Studying the synergistic effect of some organo-halogen antimony complexes with chlorinated rubber on retard combustion of unsaturated polyester and epoxy resins

دراسة التأثيرالتآزري لبعض معقدات الانتيمون العضوية الهالوجينية مع المطاط المكلورعلى تثبيط اللهوبية لراتنجي البولي استر غير المشبع والايبوكسي

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Keyword: Flammability; Fire-Retardant; Retard combustion; Synergistic effect ; Inorganic antimony complex; Chlorinated rubber**;** Unsaturated polyester resin; Epoxy resin; Limiting oxygen index; Rate of burning; Flame height **.**

Abstract

Two groups of additives were used in this investigation, to measure the effect of these additives on retard combustion of unsaturated polyester and epoxy resins. The first group contains four complexes, from type organo-halogen antimonate compounds, and the second group, which prepared from blend 50% in weight percentage of each complex with 50% in weight percentage of chlorinated rubber. Three sheets from each resins were prepared with weight percentage (0.2, 0.4, 0.6 & 0.8 %) of additives . Three standard test methods used to measure the flame retardation, which are: (ASTM:D -2863), (ASTM:D-635) and (ASTM:D-3014) .

Results were obtained from these tests indicated that, additive VI has high efficiency as flame retardant, for both resins and additive III show low effect on flammability in both resins .

الخلاصة :-

مجموعتين من المضافات أستخدمت في هذا البحث لقياس تأثيرها على تثبيط اللهوبية لراتنجي البولي أستر غير المشبع والأيبوكسي . المجموعة الأولى ، تحتوي على أربعة معقدات من نوع مركبات أنتيمونات الهالوجين العضوية ، و المجموعة الثانية ، حضرت بخلط فيزيائي من 50% نسبة وزنية من كل من المعقدات المحضرة مع 50% نسبة وزنية من المطاط المكلور .

ثلاثة ألواح من كل من الراتنجين قد حضرت مع نسب مئوية وزنيه (0.2, 0.4, 0.6& 0.8 %) من المضافات . استخدمت ثلاثة طرق قياسية لقياس تثبيط اللهوبية هي (ASTM:D-635), (ASTM:D-3014) , (ASTM:D-2863) .

إن النتائج التي تم الحصول عليها من هذه القياسات تشير الى ان المضاف VI يمتلك كفاءة عالية في تثبيط اللهوبية في كلا الراتنجين ، أما المضاف III فقد أظهر تأثير قليل على تثبيط اللهوبية في كلا الراتنجين .

Introduction

Flame retardants are used to reduce flammability of polymeric materials, these chemical compounds are capable of imparting flame resistance to the materials and they can be classified into two general types [1] : those which do not react chemically with the polymer and the other type which are those incorporated chemically in to the basic polymer structure .

Halogens compounds are selected on the basis of economy, stability and general properties as well as their efficiency as flame retardant .Bromine and chlorine compounds occupy an important position among the fire extinguishing and flame retardant agents .The efficiency of the halogen compounds depends on the ease of relase of reactive halogen [2], the order of halogens effective being the following [3, 4]: I>Br>Cl>F . The low efficiency of florine compounds has been attributed to the stability of C-F and H-F bonds and to non –thermal stability. The efficiency of Bromine Compounds as flame retardant are much higher than those of chlorine [5].

In the absence of halogens, except for certain cellulosic, antimony oxides are a poor flame retardants. Antimony trioxide (Sb_2O_3) and antimony pentaoxide (Sb_2O_5) are widely used commercial flame retardants. Antimony oxide behaves a condensed phase flame retardant in cellulosic materials. Rhys and cleaver [6,7], studied the combustion of polyester Laminates containing pentabromotoluene , they observed that the optimum atomic ratio of (Sb: Br) for flame retardancy is (1:3) .

In the condensed phase the polymer, antimony trioxide and halogen react to form char which reduce the heat transfer from flame to the polymer and fuel transfer from the polymer to the flame, but in the vapor phase (SbX_3) endothermally decomposes to form halide radicals [8].

