Influence of some additives on flammability and mechanical properties of modified polyester containing heterocyclic ring composites

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الخلاصة

في هذا العمل، تم دراسة تأثير خمسة أنواع من أملاح الفسفور اللاعضوية على تثبيط اللهوبية والخواص الميكانيكية (قوة الشد وقوة الانحناء) لراتنج البولي استر غير المشبع المحور المتشابك جزئيا والمتراكب مع الألياف الزجاجية، كذلك تم دراسة تأثير نوعين من الألياف الزجاجية (حصائر الألياف المقطعة وحصائر الألياف المحاكة) على تثبيط اللهوبية والخواص الميكانيكية للمتراكب. تم تحضير ألواح من الراتنج المحضر المتراكب بإضافة نسب مئوية (0.5, 1.0, 1.5, 2.0 و2.5%) من المضافات وبإبعاد (15×150×5) ملم مع ثلاثة طبقات من كل نوع من الألياف الزجاجية. أربعة طرق اختبار قياسية استخدمت لحساب تثبيط اللهوبية والخواص الميكانيكية وهي:

ASTM: D-2863, ASTM: D-635, ASTM: D-790 و ASTM: D-638.

أن النتائج المستحصلة من هذه الاختبارات تشير إلى إن المضاف V يمتلك تأثيراً عالياً على تثبيط اللهوبية، حدوث إطفاء ذاتي (S.E) عند نسبة 1.5% وكذلك حدوث عدم أشتعال للعينة عند النسبة 2.5% للراتنج المتراكب مع الياف الزجاجية من نوع حصائر الياف المحاكة، وكذلك فأنه يظهر تأثيراً عالياً في خفض قيم الخواص الميكانيكية، لكن المضاف I يمتلك تأثير قليل على تثبيط اللهوبية ويظهر تأثيراً واطئاً على قيم الخواص الميكانيكية.

الكلمات المفتاحية

أملاح الفسفور اللاعضوية، المضافات، تثبيط اللهوبية، خواص ميكانيكية، البوليمرات المعدلة، البوليمر الحلقي الشاذ، المواد الأولية.

Abstract

In this work, the effect of five types of inorganic phosphors salts on flammability and mechanical properties (Flexural and Tensile) strength, of partially cross linked modified unsaturated polyester resin, were studied. Sheets of composites with different weight percentage of additives were prepared. Four standard test methods were used to measured 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 V has high efficiency as a flame retardant, self - extinguishing (S.E.) was occur at the percentage 1.5% and non - burning (N.B.) was occur at the percentage 2.5% for resin and showed high effect to reduce the values of the mechanical behaviors, but additive I has low effect on retard composition and low effect on the values of mechanical properties.

Keyword

Additives; Fire-retardant; Mechanical properties; Modified polymers; Modified polyester; Heterocyclic polymer; Composite material.

1. Introduction

A large number of synthetic polymeric materials were using in these days, with various different properties are available for medical applications and engineering matrices. Most of the common materials have sufficient mechanical stability and elasticity as well as desired stability towards degradation, and are non-toxic. [1, 4].

Heterocyclic polymers are linear high polymers comprising, heterocyclic rings, or groups of rings, linked together by one or more covalent bonds. As a group such polymers are often both mechanically rigid and inherently resistant to thermal degradation [5].

Modified polymers are widely used in the packaging industry because of their good barrier and mechanical properties, good chemical stability and processability, low costs and low toxicity. Polyethylene, polyethyleneterphthalate, polyamides and unsaturated polyester resins, are important classes of polymers with different properties [6]. When combining these polymers in multilayered structure, materials in which the favorable properties of both polymers are present can be obtained. However these polymers are not compatible and do not adhere to one another, which of course diminishes the performance of multilayered films [7].

Very wide applications for polymeric materials were extended to use them as composites that covered most aspects of life. So these materials have to modified in aspect of reducing the hazarded of heat and fire [8]. Different polymers vary in the rate of combustion and thus difference may depend on the degree of exposure to ignition source [9]. The process of combustion of polymeric materials by a heat source and a sufficient amount of oxygen of the atmosphere contains a series of physical and chemical changes that occur to both the polymer and the environment [10]. Many organic and inorganic phosphorus compounds are used as flame- retardants materials in polymeric compounds [11], Although the mechanism of action is less understood of the halogenated compounds [12], and often used phosphorus compounds synergistic with nitrogen and halogen compounds. Synergistic effect means, that using two or more of the flame - retardant materials with polymeric material for the purpose of increasing the efficiency of the disability, and in any case it is not necessary that all phosphorus compounds are flame - retardant with the same degree of efficiency, also the retarded of the flame is not linear function relative to the content of the phosphorus in the used material [13].

