Study the Synergetic Activity of Aluminium Tri Hydroxide with Zinc Oxide as Flame Retardants for Unsaturated Polyester Resin

دراسة الفعل التازري لهيدروكسيد الالمنيوم مع اوكسيد الخارصين كمثبطات للهوبية البولي استر غير المشبع

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Abstract:-

In this work, aluminum tri hydroxide (I), zinc oxide (II) and their mixture (1:1) (III) were used as flame retardants for unsaturated polyester resin in the weight ratios of (0, 2, 4, 7, 10, and 12) %, by preparing films of (130*130*3) mm in dimensions.

Three standard test methods used to measure the flame retardation which are: ASTM: D-2863 to measure the limiting oxygen index (LOI), ASTM: D-635 to measure the rate of burning (R.B) & ASTM: D-3014 to measure the maximum height of flame (H). Results obtained from these tests indicated that; ATH, ZnO and their mixture have a good effect as flame retardants for unaturated polyester resin. The synergetic effect was the best.

Key word: Unsaturated Polyester Resin; Flame Retardants; Combustion retardation.

الخلاصة :

في هذا البحث تم استخدام هيدروكسيد الالمنيوم (مضاف I), اوكسيد الخارصين(مضاف II) ومزيجهما بنسبة (1:1) مضاف (III) كمثبطات للهوبية البولي استر غير المشبع. بنسب مئوية وزنية (0, 2, 4, 7, 10و 12) % بواسطة تحضير شرائح بابعاد (130*130*3) ملم.

استخدمت ثلاث طرق قياسية لاختبار تثبيط اللهوبية وهي: الطريقة القياسية (ASTM: D-2863 LOI) لقياس معامل الاوكسجين المحدد, الطريقة القياسية ASTM: D-635 لقياس سرعة الاحتراقوالطريقة القياسية ASTM: D-3014 لقياس اقصى ارتفاع يصل اليه اللهب (H)

اظهرت النتائج المستحصل عليها ان المضافات المستعملة في هذه الدراسة تمتلك تاثير جيدا كمثبطات لهب للبولي استر غير المشبع. وان افضلها كانت عندما كان التاثيرتازريا.

Introduction:-

The polymer a giant molecule, built up by the linking together of large numbers of much smaller moleculesby chemical bonds. The small molecules that combine with each other to form polymer molecules are termed monomers and the reaction by which they combine are termed polymerization.[1-3], Where monomers (structural units) react together chemically to form linear, branched chains or three dimensional polymer networks. In the cross linked polymers, the chains are joined chemically at fastening points. The degree of cross-linking has effect on the physical and chemical properties of polymer. [4, 5]

The utilization of polymeric materials continues to increase each year, because of their unique physical properties, have rapidly replaced more traditional materials such as steel and nonferrous metals, as well as natural polymeric materials such as wood, cotton, and natural rubber.[6]These materials tend to be the most flammable because of, most of them are petroleum-based in which characterized by the presence of organic molecules made up mainly of carbon and hydrogen **[7]**. In the UK alone some 800–900 deaths and roughly 15000 injuries result from fire each year. Most of the deaths are caused by inhalation of smoke and toxic combustion gases, carbon monoxide being the most common cause, while the injuries result from exposure to the heat evolved from fires. [8] Of major interest in the plastics and textiles industries is not the fact that their products burn but how to render them less likely to ignite and, if they are ignited, to burn much less efficiently.The phenomenon is termed "flame retardance". Ideal flame retarant additive must meet following requirements: thermally stable at the processing temperature of the polymer, do not emit or at least emit low levels of toxic gases. Do not have harmful physiological and environmental effects, not alter the mechanical properties of the polymer, reduce flammability to the required polymer and be commercially available in low cost [9- 12] .

A flame retardant is designed to inhibit or prevent the material from igniting, to reduce flame spread rate, and prevent sustained burning. Flame retardant tend to retard the spread of flames by increasing the given polymer's resistance to ignition either act physical or/and chemical mechanisms. Physically by cooling, formation of a protective layer or fuel dilution, chemically reacting in the condensed or gas phase. [13, 14].

This resin is used in many important applications such as marine applications, automotive, and construction industries. Many inorganic compounds are used as fire retardants for UPR, which shows high efficiency in flame – retardancy [15- 17] . So that, in this work the influence of other additives as flame resistance on unsaturated polyester resin was studied.