In (1993) Ugal [9], prepared some organo-halogen compounds from mixed types halo-antimonates in which antimony was the central element, such as $Et_4N[PhSbCl_2Br]$, and in (2005) Al-Baiaty [10], prepared organo-halogen compound from mixed types halo-phosphours for which phosphor element was involves ,such as $Et4N[PhPCl_2Br]$, these compounds contain in their structure atoms such as bromine, chlorine, phosphor ,nitrogen and benzene ring ,the ratio between halogen atoms and antimony or phosphor atoms is (3:1), this ratio represent ratio for high efficiency in flame retardant ability and non – burning properties for the polymeric materials .

Experimental

A. Polymers:

1. Unsaturated polyester resin, hardener type (MEKP), imported from industrial chemical and resin Co. LTD, Kingdom of Sudia Arabia.
2. Epoxy resin, type (CY223), hardener type (HY956), imported from Ciba – Geigy Co. .

B. Flame – retardants materials :

All complexes were prepared using method reported in the literature [11], and chlorinated rubber, in powder form, was imported from BDH Co. .

The additives were used as flame retardant materials, which are:

1. Additive I **:** Tetraethylammonium tribromoethyl antimonate, $Et_4N[(C_2H_5)SbBr_3]$.
2. Additive II **:** Tetraethyl ammonium tribromophenyl antimonate, $Et_4N[PhSbBr_3]$.
3. Additive III **:** Tetraethylammonium trichloroethyl antimonate, $Et_4N[(C_2H_5)SbCl_3]$.
4. Additive IV **:** Tetraethyl ammonium trichlorophenyl antimonate, $Et_4N[PhSbCl_3]$.
5. Additive V : 50% additive I + 50% chlorinated rubber .
6. Additive VI : 50% additive II + 50% chlorinated rubber .
7. Additive VII : 50% additive III + 50% chlorinated rubber .
8. Additive VIII : 50% additive IV + 50% chlorinated rubber .

C. Standard tests

1. ASTM: D-2863: The measurement of limiting oxygen Index (LOI) is widely used for measuring flammability of polymers [12].
2. ASTM: D-635: This instrument deals with the measurement of rate of burning (R.B), Average time of burning (ATB), Non –burning (N.B), Self- extinguishing (S.E) and Average extant of burning (AEB) for self Supporting plastic in a horizontal position [13].
3. ASTM: D-3014: This instrument deals with the measurement of maximum flame height (H), and the ratio of loss of weight of polymeric materials [14].

D- Preparation of specimens

Specimens were prepared in dimension of (150X150X3) mm, three sheets from each unsaturated polyester and epoxy resins were prepared having percentage weight (0.2, 0.4, 0.6 & 0.8 %) of the additives. These sheets were cut according to ASTM standard tests were used in this work.

Results and Discussion

The limiting oxygen Index (LOI) for unsaturated polyester resin without additives is (20.4) [15] and for epoxy resin without additives is (19.7) [16], Tables 1 & 2, and Figures 1 & 2, indicated that. Oxygen concentration required to support a candle – like in unsaturated polyester and epoxy resins samples were increased with increasing the weight percentage of additives. The efficiency of additives studied was in the following order:

VI > VIII > V > VII > II > IV > I > III

The synergistic action of the complexes with the chlorinated rubber show high effect to reduced the flammability compared with low effect of complexes alone, that's means, the chlorinated rubber gives more power to reduced the flame, because liberated Cl˙ Free radicals and in same time the complexes contains three atoms from bromine and phenyl group, show high effect compared with complexes contains three atoms from chlorine and ethyl group, because the bromine atoms have high effect on flammability .

Tables 3&4, showed the results obtained from the rate of burning (R.B) tests of the resins with additives are of inversely proportional with the percentage weight of additives, as indicated in, Figures 3&4, respectively, which showed the flame speed curves of flame retardation for both resins.

Figures.-5&6, showed the flame-height results, the maximum flame height (H) was decreased with increasing the percentage weight of additives (inversely proportional), as indicated in Tables - 5&6, respectively.

Conclusion

The limiting oxygen index (LOI), was increased with increasing the weight percentages of the additives and the rate of burning (R.B) and flame height (H), were decreased with increasing the weight percentages of the additives and the flame retarding efficiency of the additives has the following order:

VI > VIII > V > VII > II > IV > I > III

The action of these additives due to by the formation of chare as result of removing the hydrogen atoms from the polymer with the Liberation of the acid (HCL) which acts in the gas – phase .The combustion products Like; free radicals (˙CL and ˙OH), chare…etc., will form allayer to prevent burning and displacing oxygen that help continues burning of polymers.