2. Experimental part

2. 1. Materials

a. All chemicals were used in this work analytical grade.

b. Flame-retardant; Mono ammonium phosphate, with purity 99%; Di ammonium phosphate, with purity 99.5%; Chlorinated rubber containing 72% chlorine in powder form; imported from MERCK Company.

2. 2. Standard tests

a. ASTM: D-2863: The measurement of limiting Oxygen Index (LOI), is widely used for measuring flammability of polymers [14].

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.) [15].

c. ASTM: D-790: The measurement of flexural strength, by three point method [16], 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 [17], with constant rate of displacement (crosshead speed) equal to 1 mm/Min., by using Instron–1122 instrument.

2. 3. Flame-retardant materials

1. Monoammonium phosphate (additive I).
2. Diammonium phosphate (additive II).
3. Chlorinated rubber (additive III).
4. 50% from additive I+50% from additive III (additive IV).
5. 50% from additive II+50% from additive III (additive V).

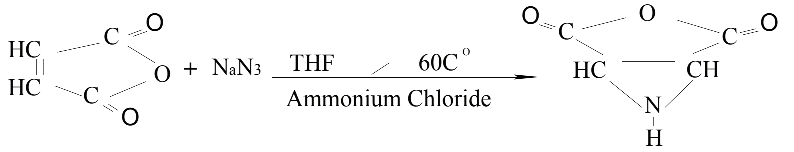
2. 4. Preparation of modified resin

a. Preparation of hetero-cyclic monomer [18]

A mixture of (147 gm, 1.5 mole) from Maleic anhydride and (79.5 gm, 1.5 mole) from Sodium azide in a 500 ml three-necked flask equipped with a thermometer, a mechanical stirrer and reflux condenser; (80.35 gm, 1.5 mole) from Ammonium Chloride and (50 ml) THF, were added to the mixture. The mixture warmed carefully with an electric heating mantle to (60 ^{o}C); heating stopped after 3hr.; and then, the mixture was filtered and the solvent was evaporated to give a yellow crystal, (m.p.144-146 ^{o}C). Equation (1) represents that reaction. Fig.(1), represents the FT-IR spectrum of this monomer, were showed the following bands: at (3308) cm^{-1} due to υ (NH) cyclic, at (2850) cm^{-1} for υ (CH) aliphatic, at (1778) cm^{-1} for υ (C=O) anhydride group, and at (1635) cm^{-1} for υ (NH) group.

b. Preparation of the linear modified resin [19]

(172.5 gm, 1.5 mole) from the monomer was prepared in (a), were dissolved in (216 gm, 3 mole) from Glycerol in a 500 ml three-necked flask equipped with a mechanical stirrer, with stirred for 1hr. in room temperature until all monomer will be dissolve in Glycerol. (222 gm, 1.5 mole) from Phthalic anhydride were add to the mixture and warmed carefully with an electric heating mantle to (160 ^{o}C), for 1hr. until a clear liquor is formed. The mixture was heated to (220 ^{o}C), under reflux and about (50 ml) of toluene was then added carefully through the condenser, and the heating was stopped after 3hr., until no more water came off. The flask was allowed to cool down to room temperature. Equation (2), represents that reaction, and Fig. (2), represents the FT-IR spectrum of the linear modified resin, showed the following bands: at (3444)cm^{-1} due to the overlapping between υ (N-H) cyclic, υ (O-H) group and υ (CH) aromatic, at (2947-2885)



Maleic anhydride Sodium azide 2,3- Aziridine-maleic anhydride

Equation (1): Preparation of the hetero-cyclic monomer.