Experimental Part:

1. Materials

A. Polymer:
Unsaturated polyester resin, hardener type (MEKP), imported from Byer company, Germany

B. Flame retardant: aluminum trihydroxidesupplied from M. Merck, Darmstadt with purity 99.5% (additive I); zinc oxide supplied from Barcelona, Espana with purity 99.9% (additive II); a combination of ATH with zinc oxide (1:1) (additive III)

2. Tests

1. The measurement of limiting oxygen index (LOI) ASTM: D-2863: It is widely using for measuring flammability of polymers. [19]
2. The measurement of rate of burning (R.B) ASTM: D- 635 average extent of burning (A.E.B) and average time of burning (A.T.B) for self-supporting plastic in a horizontal position. [20, 21]
3. The measurement of maximum flame height (H) ASTM: D-3014. [22]

3. Preparation of samples

The specimens were prepared in the dimensions of (130*130*3) mm; the sheets of unsaturated polyester resin were prepared for each percentage weight (2, 4, 7, 10, and 12) % of flame retardant materials. These sheets cut as samples according to the three ASTM test methods.

Results and Discussion:

1. Measurement of Limiting Oxygen Index (LOI) according to the ASTM: D-2863:

The limiting oxygen index (LOI) for unsaturated polyester resin without additive is (20.2), Results obtained are listed in Table-1. The oxygen concentration required to support a candle like of unsaturated polyester resin samples was increased with increasing the weight percentage of additives as shown in figure-1, and represented in Figure-1.

Table (1): Results of limited oxygen indexaccording to ASTM: D-2863 for the UPR with different percentages of additives.

Type of additive / Additives%	I	II	III
2	21.82	20.90	21.98
4	22.14	21.31	22.43
7	22.60	21.84	22.81
10	23.04	22.29	23.19
12	23.46	22.66	23.66

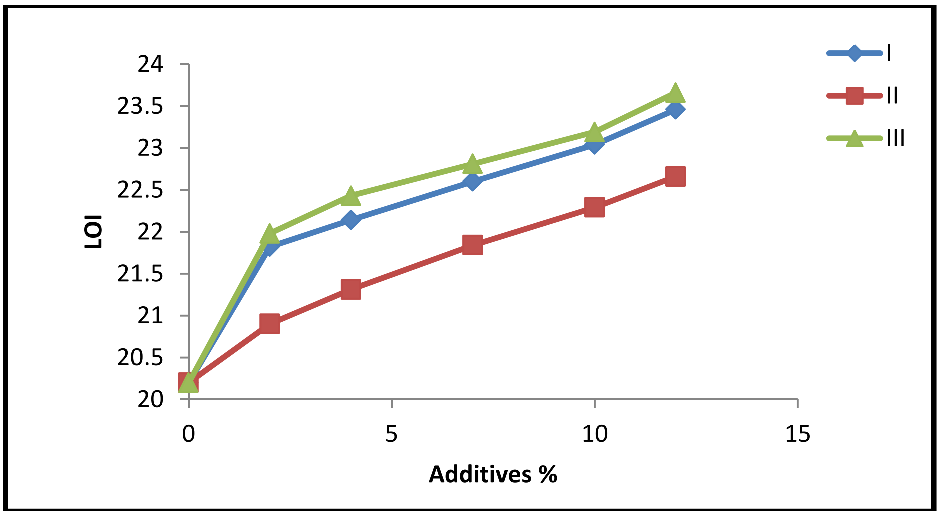

Figure-1: (LOI) of UPR with additives

2. Measurement of Rate of Burning (R.B), According to ASTM: D- 635:

The results obtained from these tests showed that, the rate of burning of the unsaturated polyester resin with the additives has a continuous reduction with increasing the percentage weight of additives, as in Tables-2, 3, and 4. Figure-2, showed the flame speed curves of flame retardation for resin.

This results indicated that, the additives (I and III) have high efficiency on self-extinguishing of the resin, especially in percentages of (10 & 12%).

