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Using of Some Inorganic Additives as Flame Retardants for Some Polymers; a Comparison Study

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Abstract

Five additives were used as flame retardants for epoxy and unsaturated polyester resins which are: Tetraethyl ammonium bromodichloro phenyl phosphonate, $(C_2H_5)_4N[PhPCl_2Br]$ (I), Ammonium phosphate (II), Borax (III), Chlorinated paraffine (IV) and a mixture of additives (I+IV) in the mole ratio (1:1) (V) to study their synergetic effect. The compounds, tetraethyl ammonium bromodichloro phenyl antimonate $(C_2H_5)_4N[PhSbCl_2Br]$ and tetraethyl ammonium chlorodibromo phenylantimonate$(C_2H_5)_4N[PhSbBr_2Cl]$ were used as flame retardantsfor polyethylene (Low density and high density) and polypropylene. These additives were used in different percentages(0-10%) and the samples of polymers were prepared in the dimensions of (3×130×130)mm. Three standard test methods (ASTM) were used to measure the limiting oxygen index (LOI), rate of burning (RB) and maximum height of flame (H). the results showed that all of these additives exhibit sufficient flame retardants and some percentage caused non burning of the polymers under study.

Keyword: Inorganic additives, flame retardants, polymers.

Introduction

In the 2stcentury, the polymer derived products are present every where in our daily life. They have substituted many matrials, composite materials in particular have slowly replaced steel and aluminium alloys in a wide range of applications such as construction, transportation, aerospace, aircrafts, autombiles, appliances and electrical and electronics [1-3]. Their numerous advantages are also associated with serious drawback, they are poorly resistance to the organic solvents and fire due to nature of the polymeric matrix.

Fires cause every year 10-20 deaths per million inhabitants in industrialized countries. The number of injured people is ten time higher [4]. Over time, different strategies have been developed in order to reduce the reaction to fire by these materials, e.g.; using of inherently flame retardant polymers [5], modification of the polymer backbone [6,7] or in corporation flame retardants into polymers. Because inherently flam retardant polymers can lead to high protection costs, the modification of already existing systems is still appreciated by industries.

The fire resistance can be improved by the addition of a flame retardant which, in the gas phase inhibiting the exothermic reaction in the flame via radical scavenging, thenby reducing the energy feedback to the polymer surface. A flame retardant can also promote the formation of a thermal barrier (charing) at the surface of the condensed phase which block the release of gaseous fuel and prevent the transfer of the fire back to the burning polymer [8].

Experimental

I- Materials

a- Polymers
  1- Epoxy resin, type (CY 223), hardner type (HY956) from Ciba Geiga Co.
  2- Unsaturated polyester resin, hardner type (MEKP) from United Arab Emirate (UAE).
  Polyethylene LDPE and HDPE supplied by PC.1, Petrochemical Company, (Basrah-Iraq).
  3- Polypropylene, from UAE.
b- Flame retardants:-
  1- $Et_4N[PhPCl_2Br]$(I)
  2- Ammonium Phosphate (II)
  3- Borax (III)
  4- Chlorinated Paraffin (IV)
  5- $Et_4N[PhPCl_2Br]$+ Chlorinated Paraffin (50:50) (V).
  6- $Et_4N[PhSbCl_2Br]$ with PE and PP.(VI)
  7- $Et_4N[PhSbBr_2Cl]$ (VII)

Additives 1,6 and 7 were prepared according to a reported methods [9].

II-Flame retardancy measurement techniques

Three techniques were employed to measure the efficiency of the flame retardants. These techniques are:-

1. Limiting Oxygen Index (LOI):- was measured according to the Standard method ASTM-D 2863 [10].

LOI% is calculated by the formula:-

$$= \frac{O_2\%}{O_2\% + N_2\%} \times 100\%$$

Where $O_2\%$ & $N_2\%$ are the rate of flow in cm^3/sec.

