Studying the Effect of Some Inorganic Phosphors Salts on Fire Retardant and Mechanical Properties of Partially Cross Linked Modified Unsaturated polyester Composite

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Abstract :

In this work, the effect of four types of inorganic phosphors salts on flammability and mechanical properties (Flexural and Tensile) strength, of partially cross linked modified unsaturated polyester reinforced with glass fibers has been studied ; also , the influence of two types form of glass fibers (chopped strand mat and woven roving), on flammability and mechanical properties of the composite, were studied . Sheets of composites with different weight percentage of additives and reinforced with two layers of each type of glass fibers, were prepared. Four standard test methods used to measure the flame retardation and mechanical properties, which are: ASTM: D – 2863, ASTM: D – 635, ASTM: D – 790 and ASTM: D – 638 .

Results obtained from these tests indicated that, additive (IV) (poly ammonium phosphate) has high efficiency as a flame retardant, self – extinguishing (S.E.) occured at the percentage of 1.5 % and non – burning (N.B.) was occured at the percentage of 2.5 % for resin reinforced with glass fiber type woven roving and showed high effect to reduce the values of the mechanical behaviors, but additive (I)(mono ammonium phosphate) have low effect on retard composition and showed low effect on the values of mechanical properties.

Key word : Polymers **;** Unsaturated polyester resin ; Modified unsaturated polyester resin ; Fire retardant ; Flammability ; Additives **;** Mechanical properties ; Fiber glass ; Composite materials **.**

Introduction :

Flame retardation is essentially on interruption of the burning process[1]. There are two distinct types of flame retardant materials[2]; Reactive flame retardants are compounds usually containing hetero elements incorporated in smaller proportions, usually during the polymerization process and the other type is additives of flame retardants incorporated in to polymers by physical mixing with the polymer, normally after the polymerization process is complete.

A good flame – retardant additive must meet the following requirements [3] ; The addative should be thermally stable up to the processing temperature of the polymer and stable to light ,does not interact with main chain of the polymer , should not be poisonous and should not inversely effect physical properties of polymer . Many inorganic phosphorus compounds are used as fire retardants in polymer compositions, the flame retardant action of which is understood less than other materials which used flame – retardants [4] . These compounds are often used synergistically with other elements especially nitrogen and halogens [3,5] . Phosphorus compounds, especially phosphate esters are the more widely used for high hydroxylated polymers[1,6] and the mechanism for their fire retardant action is to reduce the production of combustible gasses and increasing char formation, inorganic phosphate salt compounds, shows high efficiency in flame – redundancy of unsaturated polyester and epoxy resins [7,8] .

Composite is generally defined as any physical combination of two or more dissimilar materials used to produce a new component having deffrent properties. [9] Properties of composites are strongly influenced by the properties of their constituent materials, their distribution and the interaction between them. Composite material as a system is described by the geometry of reinforcement [10] . The geometry of reinforcing material may be described by some important factors [8] : shape, size and size distribution; concentration distribution and orientation of reinforcing material . Thus most composite materials developed have been fabricated to improve mechanical properties [4]. The interaction between the matrix and fibers are effective in improving the fracture resistance of the matrix. The fibers have small cross sectional dimensions so that they are embedded in matrix materials to form fibrous composites [5] . Most of reinforced plastics are glass fiber reinforced polyesters . They are used in many important applications [9,10] , so that , in this work the influence of increasing the ratio of additives as flame-resistance on mechanical properties of reinforced modified polyester composite were studied.

Experimental Part :

1-Materials

a. Glass fiber type (E-Glass), were used as a reinforcing materials in the two forms; chopped strand mat, randomly oriented, with surface density equal to (0.277 kg/M^2), and woven roving, with surface density equal to (0.5 kg/M^2), purchased from (Moulding, LTD. , UK) Company.

b. Flame-retardant; Mono ammonium phosphate, with purity 99% (additive I); Di ammonium phosphate, with purity 99.5% (additive II); Tri ammonium phosphate, with purity 98% (additive III) & Poly ammonium phosphate with purity 97% (additive IV), in powder form ;were purchased from MERCK Co. .

c. All chemicals were used in the preparation of modified resin were pure and made by BDH Co.

2-Standard Tests

a- ASTM: D-2863: The measurement of limiting oxygen index (LOI), is widely used for measuring flammability of polymers [11].

b-ASTM: D-635: The measurement of rate of burning (R.B), average extent of burning (A.E.B) , average time of burning (A.T.B), self - extinguishing (S.E) and non – burning (N.B.) [12] .

c-ASTM : D-790 : The measurement of flexural strength, by three point method[13], with constant rate of displacement (crosshead speed) equal to 1 mm/Min. , by using Instron-1122 instrument.

d-ASTM: D-638: The measurement of tensile strength[14], with constant rate of displacement (crosshead speed) equal to 1 mm/Min., by using Instron - 1122 instrument .

