Study of the Activity of Some Metal Oxides and Salts as Flame Retardants for Unsaturated Polyester Resin

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Abstract

In this work, calcium carbonate (I), ammonium dihydrogen ortho phosphate (II) and magnesium oxide (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, $CaCO_3$, $H_2NH_4PO_4$ and MgO have a good effect as flame retardants for unsaturated polyester resin. Ammonium dihydrogen ortho phosphate was the best.

Key words: Unsaturated Polyester Resin, Flame Retardants, Combustion retardation.

Introduction

The polymer is a giant molecule, built up by linking together large number of much smaller molecules by chemical bonds. These molecules are termed monomers and the reaction by which they combine is termed polymerization. [1,2,3]. Once these monomers react together chemically to a linear, branched chains or three dimensional polymer network are formed. In the cross linked polymers, the chains are joined chemically at fastening points. The degree of cross-linking has significant effect on the physical and chemical properties of polymer [4,5].

The utilization of polymeric materials continue to grow up each year, because of their unique physical properties and have rapidly replaced more traditional materials such as steel and nonferrous metals, as well as wood, cotton and natural rubber, [6]. These polymers tend to be the most flammable materials because of most of them are petroleum –based source [7]. In UK alone some 800-900 deaths and roughly 15000 injuries results 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 retardant additive must meet the 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 environment effects, not alter the mechanical properties of the polymer, reduce flammability to the required polymer and be commercially available in low cost [9,10, 11, 12].

A flame retardant is designed to inhibit or prevent the material from igniting to reduce flame spread rate, and prevent sustained burning by physical or /and chemical mechanism. Physically by cooling, formation of a protective layer or fuel dilution, chemically reacting in the condensed or gas phase [13,14].

However polyester resin is used in many important application such as marine applications, automotive and construction industries. Many inorganic compounds are used as fire retardants for UPR, which show high efficiency in flame-retardancy, [15,16,17]. So that, in this work the influence of other additives as flame resistance on unsaturated polyester resin was studied.

Experimental parts:

1- Materials

Unsaturated polyester resin, hardener type (MEKP). Imported from Byer company, Germany

Flame retardant: calcium carbonate supplied from Hopkins and Williams, with purity 98.5% (additive I); ammonium dihdrogen ortho phosphate (Merck) with purity 99% (additive II): oxide (additive III) commercial type.

2-Tests

The measurement of limiting oxygen index (LOI) ASTM:D-2863:it is widely used for measuring flammability of polymers [19]. 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]. 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

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), while the obtained results with additives are listed in Table-1. The oxygen concentration required to support a candle like of unsaturated polyester resin sample was increased with increasing the weight percentage of

additives shown in Table -1, and represented in Figure-1.

Table (1): Results of limiting Oxygen Index (LOI) according to the ASTM: D-2863 for the UPR with different percentages of additives

Type of additive / Additives%	I	II	II
2	21.42	22.35	21.32
4	21.85	22.74	21.70
7	22.23	23.16	22.09
10	22.71	23.63	22.55
12	23.41	24.07	23.02

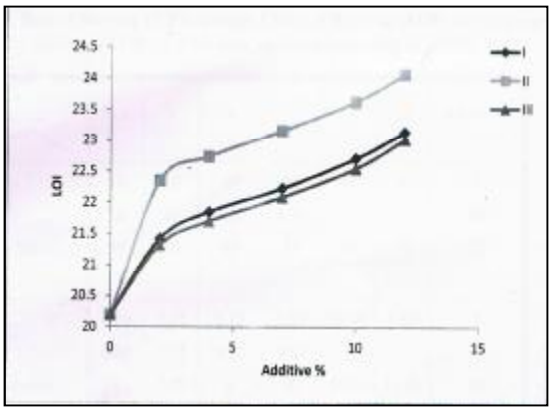

Figure-1 (L0l) of UPR with additives

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

The obtained results from these tests indicated that the rate of burning of the unsaturated polyester resin with additives decrease with increasing the weight percentage of additives, as listed in Table-2. Figure-2 showed the flame speed curve of flame retardation for resin with increasing the additives. These results indicate that, the additive (II) has high efficiency on self-extinguishing of the resin.

