

Improving the Fire Retardant Efficiency of Phosphazenes for some Constructional Materials

Hyder I. AL Taha Asaad F. Khattab
Department of Chemistry/ College of Science/ University of Mosul

(Received 14 / 3 / 2019 ; Accepted 15 / 4 / 2019)

ABSTRACT

Cyclophosphazene and Polyphosphazene have been developed as a fire retarding material by increasing the number of bromine and chlorine atoms and adding azo moieties within the chemical structure. Four azo phenolic compounds with different numbers and places of substituted bromine and chlorine atoms were prepared. The cyclophosphazene and polyphosphazene were functionalized by the azo phenolic compounds. The functionalizing was done by substituting three chlorine atoms from cyclophosphazene or one chlorine atom from polyphosphazene by the prepared azo compounds through hydroxyl group. (ratio Azo3:1Cyclophosphazene, and ratio Azo1:1 Polyphosphazene). The chemical structure of the phosphazenes were studied by IR, ¹H-NMR and elemental analysis. The fire retarding efficiency of phosphazenes compounds for many trading constructional materials was examined. The efficiency of the new phosphazenes compounds was increased for both Cyclophosphazene and Polyphosphazene as a fire retardant.

Keywords: phosphazenes, polyphosphazene, azo compound, fire retardant.

تحسين كفاءة الفوسفازينات كمثبطات للحريق لبعض المواد البنائية

الملخص

تم تطوير البولي فوسفازين والفوسفازين الحلقي كمادة مانعة للاحتراق من خلال زيادة عدد ذرات البروم والكلور المعوضة كمجاميع جانبية في مركبات الازو الفينولية المحضرة والتي تم ربطها مع الفوسفازين الحلقي وكذلك مع البولي فوسفازين. في هذه الدراسة تم تحضير اربعة من مركبات الازو الفينولية الحاوية على اعداد مختلفة من مجاميع البروم والكلور، عوضت ثلاث ذرات كلور من الفوسفازين الحلقي وذرة واحدة من البولي فوسفازين بمركبات الازو الفينولية المكلورة لانتاج مركبات الازو الفينولية للفوسفازين اي نسبة (فوسفازين حلقي 1:3مركبات الازو)، وكذلك مع البولي فوسفازين بنسبة (بولي فوسفازين 1:1مركبات الازو). شخّصت المركبات الناتجة باستخدام تقنيات IR, C.H.N و ¹H-NMR على النماذج المحضرة. أظهرت نتائج فحص مركبات الفوسفازين الحلقي والبولي فوسفازين المحضرة بعد مزجها مع بعض المواد الإنشائية كفاءة جيدة في مجال مقاومة عملية الاحتراق، وبيّنت النتائج ان مركبات الازو المهلجنة عملت على تحسين مقاومة الاحتراق لكل من الفوسفازين الحلقي والبولي فوسفازين.

الكلمات الدالة: فوسفازين الحلقي، البولي فوسفازين، مركبات الازو، مثبط الاحتراق.

INTRODUCTION

Fire retardancy of the composite materials can be achieved by inhibiting or by disrupting the continuous combustion process. Combustion process for composite materials can be interrupted in three different ways (Dittenber and Gangarao, 2012).

Firstly, by incorporating fire retardant materials that decompose endothermically when exposed to reach the pyrolysis temperature of composite materials (Camino and Cortemiglia, 1991).

Secondly, by incorporating fire retardant that produce more non-flammable byproducts and more char during pyrolysis reaction. The char layer acts as a physical barrier which hinders the heat and mass transfer between gas and condense phase. This mechanism is known as condensed phase mechanism (Camino and Cortemiglia, 1991).

Third, method is known as gas phase mechanism, in this case during combustion, the fire retardant chemicals release more non-flammable gases leading to reduction the an effective oxygen concentration in the flame zone and thus act as a fire retardant-agent (Schindler and Hauser, 2004).

Fire retardants behavior or fire performance of a composite materials can be improved in two ways. Firstly, by improving the fire performance of composite making constituents i.e. matrix and reinforcing agent. Secondly, by providing protective fire retardant coating around the core composites (Wichman, 2003). Different methods of improving fire performance of composite materials have been done through component modification as well as through providing protective coating. (Cullis and Hirschter, 1981).

Polymeric composite materials are widely used in different areas where fire retardancy one of the most important requirements. It is observed that fire retardant treatment not only affect the fire performance of composite materials it also affects the other composite properties like mechanical or physical properties (Shumao *et al.*, 2010).

EXPERIMENTAL

Materials and Equipments:

All chemical and reagents are purchased from Fluka and used as received without purification. The used constructional materials are shown in (Table 1).

Table 1: Construction materials Source

No . Sample	Commercial Materials	Source
1	Epoxy (Ep)	CALIDAD HENKEL in Greece
2	X-SBR	Durmakker.Evcrgem. in Belgium
3	Co polystyrene (AS)	Durmakker.Evcrgem. in Belgium
4	polyurethane primer(PU)	ALchimica Builing Chemicals in Greece
5	polyurethane foam(PU.F)	ALchimica Builing Chemicals in Greece
6	PVA (Polyvinyl acetate)	Shenxhen Taiqiang Chemicals in Chine
7	Pint(OD)	Local
8	Wood "saw dust"(W)	Local

¹H NMR(400 MHz) spectra were obtained by using (Bruker BioSpin GmbH in turkey). Tetramethyl saline was used as reference. FTIR spectra were accomplished by using (BRUKER FTIR Infrared Spectrophotometer).

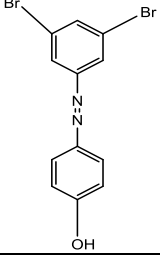
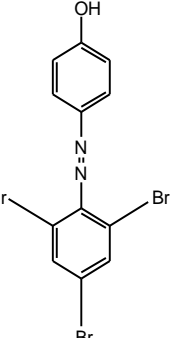
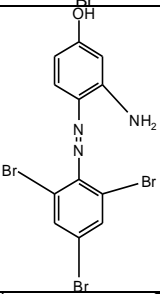
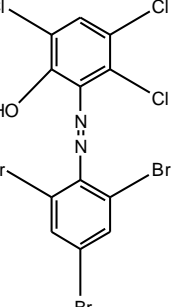
The elemental analysis were carried out by using (EuroEA3000/Italy) elemental a analyzer.

Synthetic Route

Azo compounds were prepared (Table 2) according to the following general method: (Khattab and Abbas, 2015) 0.01 mole of aniline or its derivatives were dissolved in 10 ml of concentrated hydrochloric acid at (-10 °C). An aqueous solution of 0.01M of sodium nitride was added drop wise with stirring at (-10 °C) for a period of 30 minutes. Phenol compound (0.01 mole) was dissolved in 10ml of sodium hydroxide solution (10%) and added to the suspended diazonium salt solution drop wise and stirred for 1.5hr. The precipitated azo compound was filtered, washed with cold water and dried under vacuum.