3- Preparation of modified resin [15] :

a. **Preparation of modified unsaturated polyester resin** : Two moles of glycerol and one mole phthalic anhydride were mixed together in a 500 ml three-necked flask . The mixture was heated carefully to $160C^0$ until a clear liquor is formed and then about 50 ml of toluene was added carefully through the condenser and the flask was gently heated . Heating stopped after 40 min . The flask was allowed to cool to $110C^0$. (0.5) mole of powdered maleic anhydride was added carefully . Reflux continued until no more water came off at 230 C^0 .

b. **Preparation of partially cross – linked resins** : About (0.25) mole of modified unsaturated polyester resin and 0.1 mole of maleic anhydride , was mixed together in a 250 ml three-necked flask .The mixture was heated carefully to 150 C^0 and 25ml of toluene were added carefully through the condenser and the flask was gently heated . Heating was stopped when no more water came off at $190C^0$ and (1.36×10^{-3}) mole of hydroquionone was added . The flask was cooled to approximately 65 C^0 . (2.85) mole of vinylacetate monomer was added to the partially cross linked modified unsaturated polyester resin and stirred until a pourable syrup was formed .

4-Preparation of specimens

The specimens of polymeric material containing additives and reinforced with three layers from two types of glass fibers were prepared in dimensions (150 x 150 x 5) mm, two sheets were prepared for each percentage weight (0.5, 1.0, 1.5, 2.0 & 2.5 %) of flame retardant materials with each type of glass fibers. These sheets cut as specimens according to ASTM standard were used in this work .

Results and Discussion :

Flammability Tests:

The results of the flammability tests for unsaturated polyester resin reinforced with glass fibers in the form of chopped strand mat and in the form of woven roving, are shown in Tables 1 – 4 , for limiting oxygen index and rate of burning respectively . The limiting oxygen index (LOI), was increased with increasing the weight percentage of additives, as shown in Tables 1 & 2 respectively, and illustrated in Figures 1 & 2 for two types form of glass fibers respectively.

The rate of burning (R.B) of the resin reinforced with glass fibers in two types form with the additives has a continuous reduction with increasing the percentage weight of additives (inversely proportional), as in tables 3 & 4 respectively. Figures 3 & 4 showed the flame speed curves of flame retardation for resin in two types form . These results indicated that, the additive IV has high efficiency on self-extinguishing (S.E) of resin, especially in percentage 2.0 % for the resin reinforced with glass fiber type chopped strand mat and in percentage 1.5 % for resin reinforced with glass fiber type woven roving. Non-burning (N.B) occur in percentage 2.5 % for the resin reinforced with glass fiber type woven roving .

In general , additive IV has the best efficiency on retarding combustion . This high efficiency depends basically on the structure of this material (Poly ammonium phosphate), as it containes high percentage of phosphours element and nitrogen which have high effect on retard combustion. The free radicals were form from decomposition of this material sand ($P^{\cdot}$ and $N^{\cdot}$) will reacted rapidly with the free radicals of flame chain, such as ($H^{\cdot}$,$O^{\cdot}$,$O^{\cdot}OH$,…,etc.) to form inert compounds like (HPO, NH_4OH ,…., etc.) and work on inhabitation of thermal decomposition will occur in flame front, because decreases of amount of generation heat and to formed a group from the non-flammable gases, such as (CO,CO_2 , H_2O,…,etc) thus will decreases from volatile materials flammablity. The char will form as results from the thermal decomposition of the specimen;and it will cover the polymer specimen's roof.

The difference in the results of the flammability tests between the polyester reinforced with chopped strand mat and that reinforced with woven roving, results from the difference in the form and size distribution of glass fibers. The layers of glass fibers in the resin reinforced with the woven roving of glass fiber would move away from one another during the burning of the composite due to the presence of the resin – rich layers between the plies, this movement led to facility in the flame spread, while that did not occur in the case of the resin reinforced with the chopped strand mat of glass fiber.

B/ Mechanical Properties Tests

The mechanical properties of polymers depend on many factors like: molecular structure, types of branching, space distribution between main chains which contains molecular groups and the percentage of cross linking density between these back-bones chains [16].

In this work, the mechanical properties of composites depend on two factors; the types form of glass fibers and the structure of additives. The woven roving form of glass fibers caused increase in the mechanical behavior comparing with the chopped strand mat form, because regularly distribution of fibers in woven roving form, caused high density cross linking of this composite . The results of the mechanical tests for the resin reinforced with two types form of glass fibers and containing different percentage of additives, shows that the mentioned additives would led to lower values, as illustrated in Figures 5 & 6 . This reduction in the mechanical behaviors is attributed to influence of these additives on matrix, because the hard particles placed in brittle material lead to stress concentration in adjacent matrix and the presence of these additives between polymer chains obstructs local mobility of chains and thus, the polymer will show little strain, and their effect on the interface where they reduce the adhesion (interfacial bonding) between the fibers and matrix. Also, results of tests showed that the additives caused decrease in mechanical strength and modulus for composites with increasing of the percentage of additives, as shown in Tables 5 & 6 for both tests (flexural and tensile) respectively.

Conclusions:

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

1- The efficiency of the flame retardation for additives were in the following order:
IV > III > II > I
2- Limiting oxygen index (LOI) was increased with increasing of weight percentage of additives, but the rate of burning (R.B) was decreased with increasing of weight percentage of additives.
3- Additive IV has high effect on retarding combustion for two type of composite, but it reduces the mechanical properties.
4- Additive I showed low effect on retarding combustion for two types of composite, and it showed little effect on the values of mechanical properties comparing with additive IV.
5- The glass fiber type woven roving showed high effect in both tests (flammability and mechanical properties) comparing with chopped strand mat form.
6- The ideal percentage of additive is 1.5% from additive IV with woven roving form of glass fiber, is suffecient for using for the general propose, as shown in the following tables and figures.