2. Rate of burning

The rate of burning (RB) in cm/ min .was measured according to the standard methodASTM-635[11].

$$RB = \frac{x}{t}$$

Where x is the length of the sample (in cm) that completely burn in time (t) in minutes.

3. Maximum flame height(H)

This was measured according to the ASTM-D-3014 standard method [12].The maximum flame height was measursed by metal ruler in centimeter, after 10 second from starting the buring process.

III- Preparation of samples

The samples were prepared in the dimensions of (130×130×3) mm, three sheets of each sample were prepared using different percentage of the flame retardants (1-10%) which were mixed with polymers.

Results and Discussion

The additive rout has always been widely used to fire-retard polymers, in particular epoxies, polyesters, polyethylene, polypropylene, polystyrene, polyvinyl chloride (pvc), …..etc., because of their wide range of applications in our life .It is generally a cheap and easy way of achieving sufficient levels of flame retardancy.

For the evaluation of the efficiency of flame retardants, several methods of testing were used. The most important measured parameters were:-

1) Limiting Oxygen Index(LOI) for epoxy and unsaturated polyester resins:

LOI is the percentage of oxygen gas in nitrogen – oxygen gas mixture, necessary to bring about the flame height of 5 cm minimum.

Results of LOI are reported in Tables (1 and 2) which show that all the additives used as flame retardants were efficient to decrease flammability of polymers, some of them were so efficient (in percentage of, 5-10%) to stop combustion causing non burning.

The efficiency of flam retardants is following the order:-

V > I > II > IV > III

2) Rate of burning (RB) for epoxy and unsaturated polyester resins:

The results of rate of burning (RB) measured for the polymers under examination clearly indicate the effectiveness of the flame retardants used in this work, the results reported in Tables (5 and 6) show that the rate of burning is effectively decreased as the weight % of the additives increased and the efficiency in flame retardancy, for all polymers at fixed weight ratio follows the order:-

V > I > II > IV > III

3) Maximum flame height (H) for epoxy and unsaturated polyester resins:

The flame heights during the polymers burning were also monitored using different weight ratio of the additives. The results listed in Tables (3 and 4) show that (H) is gradually decreased as the % additive increased for all the polymers with all types of additives. Again the effectiveness of these additives are in agreement with the results obtained in case of LOI and RB mentioned earlier; the most active FR is that gives the lowest (H). The order of effectiveness is :-

V > I > II > IV > III

These results and others discussed before indicate that these additives can effectively reduce the flammable gases produced in the flame region during flammability of the polymers. These additives can also interfere with the chain reaction usually occurs in the vapor phase during the oxidation process; i.e. can terminate the free radicals

$(OH^{\cdot}, O^{\cdot}, OOH^{\cdot}, OR^{\cdot}, \ldots\ldots etc)$ as a chain carrier and transfer them to non radical species.

4) Limiting Oxygen Index (LOI) for PE and PP polymers was measured according to ASTM-D: 2863. The results are listed in Tables (7, 8 and 9) which show that the additives are active to retard the flammability of these polymers. The Et_4N [$PhSbBr_2Cl$] additive was more active than Et_4N[$PhSbCl_2Br$], this is because of their composition where the first one containing more than bromine than the second because the bromine compounds are more active than chlorine compounds as flam retardants[13].

5) Maximum height of flame (H) for PE and PP.

The results are reported in Table (7,8 and 9). Also these results indicated that Et_4N [$PhSbBr_2Cl$] is more active than Et_4N[$PhSbCl_2Br$], due to bromine content.

6) Rate of burning (RB) for LDPE

The results showed that Et_4N [$PhSbBr_2Cl$] is more active than Et_4N[$PhSbCl_2Br$] for the same reason discussed before .The results are reported in Table (10).

Table (1)
LOI for epoxy resins with additives.

% *Additives*	*1*	*3*	*5*	*7*	*10*
I.	22.35	23.44	24.51	25.68	27.25
II.	21.74	22.81	23.85	24.65	26.10
III.	20.66	21.48	22.13	22.91	24.00
IV.	20.95	22.00	22.86	23.93	25.00
V.	23.67	24.86	25.97	26.84	28.51

LOI for epoxy without additive = 19.7.

