088 m	1148 m	572 w	2690 br	1650 m

br: broad, m: medium, sh: sharp, s: small, w: weak.

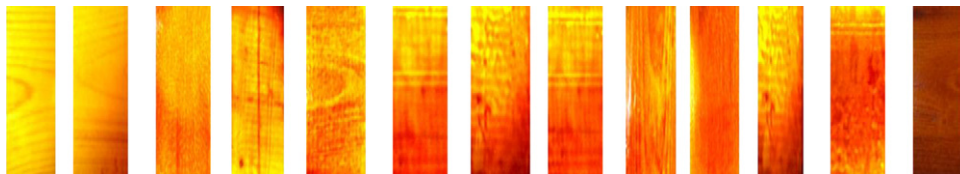


Fig. 1. Coated wood specimens before ignition.



Fig. 2. Limiting oxygen index (LOI) chamber.

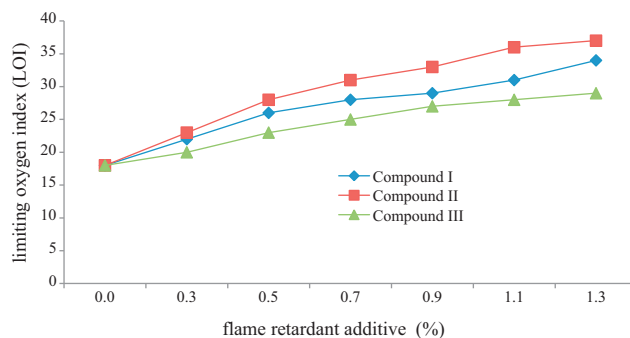


Fig. 3. Limiting oxygen index (LOI) characteristics of polyurethane varnish incorporated flame retardant additives.

Table 4
¹H NMR spectra of cyclodiphosph(V)azane of types (I–III).

Compound	Chemical shift δ (ppm)	Assignment
I	7.63	d, 4H, Ar H's, $J=8.58$ Hz
	6.92	d, 4H, Ar H's, $J=8.68$ Hz
	5.82	br, 4H, $-\text{C}=(\text{NH})(\text{NH}_2)$
	7.16	br, 2H, $-\text{SO}_2\text{NH}$
	7.37	s, 2H, $-\text{C}=(\text{NH})$
II	7.12	d, 4H, ArH's, $J=8.80$ Hz
	7.60	d, 4H, ArH's, $J=8.40$ Hz
	6.97	br, 2H, $-\text{SO}_2\text{NH}$
	8.47	s, CH, hetero
	9.80	br, H, heterocycle proton
III	6.59	d, 4H, ArH's, $J=8.90$ Hz
	7.60	d, 4H, ArH's, $J=8.70$ Hz
	2.50	s, 2H, glycine CH_2 protons
	7.30	br, 2H, $-\text{SO}_2\text{NH}$
	8.30	br, 2H, glycine NH protons
	6.98	t, CH hetero
8.40	s, 2H, CH heterocycle protons	

Table 5
Flame retardant characteristics of polyurethane varnish incorporated flame retardant additives.

Formulation	FR %	Limiting oxygen index (LOI)
Blank polyurethane	–	18
Polyurethane and comp. I	0.3	22
	0.5	26
	0.7	28
	0.9	29
	1.1	31
1.3	34	
Polyurethane and comp. II	0.3	23
	0.5	28
	0.7	31
	0.9	33
	1.1	36
1.3	37	
Polyurethane and comp. III	0.3	20
	0.5	23
	0.7	25
	0.9	27
	1.1	28
1.3	29	

Table 6
Physical and mechanical characteristics of polyurethane varnish incorporated flame retardant additives.

Formulation	FR %	Gloss at 60°	Hardness (kg)	Adhesion	Flexibility	Impact (J)
Blank polyurethane	–	85	2.0	5B	Pass	1.75
Polyurethane and comp. I	0.3	85	1.8	5B	Pass	1.75
	0.5	85	1.8	5B	Pass	1.57
	0.7	87	1.7	5B	Pass	1.48
	0.9	89	1.7	5B	Pass	1.39
	1.1	89	1.7	5B	Pass	1.31
	1.3	92	1.6	5B	Pass	1.22
Polyurethane and comp. II	0.3	86	2.0	5B	Pass	1.75
	0.5	86	2.0	5B	Pass	1.75
	0.7	90	1.8	5B	Pass	1.66
	0.9	93	1.8	5B	Pass	1.57
	1.1	96	1.8	5B	Pass	1.48
1.3	97	1.7	5B	Pass	1.39	
Polyurethane and comp. III	0.3	85	2.0	5B	Pass	1.75
	0.5	86	1.8	5B	Pass	1.66
	0.7	89	1.8	5B	Pass	1.57
	0.9	93	1.7	5B	Pass	1.48
	1.1	94	1.7	5B	Pass	1.48
1.3	94	1.7	5B	Pass	1.31	