Results obtained from these tests indicated that, the bromine atoms and the phenyl group were more effective from chlorine atoms and the ethyl group, respectively, to retard combustion for both resins, and present the chlorinated rubber give the additives more power to reduced the flammability, because contain on very large amount from chlorine (70 – 72 %) .

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Table -1: Limiting Oxygen Index (LOI) for unsaturated polyester resin with additives

% / Additives	Non	0.2	0.4	0.6	0.8
I	20.4	21.08	21.76	22.44	23.12
II	20.4	21.24	22.09	22.92	23.78
III	20.4	20.95	21.63	22.18	22.73
IV	20.4	21.17	21.94	22.73	23.48
V	20.4	21.92	23.44	24.46	25.69
VI	20.4	22.36	24.32	26.25	27.15
VII	20.4	21.60	22.85	24.10	25.40
VIII	20.4	22.13	23.86	25.58	26.61

Table - 2: Limiting Oxygen Index (LOI) for epoxy resin with additives.

% / Additives	Non	0.2	0.4	0.6	0.8
I	19.7	20.14	20.76	21.39	22.01
II	19.	20.61	21.30	21.98	22.60
III	19.7	20.05	20.58	21.11	21.74
IV	19.7	20.36	21.02	21.66	22.35
V	19.7	21.20	21.97	22.74	23.51
VI	19.7	21.90	22.74	23.88	24.65
VII	19.7	20.93	21.52	22.15	23.39
VIII	19.7	21.57	22.34	23.21	23.80

Table -3: Rate of Burning (R.B.) for unsaturated polyester resin with additives.

% / Test	Non	o.2	0.4	0.6	0.8	Additives
AEB (cm)	10	10	10	9.1	8.2	I
	10	10	9.5	8.7	7.0	II
	10	10	10	9.8	8.9	III
	10	10	10	9.4	7.7	IV
	10	10	8.9	7.3	-	V
	10	9.4	7.5	-	-	VI
	10	10	9.2	7.8	-	VII
	10	9.7	8.3	-	-	VIII

ATB (Min.)	6.92	8.26	9.00	8.50	9.01	I
	6.92	9.09	10.21	14.26	16.27	II
	6.92	8.00	8.77	8.99	9.08	III
	6.92	8.54	9.17	11.32	11.66	IV
	6.92	10.63	11.86	13.03	-	V
	6.92	13.05	19.73	-	-	VI
	6.92	10.52	10.69	18.57	-	VII
	6.92	12.12	12.96	-	-	VIII
R.B (cm/ Min.)	1.44	1.21	1.11	1.07	0.91	I
	1.44	1.1	0.93	0.61	0.43	II
	1.44	1.25	1.14	1.09	0.98	III
	1.44	1.17	1.09	0.83	0.66	IV
	1.44	0.94	0.75	0.56	-	V
	1.44	0.72	0.38	-	-	VI
	1.44	0.95	0.86	0.42	-	VII
	1.44	0.80	0.64	-	-	VIII
S.E	-	-	-	-	yes	I
	-	-	yes	yes	yes	II
	-	-	-	-	yes	III
	-	-	-	yes	yes	IV
	-	yes	yes	yes	yes	V
	-	yes	yes	yes	yes	VI
	-	yes	yes	yes	yes	VII
	-	yes	yes	yes	yes	VIII
N.B	-	-	-	-	-	I
	-	-	-	-	-	II
	-	-	-	-	-	III
	-	-	-	-	-	IV
	-	-	-	-	Yes	V
	-	-	-	yes	yes	VI
	-	-	-	-	yes	VII
	-	-	-	ves	yes	VIII

Table -4 : Rate of Burning (R.B.) for epoxy resin with additives.