Table (2)
LOI for UPE with additives.

% *Additives*	*1*	*3*	*5*	*7*	*10*
I.	23.00	24.03	25.00	25.92	27.41
II.	22.54	23.62	24.30	25.41	25.90
III.	21.36	22.28	22.93	23.71	24.80
IV.	21.80	22.54	23.57	24.00	25.21
V.	24.18	25.24	26.53	27.50	28.91

LOI for UPE without additive = 20.4.

Table (3)
Maximum flame height (H) for UPR.

Additives / *%*	*I*	*II*	*III*	*IV*	*V*
Non	14.0	14.0	14.0	14.0	14.0
1	10.0	11.0	13.5	12.5	9.0
3	8.0	8.5	12.5	12.0	6.5
5	6.5	8.0	11.0	10.5	N.B
7	N.B	6.5	9.5	9.5	N.B
10	N.B	5.0	8.0	7.0	N.B

Table (4)
Maximum flame height (H) for Epoxy resin.

Additives / *%*	*I*	*II*	*III*	*IV*	*V*
Non	12.0	12.0	12.0	12.0	12.0
1	9.5	10.0	11.5	11.0	8.0
3	7.5	8.0	10.0	9.5	6.5
5	6.0	6.5	8.5	8.0	3.5
7	4.0	5.5	8.0	7.5	N.B
10	N.B	4.0	7.0	6.0	N.B

Table (5)
R B for epoxy resin with additives.

Additives / *%*	*I*	*II*	*III*	*V*	*IV*
1	1.29	1.35	1.86	1.71	0.79
3	0.66	0.75	1.63	1.51	0.41
5	0.60	0.64	1.44	1.22	0.24
7	0.49	0.51	1.34	1.04	N.B
10	N.B	0.32	1.07	0.86	N.B

R.B for epoxy without additives = 1.95.

Table (6)
R B for UPE with additives.

Additives / *%*	*I*	*II*	*III*	*IV*	*V*
1	1.02	1.10	1.4	1.30	0.53
3	0.62	0.70	1.27	1.17	0.28
5	0.46	0.52	1.15	1.0	N.B
7	N.B	0.42	1.0	0.83	N.B
10	N.B	0.23	0.87	0.71	N.B

R.B for UPE without additives = 1.44.

Table (7)
LOI and maximum flame height for LDPE with additives (I) and (II).

Test / *%*	*LOI (I)*	*H(I)*	*LOI(II)*	*H(II)*
1	19.5	10	20.66	9.5
3	21.42	9	22.71	8.0
5	22.31	7.5	23.37	6.5
7.5	22.75	6.5	23.78	5.5
10	22.97	6	24.35	5.0

LOI for LDPE without additives = 18.8.

Table (8)
LOI and maximum flame height for HDPE with additives (I) and (II).

Test / *%*	*LOI (I)*	*H(I)*	*LOI(II)*	*H(II)*
1	18.91	11	19.64	10
3	20.44	10	21.70	7.5
5	21.61	9	22.55	6.5
7.5	22.70	7.5	23.73	5.0
10	23.40	5.5	24.36	4.0

LOI for HDPE without additives = 17.13.

Table (9)
LOI and maximum flame height for polypropylene (PP).

Test / %	LOI (I)	H(I)	LOI(II)	H(II)
1	20.70	11.5	21.07	10.5
3	21.25	8.25	21.81	7.5
5	21.91	7.5	22.73	6.5
7.5	23.48	6.5	24.65	5.5
10	26.00	6	26.76	5.0

LOI for PP without additives, H = 13.5.

Table (10)
Rate of Burning (R.B) for LDPE.

