The Combined Action of Zeolite and Chlorinated Rubber as Flame Retardants for Epoxy Resin

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Abstract :

In this work , the effect of chlorinated rubber (additive I), zeolite 3A with chlorinated rubber (additive II), zeolite 4A with chlorinated rubber (additiveIII), and zeolite 5A with chlorinated rubber (additive IV), on flammability for epoxy resin studied, in the weight ratios of (2, 4, 7,10 & 12%) by preparing films of (130x130x3) mm in diameters, three standard test methods used to measure the flame retardation which are ; ASTM : D-2863 , ASTM : D-635 & ASTM : D-3014.

Results obtained from these tests indicated that all of them are effective and the additive IV has the highest efficiency as a flame retardant.

Key word : Polymers ; Epoxy resin ; Flame retardant ; Flammability ; Additives ;Composite materials .

Introduction:

Polymers, also called macromolecules are giant molecules in which atoms are linked together by covalent bonds along molecules. [1]

Composite materials are those formed by the combination of two or more materials to achieve properties that are superior to those of its constituents. The design goal of a composite is to achieve a combination of properties that is not displayed by any single material, and also to incorporate the best characteristics of each of the component materials. [2] Polymers find many uses and add greatly to the quality of modern day life. However, a major problem arises because most of the polymers on which these materials are based are organic and thus flammable. In the UK alone some 800–900 deaths and roughly 15 000 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. [3] 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'.The ideal flame retardants should be compatible i.e. not alter the mechanical properties of the plastic, not change colour, have good light stability, resistant towards ageing and hydrolysis, match and begin its thermal behavior before the thermal decomposition of plastics, not cause corrosion, not have harmful physiological effects, not emit or at least emit low levels of toxic gases and be as cheap as possible. [4] Many inorganic compounds are used as fire retardants for epoxy resin, which shows high efficiency in flame – retardancy of epoxy resin. [5-7] Epoxy resins are widely used as a matrix in composites in different applications where chemical, mechanical, thermal, and dielectric properties are necessary.

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It is used in aircraft-aerospace demand, in military and commercial applications and is also used in construction. [8], so that, in this work the influence of another additives as flame-retardants for epoxy resin were studied.

Material and Methods:

Materials

a. Epoxy resin, type (CY223), hardener type (HY956), imported from Ciba-Geigy Company.
b. Flame-retardants; Chlorinated rubber supplied from Industries Modern Painting Company (additive I); Zeolite type 3A with chlorinated rubber (1:1)(additive II); Zeolite type 4A with chlorinated rubber (1:1) (additive III) & Zeolite type 5A with chlorinated rubber (1:1) (additive IV), the three type of zeolite were laboratory prepared according to reported method.[9-11]

Tests

a- ASTM: D-2863: The measurement of limiting oxygen index (LOI), is widely used for measuring the flammability of polymers. [12]
b- ASTM: D-635 : The measurement of rate of burning (R.B), extent of burning (E.B) and time of burning (T.B) [13] were achieved by this method.
c- ASTM : D-3014: Measurement of maximum height of flame (H) of the burning polymer, and the amount of loss in weight of polymer as a result of combustion[14] were done according to this test.

Preparing of specimens

The samples were prepared in the dimensions of (130x130x3) mm, three sheets of epoxy resins were prepared for each percentage weight (2, 4, 7, 10 & 12%) with the additives I , II , III , and IV.

Results and Discussions :

1-Measurement of LOI using ASTM : D-2863 :

Limiting oxygen index (LOI) is defined as the minimum percentage of O_2 in a mixture of (oxygen + nitrogen) that will just support flaming combustion, which is necessary for the continuation flammable of specimen for more than three minutes at least. The efficiency of I, II, III and IV additives are in the following order :
IV> III > II > I

The results are listed in table (1) and reresented by Fig. (1).

2- Measurement of rate of burning (R.B), usingASTM : D-635 :

The results obtained from these tests showed that the rate of burning (R.B) of the epoxy resin with the additives has a continuous reduction with increasing the percentage weight of additives, as in Table (2), Fig. (2), showed the flame speed curves of flame – retardation for resin. These results indicated that, the additive IV has the highest efficiency causing self-extinguishing at the percentages of 2&4%. Non-burning occured in the percentages of 7, 10&12% .

