EFFECT OF FLAME RETARDANT ADDITIVE ON THE FLAMMABILITY OF UNSATURATED POLYESTER RESIN [+]

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Abstract:

Diammonium Phosphate (DAP) was used as a flame retardant additive to unsaturated poly -ester UPE resin and to increase it's combustion resistance . It was added to the resin with weight percent ratios (2 , 4 , 6 , 8 , 10 , 12 , 14 , 16) % to obtain different samples . From the results , good flame retardant to unsaturated polyester was obtained in all weight percent ratios of the additive .

Self – Extinguishing was observed at additive ratios (8 , 10 , 12 , 14) % , and No – Burning phenomenon for unsaturated polyester resin was observed at (16) % .

Rockwell – B hardness and flexural strength were measured for preparing polymeric samples , the polyester hardness without additive was (88) HRB , and (42) HRB with (16)% ratio of the additive , and it's flexural strength was (146.93) MPa without additive and (44.08) MPa with (16)% ratio of the additive .

Iraqi kaolin ($Al_2O_3.2SiO_2.2H_2O$) with (7.5) % weight percent ratio was added to polymeric samples , which self extinguishing was obtained at (8 , 10 , 12 , 14) % DAP , for studying it's effect on polymeric samples hardness , flexural strength and combustion resistance , from results it was noticed that samples mechanical and thermal properties were enhanced , that is, the Rockwell-B hardness was increased from (60 to 76)HRB at (8)% weight DAP , and flexural strength was increased from (102.85 to 117.55) MPa at the same ratio , the enhancement was occurred also at the ratios (10 ,12) % .

The self extinguishing at (8)% weight DAP after (2) cm from test sample length , it appeared at (0.3) cm from test sample length , and the self extinguishing at (12)% DAP after (0.5) cm from sample length was converted to no – burning, that is the aim of the work , so the kaolin addition was stopped after (12) % DAP.

تأثيرالمضاف المعيق للهب على لهوبية راتنج البولي أستر غير المشبع

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المستخلص:

تم أستخدام مادة فوسفات ثنائي الامونيوم (DAP) كمضاف معيق للهب راتنج البولي أستر غير المشبع UPE ولزيادة مقاومة أشتعاله , بنسب مئوية وزنية (2 , 4 , 6 , 8 , 10 , 12 , 14 , 16) للحصول على نماذج

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مختلفة . من النتائج المقاسة , تبين ان هناك أعاقة جيدة للهب راتنج البولي أستر غيرالمشبع بكل النسب المئوية الوزنية للمضاف .تمت ملاحظة الاطفاء الذاتي عند النسب الوزنية (8 , 10 , 12 , 14) % , وان ظاهرة عدم الاشتعال تمت ملاحظتها عند النسبة الوزنية (16) % .

تم قياس صلادة روكويل – B ومقاومة الانحناء للنماذج البوليميرية المحضرة , فقد كانت صلادة البولي أستر بدون مضاف (88) HRB و(42) HRB عند النسبة (16) % , وان مقاومة الانحناء كانت (146.93) MPa بدون مضاف و (44.08) MPa عند النسبة (16) % للمضاف .

كما أضيف الكاؤولين العراقي بنسبة مئوية وزنية قدرها (7.5) % , للنماذج البوليميرية التي حصل فيها الاطفاء الذاتي عند (8 , 10 , 12 , 14) % (DAP) , لدراسة تأثيره على صلادة ومقاومة الانحناء ومقاومة أشتعال النماذج البوليميرية . من نتائج الاختبار لوحظ تحسن الخواص الميكانيكية والحرارية , حيث ان الصلادة أزدادت من (60 الى 76) HRB عند النسب 8 % وزنا DAP , ومقاومة الانحناء عند نفس النسبة أزدادت من (102.85 الى 117.55) MPa , وحدث التحسن أيضا عند النسبة (10 و 12) % .

أن الاطفاء الذاتي الذي حدث عند النسبة 8 % وزنا DAP بعد (2) سم من طول نموذج الفحص , ظهربعد (0.3) سم من طول النموذج , وأن الاطفاء الذاتي عند النسبة (12) % DAP بعد (0.5) سم من طول عينة الاختبار تحول الى عدم الاشتعال , وهذا هو هدف العمل , لذلك توقفت أضافة الكاؤولين بعد (12) % DAP .

Introduction

Afire retardant is a substance other than water that reduces flammability of fuels or delays their combustion , this typically refers to chemical retardants , but may also include substances that work by physical action , such as cooling the fuels .These substances have been used to retard the burning of a wide variety of synthetic and naturally occurring polymers .[1] . There are two distinct types of flame retardant :

1- Reactive Flame Retardant*s*

Reactive flame retardants are chemically added during the polymerization and they are incorporated in the polymer structure during the polymerization process.