Table-1: Rate of Burning (R.B), Average Extent of Burning (AEB), and Average Time of Burning (ATB) for UPR with additives According to ASTM: D-653

% Test	Non	2	4	7	10	12	Additives
AEB (cm)	10	10	10	10	3.33	2.54	I
	10	10	10	10	10	10	II
	10	10	10	10	3.1	2.75	III
ATB (min)	6.89	7.51	8.92	11.23	4.26	4.53	I
	6.89	7.09	7.24	7.75	8.33	9.09	II
	6.89	7.46	8.47	10	5.18	4.58	III
R.B (cm/min)	1.45	1.34	1.18	1	0.83	0.59	I
	1.45	1.41	1.38	1.29	1.20	1.1	II
	1.45	1.33	1.12	0.89	0.59	0.48	III
S.E	-	-	-	-	yes	yes	I
	-	-	-	-	-	-	II
	-	-	-	-	yes	yes	III

Note:

A.E.B: Average Extent of Burning.
A.T.B: Average Time of Burning.
S.E:Self-Extinguishing.

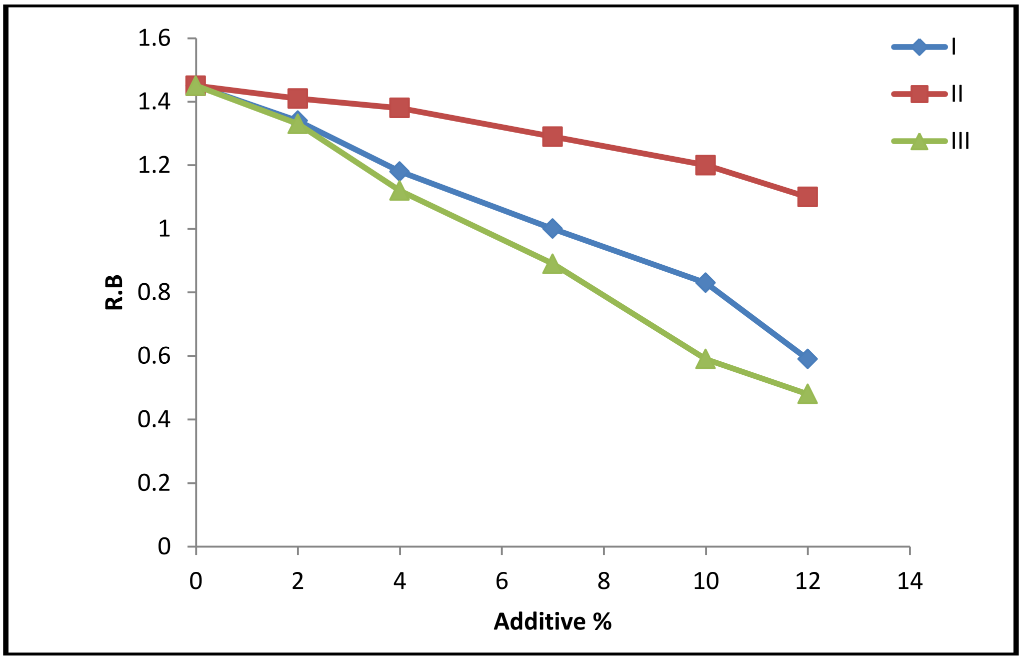

Figure-2: Rate of Burning (R.B) of UPR with Additives

3. Measurement of maximum flame height(H), according to the ASTM: D-3014:

Figure-3 showed that, the maximum flame height (H) was decreased with increasing the percentage of additives (inversely proportional), the effectiveness and retardancy were increased with increasing the percentage of the additives which led to the reduction in the flame height and persist the continuation in the ignitionas listed in Tables-

Also, the amount of residue from the combustion of UPR with additives in all percentages is higher than those of remaining materials without additives, the reason is that the additives are thermally degradable and fly to the flame zone to prevent the continuation of combustion.