the removal of the fire or ignition source. The increased amount of cyclodiphosph(V)azane of types (I–III) additives increases the LOI value of the polyurethane varnish formulation. This is due to the incorporation of the cyclodiphosph(V)azanes into the network of the thermoset polyurethane varnish, which increases the flame retardancy of the polymer. This is due to the flame retardant synergy of the phosphorus and nitrogen content. An interesting point associated with the results is that the LOI curves for the three compounds (I–III) are more or less linear. This is as a result of the fact that they are high molecular weight compounds containing chlorine, nitrogen and phosphorus, and therefore provide superior flame retardant properties compared to low molecular weight flame retardants. A further interesting point is that the LOI values of compound II is the highest, whilst compound III is the lowest.

3.3.2. Evaluation of the physical and mechanical properties of polyurethane varnish incorporated the flame retardant additives

The effects of adding flame retardant to the polyurethane varnish, in respect of the physical and mechanical properties, were evaluated as per the standard test methods. This was done to ascertain any negative aspects that might arise due to the presence of the additives. The gloss, scratch hardness, adhesion, flexibility and impact were all measured. The resulting data is shown in Table 6.

(a) *Gloss*: This was measured using a Sheen UK glossmeter. On observing the films using a 60° angle, it could be seen that the flame retardant additives actually increased the gloss levels. This is obviously a positive result which may be attributed to the introduction of aromatic rings, present in the additive structure.

(b) *Scratch hardness test*: This was determined by using a Sheen UK hardness tester. The scratch hardness is observed to vary between 1600 and 2000 g and it is clear from the data that as we increase the flame retardant additive, the scratch hardness of the film decreases.

(c) *Cross-hatch adhesion test*: This was measured by using a Sheen UK crosscut adhesion tester. For this test method a lattice with six cuts in each direction was made in the film (the cuts were spaced at 2 mm). Pressure-sensitive tape was then applied over the lattice and subsequently removed. All the coating film demonstrated good cross-hatch adhesion. The flame retardant additives did not change the adhesion properties of the polyurethane varnish formula.

(d) *Flexibility (bend) test*: Flexibility was determined by using a 1/4 in. Mandrel bend tester from Sheen UK, in such a way that the surface of the panel was directed outside. The films for all the coating compositions passed the 1/4 in. Mandrel bend test. The varnish was considered satisfactory if no cracking marks, or dislodging, are observed following the bending procedure. Based on this qualitative measurement, it can be stated that all the films showed reasonably good flexibility.

(e) *Resistance to mechanical damage (impact resistance) test*: This was measured using a Sheen UK impact tester. The impact resistance of the coating on the steel panels was tested by means of dropping a 890 g steel ball from a height of 1 m. The impact strength was shown to decrease in the presence of the additive due to the decrease in the bulk elasticity of the polyurethane varnish.

4. Conclusion

In this study a new flame retardant additive based on cyclodiphosph(V)azane of sulfaguanidine, 1, 3-di-[N/-2-pyrimidinylsulfanilamide]-2, 2, 2, 4, 4, 4-hexachlorocyclodiphosph(V)azane and 1,3-di-[N/-2-pyrimidinylsulfanilamide]-2, 4-di[aminoacetic acid]-2, 4-dichlorocyclodiphosph(V)azane was physically applied to a polyurethane varnish. The non-flammability of these flame retardants was characterized by the limiting oxygen index (LOI) test, and the physical and mechanical properties were examined to ascertain any drawbacks. The incorporation of these additives into a polyurethane varnish results in excellent flame retardancy properties when compared to a blank polyurethane equivalent. This improvement may be attributed to a number of key factors. Firstly, the introduction of high molecular weight compounds containing chlorine, nitrogen and phosphorus, provides superior flame retardant properties. Secondly, the presence of N–P bonds render most nitrogen–phosphorus compounds exceptionally thermally stable, and their gases or vapors, which evolve during combustion, have low toxicity which means that less corrosive gases are produced during the fire. Thirdly, it is also known that the binding of halogens and/or nitrogen–phosphorus to the polymeric backbone by covalent bonds, will improve the flame retardancy of the polymers (also referred to as the reactive route) making the polymer itself fire retardant. Finally, the aromaticity of the three compounds imparts a kind of flame retardancy. The results obtained indicate that cyclodiphosph(V)azane of 1,3-di-[N/-2-pyrimidinylsulfanilamide]-2, 2, 2, 4, 4, 4-hexachlorocyclodiphosph(V)azane (compound II) showed the best flame retardant capability and mechanical properties. Cyclodiphosph(V)azane of 1,3-di-[N/-2-pyrimidinylsulfanilamide]-2, 4-di[aminoacetic acid]-2, 4-dichlorocyclodiphosph(V)azane on the other hand was shown to have the least flame retardant properties.