2- Additive Flame Retardant

Generally, these groups of materials are incorporated into polymers by physically mixing with the polymer, normally after the polymerization process [2].

Diammonium Phosphate (NH4)2PO4 , can be used as fire retardant , it lowers the combustion temperature of the material , and causes an increase in the production of residue or char [3] .

Kaolin and various types of clays are important ceramic raw materials. The most principal constituent of kaolin is mineral kaolinite which has the compositions $Al_2O_3.2SiO_2.2H_2O$ [4]

Kaolin is highly refractory clay and has a melting point above 1600^oC [□].

Through melt compounding method , a novel flame retardant system composed of nano-kaolin and nano – HAO (hydroxyl aluminum oxalate) was used for flame retarding the low density polyethylene (LDPE) ethylene propylene diene rubber (EPDM) blends . From the LOI tests , it was found that when 12 wt% nano – kaolin took the place of 12 wt% nano – HAO in the composite , the LOI was increased from 31.0 % to 3□□ % and the thermal stability of the composites was enhanced [6] .

The unsaturated polyester resins belong to the most used thermosetting materials for

composite applications , structural parts of automobiles , building and coating materials and electrical parts [7 , 8] .
The activity of flame retardant additives consist in : (a) dilution of polymer in the condensed phase , (b) decreasing the amount of available fuel , (c) increasing the amount of thermal energy needed to raise the temperature of the composition to the pyrolysis level , due to the high heat capacity of the fillers , (d) enthalpy of decomposition – emission of water vapor , (e) decrease of feedback energy to the pyrolyzing polymer , (f) insulative effect of the oxides remaining in the char [9] .
Literature show that there are some studies about adding flame retarding additives ,
Al – Bayatee [10] studied the use of some inorganic additives as a flame retardants in weight percentages (0 , 1 , 3 , □, 7 , 10) % , with unsaturated polyester resin and epoxy resin , in these percentages the self extinguishing was occurred , and the mechanical properties don't examine . The results indicated that the additive which contains of (□0%Tetraethyl ammonium bromodichlorophenyl phosphine and □0% chlorinated paraffin) had the highest efficiency .
Habaib [11] studied the use of novolac resin and borax as flame retardant materials of epoxy resin .
Ricciardi et.al [1] investigated the addition of three phosphorus-based fire-retardant materials , (ammonium polyphosphate (APP), silane-coated APP, and melamine pyrophosphate) at two concentration levels (20% w/w, 3□% w/w) . Results demonstrated that the incorporation of the fire retardants at 3□% w/w has a strong effect on flammability and smoke suppressant properties with respect to both the neat resin and the loaded systems at 20% (w/w). In particular, the smoke formation and smoke parameters are reduced by □0% and 80%, respectively, leading to the conclusion that APP can be used single-handedly without combination with specific smoke suppressors.
Ngakan et.al [12] measured the flammability , thermal stability of natural fiber reinforced thermoplastic bio – composites . Various diammonium phosphates (DAP) were treated into the fibers ,to improve the flame retardancy of the bio – composites , the results indicate that increasing the percentage of DAP improves the flame resistant , weight loss rate .
In this work the fire behavior and the smoke emission of an unsaturated polyester resin modified by addition of diammonium phosphate , with different weight ratios until no burning phenomenon was happened. Kaolin was selected to enhance the polyester resin mechanical and thermal properties .

Experimental Work:

1- Materials

A- Unsaturated polyester UPE .
Traditional unsaturated polyester was used , it was supplied by (SER) company .
B- Flame Retardant Materials
1- Diammonium Phosphate (DAP) (NH_4)$_2PO_4$ was used , it was supplied by Merk company with (98.8) % purity , it was added to (USP) resin with weight percent ratios (2 , 4 , 6 , 8 , 10 , 12 , 14 , 16) .
2- Iraqi kaolin was used , It was produced by General Establishment for Construction Industries / Mosuel with (98)% purity . It was added with (7.□) % weight ratio to polymeric samples which were mixed with (8, 10 , 12 , 14) % DAP .

2- Samples Preparation

A- Polyester samples were prepared by mixing them with (2) % hardener .

B- Diammonium Phosphate weight percent ratios mentioned before were added to polyester resin with hardener .

C- Another samples were prepared from polyester with hardener and (8 , 10 , 12 , 14 , 16) % DAP plus (7.□) % kaolin .