Test \ %	Non	o.2	0.4	0.6	0.8	Additives
AEB (cm)	10	10	10	9.3	8.4	I
	10	10	9.8	8.5	7.2	II
	10	10	10	9.6	8.8	III
	10	10	10	8.9	7.6	IV
	10	10	9.0	7.8	-	V
	10	9.7	8.3	7.1	-	VI
	10	10	9.4	8.2	-	VII
	10	10	8.7	7.5	-	VIII
ATB (Min.)	5.12	7.93	8.47	8.53	9.33	I
	5.12	8.84	10.76	11.18	13,58	II
	5.12	7.81	8.19	8.72	8.71	III
	5.12	8.40	8.92	9.56	9.38	IV
	5.12	12.04	12.67	13.00	-	V
	5.12	12.43	15.09	16.90	-	VI
	5.12	11.62	12.20	12.81	-	VII
	5.12	12.34	12.79	14.70	-	VIII
R.B (cm/ Min.)	1.95	1.26	1.18	1.09	0.90	I
	1.95	1.13	0.91	0.76	0.53	II
	1.95	1.28	1.22	1.10	1.01	III
	1.95	1.19	1.12	0.93	0.81	IV
	1.95	0.83	0.71	0.60	-	V
	1.95	0.78	0.55	0.42	-	VI
	1.95	0.86	0.77	0.64	-	VII
	1.95	0.81	0.68	0.51	-	VIII
S.E	-	-	-	-	yes	I
	-	-	yes	yes	yes	II
	-	-	-	-	-	III
	-	-	-	yes	yes	IV
	-	yes	yes	yes	yes	V
	-	yes	yes	yes	yes	VI
	-	yes	yes	yes	yes	VII
	-	yes	yes	yes	yes	VIII
N.B	-	-	-	-	-	I
	-	-	-	-	-	II
	-	-	-	-	-	III
	-	-	-	-	-	IV
	-	-	-	-	yes	V
	-	-	-	-	yes	VI
	-	-	-	-	yes	VII
	-	-	-	-	yes	VIII

Table -5 : Flame High (H) for unsaturated polyester resin with additives.

Test \ %	Non	o.2	0.4	0.6	0.8	Additives
W1 (gm)	5.63	5.94	5.96	5.98	6.00	I
	5.63	5.98	6.00	6.02	6.04	II
	5.63	5.92	5.94	5.96	5.98	III
	5.63	5.96	5.98	6.00	6.02	IV
	5.63	6.02	6.04	6.06	-	V
	5.63	6.04	6.07	-	-	VI
	5.63	6.00	6.02	6.04	-	VII
	5.63	6.03	6.05	-	-	VIII
W2 (gm)	2.57	1.87	1.92	1.96	2.00	I
	2.57	1.95	1.98	2.01	2.05	II
	2.57	1.83	1.88	1.92	1.97	III
	2.57	1.91	1.94	1.99	2.02	IV
	2.57	2.03	2.06	2.11	-	V
	2.57	2.11	2.14	-	-	VI
	2.57	1.99	2.03	2.06	-	VII
	2.57	2.07	2.10	-	-	VIII
P.W.R (%)	54.35	68.51	67.78	67.22	66.66	I
	54.35	67.39	67.00	66.61	66.05	II
	54.35	69.08	68.35	67.78	67.05	III
	54.35	67.95	67.55	66.83	66.44	IV
	54.35	66.27	65.89	65.18	-	V
	54.35	65.06	64.74	-	-	VI
	54.35	66.83	66.27	65.89	-	VII
	54.35	65.67	65.28	-	-	VIII
H (cm)	14.0	5.8	5.5	5.0	4.5	I
	14.0	5.0	4.5	4.0	3.5	II
	14.0	6.4	6.0	5.5	5.0	III
	14.0	5.5	5.0	4.5	4.0	IV
	14.0	4.0	3.5	3.0	-	V
	14.0	3.0	2.0	-	-	VI
	14.0	4.5	4.0	3.5	-	VII
	14.0	3.5	3.0	-	-	VIII

NOTE:
W1: weight of sample before burning (gm) .
W2: weight of the loss from sample after burning (gm).
PWR: The percentage of Weight Ratio (%) , where PWR= (W1-W2/ W1) × 100 **.**

Table -6 : Flame High (H) for epoxy resin with additives.