% / Additives	Non.	1	3	5	7.5	10
$Et_4N[PhSbCl_2Br]$	1.09	0.91	0.80	0.71	0.59	0.56
$Et_4N[PhSbBr_2Cl]$	1.09	0.83	0.73	0.61	0.52	0.43

The results discussed before are also shown in the Figs.(1-6) which confirm the behavior of the flame retardants according to their compositions and their percentages.

A flame retardant can also promote the formation of a thermal barrier (charring) at the surface of the condensed phase which blocks the release of gaseous fuel and prevents the transfer of heat back to the burning polymer. An increased char yield results in a reduced amount of a combustible gases reaching the flame which in turn leads to extinction. Flame retardants acting via the latter mechanism are known as a condensed phase active because they catalyse the formation of char [14].

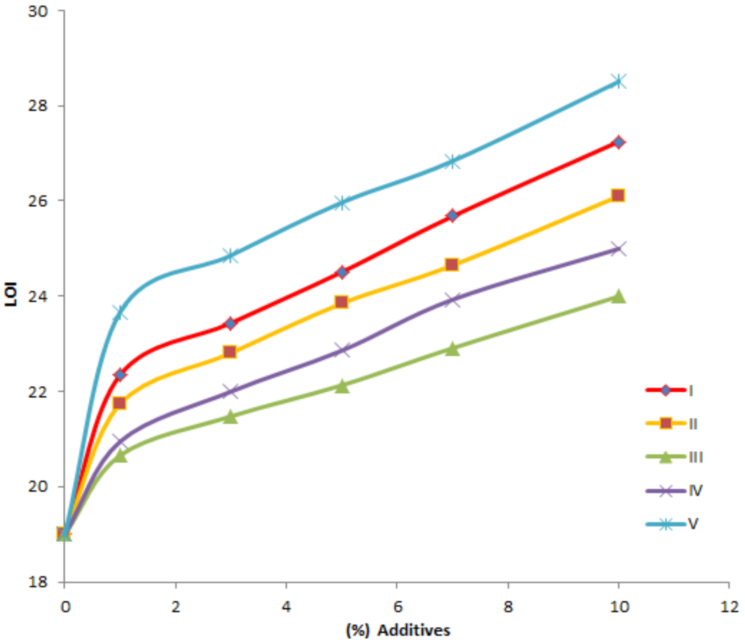

Fig. (1) LOI of epoxy resin with additives.

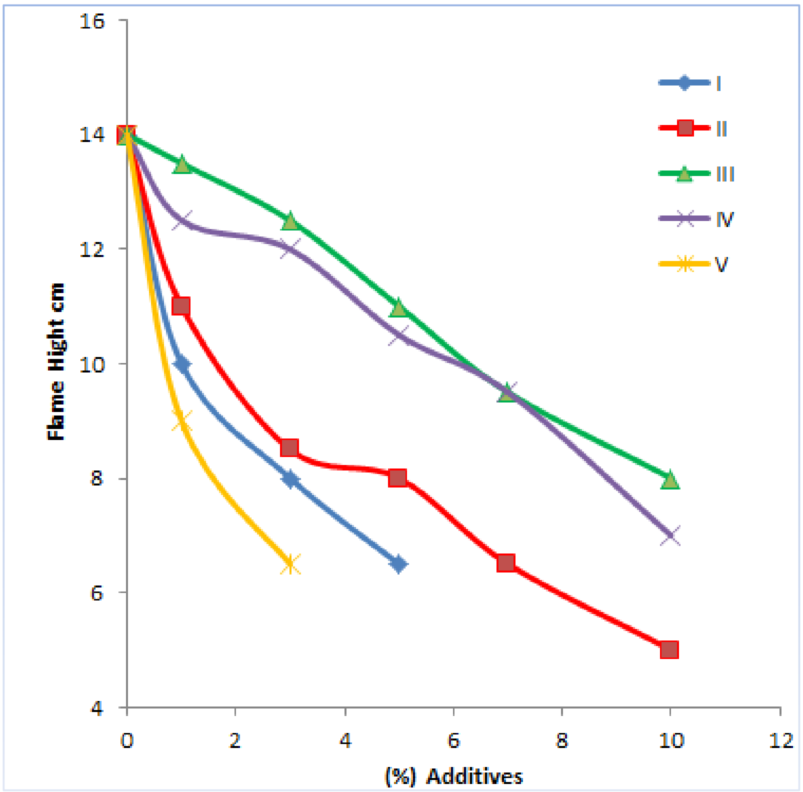

Fig. (2) Maximum flame height (H) of epoxy resin.