All samples were molded in a mold with dimensions (1□* □* □) cm , they put in it to be solidified at atmospheric pressure and room temperature . Rate of burning test samples were prepared in (1□* 1.2 * 0.3) cm according to ASTM – D 63□-03 [13] , and flexural strength test samples were prepared too , in (68 * 14 * 3.□) mm according to ASTM D790 – 03 [14] .

Mechanical Testing:

A- Hardness Test

Hardness is defined as the resistance of material to deformation , particularly permanent deformation , indentation ,or scratching [1□] .

Rockwell – B Hardness Test (HRB) was followed , as ASTM – D 78□– 08 [16] .

B- Flexural Strength

Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis . The stresses induced due to the flexural load are a combination of compressive and tensile stresses [1□] . A three – point loading system utilizing center loading on a simple supported beam , as ASTM D790 – 03 [14] :

4- Rate of burning

Rate of burning measured according to ASTM D63□– 03 [13]:

1-A bar of UPE resin without and with additives were prepared , in (12□± □mm) length by (12.□±0.2 mm) in width, and of thickness (3mm ± 0.2 mm) .

2- Each test bar marked by scribing two lines, 2□ mm, and 100mm far from one end of the specimen.

3-The test bar clamped at the end nearest to the 100 mm mark, in a support with its longitudinal axis horizontal and its transverse axis inclined at 4□° to the a horizontal. Under the test specimen clamp, a screen of wire gauzes was placed ,in a horizontal position 10 mm below the edge of the specimen.

4-The burner adjusted with air ports open to produce a blue flame approximately 2□ mm high. □-The burner placed so that the flame contacts the end of test specimen , for 30 s or until the flame front reaches the 2□ mm mark . The time recorded in seconds , as burning time, (t_o) , and when the flame front reaches the 100 mm mark from the free end , the time recorded in seconds, as burning time (t) . If the burning has not reached the 100 mm mark, the unburned length is measured (X), the length of extent of burning is equal to (100 mm minus the unburned length mm).

The calculated variables as ASTM D-63□are :

1 – Average time of burning (ATB)

$ATB = \sum (t - t_o) /$ number of specimens ------ 1)

2- Average extent of burning (AEB)

$AEB = \sum (100 – X) /$ number of specimens,

where : X is the unburned length in (mm) ------ 2)

3- Rate of burning (R . B) .

R . B = AEB / ATB -------3)

4- Self –Extinguishing (S . E)

- No – burning (N . B)

Results and Discussion:

1- The results were decreasing in average extent of burning (AEB) and in the rate of burning (R.B.) of unsaturated polyester resin , proportional with increasing of the flame retardant additive (Diammonum Phosphate DAP) .

The active ratio of DAP was (8)% , this ratio caused self extinguishing to (UPE) after (1.78) min , and the no – burning phenomenon (N.B.) was obtained in (16) % weight ratio of DAP , as shown in table (1) .

Table (1) : (R.B.) , (AEB) and (ATB) tests , for (UPE) resin with the weight ratios of the additive (DAP)

Additive (Borax)	**Non**	**2**	**4**	**6**	**8**	**10**	**12**	**14**	**16**
AEB cm	10	10	10	10	2	1	0.	0.4	–
ATB min	4.73	79	7.	8.83	1.78	1.3	1.08	1.6	–
R.B. cm / min	2.11	1.72	1.33	1.13	1.12	0.74	0.46	0.2	–
S.E.	–	–	–	–	Yes	Yes	Yes	Yes	Yes
N.B.	–	–	–	–	–		–	–	Yes

From table (1) , the (R. B.) of UPE without additive was (2.11) cm\ min , it became (0.2) cm / min after adding the additive (DAP) at (14) % because diammonium phosphate is used as flame-retardants , this salt decompose into ammonia and phosphoric acid on heating. The phosphoric acid loses water and is converted to pyrophosphoric acid at approximately 200^{o}C. At higher temperature, the latter loses more water and is converted to metapyrophosphoric acid, which can form a glassy melt ,besides it causes an increase in the production of residue of char , this amount of char formed reduces that a mount of available fuel and can lead to the formation of a fire break [9 , 17] .

2- The mechanical properties to UPE resin were examined , Rockwell – B hardness and flexural strength , without and with additive as shown in table (2) and (3) .

Table (2) : UPE hardness with and without DAP .

UPE with weight percent ratio of DAP	Rockwell –B hardness (HRB)
UPE without additive	88
UPE + 2% DAP	76
UPE + 4% DAP	68
UPE + 6% DAP	63
UPE + 8% DAP	60
UPE + 10% DAP	4
UPE + 12% DAP	49
UPE + 14% DAP	46
UPE + 16% DAP	42

Table (3) : UPE flexural strength with and without DAP .