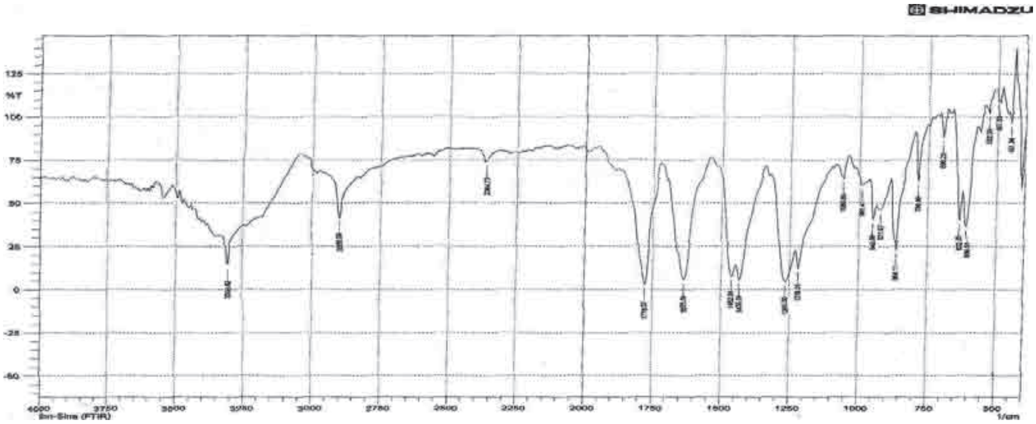
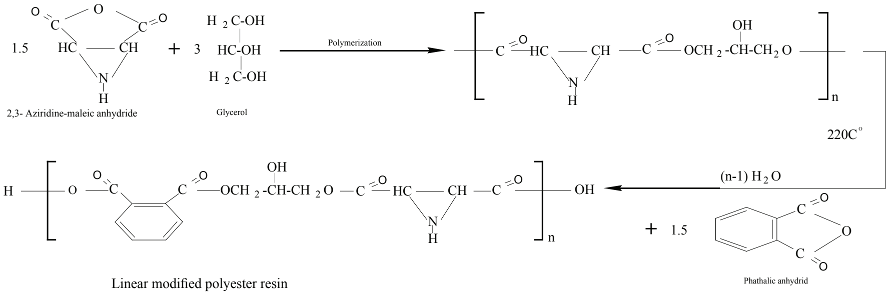


Fig. (1): The FT-IR spectrum of the prepared monomer.

Table (1): Physical properties of the modified resins after the addition of vinyl monomer.

Physical properties	Values
Molecular Weight ($\overline{Mn}$)	Around 2100 (gm/mole)
Solid content	46 %
Viscosity	17 poise
Gel time	13 min. at 25 ^{o}C
Acid Value	27
Density	1. 2 (gm/cm^3)



Equation (2): Preparation of the linear modified resin.

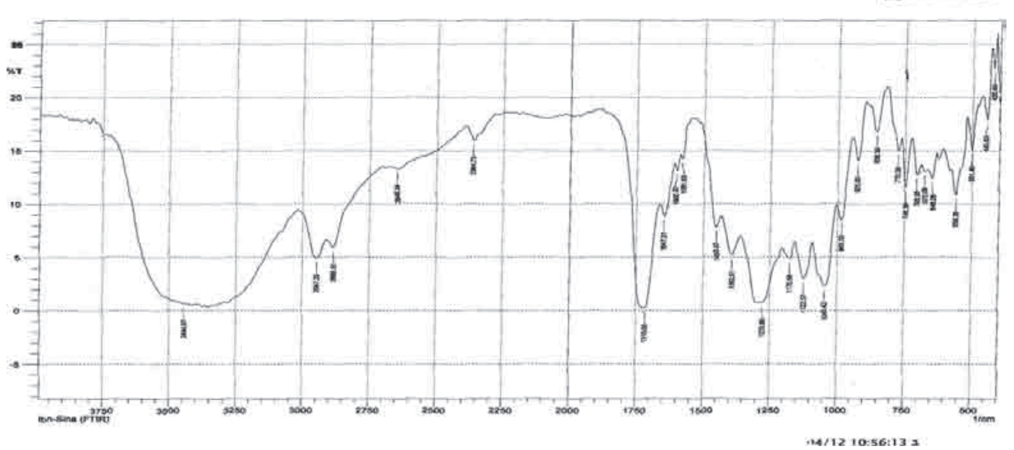


Fig. (2): The FT-IR spectrum of the linear modified resin.