Table-2: Rate of Burning (R.B), Average Extent of Burning (AEB), and Average Time of Burning (ATB) for UPR with additives According to ASTM:D-635

% / Test	Non	2	4	7	10	12	additives
AEB(cm)	10	10	10	10	10	6	I
	10	10	9.20	4.35	-	-	II
	10	10	10	10	10	10	III
ATB(min)	6.89	7.35	8.13	9.52	10.98	7.59	I
	6.89	7.75	9.23	5.87	-	-	II
	6.89	7.29	8	9	10.30	11.36	III
R.B(cm/min)	1.45	1.36	1.23	1.05	0.91	0.79	I
	1.45	1.29	0.99	0.74	-	-	II
	1.45	1.37	1.25	1.08	0.97	0.88	III
S.E	-	-	-	-	-	yes	I
	-	-	yes	yes	yes	yes	II
	-	-	-	-	-	-	III
N.B	-	-	-	-	-	-	I
	-	-	-	-	yes	yes	II
	-	-	-	-	-	-	III

Note:
A.E.B: Average Extent of burning.
A.T.B: Average Time of Burning.
S.E: Self-Extinguishing.
N.B: Not-Burning.

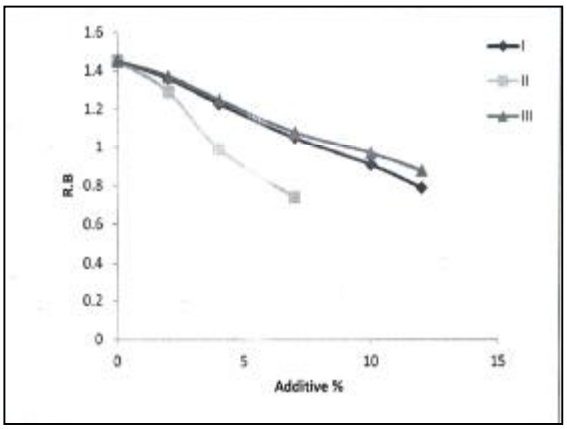

Figure-2: Rate of Burning (R.B) of UPR with additives

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

Maximum flame height was measured according to the ASTM D-3014 and the results are listed in Table-3 and Figure-3. These result show 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 ignition as listed in Table-2.

Also, the amount of residue from the combustion of unsaturated polyester resin (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-3: 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	6.10	6.22	6.29	6.53	6.48	I
	5.52	6.15	6.18	6.25	6.52	6.76	II
	5.52	6.30	6.44	6.59	6.70	6.74	III
W_2	2.43	2.46	2.34	2.41	2.36	2.54	I
	2.43	2.36	2.43	2.50	-	-	II
	2.43	2.46	2.60	2.45	2.55	2.38	III
PWR	55.97	59.67	62.37	61.68	62.83	60.80	I
	55.97	61.62	60.67	60.00	-	-	II
	55.97	56.80	59.62	62.82	61.94	64.68	III
H	15.0	14.5	13.0	11.5	9	8	I
	15.0	12	10	7.5	-	-	II
	15.0	14.5	13.5	12	10	9	III

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

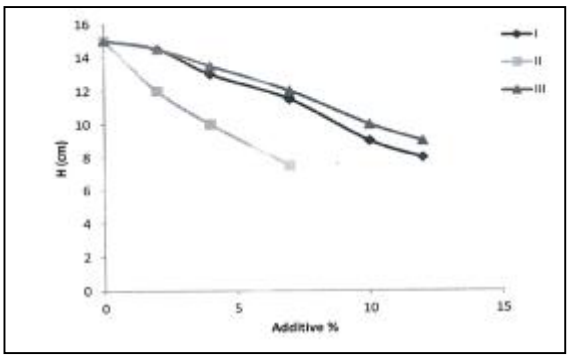

Figure-3: Flame Height (H) of UPR with additives

The obtained results showed that, additives I, II, and III have a good efficiency to retard combustion. The mode of action for these additives basically depend on structure of these additives, the retardation of additive (I) [23, 24, 25, 26] depends on its endothermic decomposition which occurs up to 600 C° due to its higher thermal stability and coverts to CaO as a protective layer offers protection to the underlying substrate from further decomposition. Also, liberating CO_2 a nonflammable gas cools substrate of polymer and reduce the amount of flammable volatile materials.