UPE with weight percent ratio of DAP	Flexural strength (MPa)
UPE without additive	146.93
UPE + 2% DAP	137.14
UPE + 4% DAP	127.34
UPE + 6% DAP	122.4□
UPE + 8% DAP	102.8□
UPE + 10% DAP	73.47
UPE + 12% DAP	48.98
UPE + 14% DAP	44.08
UPE + 16% DAP	39.02

Table (2) illustrated that the UPE hardness decreasing with increasing the weight percent ratio of DAP, UPE hardness without additive was (88) HRB , it became (42) HRB , and the flexural strength of UPE without additive was (146.93) MPa and (39.02) MPa with 16 % MPa , because the interface bonding between the additive and the polymer was adversely affected by an increase in weight percent of the additive [18] .

3- There was a demand for selection a material , to mix it with DAP , for enhancing the mechanical properties of UPE resin , and in the same time it doesn't decrease the DAP flame retardancy . The ceramic material " kaolin " $Al_2O_3.2SiO_2.2H_2O$ with (7.□) % was choiced , to adding it to UPE resin samples which were mixed with (8 , 10 , 12 , 14) % DAP, which the self extinguishing was occurred at them , and with ratio (16) % DAP , which was no – burning happened .

From the results there were synergetic action between DAP and kaolin to decrease UPE resin rate of burning , which was reflexed on self extinguishing and no – burning , as in table (4) .

Table (4) : Effect of (7.5) % kaolin with the UPE resin on the AEB , ATB and R.B.

Additive DAP %	**8**	**10**	**12**
AEB cm	0.3	0.2	_
ATB min	1.22	0.9□	_
R.B. cm □min	0.2□	0.21	_
S.E	Yes	Yes	Yes
N.B.	_	_	Yes

The self extinguishing that happened at (8)% weight DAP at (2) cm from test sample length , it happened at (0.3) cm from test sample length , and the self extinguishing at (12)% DAP after (0.□) cm from sample length , was converted to no – burning , that is the aim of the work , so the kaolin addition was stopped after (12) % DAP . This enhancement of UPE resin no-burning was happened because Kaolinite is converted to so-called metakaolinite with a less distinct crystalline structure, similar to kaolinite, at elevated temperature, with the first endothermal effect due to the loss of structural water as shown below [4] :

$$Al_2O_3 + 2SiO_2 \,.\, 2H_2O \xrightarrow{(500\text{-}600)^0C} Al_2O_3 \,.\, 2SiO_2 + 2\,H_2O$$

Besides , the water vapor has low thermal conductivity (0.020 W \ m .°K) , comparing with air which has (0.024 W \ m .°K) , at same temperature [19] , the gaseous phase was diluted by water vapor which decrease the amount of fuel and oxygen in the flame , and possible

endothermic interactions between the water and decomposition products in the flame so it was decreased the flame effect on UPE resin [9].
Hardness and flexural strength samples after mixing them with the kaolin were examined , as shown in table (□) and (6) , they were increased , comparing with same ratios of DAP as shown in table (2) and (3) . It can be noticed that the presence of hard ceramic particles would increase the hardness and the strength of the polymeric samples , because the resin has the lowest hardness of the other types of engineering materials i.e. , metals and ceramics [20] .

Table (5) : UPE resin hardness with (7.5) % kaolin .

UPE with percent ratio DAP	Rockwell –B hardness (HRB)
UPE + 8% DAP	76
UPE + 10% DAP	71
UPE + 12% DAP	67

Table (6) : UPE resin flexural strength with (7.5) % kaolin .

UPE with percent ratio DAP	Flexural strength (MPa)
UPE + 8% DAP	117.□□
UPE + 10% DAP	83.27
UPE + 12% DAP	□6.33

Conclusions :

1- Diammonium Phosphate (DAP) is an active flame retardant additive , for unsaturated polyester UPE , the self extinguishing was happened at (8) % weight ratio , and no-burning at (16) % .
2- Unsaturated polyester resin hardness and flexural strength were decreased with increasing weight ratio of additive DAP. UPE resin hardness without additive was (88) HRB ,and after adding (16) % weight ratio ,it became (42) HRB , and it's flexural strength was (146.93) MPa without additive and (39.02) MPa .
3- Kaolin has a synergetic action with DAP in decreasing the rate of burning of USP .The no- burning was occurred at (16) % DAP , it became at (12) % DAP when kaolin was added , the hardness and flexural strength values were increased .
4- Kaolin addition was effect because it's price is less than DAP price .

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