Table-2: The Maximum Flame Height (H) according to ASTM: D-3014 for UPR with additives

% Test	Non	2	4	7	10	12	Additives
W_1	5.52	5.89	6.11	6.20	6.32	6.39	I
	5.52	6.12	6.28	6.31	6.39	6.44	II
	5.52	6.26	6.38	6.43	6.56	6.67	III
W_2	2.43	2.31	2.35	2.31	2.365	2.48	I
	2.43	2.40	2.56	2.45	2.52	2.43	II
	2.43	2.40	2.54	2.32	2.44	2.40	III
PWR	55.97	60.78	61.53	62.74	62.57	61.18	I
	55.97	60.78	59.23	61.17	60.56	62.26	II
	55.97	61.66	60.18	63.91	62.80	64.01	III
H	15.0	13.5	12.0	9.5	8	7	I
	15.0	15.0	14.5	13.5	11.5	11	II
	15.0	13.0	11.5	8.5	7	6	III

Note:
W_1: Weight of sample before burning (gm).
W_2: Weight the loss from sample after burning (gm).
H: Maximum Flame Height (cm).
PWR: The Percentage of Weight (%).

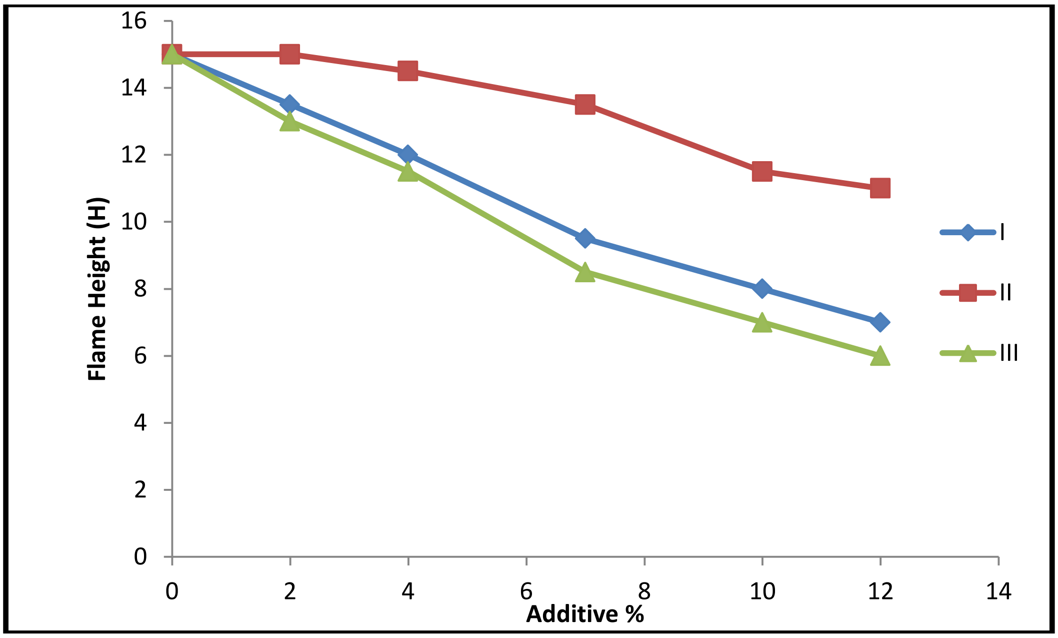

Figure-3: Flame Height (H) of UPR with additives

The results obtained showed that, additives I, II, and III have a good efficiency to retard combustion mode of action for these additives basically depend on structure of these additives; the retardation of additive (I) depends on its endothermic decomposition which takes place in the temperature range of 180-200°C, it has the ability to absorb heat and promoting a cooling effect of the host polymer by releasing at least (34.5%) of its crystallization water, which hinder the combustion process by diluting the concentration of flammable evolving gases and restricting the access of oxygen through the composite surface. Also the formation of Al_2O_3 as a protective char layer formed on the surface of the substrate, which limits both heat transfer and the diffusion of fuel and oxygen [23- 26] .

$$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$$

In the case of additive (II) a little effect on impart flammability for UPR was demonstrated, but this additive in combination with ATH enhanced flame retardancy of UPR, as it is clear in results of additive (III), which reflect the synergetic effect of them.

The increase in limiting oxygen index (LOI) values and decrease in rate of burning (R.B) and maximum flame height (H) of UPR with increasing the percentage weight for the used additives indicated the reduction of the flammability of UPR. These additives form an inert atmosphere which reduces and inhibits the oxygen from reaching to flame zone that required for maintaining the ignition.The efficiency behavior of the additives in increasing limiting oxygen index, decreasing rate of burning, and maximum flame height is follows the order:

III > I > II

Also these additives have the ability on inhibition of thermal decomposition that occur in flame front, due to the formation of non-flammable gases such as CO_2, H_2O…etc.