Table (1) Limiting Oxygen Index (LOI) of modified resin reinforced with glass fiber type chopped strand mat, with additives

% / Additives	(LOI)					
	Non	0.5	1.0	1.5	2.0	2.5
I	19.9	20.36	20.89	21.37	21.90	22.38
II	19.9	20.57	21.22	21.73	22.26	22.74
III	19.9	20.83	21.53	22.24	22.93	23.61
IV	19.9	21.06	21.94	22.75	23.77	24.40

Table (2): Limiting Oxygen Index (LOI) of modified resin reinforced with glass fiber type woven roving, with additives

% / Additives	(LOI)					
	Non	0.5	1.0	1.5	2.0	2.5
I	20.2	20.79	21.33	21.78	22.30	22.85
II	20.2	20.98	21.71	22.39	23.11	23.78
III	20.2	21.30	21.90	22.67	23.50	24.69
IV	20.2	21.88	22.29	23.26	24.41	25.40

<u>Table (3)</u> : Rate of burning (R.B) of modified resin reinforced with glass fiber type (chopped strand mat) with additives

Test \ Additives %	Non	0.5	1.0	1.5	2.0	2.5	Additives
AEB (cm)	10	10	10	9.7	9.0	8.3	I
	10	10	10	9.1	8.2	7.1	II
	10	10	9.8	8.5	7.4	6.6	III
	10	10	9.3	7.8	6.5	4.9	IV
ATB (Min.)	5.03	5.81	6.09	6.34	6.21	6.34	I
	5.03	5.95	6.41	6.15	6.03	5.92	II
	5.03	6.13	6.53	6.40	6.22	6.17	III
	5.03	7.09	7.75	7.03	7.65	7.78	IV
R.B (Cm/Min.)	1.988	1.72	1.64	1,53	1.45	1.31	I
	1.988	1.68	1.56	1.48	1.36	1.20	II
	1.988	1.63	1.50	1.33	1.19	1.07	III
	1.988	1.41	1.20	1.11	0.85	0.63	IV
S.E	-	-	-	-	-	-	I
	-	-	-	-	-	-	II
	-	-	-	-	-	yes	III
	-	-	-	-	yes	yes	IV
N.B	-	-	-	-	-	-	I
	-	-	-	-	-	-	II
	-	-	-	-	-	-	III
	-	-	-	-	-	-	IV

<u>Table(4) :</u> Rate of burning (R.B) of modified resin reinforced with glass fiber type (woven roving) with additives

Tests \ Additives %	Non	0.5	1.0	1.5	2.0	2.5	Additives
AEB (cm)	10	10	10	9.2	8.4	7.2	I
	10	10	9.6	8.5	7.9	6.8	II
	10	10	9.0	8.0	7.1	5.7	III
	10	10	8.8	7.2	6.0	-	IV
ATB (Min.)	5.08	6.02	6.36	6.43	6.22	6.05	I
	5.08	6.25	6.32	6.03	6.12	6.07	II
	5.08	6.49	6.16	6.20	6.17	5.64	III
	5.08	7.52	7.65	6.92	7.69	-	IV
R.B (cm/Min.)	1.968	1.66	1.57	1.43	1.35	1.19	I
	1.968	1.60	1.52	1.41	1.29	1.12	II
	1.968	1.54	1.46	1.29	1.15	1.01	III
	1.968	1.33	1.15	1.04	0.78	-	IV
S.E	-	-	-	-	-	-	I
	-	-	-	-	-	-	II
	-	-	-	-	-	yes	III
	-	-	-	yes	yes	yes	IV
N.B	-	-	-	-	-	-	I
	-	-	-	-	-	-	II
	-	-	-	-	-	-	III
	-	-	-	-	-	yes	IV

<u>Table (5):</u> Flexural Strength (S_F) and Flexural Modulus (E_F) of modified resin reinforced with glass fiber (in two forms) with additives

Form of glass fiber	Test of mechanical properties	Additives %						Additives
		Non	0.5	1.0	1.5	2.0	2.5	
Chopped strand mat	Flexural strength (S_F) MPa	3.58	3.55	3.52	3.49	3.46	3.43	I
		3.58	3.54	3.51	3.48	3.45	3.42	II
		3.58	3.53	3.50	3.47	3.44	3.41	III
		3.58	3.51	3.48	3.45	3.42	3.38	IV
	Flexural Modulus (E_F) MPa	143.4	141.0	139.6	137.3	135.4	133.0	I
		143.4	140.2	138.0	136.1	134.3	132.9	II
		143.4	139.4	137.1	135.3	133.2	130.7	III
		143.4	138.0	135.8	134.0	132.0	128.9	IV
Woven roving	Flexural strength (S_F) MPa	4.32	3.29	3.26	3.23	3.20	3.17	I
		4.32	3.28	3.25	3.22	3.19	3.16	II
		4.32	3.27	3.23	3.21	3.18	3.15	III
		4.32	3.25	3.21	3.18	3.15	3.12	IV
	Flexural Modulus (E_F) MPa	231	229.8	227.6	225.0	223.8	221.1	I
		231	228.0	226.2	224.5	221.6	219.8	II
		231	227.3	225.1	223.0	220.7	218.4	III
		231	226.5	224.0	222.4	219.6	217.1	IV