Hexachlorocyclophosphazene (NPCl_2)₃ was prepared by refluxing equimolar of phosphorous pentachloride with ammonium chloride in chlorobenzene for 8 hrs. The reaction mixture was filtered from unreacted ammonium chloride, and the filtrate was distilled under vacuum. The residue phosphazene was recrystallized from hexane (yield 26%). Polyphosphazene [NPCl_2]_n was prepared by heating the cyclophosphazene (NPCl_2)₃ at 200 °C for 3 hour under vacuum. (Allcock, 2006).

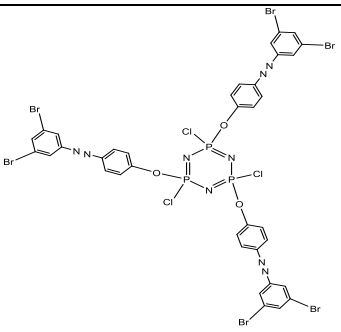
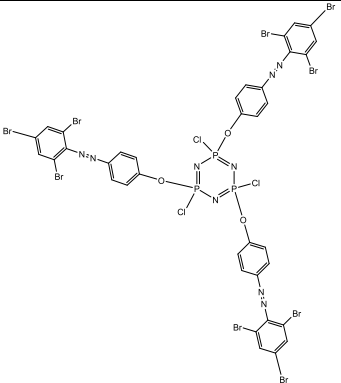
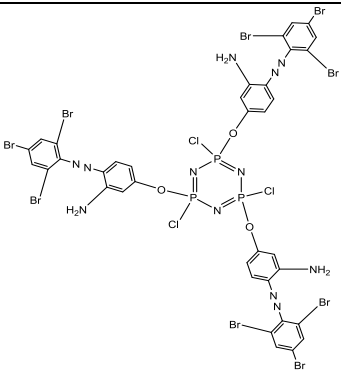
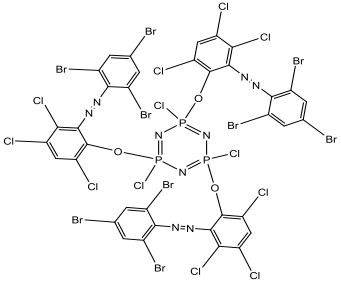
Table 2: The chemical structure of azo compounds and their physical properties

No.C	Name Compound	Structure	Color	m.p C°	Yield %
1	2,6- Dibromo-4-(4-hydroxy-phenylazo)-phenol		Brown	171	87
2	4-(2,4,6-Tribromo-phenylazo)-phenol		Brown	174	75
3	3- Amino-4-(2,4,6-tribromo-phenylazo)-phenol		Brown	167	85
4	3,4,6- Trichloro-2-(2,4,6-tribromo-phenylazo)-phenol		Brown	184	63

Functionalizing $(\text{NPCl}_2)_3$ with Azo Compounds

In a porcelain crucible 2mmole of $(\text{NPCl}_2)_3$ was fused by using a sand bath (at 112°C) followed by adding 6mmole of azo compound. Heating the mixture was continued until vapor of hydrochloric acid was noticed (tested by litmus paper). The precipitate was cooled and stored in a vacuum dryer (Allcock 2012) . (Table 3).

Table 3: The chemical structure of phosphazenes compounds (M) and some of its physical properties

Samples	Compound Name	Chemical Stricture	M.P C°	Yield %
M1	2,4,6-trichloro-2,4,6-tris(4-((3,5-dibromophenyl)diazenyl)phenoxy)-1,3,5,2λ ⁵ ,4λ ⁵ ,6λ ⁵ -triazatriphospha-2,4,6-trichloro-2,4,6-tris(2,5-dichloro-4-((3,4-dichlorophenyl)dienyl)phenoxy)-1,3,5,2λ ⁵ ,4λ ⁵ ,6λ ⁵ -triazatriphosphazene		204	74
M2	2,4,6-trichloro-2,4,6-tris(4-((2,4,6-tribromophenyl)diazenyl)phenoxy)-1,3,5,2λ ⁵ ,4λ ⁵ ,6λ ⁵ -triazatriphosphinine		171	89
M3	5,5',5''-((2,4,6-trichloro-1,3,5,2λ ⁵ ,4λ ⁵ ,6λ ⁵ -triazatriphosphinine-2,4,6-triyl)tris(oxy)) tris(2-((2,4,6-tribromophenyl)diazenyl)aniline)		217	65
M4	2,4,6-trichloro-2,4,6-tris(3,4,6-trichloro-2-((2,4,6-tribromophenyl)diazenyl)phenoxy)-1,3,5,2λ ⁵ ,4λ ⁵ ,6λ ⁵ -triazatriphosphinine		174	56

Functionalizing $[\text{NPCl}_2]_n$ with Azo Compounds

Dissolved 17.0 mmol of Polyphosphazene $[\text{NPCl}_2]_n$ in 50 ml THF (Tetrahydrofuran) and dissolve 34.0 mmol from azo compounds in 50 ml THF, add 20 gm K_2CO_3 . Refluxing the mixture for 9 hour and filtration the mixture to remove KCl salt, deposit polyphosphazene was obtained by using petroleum ether 60-80. (Arvind *et al.*, 2010). (Table 4)

Table 4: Name and structure of the polyphosphazenes compounds (Pz)

No. comp.	Name compounds	Structure compounds
Pz:1	4-((3,5-dibromophenyl)diazenyl)phenyl <i>N,P</i> -dimethylphosphazene	
Pz:2	4-((2,4,6-tribromophenyl)diazenyl)phenyl <i>N,P</i> -dimethylphosphazene	
Pz:3	3-amino-4-((2,4,6-tribromophenyl)diazenyl)phenyl <i>N,P</i> -dimethylphosphazene	
Pz:4	3,4,6-trichloro-2-((2,4,6-tribromophenyl)diazenyl)phenyl <i>N,P</i> -dimethylphosphazene	

Fire Retarding Test

This test was accomplished according to method ASTM E 285-80 for all phosphazenes compounds with the some construction materials (Table 1) The mixing percentage was 1%. The wood was prepared by curing the saw dust with resole in presence of phosphazenes compounds. The properties of fire retarding were calculated as following:

Insulation Index (I.I) was recorded according to the equation:

$$I.I = B.T(\text{sac})/4 \text{ (mm) where } B.T = \text{Burning Time /sec, } 4 \text{ mm} = \text{Sample thick}$$

Erosion Rate (E.R) was calculated according to the equation:

$$E.R = 4 \text{ mm/B.T sec}$$

The Percentage of residual weight of combustion was calculated according to the equation:

$$RWR = (W1 - W2 / W1) * 100$$

Where : W1 = Sample weight before burning (gm), W2 = Weight of the missing material (gm).