3- Measurement of maximum flame hight (H) using ASTM: D-3014:

Figure (3) showed that, the maximum flame hight (H) decreased with increasing the percentage of additives (inversely proportional), as showen in table (3).For the additive IV the flame hight was 4.0 cm in the percentage 12%.The amount of residue from the combustion of epoxy resin with additives in all percentages is higher than those of remaining material without additives, the reason is that the additives are thermally degradable and fly to the flame zone retarding the combustion.In general, the results obtained indicated that, additive IV has the best efficiency to retarder combustion. Depending on the structure of additives, the highly effectiveness of the additive IV can be attributed to the synergistic effect of zeolite 5A with chlorinated rubber which consists of a high percentage of halogen (Chlorine 67%) as well as the presence of silicon, aluminum and calcium oxides account for 94% of the total chemical composition of the clay. Halogen-containing flame retardants are releasing halogen radicals, which react with the high energy H • and •OH radicals which are responsible of combustion continuation of polymeric material chain reaction of the burning organic gases, chlorine are very efficient flame inhibitors[15].Also the additives can promote the formation of a good carbon char residue, which can isolate heat and oxygen from flame zone to the polymeric material and as a barrier combustible gas degraded from the polymeric material to flame.In addition to that, liberation of a group of non-flammable gases, e.g. H_2O, CO, CO_2 and carbonceos char, insulating the heat transfer and isolate combustible gas, which results in the high flame retardancy.

Conclusions:

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

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

2- The synergistic effect of zeolite 5A with chlorinated rubber and zeolite 4A with chlorinated rubber gave the best results in blocking the flammability of epoxy resin comparing with the other additives.

3- Self-extinguishing (S.E) occurred at the percentage (2%) of the additives (IV), and at the percentage (4%) for the additives (III)

4- Non-burning (N.B) occurred at the percentage (7, 10&12%) of the additive (IV).

5- 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.

Table (1)Limiting Oxygen Index (LOI) of epoxy resin, with additives.

% Additives	(LOI)					
	Non	2	4	7	10	12
I	19.3	22.17	23.29	24.31	25.91	26.54
II	19.3	23.41	24.57	25.45	26.87	28.20
III	19.3	23.56	24.83	25.60	27.08	28.31
IV	19.3	23.90	25.00	26.05	27.45	28.69

Table(2) : Rate of burning (R.B), Average Extent of Burning (AEB), and Average Time of Buning (ATB) of epoxy resin with additives .

% Test	Non	2	4	7	10	12	Additives
AEB (cm)	10	10	10	3.8	-	-	I
	10	10	3	1.2	-	-	II
	10	10	2.9	-	-	-	III
	10	4.8	3.5	-	-	-	IV
ATB (min)	5.23	7.04	9.34	4.31	-	-	I
	5.23	10.20	4.54	2.26	-	-	II
	5.23	10.98	6.04	-	-	-	III
	5.23	6.00	8.33	-	-	-	IV
R.B (cm/min)	1.91	1.42	1.07	0.88	-	-	I
	1.91	0.98	0.66	0.53	-	-	II
	1.91	0.91	0.48	-	-	-	III
	1.91	0.80	0.42	-	-	-	IV
S.E	-	-	-	yes	yes	yes	I
	-	-	yes	yes	yes	yes	II
	-	-	yes	yes	yes	yes	III
	-	yes	yes	yes	yes	yes	IV
N.B	-	-	-	-	yes	yes	I
	-	-	-	-	-	yes	II
	-	-	-	yes	yes	yes	III
	-	-	-	yes	yes	yes	IV

Table(3) : Maximum flame height (H) of epoxy resin with additives.

% Test	Non	2	4	7	10	12	Additives
W_1	4.50	5.23	5.28	5.31	5.35	5.37	I
	4.50	5.28	5.30	5.32	5.35	5.38	II
	4.50	5.30	5.32	5.35	5. 38	5.40	III
	4.50	5.33	5.35	5.42	5.49	5.58	IV
W_2	1.43	1.44	1.47	1.51	-	-	I
	1.43	1.46	1.53	1.59	-	-	II
	1.43	1.45	1.54	-	-	-	III
	1.43	1.50	1.54	-	-	-	IV
PWR	68.22	72.46	72.15	71.56	-	-	I
	68.22	72.34	71.13	70.11	-	-	II
	68.22	72.64	71.05	-	-	-	III
	68.22	71.85	71.21	-	-	-	IV
H	12.0	8.5	7.5	6.5	-	-	I
	12.0	7.5	6.5	5	-	-	II
	12.0	7	6	-	-	-	III
	12.0	6	4	-	-	-	IV

W_1: the weight of the sample before combustion.
W_2: the weight of lost material.
PWR: percentage weight of the remainder of the burning material.