Test \ %	Non	o.2	0.4	0.6	0.8	Additives
W1 (gm)	4.52	4.90	4.92	4.94	4.96	I
	4.52	4.94	4.96	4.98	5.00	II
	4.52	4.88	4.90	4.92	4.94	III
	4.52	4.92	4.94	4.96	4.98	IV
	4.52	4.98	5.00	5.02	-	V
	4.52	5.02	5.04	5.06	-	VI
	4.52	4.96	4.98	5.00	-	VII
	4.52	5.00	5.02	5.04	-	VIII
W2 (gm)	1.43	0.90	0.93	0.96	0.99	I
	1.43	0.94	0.97	1.01	1.04	II
	1.43	0.88	0.91	0.94	0.97	III
	1.43	0.92	0.96	1.00	1.03	IV
	1.43	1.00	1.03	1.06	-	V
	1.43	1.03	1.05	1.07	-	VI
	1.43	0.98	1.00	1.03	-	VII
	1.43	1.01	1.04	1.09	-	VIII
P.W.R (%)	68.36	81.63	81.09	80.56	80.04	I
	68.36	80.79	80.44	79.71	79.20	II
	68.36	81.96	81.42	80.89	80.36	III
	68.36	81.30	80.56	79.83	79.31	IV
	68.36	79.91	79.40	78.88	-	V
	68.36	79.48	79.16	78.85	-	VI
	68.36	80.24	79.91	79.40	-	VII
	68.36	79.80	79.28	78.37	-	VIII
H (cm)	12.0	5.0	4.8	4.5	4.0	I
	12.0	4.0	3.5	3.0	2.5	II
	12.0	5.5	5.0	5.0	4.5	III
	12.0	4.5	4.5	4.0	3.5	IV
	12.0	3.0	2.5	2.0	-	V
	12.0	2.0	1.5	1.0	-	VI
	12.0	3.5	3.0	2.5	-	VII
	12.0	2.5	2.0	1.5	-	VIII

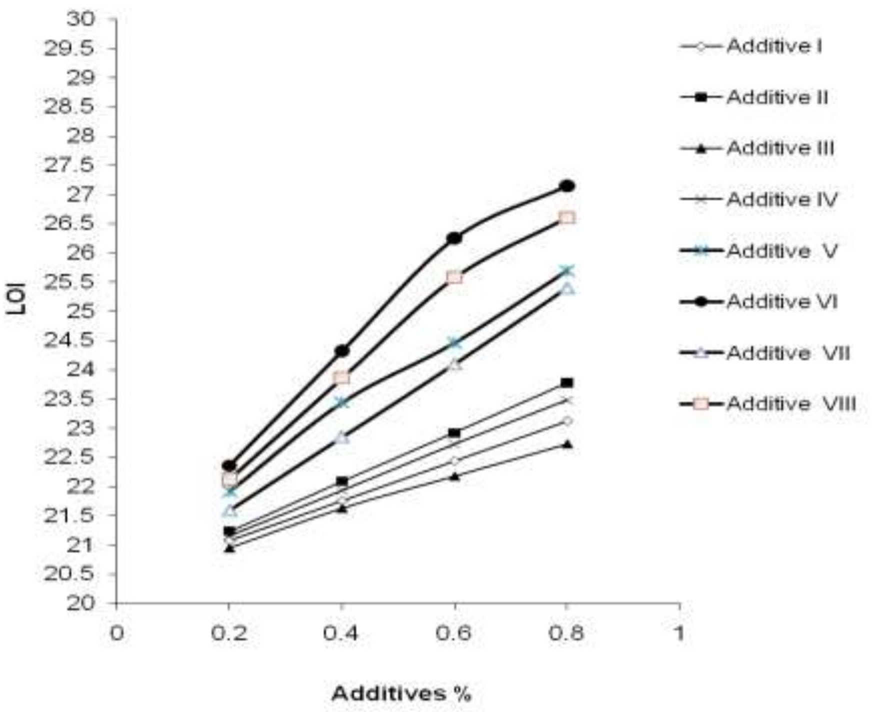

Figure – 1 : The limiting oxygen index for unsaturated polyester resin with additives .