RESULTS AND DISCUSSION

Preparation polyphosphazene and cyclophosphazene coupled with azo phenolic compounds is involved abbreviate and rapid method in comparing with the general method (Allcock, 2006). Method preparing cyclophosphazene with azo phenolic compounds involved fusing mixture of hexachlorocyclotriphosphazene (NPCl_2)₃ with the phenolic compounds. Accordingly, (NPCl_2)₃ was treated with three molar equivalents of phenolic compounds (Table 2) to yield triphenyl diazenyl phenoxy phosphazene (Table 3).

The reaction of polyphosphazene with azo phenolic compounds was carried out by refluxing involved dissolved polyphosphazene and azo phenolic compounds in THF in presence of K_2CO_3 .

The prepared azo compounds is diagnosed by IR (Table 5), Fig. (1). The molecular structure of the resulted cyclophosphazenes were assessed by IR (Table 6), Fig. (2) and $^1\text{H-NMR}$ (Table 7), Fig. (3) spectroscopy, as well as elemental analysis.

Table 5: F.T. IR band frequencies of the prepared azo phenolic compounds

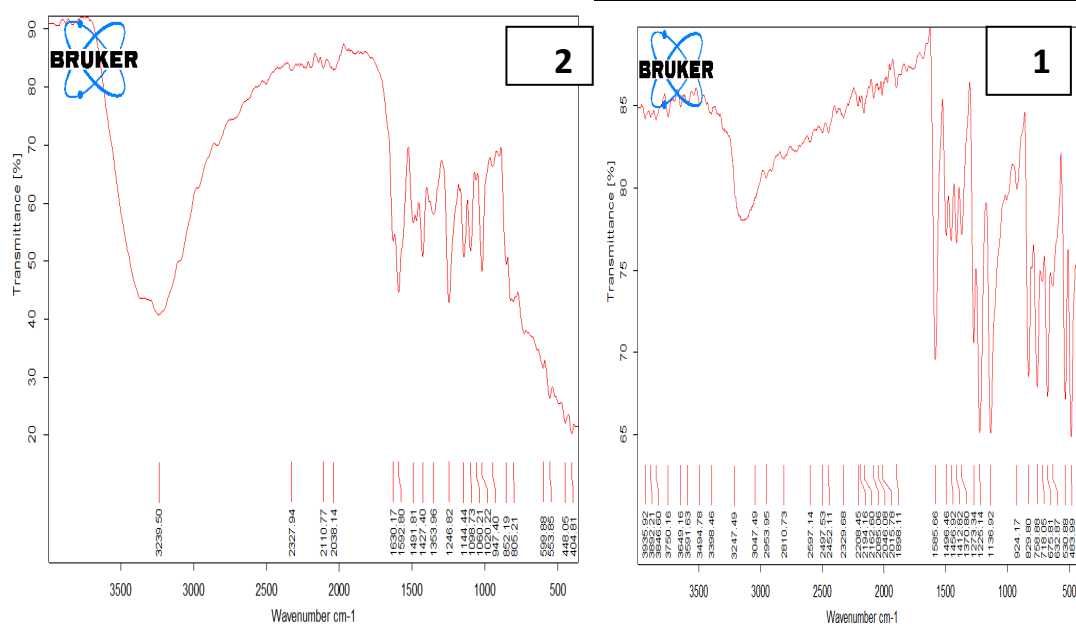
Compounds	$\nu \text{ O-H}$ Cm^{-1}	$\nu \text{ N=N}$ Cm^{-1}	$\nu \text{ C=C}$ Cm^{-1}	$\nu \text{ C-Br}$ Cm^{-1}	$\nu \text{ C-N}$ Cm^{-1}
1	3247	1585	1225-1496	483	1136
2	3239	1592	1370-1243	599	1144
3	3186	1500	1602-1237	467	1091
4	3362	1591	1544-1201	444 $\nu \text{ C-Cl}$ 753	1108

Table 6: F.T. IR band frequencies of the prepared cyclophosphazenes compounds (M)

Compound	$\nu \text{ P-O-C}$ Cm^{-1}	$\nu \text{ N=N}$ Cm^{-1}	$\nu \text{ C=C}$ Cm^{-1}	$\nu \text{ C-Br}$ Cm^{-1}	$\nu \text{ C-N}$ Cm^{-1}
M1	999	1585	1225-1496	483	1136
M2	993	1592	1370-1243	599	1144
M3	976	1500	1602-1237	467	1091
M4	999	1591	1544-1201	444 $\nu \text{ C-Cl}$ 753	1108

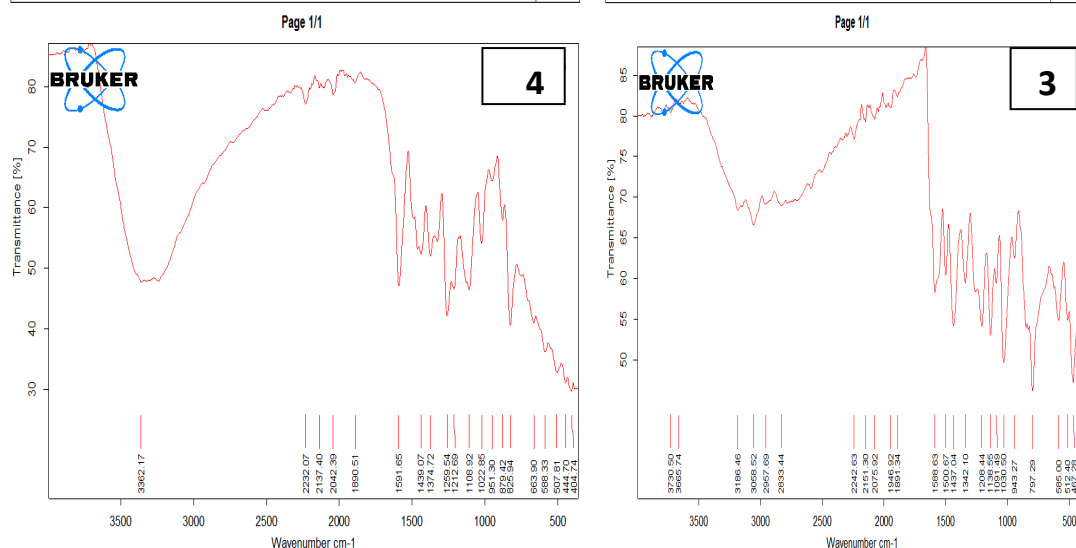
Table 7: ^1H -NMR bands of some prepared phosphazenes (M)