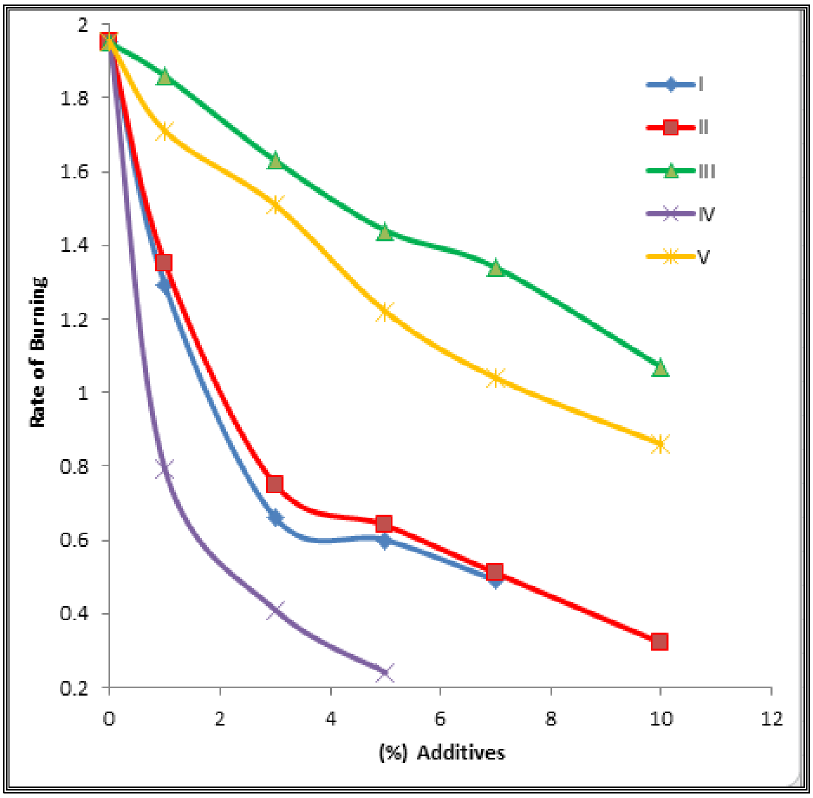

Fig. (3) Rate of burining for epoxy resin with additives.