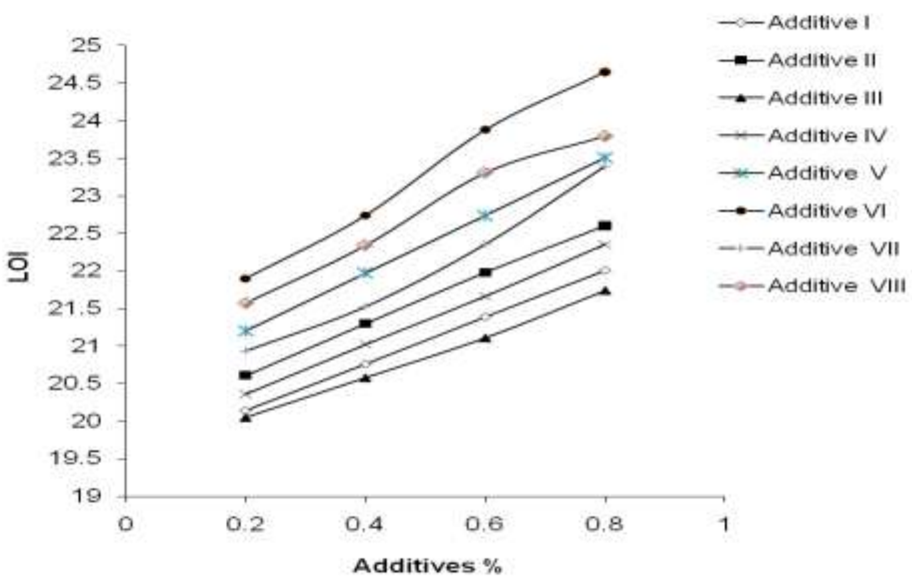

Figure – 2 : The limiting oxygen index for epoxy resin with additives .

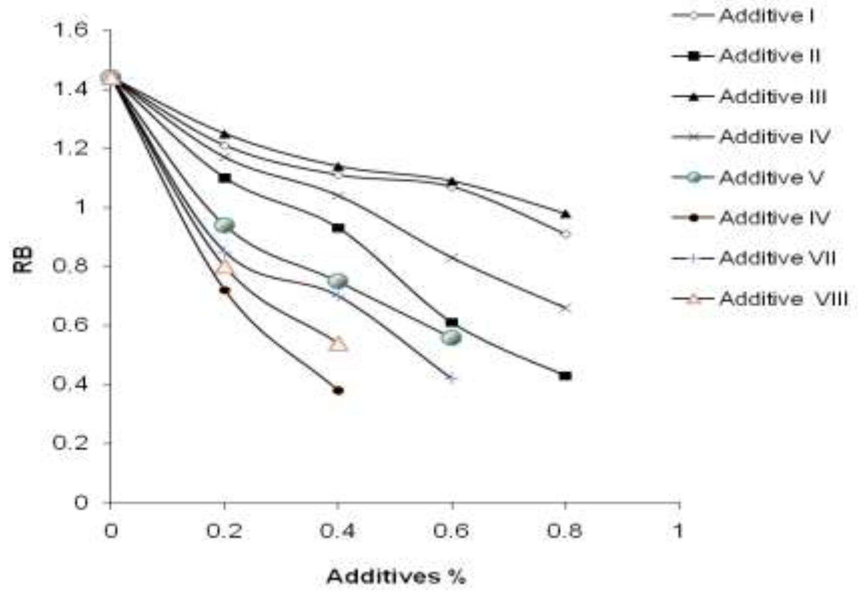

Figure-3 : Rate of burning (R.B.) of unsaturated polyester resin with additives .

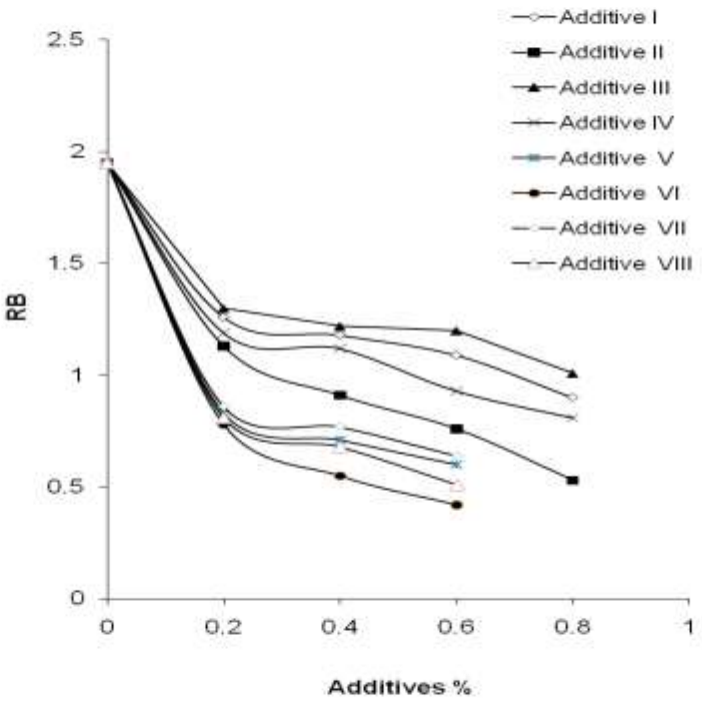

Figure-4 : Rate of burning (R.B.) of epoxy resin with additives .