No. M	Chemical Structure	Frequency
M1		(1,2) 7.41 (3,4) 7.61 (5,6) 7.63 (7) 7.64
M2		(1,2) 7.45 (3,4) 7.65 (5,6) 8.00



C:\Haider\15.0	15	Instrument type and / or accessory	12/06/2017
----------------	----	------------------------------------	------------

C:\Harder\14.0	14	Instrument type and / or accessory	12/06/20
----------------	----	------------------------------------	----------



C:\Haider\48.0	48	Instrument type and / or accessory	12/06/201
----------------	----	------------------------------------	-----------

C:\Harder16.0	16	Instrument type and / or accessory	12/06/20
---------------	----	------------------------------------	----------

Fig. 1: FTIR Spectra of azo compounds

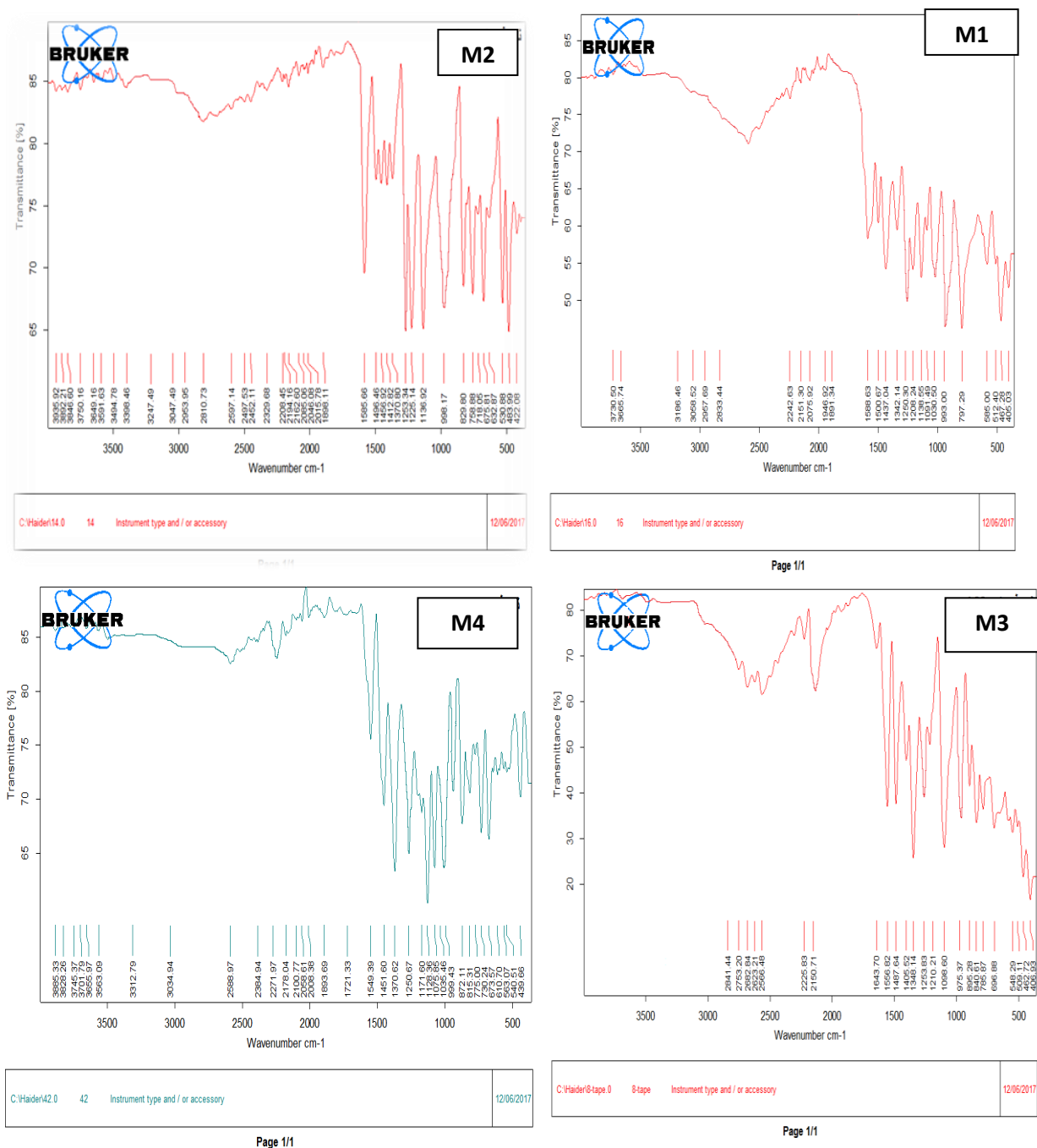


Fig. 2: FTIR Spectra of cyclophosphazenes compounds (M)