<u>Table (6):</u> Tensile Strength (σ_T) and Young Modulus (E) of modified resin reinforced with glass fiber (in two forms) with additives

Form of glass fiber	Test of mechanical properties	Additives %						Additives
		Non	0.5	1.0	1.5	2.0	2.5	
Chopped strand mat	Flexural strength (S_F) MPa	14.65	14.62	14.59	14.56	14.53	14.49	I
		14.65	14.61	15.58	14.55	14.52	14.48	II
		14.65	14.60	14.57	14.54	14.51	14.47	III
		14.65	14.56	14.53	14.49	14.45	14.44	IV
	Flexural Modulus (E_F) MPa	205.3	203.6	201.4	198.2	196.0	194.3	I
		205.3	202.3	200.1	197.8	195.3	193.1	II
		205.3	201.4	199.6	196.4	194.2	192.0	III
		205.3	195.1	193.2	191.0	189.4	187.5	IV
Woven roving	Flexural strength (S_F) MPa	15.90	15.80	15.51	15.20	14.96	14.93	I
		15.90	15.71	15.40	15.11	14.84	14.80	II
		15.90	15.60	15.29	15.09	14.75	14.72	III
		15.90	15.53	15.5	15.47	15.43	15.38	IV
	Flexural Modulus (E_F) MPa	390.2	387.8	384.3	381.5	378.0	374	I
		390.2	386.4	383.1	380.7	377.3	373.4	II
		390.2	385.0	382.4	379.6	376.1	372.0	III
		390.2	379.4	377.1	375.6	372.4	369.7	IV

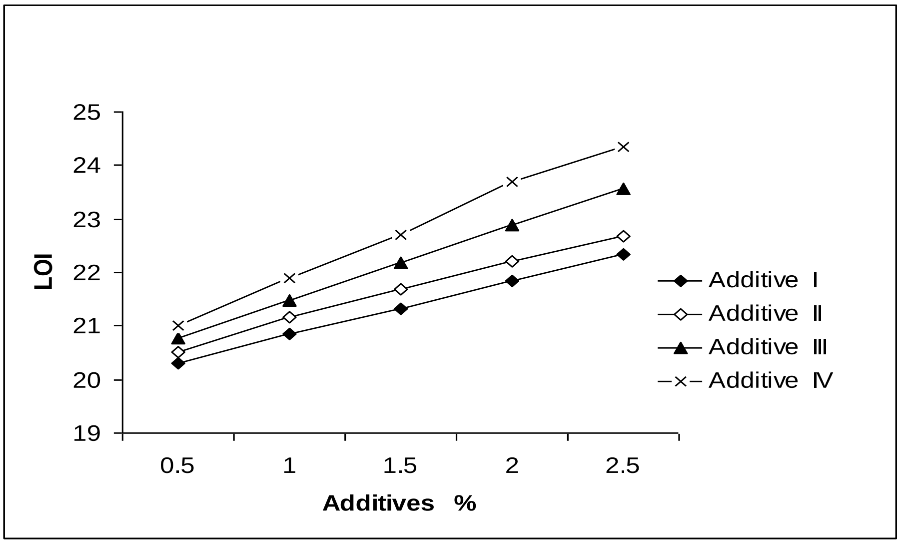

Figure – 1 : Limiting oxygen index (LOI) for resin reinforced with glass fiber from type chopped strand mat with different percentage of additives .

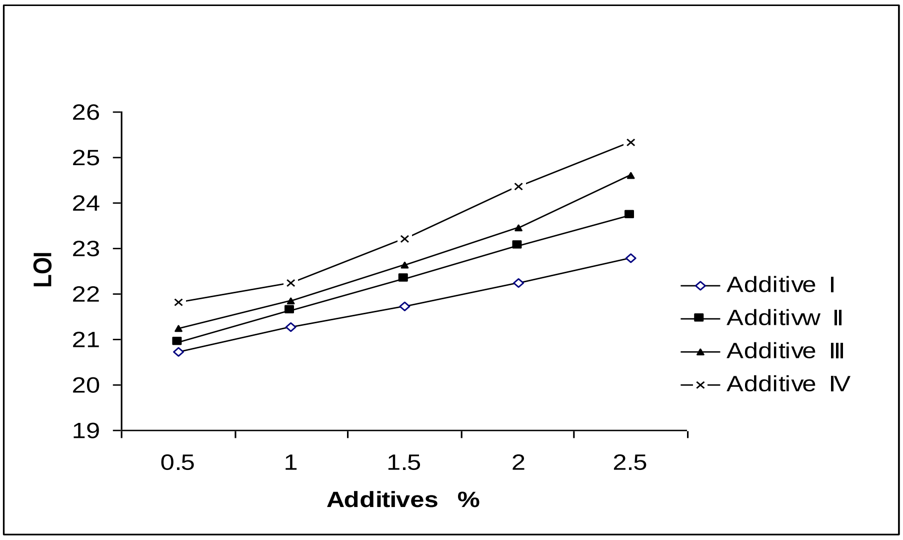

Figure – 2 : Limiting oxygen index (LOI) for resin reinforced with glass fiber from type woven roving with different percentage of additives .