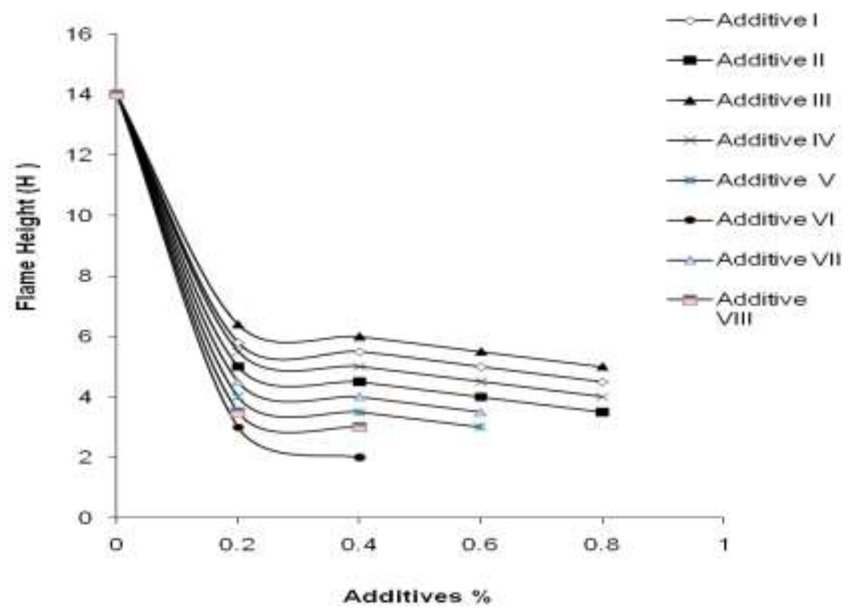

Figure-5 : Flame height (H) of unsaturated polyester resin with additives .

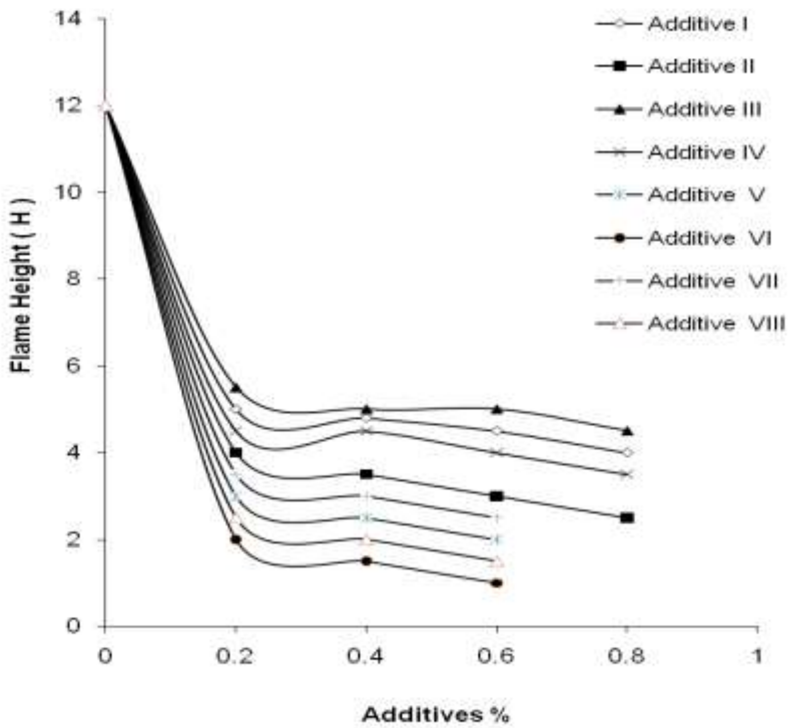

Figure-6 : Flame height (H) of epoxy resin with additives .