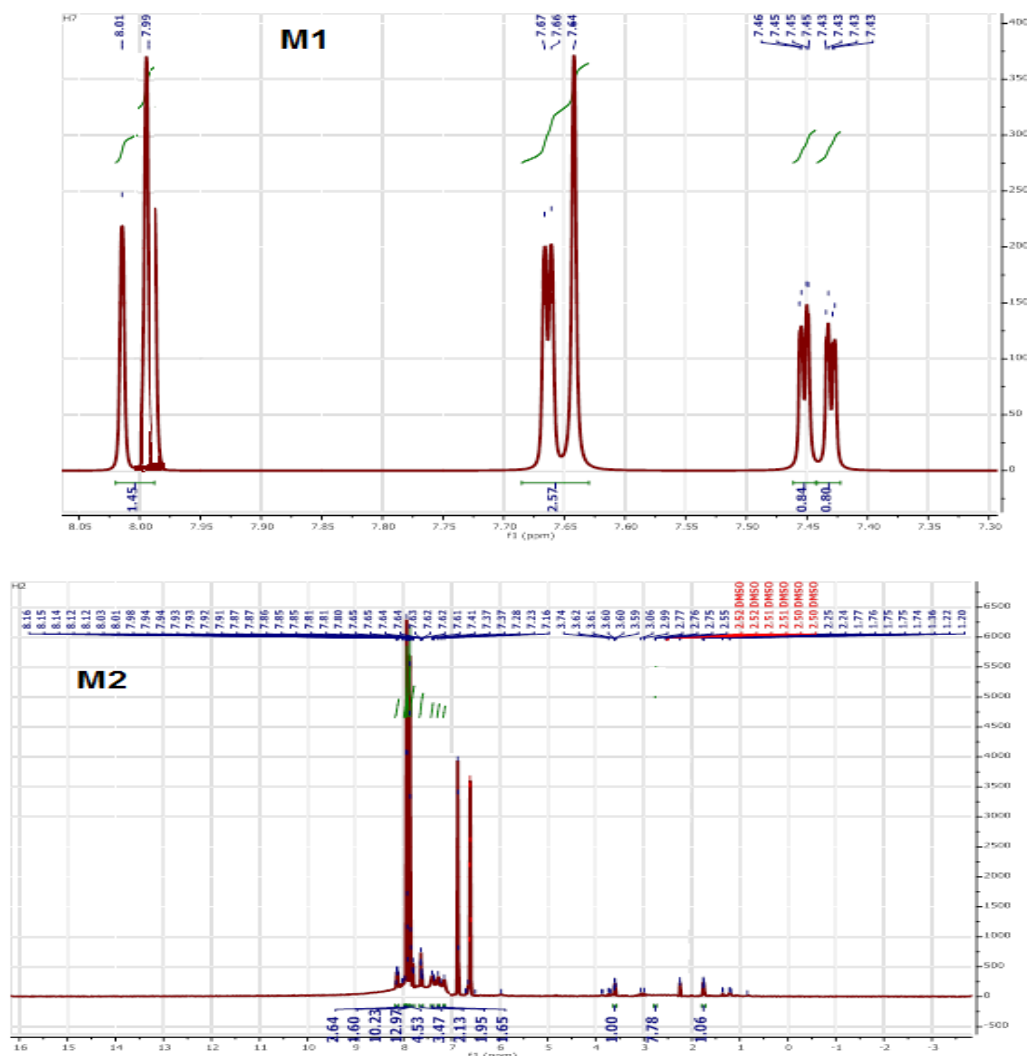


Fig. 3: ^1H -NMR spectra of some prepared cyclophosphazenes compounds (M1, M2)

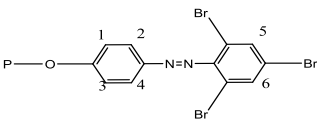
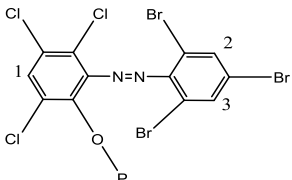
Polyphosphazenes were assessed by IR (Table 8), Fig. (4) and ^1H -NMR (Table 9), Fig. (5) spectroscopy, as well as elemental analysis (Table 9). In comparison with the IR spectra of azo compounds, the spectra of the functionalized polyphosphazene and phosphazenes show the disappearance of (OH) bands and appearance of new bands at about $1010\text{-}930\text{ cm}^{-1}$ for Ar-O-P, $1250\text{-}1150\text{ cm}^{-1}$ for str (P=N) and $1256\text{-}1200\text{ cm}^{-1}$ for str.⁽¹¹⁾ (P-N) for all compounds.

These results presented the certainty that azo compounds were connected to cyclic phosphazene through (P-O-C) bonds.

Table 8: F.T. IR band frequencies of the prepared polyphosphazenes compounds(Pz)

Compound	ν P-O-C Cm ⁻¹	ν N=N Cm ⁻¹	ν C=C Cm ⁻¹	ν C-Br Cm ⁻¹	ν C-N Cm ⁻¹
Pz 1	999	1585	1225-1496	483	1136
Pz 2	993	1592	1370-1243	599	1144
Pz 3	976	1500	1602-1237	467	1091
Pz 4	999	1591	1544-1201	444 ν C-Cl 753	1108

Table 9: ¹H-NMR bands of some prepared phosphazenes

No. Pz	Chemical Structure	Frequency
Pz 2		(1,3) 2.99 (2,4) 3.49 (5,6) 7.88
Pz 4		(1) 4.71 (2,3) 7.49

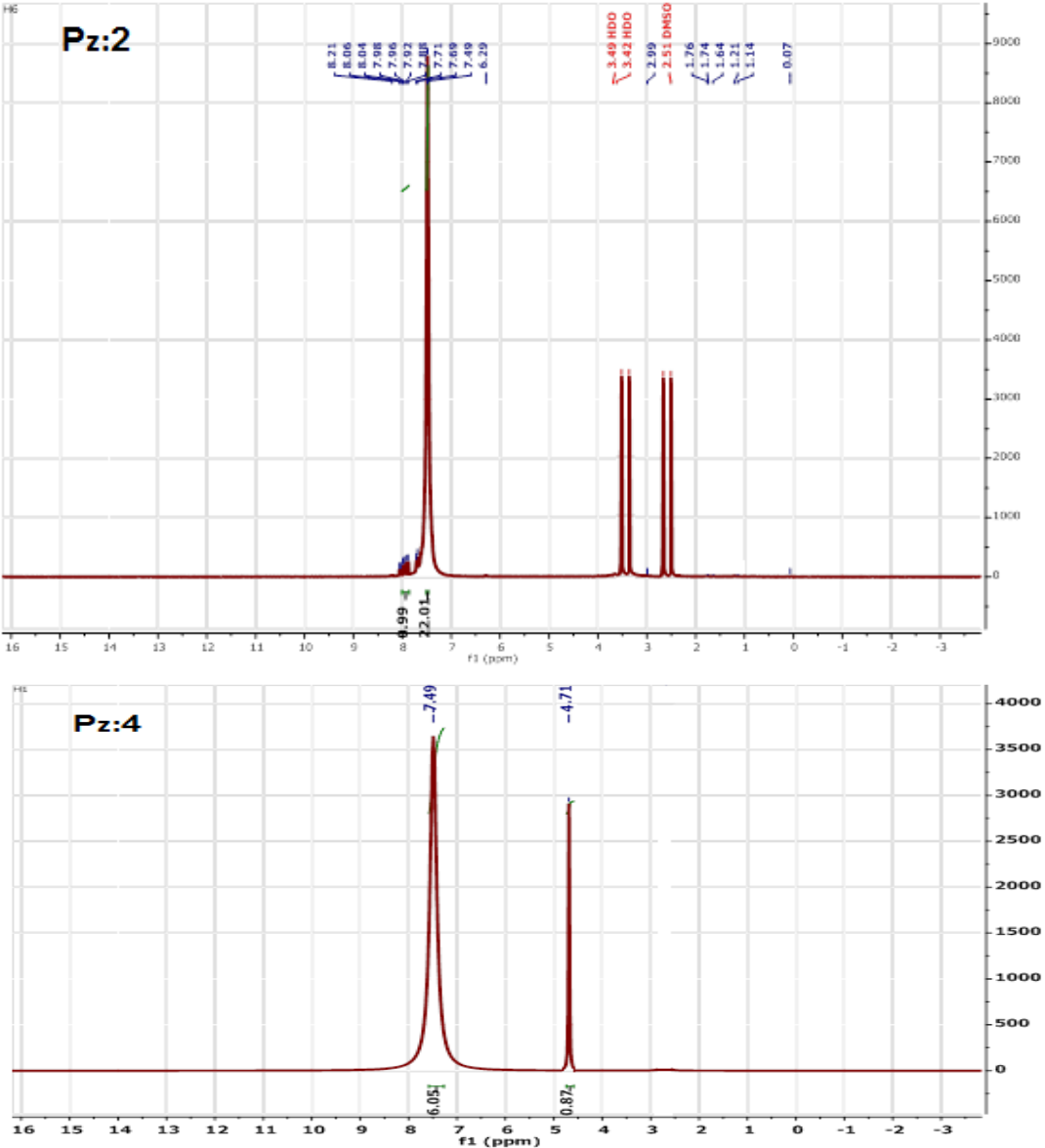


Fig. 5: ¹H-NMR spectra of some prepared Polyphosphazenes compounds (Pz)