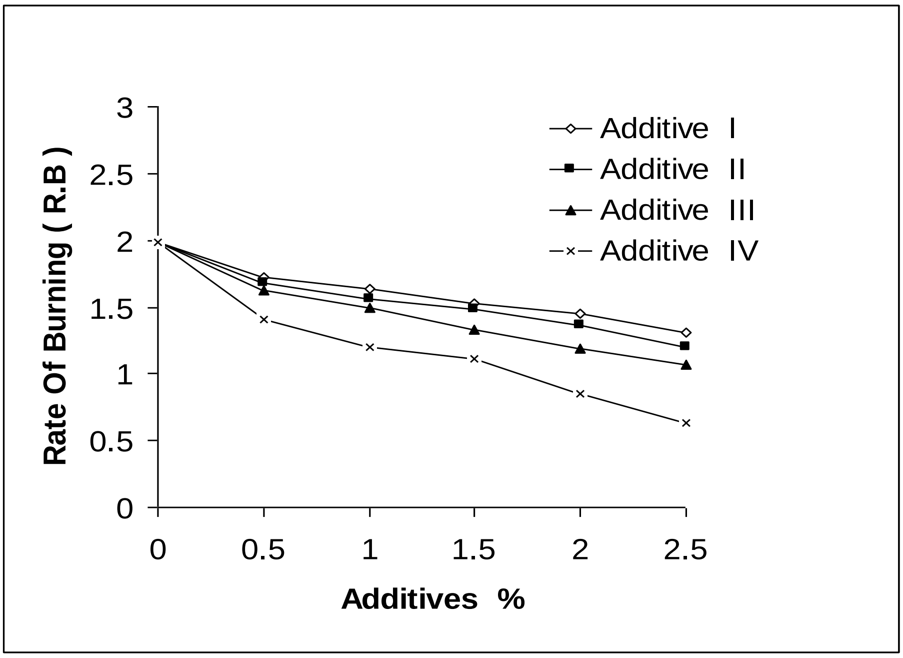

Figure – 3 : Rate of burning (R.B.) for resin reinforced with glass fiber from type copped strand mat with different percentage of additives .

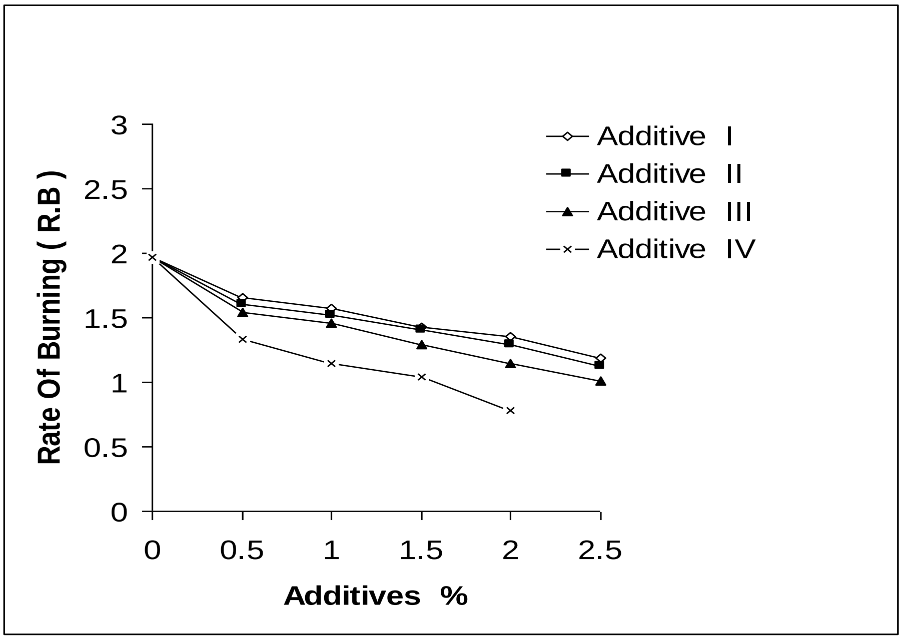

Figure – 4 : Rate of burning (R.B.) for resin reinforced with glass fiber from type woven roving with different percentage of additives .