Conclusions:

The main conclusions of this work can be summarized as follows:

1- The flame-retardancy efficiency of the additives I, II, and III appeared to follow the order:

III > I > II

2- The synergistic effect of ATH with Zinc Oxide gave the best results in blocking the flammability of UPR comparing with the other additives.

3- Self-extinguishing (S.E) occurred at the percentages (10 & 12%) of the additives (III & I).
4- The (LOI) increased with increasing the weight percentages of the additives.
6- The rate of burning (R.B) and the flame height (H), decreased with increasing the weight percentages of the additives.

References:

1. Ch. E. Carraher, " Introduction to Polymer Chemistry ", Taylor & Francis Grp., (2007).
2. S. A. Felemban, " M. Sc. Thesis ", University of Umm Al- Qura, College of Applied Sciences, (2009).
3. A. B. Strong, " Plastics Materials & Processing ", 2nd edition, Prentice-Hall, (2000).
4. D. W. Van Kervelen& P. J. Hoftyzer; Properties of Polymers Correlation with Chemical Structure ; by Elservies Publishing Company, Amsterdam, 15, 1972.
5. D. J. William: Polymer Science and Engineering; Prentaice-Hall Inc., NewYork, 29, 1971.
6.T. Kashiwagi, A. Inaba, J. E. Brown, K. Hatada, T. Kitayama, & E. Masuda, "Macromolecules ", 19, 2160-2168, (1986).
7.M. Alaee, P. Arias, A. Sojdin, and A. Bergmam, " Environment Inter. ", Elsevier, 29, 683-689, (2003).
8. A. R. Horrocks and D. Price," *Fire retardant Materials*", 2nd *ed*., CRC Press LLC, Cambridge England,(2001).
9.S.Posner,L.Börås," *Survey and Technical Assessment of Alternatives to Decabromodiphenyl Ether (decaBDE) in plastics"*. Report, The Swedish Chemicals Inspectorate, Stockholm,June (2005).
10. M., L., Bras, Ch., A., Wilkie, S., Bourbigot, S., Duquesne,& Ch., Jama, " Fire Retardancy of Polymers: New Applications of Mineral Fillers ", Royal Society of Chemistry, UK,P. 432, (2007).
11. T.M. Aminabhavi& P. E. Cassidy, " Polym. Plast. Technol. Engg. ", 28. 717-751, (1989).
12. H. F. Mark & N. M. Bkales, " Encyclopedia of Polymer Science & Engineering ", Vol. 7, 154-204, Jhon Wiley & Sons Inc., New York, (1987).
13.E. Gallo, " Ph. D. Thesis ", University of Napoli Federico II, College of Industerial Engineering, (2009).
14.B. J. Sutker, "Flame Retardant " in Ullman's Encyclopedia of Industerial Chemistry , Vol. A11, P.123-140, 5th edition, VCH Verslag, Weinheim, (1988).
15.Hapuarachchi, T. D &Peijs, T., "Express Polm. Letters", 3(11): 743-751, (2009).
16.H.-T.. Chiu, S.-H. Chiu, R.- E. Geng, and J.-S, Chung, " Polym. Degrad. And Stabilit ", 70, 504-514, (2000).
17.E. Kicko-Walczak, " Fire and Mater ", 22, 253-255, (1998).
18. 12. G. Gamino, L. Costa & E. Casovati, " J. Appl. Polym. Sci. ", 35, 1863, (1988).
20. Annual Book of ASTM Standards, Vol. 08, 01, (1986).
21. Annual Book of ASTM Standards, Part-35, (1981).
22. Annual Book of ASTM Standards, Part-35, (1976).
23. T. D. Hapuarachchi, " *Ph. D. Thesis* ", University of Queen Mary, College of Engineering & Materials Science, London, (2010).
24.R. N. Rothon, " *Particulate-Filled Polymer Composites* ", 2nd edition, Repra Technology Limited, (2003).
25. E. A. Woycheshin, I. Sobolev, " J. Fire. Retardant. Chem. ", 2, 224, (1975).
26.T. R. Hull & B. K. Kandola, " Fire Retardancy of Polymers: New Strategies Mechanisms ", Royal Society of Chemistry, (2009).