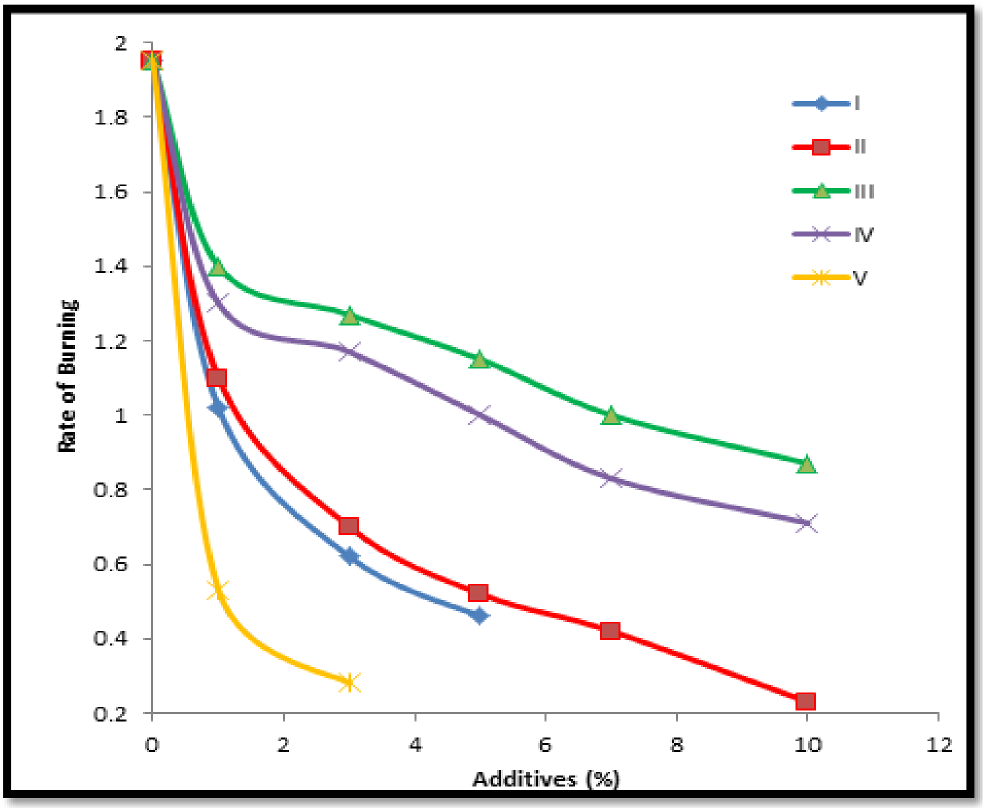

Fig. (4) Rate of burining for UPE with additives.

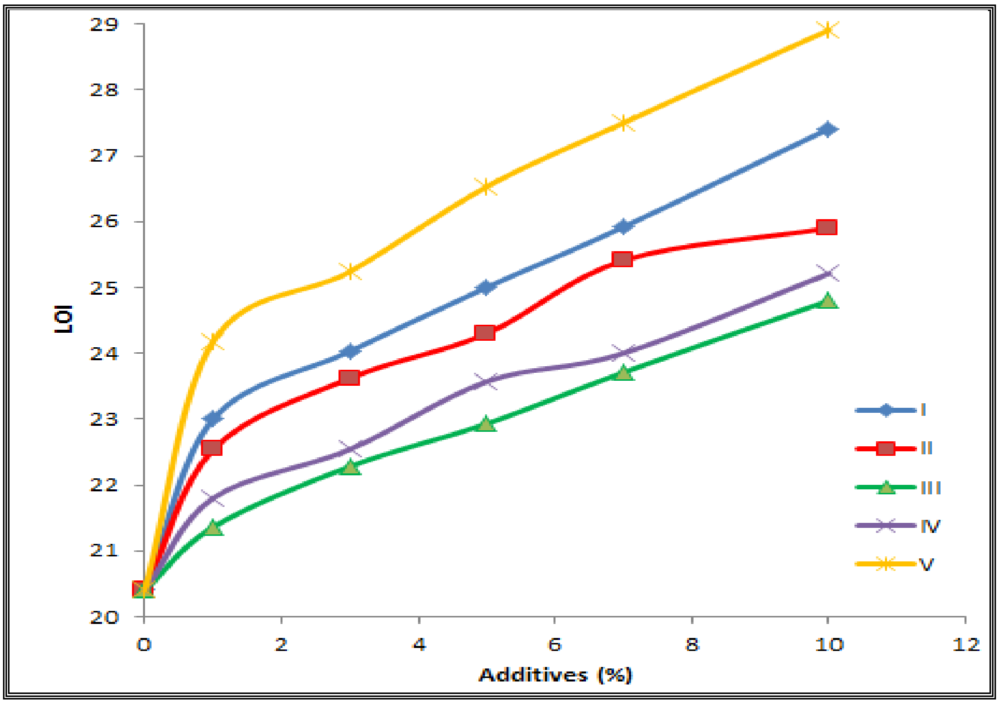

Fig. (5) LOI for UPE with additives.