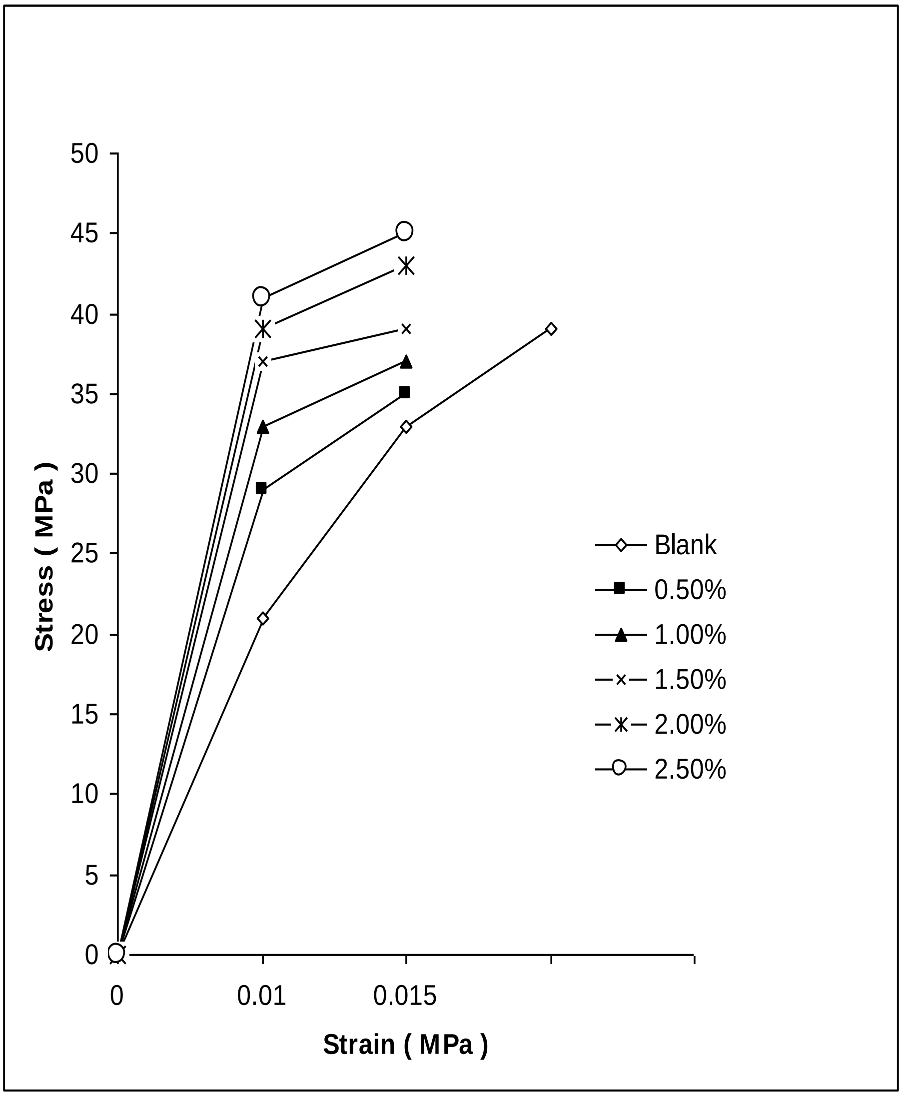

Figure – 5 : Stress – strain curve for resin reinforced with glass fiber type chopped strand mat with different percentage of polyammoniumphosphate