Elemental analysis of the functionalized cyclophosphazene and polyphosphazene, (Table 10), (Table 11) respectively, revealed certainly that the half amount of chlorine atom of (NPCl₂)₃ and [NPCl₂]_n were replaced by azo phenolic compounds.

Table 10: Elemental analysis (C.H.N) of cyclophosphazenes compounds(M)

No . Sample	% Found			% Calculated		
	% N	% H	% C	% N	% H	% C
M1	13.029	2.989	33.997	13.524	2.986	33.500
M2	8.797	1.432	30.810	8.800	1.301	30.00
M3	10.974	1.491	27.116	10.518	1.389	26.856
M4	7.120	0.754	23.733	6.710	0.500	23.300

Table 11: Elemental analysis (C.H.N) of Polyphosphazenes compounds(Pz)

No . Sample	% Found			% Calculated		
	% N	% H	% C	% N	% H	% C
Pz 1	9.790	1.921	33.997	9.644	1.607	33.065
Pz 2	11.028	1.022	27.500	10.576	1.322	27.988
Pz 3	10.974	1.491	27.210	10.576	1.322	27.988
Pz 4	6.820	0.500	23.703	6.796	0.485	23.301

Flame Retarding Tests

Construction materials have been mixed with 1% of fire retardant materials in order to improve their fire retarding characteristics. The homogeneity was rationalized via Atomic Force Microscopy (AFM) Fig. (6).

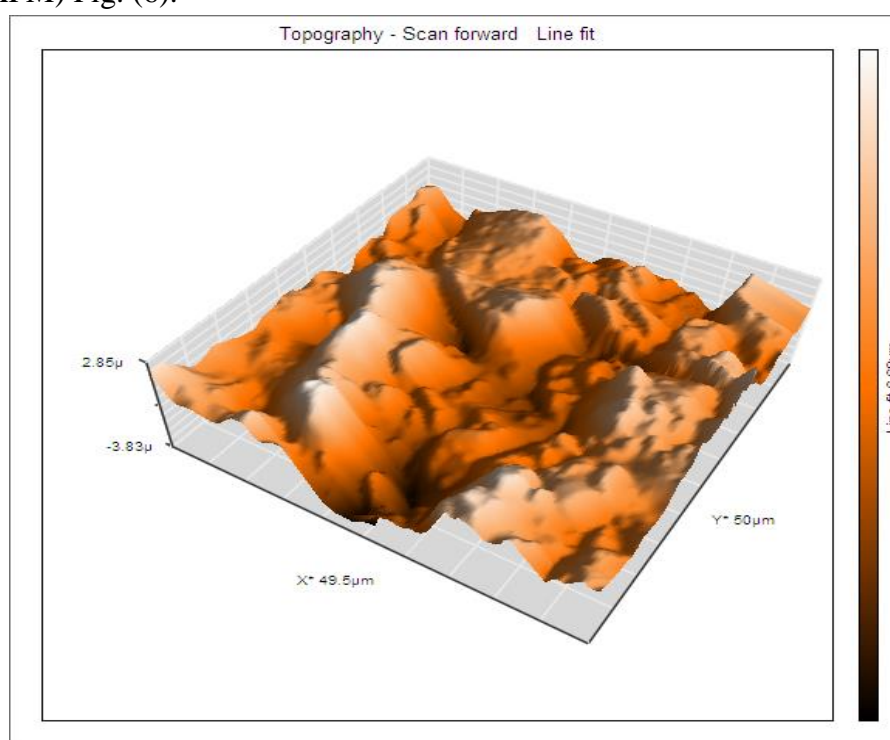
**Fig. 6: AFM of mixing SBR with %1 of phosphazene compound (M2)**

Table (12) revealed the efficiency for fire retardant of the constructional materials with the prepared azo compounds. It was noticed very clear that increasing the number of halogen atoms will increased the efficiency of retarding the fire.

The efficiency was increased by many order of magnitude when their compounds are linked with the cyclotriphosphazene (Table 13). The result show also that cyclophosphazenes as a fire retardant was improved when its chemical structure was developed by the azo compounds whereas the number of halogen atoms have been increased.

The fluctuation in result is belong to the sites of substitution Polyphosphazenes compounds (Table 14) give a good satisfaction for fire retardency in comparison with the cyclophosphazenes or pure azo compounds.

Table 12: The variables of fire retarding test for the construction materials composites with Azo compounds