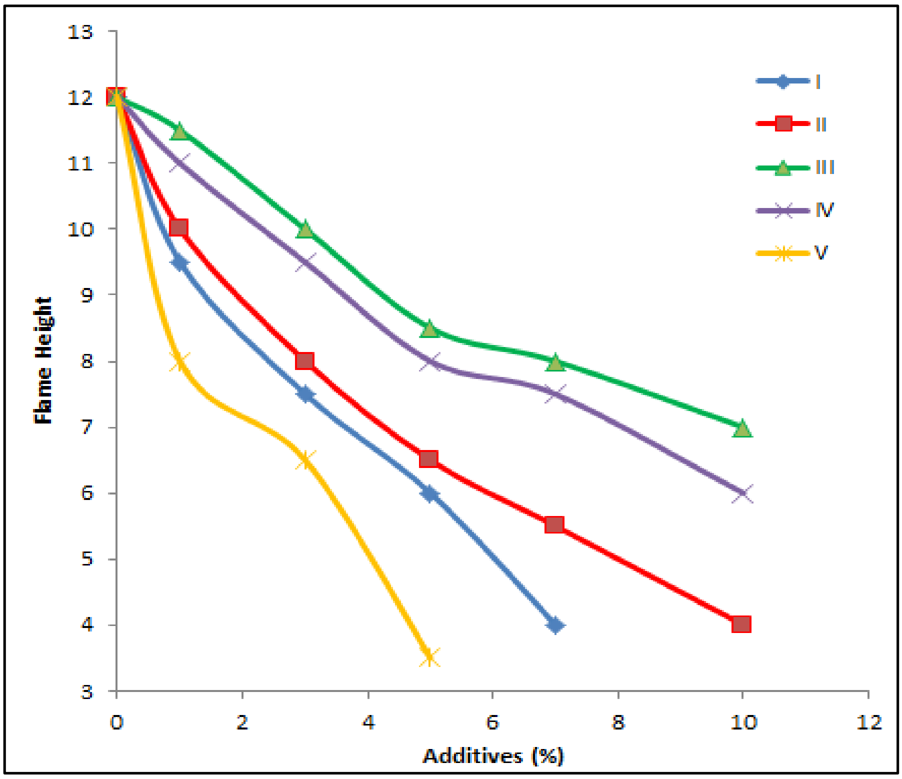

Fig. (6) Flameheight for UPE.

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الخلاصة

استخدمت خمسة مضافات لتثبيط لهوبية راتنجي الايبوكسي والبولي استر غير المشبع وهي : رباعي اثيل امونيوم برومو ثنائي كلورو فنيل فوسفونيت $(C_2H_5)_4N\ [PhPCl_2Br]$ (I) فوسفات الامونيوم (II)، البوراكس (III)، البارافين المكلور (IV) ومزيج من المضافين (IV+I) بنسبة مولية (V)(1:1) لدراسة فعلهما التازري. استخدم المركبان رباعي اثيل امونيوم برومو ثنائي كلوروفنيل انتيمونيت $(C_2H_5)_4N\ [PhSbCl_2Br]$ ورباعي اثيل امونيوم كلورو ثنائي بروموفنيل انتمونيت $(C_2H_5)_4N[PhSbBr_2Cl]$ لتثبيط لهوبية البولي اثلين (واطئ الكثافة وعالي الكثافة) والبولي بروبلين. استخدمت هذه المضافات بنسب وزنية مختلفة (٠−١٠ %) وزناً وتم تحضير النماذج البوليمرية بابعاد (٣* ١٣٠ * ١٣٠) ملم. استخدمت ثلاث طرائق قياسية للفحص (ASTM) لقياس معامل الاوكسجين المحدد (LOI)، معدل الاحتراق (RB) واقصى ارتفاع للهب (H) بينت النتائج بان جميع هذه المضافات اظهرت كفاءة في تثبيط اللهوبية وقسم من النسب تسببت في عدم اشتعال البوليمرات قيد الدراسة.