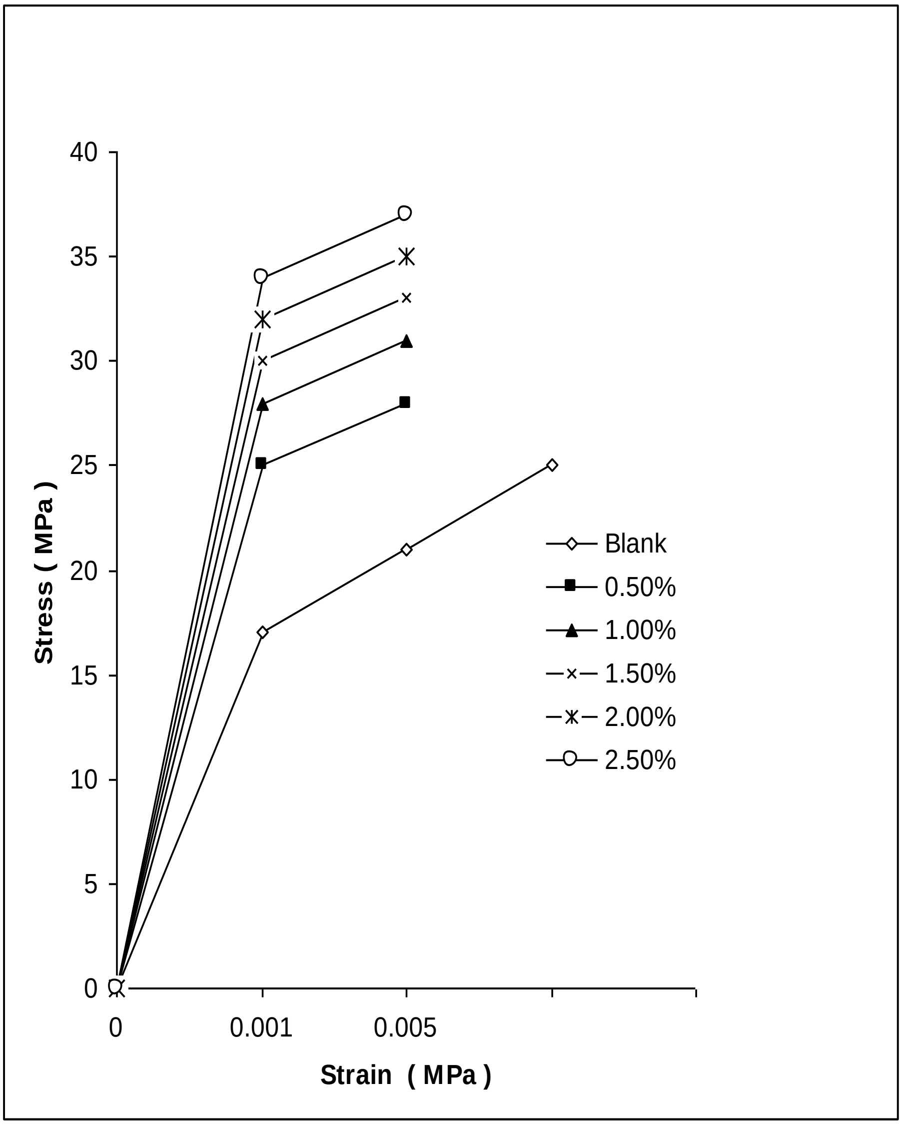

Figure – 6 : Stress – strain curve for resin reinforced with glass fiber type woven roving with different percentage of polyammoniumphosphate

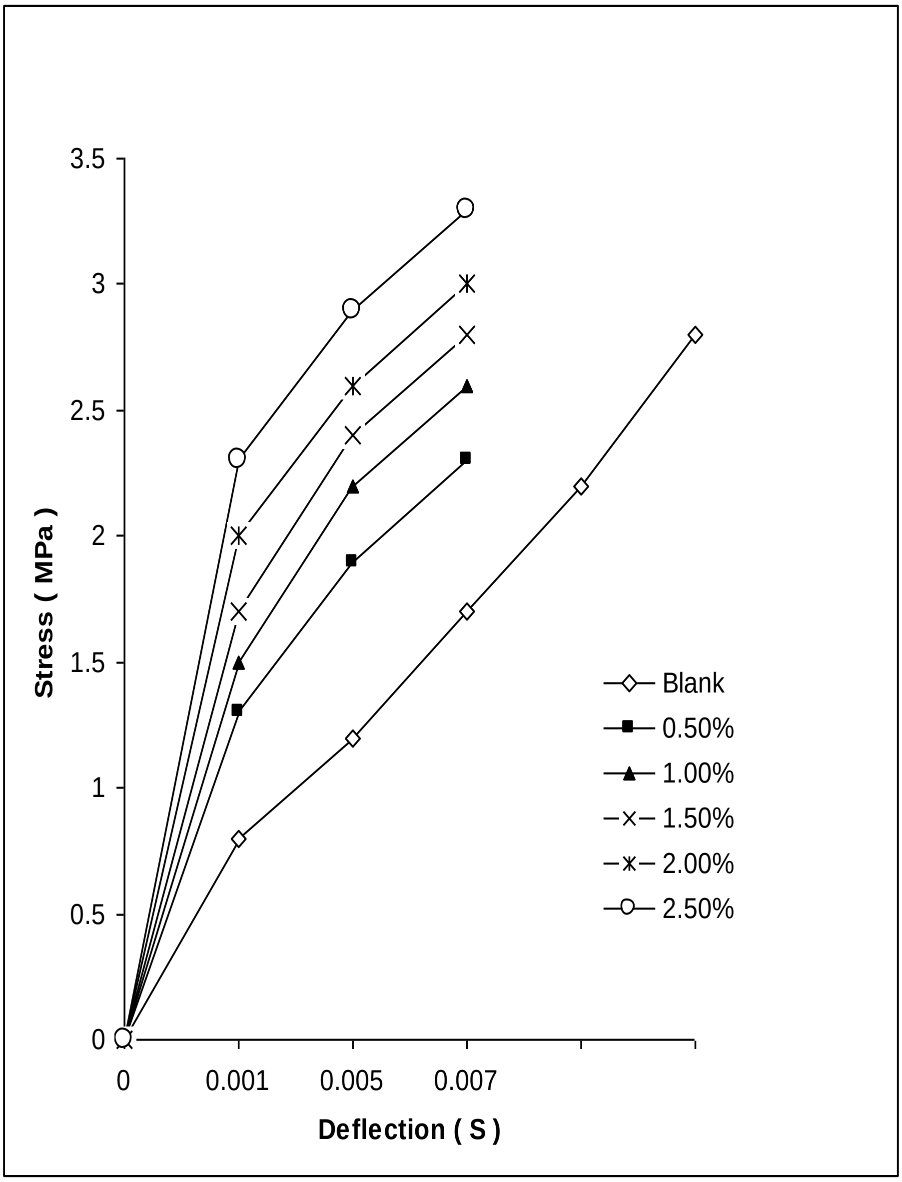

Figure – 7 : Stress – deflection curve for resin reinforced with glass fiber type chopped strand mat with different percentage of polyammoniumphosphate