Material	Azo	B.T/ sec	I.I/ sec/mm	E. R/ mm/sec	H/ cm	AEB/ cm	W1/ gm	W2/ gm	RWR %	E.S	N.B
E.P	Without	46	11.5	0.086	5	8.5	5	2.00	60	-	-
	1	48	12	0.083	5.0	8	5	1.80	64	Yes	-
	2	33	8.25	0.121	4.0	5.5	5	1.29	74	Yes	-
	3	27	6.75	0.148	4.0	4.5	5	1.00	80	Yes	-
	4	28	7	0.142	3.5	5	5	1.09	78	Yes	-
P.U	Without	299	74.75	0.013	6.0	15	5	4.5	10	-	-
	1	294	73.5	0.013	5.7	15	5	4.3	14	-	-
	2	277	69.25	0.014	5.0	13	5	3.8	24	-	-
	3	267	66.75	0.014	4.0	13	5	3.0	40	-	-
	4	216	54	0.018	4.5	10	5	3.3	34	-	-
SBR	Without	575	143.75	0.006	12	15	5	4.6	8	-	-
	1	542	135.5	0.007	11.5	14.8	5	4.4	12	-	-
	2	451	112.75	0.008	10.6	11.4	5	3.8	24	-	-
	3	446	111.5	0.008	9.5	8.7	5	3.1	38	-	-
	4	441	110.25	0.009	9.6	9.4	5	3.3	34	-	-
A.S	Without	498	124.5	0.008	10.0	15.0	6	5.1	15	-	-
	1	463	115.75	0.008	9.0	15	6	4.6	23	-	-
	2	328	82	0.012	6.5	10.5	6	3.3	45	-	-
	3	331	82.75	0.012	7.0	10.8	6	3.4	43	-	-
	4	320	80	0.012	6.5	10.6	6	3.3	45	-	-
P.U.F	Without	306	76.5	0.013	12	15	4	3.6	10	-	-
	1	295	73.75	0.014	11.4	14.5	4	3.4	15	-	-
	2	271	67.75	0.014	10.6	13.3	4	3.1	22	-	-
	3	283	70.75	0.014	11.2	14.0	4	3.3	17	-	-
	4	277	69.25	0.014	10.8	13.5	4	3.4	20	-	-
OD	Without	362	90.5	0.011	8.0	15	6	5.3	10	-	-
	1	354	88.5	0.011	8.0	14.6	6	4.2	30	-	-
	2	278	69.5	0.014	6.0	11.6	6	3.3	45	-	-
	3	281	70.25	0.014	6.5	11.5	6	3.4	5343	-	-
	4	285	71.25	0.0140	6.0	10.8	6	3.4	43	-	-
W	Without	588	147	0.007	12.0	15	5	4.8	4	-	-
	1	510	127.5	0.0078	10.5	13.7	5	4.3	14	-	-
	2	396	99	0.0101	8.0	10.0	5	4.1	18	-	-
	3	426	106.5	0.0093	8.5	10.5	5	3.4	32	-	-
	4	473	118.25	0.008	9.5	2.5	5	4.1	18	-	-
PVA	Without	372	93	0.011	13.0	15	6	4.5	25	-	-
	1	368	92	0.011	13.0	15.0	6	4.5	25	-	-
	2	338	84.5	0.012	12.0	14.6	6	4.0	33	-	-
	3	341	85.25	0.012	12.0	4.4	6	4.3	28	-	-
	4	329	82.25	0.012	11.5	14.2	6	3.9	35	-	-

Table 13: The variables of fire retarding test for the construction materials composites with phosphazenes (M)

Material	M	B.T sec	I.I sec/mm	E.R mm/sec	H cm	AEB Cm	W1 gm	W2 gm	RWR %	E.S	N.B
E.P	Without	46	11.5	0.086	5.0	8.5	5	2.0	60	YES	-
	P*	32	8	0.125	3.5	5.8	5	1.3	74	YES	
	M1	36	9	0.111	4.0	6.5	5	1.4	72	YES	-
	M2	23	5.75	0.173	2.5	4.0	5	0.9	82	YES	-
	M3	8	2	0.5	1.0	1.5	5	0.3	94	YES	-
	M4	4	1	1	0.5	1.0	5	0.1	98	YES	-
P.U	Without	299	74.75	0.013	6.0	15.0	5	4.5	10	-	-
	P*	162	40.5	0.025	3.0	8.0	5	2.4	52	Yes	-
	M1	168	42	0.023	3.5	8.4	5	2.5	50	Yes	-
	M2	153	38.25	0.026	3.0	7.6	5	2.3	54	Yes	-
	M3	44	11	0.090	1.0	2.2	5	0.7	86	Yes	-
	M4	29	7.25	0.137	0.5	1.5	5	0.4	92	Yes	-
SBR	Without	575	143.75	0.006	12	15	5	4.6	8	-	-
	P*	284	72	0.013	5.5	7.6	5	2.5	50	Yes	-
	M1	398	99.5	0.010	8.5	10.4	5	3.2	36	-	-
	M2	317	79.25	0.012	6.5	8.3	5	2.5	50	Yes	-
	M3	97	24.25	0.041	2.0	2.5	5	0.8	84	Yes	-
	M4	83	20.75	0.048	2.0	2.2	5	0.6	88	Yes	-
A.S	Without	498	124.5	0.008	10.0	15	6	5.1	15	-	-
	P*	182	45.5	0.022	3.5	5.3	6	1.7	71	Yes	-
	M1	302	75.5	0.013	6.0	9.2	6	3.0	50	Yes	-
	M2	164	41	0.024	3.5	5.0	6	1.6	73	Yes	-
	M3	126	31.5	0.031	2.5	3.8	6	1.3	78	Yes	-
	M4	21	5.25	0.190	0.5	0.6	6	0.2	95	Yes	-
P.U.F	Without	306	76.5	0.013	12	15	4	3.6	10	-	-
	P*	147	36.75	0.027	5.5	6.8	4	2.0	50	Yes	-
	M1	128	32	0.031	5.0	6.3	4	1.5	62	Yes	-
	M2	118	29.5	0.033	4.5	6.0	4	1.4	65	Yes	-
	M3	63	15.75	0.063	2.5	3.1	4	0.7	82	Yes	-
	M4	30	7.5	0.133	1.5	1.5	4	0.4	90	Yes	-
OD	Without	362	90.5	0.011	8.0	15	6	4.3	28	-	-
	P*	163	40.75	0.025	4.0	7.0	6	2.1	65	Yes	-
	M1	204	51	0.019	4.5	8.5	6	2.2	63	Yes	-
	M2	156	39	0.025	3.5	6.5	6	1.7	71	Yes	-
	M3	113	28.25	0.035	2.5	4.6	6	1.2	80	Yes	-
	M4	20	5	0.2	0.5	0.8	6	0.2	96	Yes	-
W	Without	588	147	0.006	12.0	15	5	4.8	4	-	-
	*P	298	74.5	0.013	6.0	6.4	5	2.4	53	-	-
	M1	355	88.75	0.011	7.5	9.0	5	2.8	44	-	-
	M2	312	78	0.012	6.5	6.3	5	2.5	50	Yes	-
	M3	66	16.5	0.060	1.5	1.6	5	0.5	90	Yes	-
	M4	14	3.5	0.285	0.5	0.4	5	0.1	98	Yes	-
PVA	Without	372	93	0.010	13	15	6	4.5	25	-	-
	*P	192	48	0.021	6.5	8.0	6	2.5	50	Yes	-
	M1	207	51.75	0.019	7.0	8.3	6	2.5	58	Yes	-
	M2	174	43.5	0.022	6.0	7.0	6	2.1	65	Yes	-
	M3	54	13.5	0.074	2.0	2.2	6	0.7	88	Yes	-
	M4	7	1.75	0.571	0.5	0.3	6	0.1	98	Yes	-

Table 14: The variables of fire retarding test for the construction materials composites with Polyphosphazenes compounds (Pz)