Acknowledgment

The authors would like to thank Dr. Algy Kazlauciusas of the University of Leeds Faculty of Maths and Physical Science, School of Chemistry, for his invaluable contribution to the written part of the paper.

References

- [1] J. Kracklauer, in: M. Lewin, S.M. Atlas, E.M. Pearce (Eds.), *Flame-Retardant Polymeric Materials*, vol. 2, Plenum press, New York, 1978.
- [2] W.C. Kuryla, A.J. Papa, *Flame Retardancy of Polymeric Materials*, vol. 4, Marcel Dekker, New York, 1978.
- [3] *Handbook of Fire Retardant Coatings and Fire Testing Services*, Technomic Publishing, Lancaster, 1994.
- [4] J. Wartusch, *Chances and limitations of high-performance polymers*, *Makromolekulare Chemie Macromolecular Symposia* 75 (1993) 67–71.
- [5] D. Weil, Z. Weiming, P. Navin, S.M. Mukhopadhyay, A systems approach to flame retardancy and comments on modes of action, *Polymer Degradation and Stability* 54 (2–3) (1996) 125–136.
- [6] B.K. Kandola, A.R. Horrock, Complex char formation in flame-retarded fiber-intumescent combinations: physical and chemical nature of char, *Textile Research Journal* 69 (5) (1999) 374–381.
- [7] S. Lu, I. Hamerton, Recent developments in the chemistry of halogen-free flame retardant polymers, *Progress in Polymer Science* 27 (8) (2002) 1661–1712.
- [8] J. Green, Mechanisms for flame retardancy and smoke suppression—a review, *Journal of Fire Sciences* 14 (6) (1996) 426–442.
- [9] N. Lejeune, I. Dez, P.A. Jaffres, J.F. Lohier, P.J. Madec, J. Sopkova-de Oliveira Santos, Synthesis, crystal structure and thermal properties of phosphorylated cyclotriphosphazenes, *European Journal of Inorganic Chemistry* 2008 (January (1)) (2008) 138–143.
- [10] D. Kumar, M. Khullar, A.D. Gupta, Synthesis and characterization of novel cyclotriphosphazene-containing poly (ether imide)s, *Polymer* 34 (14) (1993) 3025–3029.
- [11] S.V. Levchik, G. Camino, M.P. Luda, L. Costa, A. Lindsay, D. Stevenson, Thermal decomposition of cyclotriphosphazene, *Journal of Applied Polymer Science* 67 (3) (1998) 461–472.
- [12] P. Potin, R.D. Jaeger, Polyphosphazenes synthesis, structure, properties, application, *European Polymer Journal* 27 (4–5) (1991) 341–348.
- [13] D. Kumar, A.D. Gupta, M. Khullar, Synthesis and characterization of novel cyclotriphosphazene-containing poly (ether imides)s, *Polymer* 34 (14) (1993) 3025–3029.
- [14] D. Kumar, A.D. Gupta, Aromatic cycloliner phosphazene polyimides based on a novel bis-spiro substituted cyclotriphosphazene diamine, *Macromolecules* 28 (18) (1995) 6323–6329.
- [15] J. Ding, W. Shi, Thermal degradation and flame retardancy of hexaacrylated/hexaethoxy cyclophosphazene and their blends with epoxy acrylate, *Polymer Degradation and Stability* 84 (1) (2004) 159–165.
- [16] C.W. Allen, Regio- and stereochemical control in substitution reactions of cyclophosphazenes, *Chemical Reviews* 91 (2) (1991) 119–135.
- [17] D. Kumar, G.M. Fohlen, J.A. Parker, Fire- and heat-resistant laminating resins based on maleimido-substituted aromatic cyclotriphosphazenes, *Macromolecules* 16 (8) (1983) 1250–1257.
- [18] C.J. Orme, J.R. Klaehn, M.K. Harrup, R.P. Lash, F.F. Stewart, Characterization of 2-(2-methoxyethoxy) ethanol-substituted phosphazene polymers using pervaporation, solubility parameters, and sorption studies, *Journal of Applied Polymer Science* 97 (3) (2005) 939–945.