Table (2): Mechanical properties of the prepared resin with additives

Type of tests	Tests of mechanical properties	Additives %					Additives
		Non	1. 0	1. 5	2. 0	2. 5	
Tensile Tests	Tensile Strength (σ_T) MPa	71	67	63	59. 6	53. 4	I
		71	65	61	57	52	II
		71	62. 7	57	54	49. 6	III
		71	60	55	50. 4	46	IV
		71	58. 4	53. 7	49	44. 8	V
	Young Modulus (E) GPa	3. 32	2. 97	2. 53	2. 39	1. 97	I
		3. 32	2. 75	2. 29	2. 10	1. 71	II
		3. 32	3. 52	2. 06	1. 85	1. 53	III
		3. 32	2. 36	1. 81	1. 64	1. 26	IV
		3. 32	2. 18	1. 59	1. 42	1. 05	V
Flexural Tests	Flexural strength (S_F) MPa	125	120. 6	115. 8	110. 3	106	I
		125	117	112	107	104	II
		125	114. 6	108. 9	105	101. 8	III
		125	112	106	102. 7	98. 1	IV
		125	109. 7	103. 7	99. 5	96	V
	Flexural Modulus (E_F) GPa	3. 19	2. 83	2. 35	1. 94	1. 47	I
		3. 19	2. 61	2. 14	1. 69	1. 22	II
		3. 19	2. 39	1. 86	1. 44	1. 05	III
		3. 19	2. 15	1. 64	1. 26	0. 82	IV
		3. 19	1. 87	1. 38	1. 02	0. 64	V

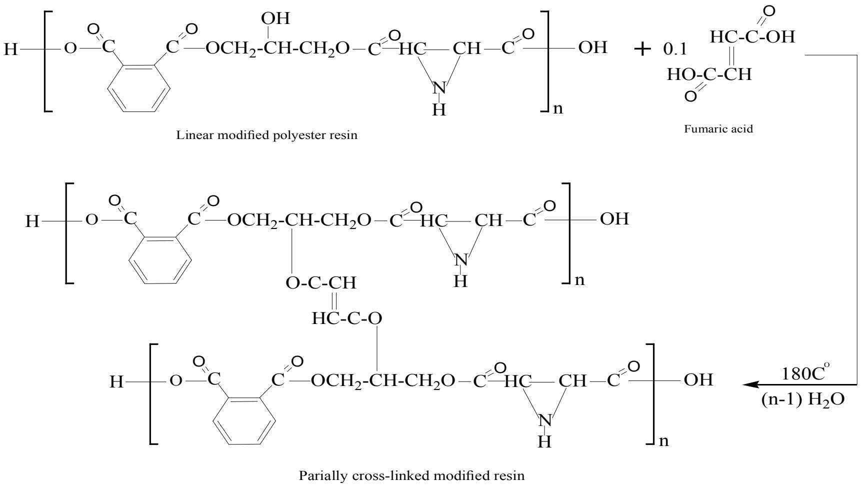
cm^{-1} for asymmetric and symmetric stretching vibrations of (CH) aliphatic, at (1716) cm^{-1} for υ (C=O) ester group, at (1643) cm^{-1} for υ (NH) group, and at (1581) cm^{-1} for υ (C=C) aromatic. The negative test of $NaHCO_3$ solution proves that the prepared modified polyester resin does not contain any un-reacted anhydride.

c. Preparation of Partially cross-linked modified resin [19]

(154. 5 gm, 0. 5 mole) from the linear resin, was prepared in (b), and mixed with (11.6 gm, 0.1 mole) from Fumaric acid in a 500 ml three-necked flask equipped with a mechanical stirrer and a thermometer, with stirred and warmed carefully with an electric heating mantle to (180 ^{o}C), under reflux and about (20 ml) of toluene was then added carefully through the condenser, and the heating was stopped after 1hr., until no more water came off. The flask was allowed to cool to (80 ^{o}C), and about (1.36×10^{-3} mole)

from Hydroquinone, and Cobalt Octoate (6%) as accelerator, were added with stirred. The flask was allowed to cool down approximately (35 ^{o}C), and added (216 gm, 2.08 mole) from Styrene monomer to the partially cross- linked modified resin and stirred for half hours until pourable syrup was formed. The viscosity and density of the prepared resins were calculated using, Brookfild digital viscometer instrument and Hydrometer instrument respectively, and the average number molecular weight ($\overline{Mn}$) was determined using the end group analysis method [20]. Equation (3), represents that reaction and Fig.(3), showed the FT-IR spectrum of the partially cross-linked modified resin; this chart appeared, the following bands: at (3437) cm^{-1} due to the overlapping between υ (N-H) cyclic, υ (O-H) group and υ (CH) aromatic, at (2943-2889) cm^{-1} for asymmetric and symmetric stretching vibration of (CH) aliphatic, at (1721) cm^{-1} for υ (C=O) ester group, at (1630) cm^{-1} for υ (NH) group, at (1578) cm^{-1} for υ (C=C) aromatic and at (1121) cm^{-1} for υ (C- O) ester.