$$CaCO_3 \longrightarrow CaO + CO_2$$

In the case of additive (II), the additive can be volatilize into the gas depending on its structure. It contains (P, H and N) elements that have a high effect to retard combustion. The free radicals formed ($P^{\cdot}$, $H^{\cdot}$, and $N^{\cdot}$) will react rapidly with free radicals of the flame chain, and act as scavengers of ($H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$…etc) to form inert compounds like (HPO, NH_4OH…etc) which subsequently work on inhabitation in the flame front. Moreover, this

additive has the ability to decrease amount of generation heat by forming a group of non-flammable gases, such as CO_2, H_2O, NH_3 …etc, thus decreases the volatile materials flammable. These inert gases dilute the fuel the both condensed and gaseous phases.

While additive (III) has the ability to enhance the flame retardancy of UPR[27] by promoting the formation of char, which together with any carbonaceous char produced, provided an effective thermal barrier, reducing heat transmission to the underlying substrate.

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 weight percentage for the used additives indicated the reduction of the flammability of UPR. These additives from 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 follows the order:

II > I > III

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

Conclusions

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

The additive (II) gave the best results in blocking the flammability of UPR comparing with other additives. Self-extinguishing (S.E) occurred at the percentage (12%) of the additive (I), and at the percentage (4&7%) of the additive (II). Non-burning (N.B) occurred at the percentage (10 &12%) of the additive(II). The (LOI) increased with increasing the weight percentages of the additives The rate of burning (R,B) and the flame height (H), decreased with increasing the weight percentages of the additives.

Reference

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., New York, 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 Alternative 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, John 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 Industrial Chemistry, Vol. All, P. 123-140. 5th edition, VCH Verslag, Weinheim, (1988).
15. T. D. Hapuarachchi & 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. G. Camino, L. Gosta &E. Casorti, "J. Appl. Polym. Sci. ", 35, 1864, (1988).
19. Anuual Book of ASTM, part35, 1983.
20. Anuual Book of ASTM, Vol. 08, 01, (1986).
21. Anuual Book of ASTM, Part-35, (1981).
22. Anuual Book of ASTM, 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).
27. P. R. Hornsby, and C. L. Watson, "*Polym. Degrad, Stab*. ", 30, 73-87 (1990).

دراسة فعالية بعض اكاسيد المعادن والاملاح كمثبطات للهوبية البولي استر غير المشبع

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الملخص

في هذا البحث تم استخدام كاربونات الكالسيوم (مضاف I)، امونيوم فوسفات ثنائي الهيدروجين (مضاف II) واوكسيد المغنيسيوم (مضاف III) كمثبطات للهوبية البولي استر غير المشبع بنسب مئوية وزنية (0، 2، 4، 7، 10 و12)% بواسطة تحضير شرائح بأبعاد (3*130*130) ملم.

استخدمت ثلاث طرق قياسية لأختبار تثبيط اللهوبية وهي: الطريقة القياسية ASTM:D-2863 لقياس معامل الاوكسيجين (LOI) المحدد، الطريقة القياسية ASTM:D-635 لقياس سرعة الاحتراق (R.B) والطريقة القياسية ASTM:D-3014 لقياس اقصى ارتفاع يصل اليه اللهب (H).

اظهرت النتائج المستحصل عليها ان المضافات المستعمله في هذه الدراسة تمتلك تأثراً جيداً كمثبطات لهب للبولي استر غير المشبع وان الامونيوم فوسفات ثنائي الهيدروجين كان افضلها.