- [19] J.Y. Chang, S.B. Rhee, S. Cheong, M. Yoon, Synthesis and thermal reaction of acetylenic group substituted poly(organophosphazenes) and cyclotriphosphazene, *Macromolecules* 25 (10) (1992) 2666–2670.
- [20] H.R. Allcock, P.E. Austin, Schiff base coupling of cyclic and high-polymeric phosphazenes to aldehydes and amines: chemotherapeutic models, *Macromolecules* 14 (6) (1981) 1616–1622.
- [21] G.F. Levchik, Y.V. Grigoriev, A.I. Balabanovich, S.V. Levchik, Phosphorus–nitrogen containing fire retardants for poly(butylene terephthalate), *Polymer International* 49 (10) (2000) 1095–1100.
- [22] J.W. Gu, G.C. Zhang, S.L. Dong, Q.Y. Zhang, J. Kong, Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings, *Surface and Coatings Technology* 201 (18) (2007) 7835–7841.
- [23] S. Chen, Q.K. Zheng, G.D. Ye, G.K. Zheng, Fire-retardant properties of the viscose rayon containing alkoxy cyclotriphosphazene, *Journal of Applied Polymer Science* 102 (1) (2006) 698–702.
- [24] D.A. Conner, D.T. Welna, Y. Chang, H.R. Allcock, Influence of terminal phenyl groups on the side chains of phosphazene polymers: structure–property relationships and polymer electrolyte behaviour, *Macromolecules* 40 (2) (2007) 322–328.
- [25] A.C. Chapman, N.L. Paddock, H.T. Searle, *Journal of Chemical Society* (1961) 1825–1827.
- [26] I.N. Zhurova, A.V. Kirsanov, *Zhurnal Obshchei Khimii* 32 (1962) 2576–2580, C.A. 58 (1963) 7848.
- [27] C.M. Sharaby, Preparation, characterization and biological activity of Fe(III), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO₂(II) complexes of new cyclodiphosph(V)azane of sulfaguanidine, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 62 (1–3) (2005) 326–334.
- [28] C.M. Sharaby, G. Mohamed, M.M. Omar, Preparation and spectroscopic characterization of novel cyclodiphosph(V)azane of N'-2-pyrimidinylsulfanilamide complexes: magnetic, thermal and biological activity studies, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 66 (4–5) (2007) 935–948.
- [29] C.M. Sharaby, Studies of some new cyclodiphosphazene complexes of Fe(III), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), *Synthesis and Reactivity in Inorganic Metal–Organic, and Nano-Metal Chemistry*, 35 (2) (2005) 133–142.
- [30] O. Bayer, The diisocyanate polyaddition process (polyurethanes). Description of a new principle for building up high-molecular compounds, *Angewandte Chem* A59 (1947) 257–272.
- [31] K.A. Pigott, *Kirk-Othmer Encycl. Chem. Technol.*, vol. 21, 2nd ed., 1970, p. 56.
- [32] D. Santos, C. Brites, M.R. Coasta, M.T. Santos, Performance of paint system with polyurethane (PU) topcoats, proposed for atmospheres with very high corrosivity category, *Progress in Organic Coatings* 54 (4) (2005) 344–352.

- [33] P. Radhakishnan Nair, C.P. Reghunadhan Nair, D.J. Francis, Phosphazene-modified polyurethane: synthesis, mechanical and thermal characteristics, *European Polymer Journal* 32 (12) (1996) 1415–1420.
- [34] M. Spirckel, N. Regnier, B. Mortaigne, B. Youssef, C. Bunel, Thermal degradation and fire performance of new phosphonate polyurethane, *Polymer Degradation and Stability* 78 (2) (2002) 211–218.
- [35] S. Ingo, P. Luke, Grocholl, S. Lothar, Synthesis and structures of heterocyclic bis (tert-butylamido)cyclodiphosph(III)azane compounds having phosphorous (III) and arsenic (III) centres, *Inorganic Chemistry* 39 (14) (2000) 3037–3041.
- [36] N.G. McCrum, C.P. Buckley, C.B. Bucknall, *Principles of Polymer Engineering*, second edition, Oxford Science Publications, 1997.