The negative test of $NaHCO_3$ solution proves that the prepared modified polyester resin don't contain any un-reacted Fumaric acid, and Table (3), represents the physical properties measured of the prepared modified resin after addition of Styrene monomer. The addition of certain Molar percentage of Fumaric acid to the modified resin, this acid is linked by esterification process with two sets of hydroxyl dangling in two series of parallel polymer to formed a bridge between these two chains and the Fumaric acid containing double bond, this bond great benefit in cross linking with styrene monomer to formed the curing polymer, the formation of this bridge leads to reduce the number of hydroxyl groups in the polymer chains and this was confirmed by test of hydroxyl groups analysis. Using hydroxyl group analysis to determined the percentage of hydroxyl content of partially cross linked modified resin, by using, ASTM: D-2849. This standard test depends on two types of reaction (acetylation and phthalation) reactions; That test showed the percentage of hydroxyl content were decreasing from 218. 406%, to 48. 049%, with addition of the Fumaric acid to formed partially cross-linked modified resin.



Equation (3): The partially cross-linked modified resin.

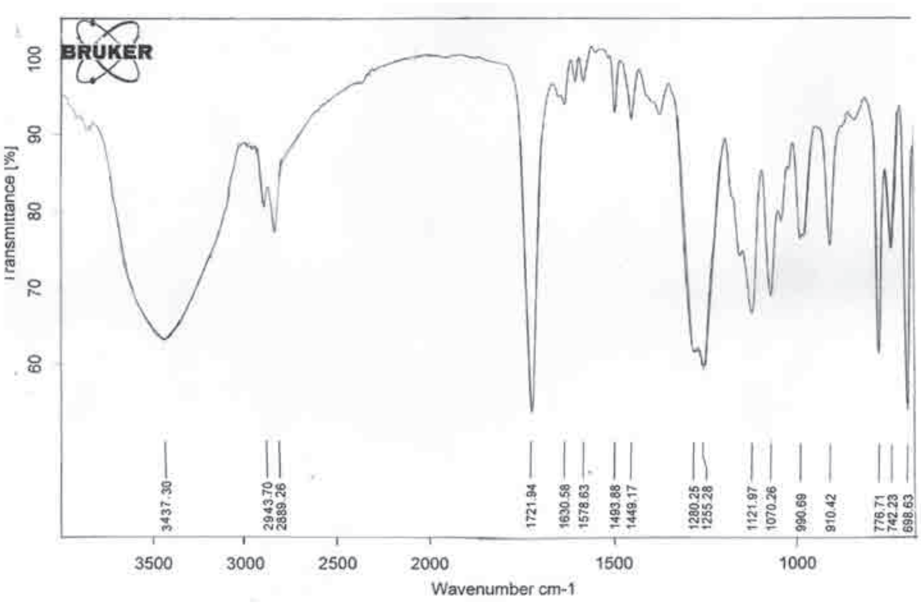


Fig. (3): The FT-IR spectrum of the partially cross- linked modified resin.

Table (3): The limiting Oxygen Index (LOI) of the partially modified resin with additives

% Additives	(LOI)				
	Non	1. 0	1. 5	2. 0	2. 5
I	20. 7	22. 65	23. 34	24. 03	24. 77
II	20. 7	22. 78	23. 63	24. 40	25. 32
III	20. 7	22. 95	23. 76	24. 56	25. 67
IV	20. 7	23. 14	24. 28	25. 32	26. 56
V	20. 7	23. 49	24. 75	26. 01	26. 83

2. 5. Preparation of polymeric specimens

The specimens of polymeric material containing additives, were prepared in dimensions (20 x 20 x 0. 5) cm; Two sheets were prepared from each percentage weight (1. 0, 1. 5, 2. 0 and 2. 5 %), of flame retardant materials (as additives) and using Methylethy lketone peroxide (MEKP) as a hardener. These sheets were cut as a samples according to ASTM standard were used in this study.