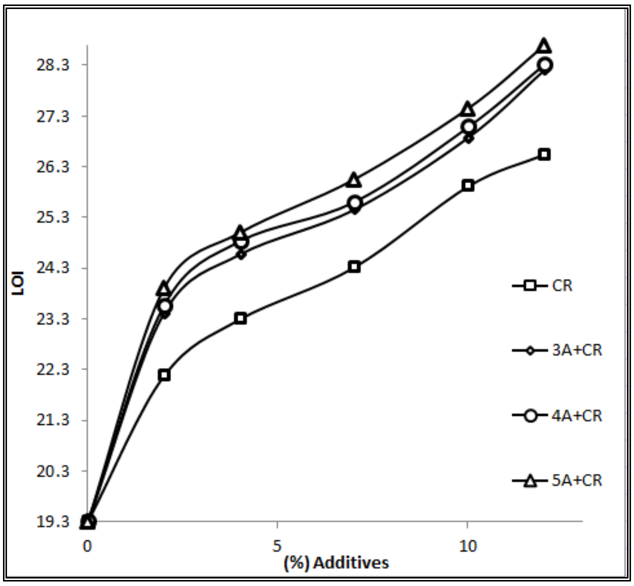

Fig. (1)
LOI of the epoxy resin with additives.

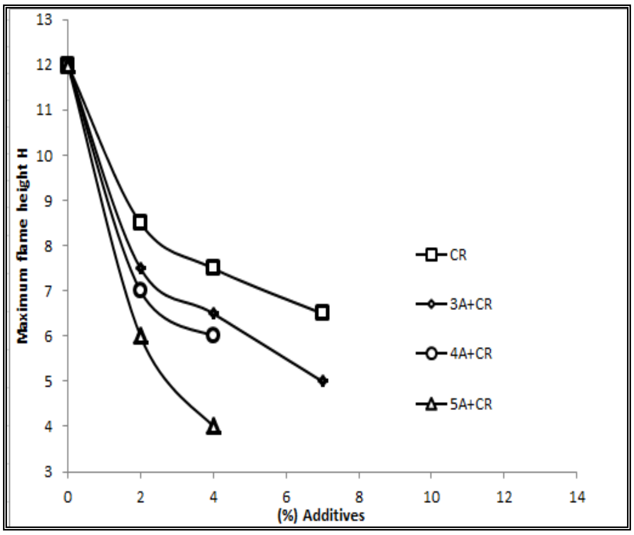

Fig. (2)
Rate of Burning of the epoxy resin with additives.

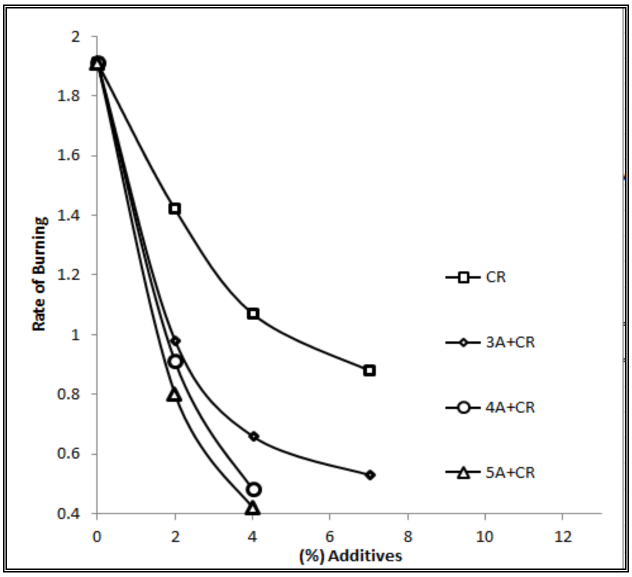

Fig. (3)
(H) of the epoxy resin with additives.

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التأثير التآزري للزيولايت والمطاط المكلور كمثبطات لهب لراتنج الايبوكسي

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الخلاصة:

في هذا العمل، تم أستخدام المطاط المكلور (مضاف I) ، زيولايت نوع 3A مع المطاط المكلور (مضاف II) ، زيولايت نوع 4A مع المطاط المكلور (مضاف III) و زيولايت نوع 5A مع المطاط المكلور (مضاف IV)وبنسب مختلفة(10,7,4,2و 12)% بوصفها مضافات لتثبيط لهوبية وزيادة مقاومة اشتعال راتنج الايبوكسي

تم تحضير شرائح بابعاد (3×130×130) ملم. واستخدمت ثلاث طرق قياسية لاختبار تثبيط اللهوبية وهي : الطريقة القياسية ASTM : D-2863 ، الطريقة القياسية ASTM : D-635 والطريقة القياسية ASTM : D-3014

ان النتائج التي تم الحصول عليها تشير الى ان جميع المضافات فعالة وأن المضاف IV يمتلك كفاءة اعلى في تثبيت لهوبية راتنج الايبوكسي.