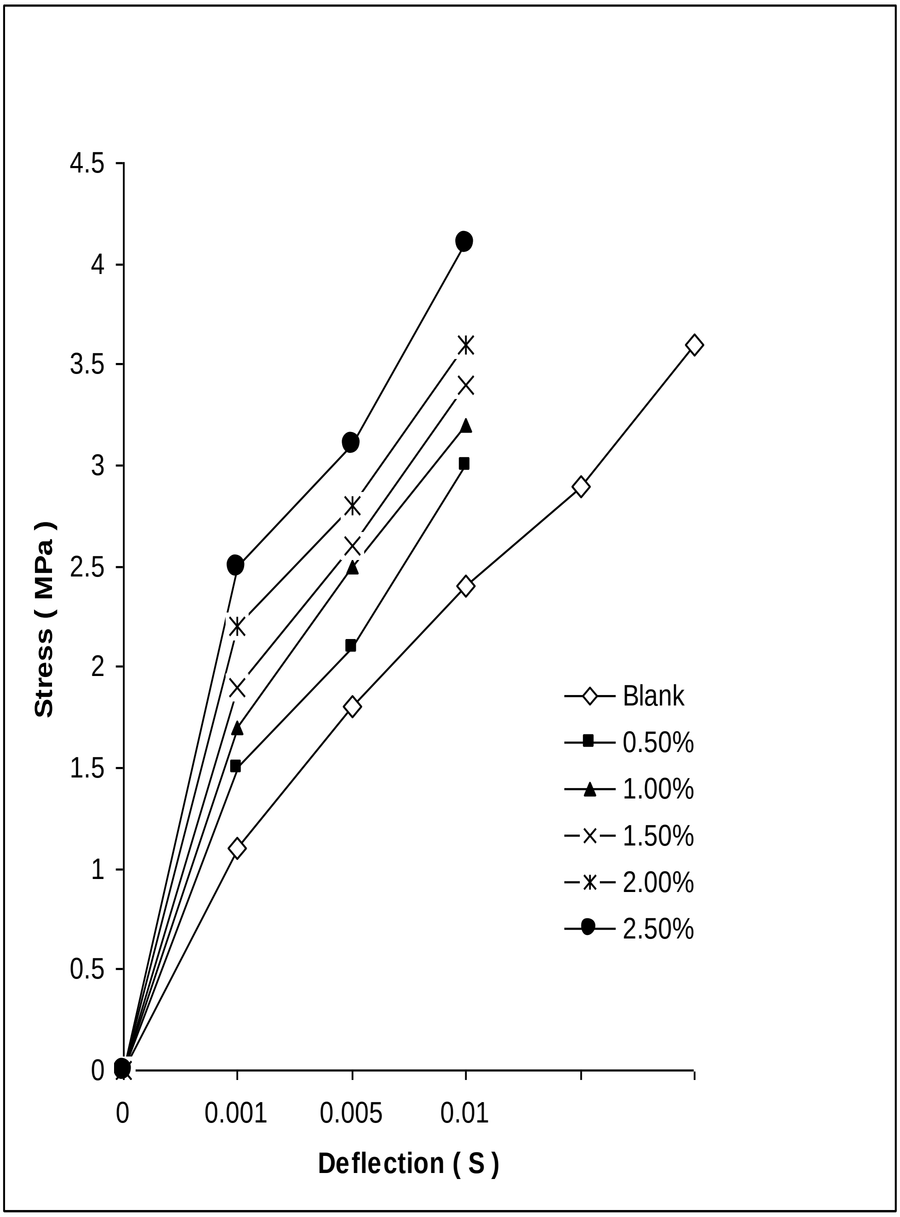

Figure – 8 : Stress – deflection curve for resin reinforced with glass fiber type woven roving with different percentage of polyammoniumphosphate

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دراسة تأثير بعض أملاح الفسفور اللاعضوية على تثبيط اللهوبية و الخواص الميكانيكية لمتراكب البولي استر غير المشبع المحور المتشابك جزئيا

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الملخص

في هذا العمل، تم دراسة تأثير أربعة أنواع من أملاح الفسفور اللاعضوية على تثبيط اللهوبية و الخواص الميكانيكية (قوة الشد و قوة الانحناء) لراتنج البولي استر غير المشبع المحور المتشابك جزئيا و المتراكب مع الألياف الزجاجية، كذلك تم دراسة تأثير نوعين من الألياف الزجاجية (حصائر الألياف المقطعة و حصائر الألياف المحاكة) على تثبيط اللهوبية و الخواص الميكانيكية للمتراكب . تم تحضير ألواح راتنج البولي استر غير المشبع المتراكب بإضافة نسب مئوية (0.5 ، 1.0 ، 1.5 ، 2.0 و 2.5 %) من المضافات و بإبعاد (5 × 150 × 150) ملم مع طبقتين من كل نوع من الألياف الزجاجية.

استخدمت أربعة طرق اختبار قياسية لحساب تثبيط اللهوبية و الخواص الميكانيكية وهي : ASTM:D-2863 ، ASTM:D-635 ، ASTM:D790 و ASTM-D638 .

ان النتائج المستحصلة من هذه الاختبارات تشير إلى إن المضاف (IV) يمتلك تأثيرعالي على تثبيط اللهوبية ، حدوث إطفاء ذاتي (S.E) عند نسبة 1.5% و كذلك حدوث عدم أشتعال للعينة عند النسبة 2.5% للراتنج المتراكب مع الياف الزجاجية من نوع حصائر الياف المحاكة ، وكذلك فأنه يظهر تأثير عالي في خفض قيم الخواص الميكانيكية ، أما المضاف (I) يمتلك تأثير قليل على تثبيط اللهوبية و يظهر تأثير واطئ على قيم الخواص الميكانيكية .