3. Results and Discussion:

3. 1. Mechanical Properties

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-bone chains [21, 23].

Table (2), listed the values of Young Modulus and the maximum stress (Tensile strength) the values of Bending Modulus and the maximum stress (Flexural strength) for partially cross linked modified resin with percentages (1. 0, 1. 5, 2. 0 and 2. 5 %) of additives; these results indicated that, increased in the percentages of additives will be decreased the behavior of mechanical properties of composite resin. This is attributed to the fact, when a stress is applied on the composite material, it will distribute on each of the matrix [24].

The result of tests obtain that, the behavior of the mechanical properties increased with increasing the percentage of additives [25]. The failure of the material under the mechanical tests, may result from the effect of stress of tensile strength, and shear together, in which the cracks appear in the positions of defects in which the stresses are concentrated, then, these cracks rapidly propagate after occurring the simple fracture [26, 27]. The results of mechanical properties tests for resin containing different weight percentage of additives, shown that the mentioned additives would lead to lower values. This reduction in the values of mechanical properties is attributed to influence of these additives on matrix, because the hard particles placed in brittle material lead to stress concentration in adjacent matrix [28]. Fig. (4), showed the stress-strain curve of prepared resin containing different percentage of additives, and Fig.(5), showed the stress-deflection curve of prepared resin containing different percentage of additives; these curves improved that behavior of mechanical properties of partially cross linked modified resin.

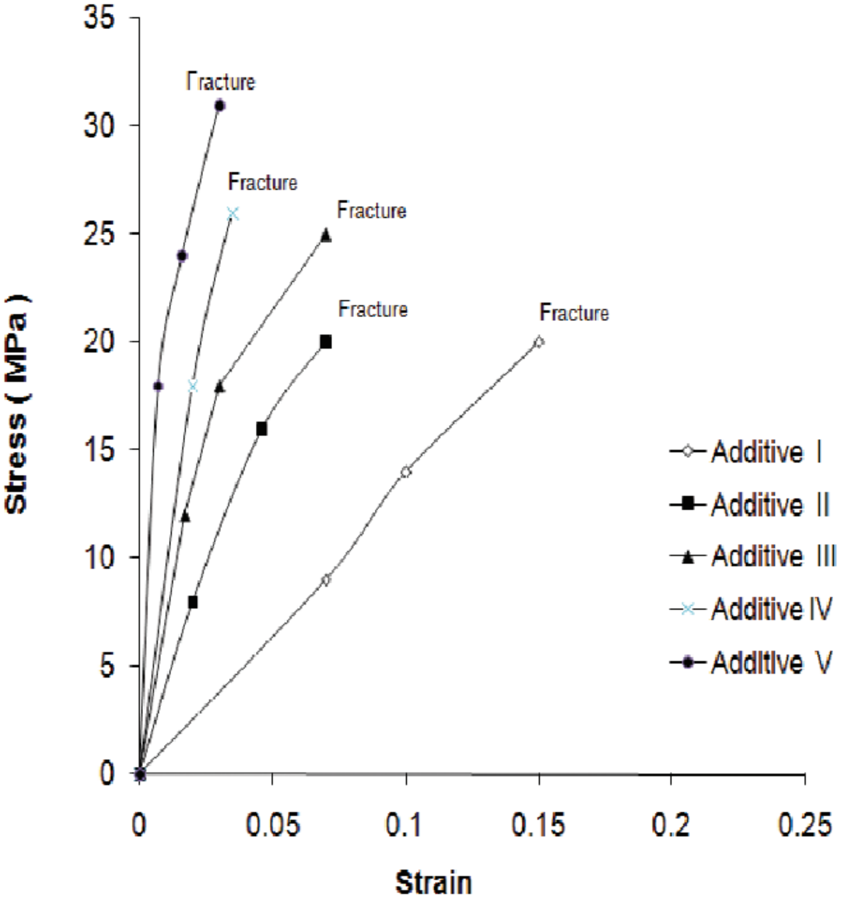


Fig. (4): Stress-strain curve of the prepared resin with additives.