Material	Pz	B.T/ sec	I.I/ sec/mm	E.R/ mm/sec	H/ cm	AEB/ cm	W1/ gm	W2/ gm	RWR %	E.S	N.B
E.P	without	46	11.5	0.086	5	8.5	5	2.0	60	-	-
	1Pz:	24	6	0.167	2.5	4.5	5	0.90	82	Yes	-
	2 Pz:	10	2.5	0.400	1.0	2.0	5	0.82	83	Yes	-
	3 Pz:	5	1.25	0.800	0.5	1.0	5	0.21	95	Yes	-
	4 Pz:	7	1.75	0.572	1.0	1.2	5	0.27	94	Yes	-
P.U	without	299	74.75	0.013	6.0	15	5	4.5	10	-	-
	1Pz:	113	28.25	0.035	2.5	5.6	5	1.70	66	Yes	-
	2 Pz:	94	23.5	0.042	2.0	4.7	5	1.41	71	Yes	-
	3 Pz:	87	21.75	0.045	2.0	4.3	5	1.31	73	Yes	-
	4 Pz:	31	7.75	0.129	1.0	1.6	5	0.47	90	Yes	-
SBR	without	575	143.75	0.006	12.0	15.0	5	4.6	8	-	-
	1Pz:	126	31.5	0.031	3.5	3.3	5	1.01	79	Yes	-
	2 Pz:	90	22.5	0.044	1.5	1.8	5	0.72	85	Yes	-
	3 Pz:	75	18.75	0.053	1.5	2.0	5	0.60	88	Yes	-
	4 Pz:	84	21	0.047	1.5	2.2	5	0.67	86	Yes	-
A.S	without	498	124.5	0.008	10.0	15	6	5.1	15	-	-
	1Pz:	78	19.5	0.051	1.5	2.3	6	0.78	87	Yes	-
	2 Pz:	57	14.25	0.070	1.5	1.5	6	0.56	90	Yes	-
	3 Pz:	59	14.75	0.067	1.5	1.7	6	0.58	90	Yes	-
	4 Pz:	53	13.25	0.075	1.0	0.6	6	0.53	91	Yes	-
PUF	without	306	76.5	0.013	12	15	4	3.60	10	Yes	-
	1Pz:	65	16.25	0.061	2.5	3.2	4	0.76	81	Yes	-
	2 Pz:	36	9	0.111	1.5	1.7	4	0.43	89	Yes	-
	3 Pz:	38	9.5	0.105	1.5	1.9	4	0.45	88	Yes	-
	4 Pz:	40	10	0.100	2.0	2.2	4	0.47	88	Yes	-
OD	without	362	90.5	0.011	8.0	15	6	4.3	28	-	-
	1Pz:	70	17.5	0.057	1.5	3.0	6	0.83	86	Yes	-
	2 Pz:	34	8.5	0.117	1.0	1.4	6	0.40	93	Yes	-
	3 Pz:	41	10.25	0.097	1.0	1.7	6	0.49	91	Yes	-
	4 Pz:	45	11.25	0.089	1.0	1.8	6	0.53	91	Yes	-
W	without	588	147	0.006	12	15	5	4.8	4	-	-
	1Pz:	84	21	0.047	2.0	2.2	5	0.68	86	Yes	-
	2 Pz:	54	13.5	0.074	1.0	1.5	5	0.44	91	Yes	-
	3 Pz:	40	10	0.100	1.0	1.0	5	0.33	93	Yes	-
	4 Pz:	37	9.25	0.108	1.0	0.9	5	0.31	93	Yes	-
PVA	without	372	93	0.011	13	15	6	4.5	25	-	-
	1Pz:	56	14	0.071	2.0	2.3	6	0.68	88	Yes	-
	2 Pz:	23	5.75	0.173	1.0	1.0	6	0.28	95	Yes	-
	3 Pz:	21	5.25	0.190	1.0	0.9	6	0.25	95	Yes	-
	4 Pz:	23	5.75	0.173	1.0	1.1	6	0.28	95	Yes	-

Where:

$B.T$ = Burning Time (sec).

$I.I$ = Insulation Index (sec/mm).

$E.R$ = Erosion Rate (mm/sec).

H = High flame (cm).

$A.E.B$ = Average extent of burning (cm).

$W1$ = Sample weight before burning (gm).

$W2$ = Weight of the missing material (gm).

RWR = Percentage of residual weight after combustion (%).

$E.S$ = Self-Extinguishing.

$N.B$ = Non Burning.

* P = only Cyclohexachlorotriphosphazene without Azo phenolic compounds.

M = cyclophosphazenes

Pz = Polyphosphazenes

CONCLUSIONS

Many constructional materials can be inhibited to fire extinguishing by using cyclophosphazene or polyphosphazene. The efficiency of phosphazenes as fire retarding materials can be developed by many order of magnitude throughout the improving of their chemical structure. The chemical structure of phosphazenes have been improved by increasing the number of halogen atoms with the molecule by linking with different azo moieties. It was noted that polyphosphazenes compounds were better than phosphazenes and azo compounds as fire retardant.

REFERENCES

- Allcock, H.R.; Morozowich, N.L. (2012). Biodegradable Polyphosphazenes and their medical potential. *Polum. Chem.* **3**, 578-590.
- Allcock, H.R. (2006). Recent development in phosphazene materials science. *Curr. Op. Solid st. M.*, **10**, 231-240.
- Arvind, S.A.; Dhiman, S.; Sandeep, A.; Kapoor, A. (2010). Synthesis of colon specific N,N-Bis-(2-Chloroethyl) Aniline Polyphosphazene Copolymer conjugates. *International J. Pharm. and Pharmaceut. Sci.*, **2**(4), ISSN-0975-1491.
- Camino, G.; Costa, L.; Cortemiglia, L.P. (1991). Stability of polymers. *Polym. Degrad. Stabil.*, **33**, 131
- Cullis, F.C.; Hirschter, M.M. (1981). "The Combustion of Organic Polymers". Clarendon Press, Oxford, London, pp. 1-10.
- Dittenber, B.D.; Gangarao, S.H.; Compos, Pt. (2012). Fire retardant materials. *Appl. Sci. Manuf.*, **43**, 1419
- Khattab, A.F.; Abbas, M.F. (2015). Studies on storing and releasing the optical energy via azo polymers and its relation with the electrical conductivity. *International J. Enhanced Research in Sci., Technol. Eng.*, **4**(8), 1-10. August.
- Schindler, W.D.; Hauser, P.J. (2004). "Chemical Finishing of Flame". Wood head, Cambridge, 1st ed., 98 p.
- Shumao, L.; lie, R.; Hua, Y.; Taa, Y.; Weixhong, Y. (2010). Some using of polymers. *Polym. Int.*, **59**, 242,
- Wichman, I.S. (2003). Fire performance of a composite materials. *Prog. Energy Combust. Sci.*, **29**, 247.