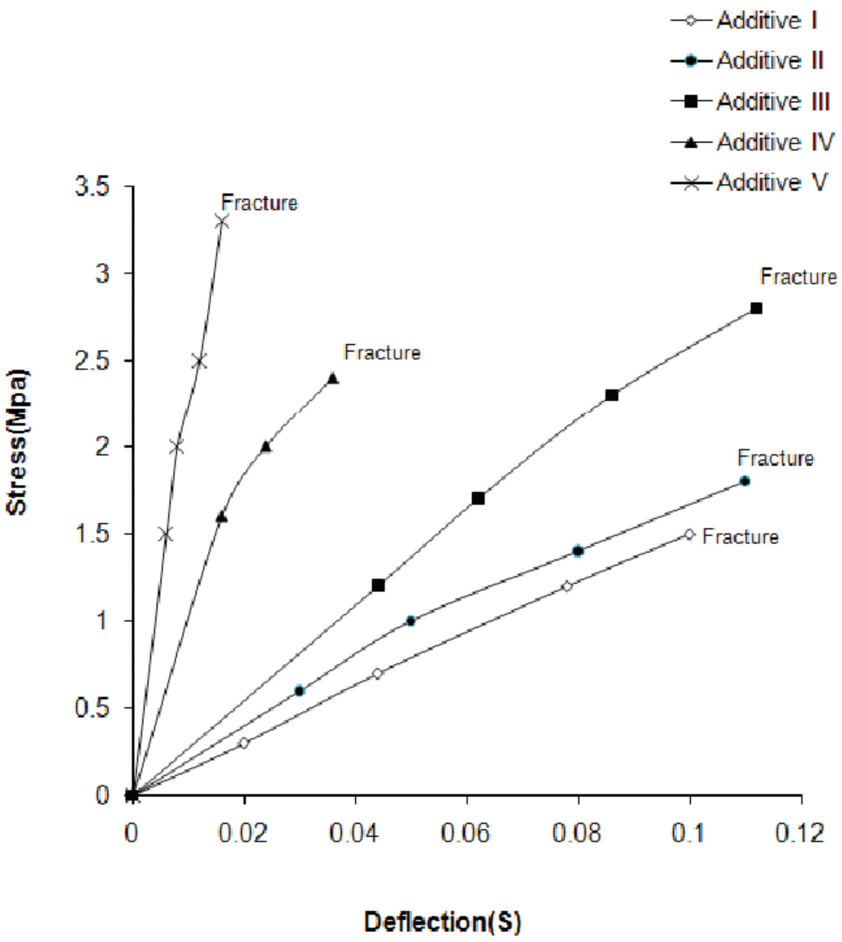


Fig. (5): Stress-deflection curve of the prepared resin with additives.

3. 2. Flammability Tests

Thermosetting polymer such as polyesters and epoxides, are generally less flammable than thermoplastic polymers, because of the difficulty of formed volatile flammable gases from highly cross-linked structures of the former and their greater tendency to the thermolze to the difficulty flammable char [29].

Table (3), listed the values of the limiting oxygen index (LOI), for partially cross linked modified resin with percentages (1.0, 1.5, 2.0 and 2.5%) of additives and Fig.(6), showed the behavior of reduced the flame. The oxygen concentration required to support a candle – like of prepared resin specimen was increased with increasing the weight percentages of additives. The efficiency of I, II, III, IV and V additives in the following order:

V > IV > III > II > I

The results obtained from that Table indicated that, the high efficiency of additive V (synergistically additive), in the weight percentage 1.5%, and decreased that effect (very weak efficiency) of additive I, in the weight percentage 1.0%; these results can be explained due to, presence of phosphor, nitrogen and chlorine elements in their structure, which have high effect on retard combustion. The free radicals were form from decomposition of material ($P^{\cdot}$, $N^{\cdot}$ and $Cl^{\cdot}$), will reacted rapidly with the free radicals of flame

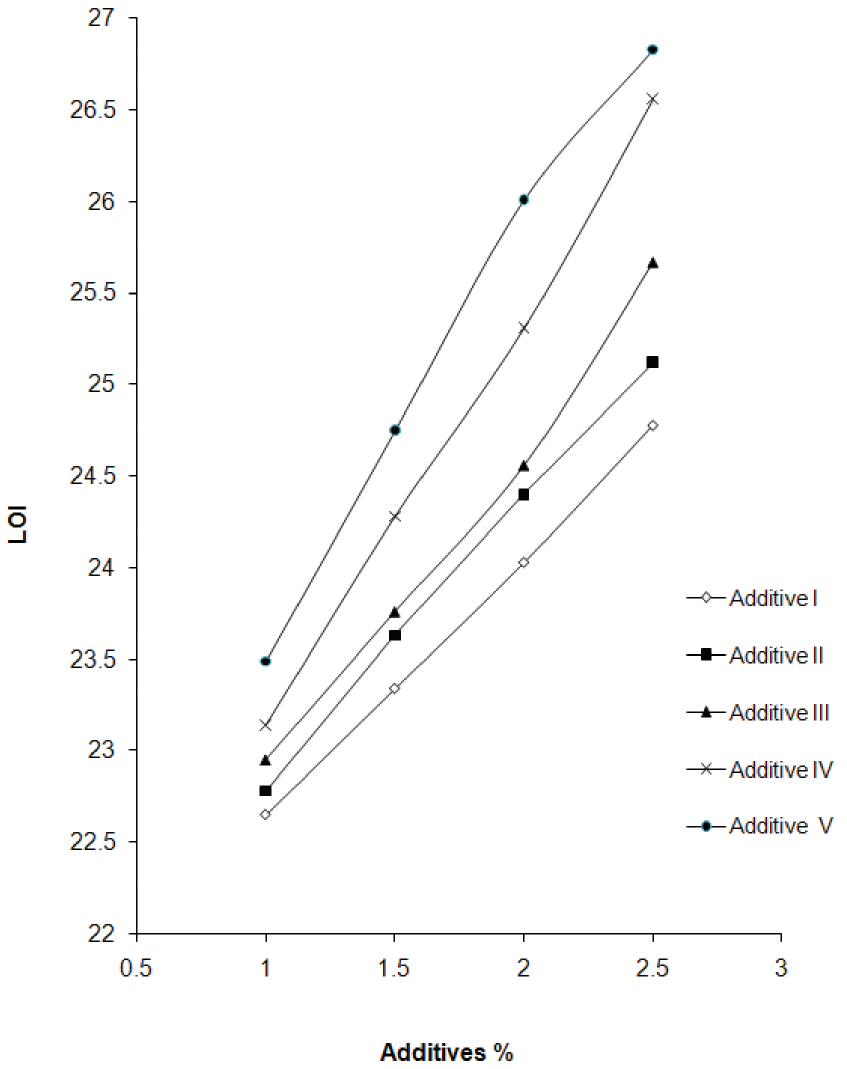


Fig. (6): Limiting oxygen index (LOI) of the prepared resin with additives.

chain, such as ($H^{\cdot}$, $O^{\cdot}$, $^{\cdot}OOH$, …, etc.) to form inert compounds like (HPO, NH_4, …, etc.) and work on inhibition 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 flammable. The char will form as a result from the thermal decomposition of the specimen, it covered the polymer roof.

The rate of burning (R.B) of the with the additives has a continuous reduction with increasing the weight percentage of additives (inversely proportional), as in Table (4), listed the values of the rate of burning (R.B.), for partially cross linked modified resin with percentages (1.0, 1.5, 2.0 and 2.5%) of additives. Fig. (7), showed the flame speed curves of flame retardation for partially cross linked modified resin with additives. This results indicated that, the additive V has high efficiency on self-extinguishing (S.E) of prepared resin, especially in weight percentage 1.5% and Non-burning (N.B) occurring in percentage 2.0%.

Table (4): The rate of burning (R. B) of the prepared resin with additives

Additives % Test	Non	1. 0	1. 5	2. 0	2. 5	Additives
AEB (cm)	10. 0	9. 3	8. 7	8. 3	5. 6	I
	10. 0	8. 5	8. 0	7. 5	4. 4	II
	10. 0	8. 1	7. 4	6. 2	-	III
	10. 0	7. 5	6. 8	5. 6	-	IV
	10. 0	7. 0	6. 4	-	-	V
ATB (Min.)	7. 35	8. 23	8. 53	9. 76	10. 37	I
	7. 35	7. 80	8. 42	9. 38	9. 17	II
	7. 35	7. 71	9. 14	8. 61	-	III
	7. 35	7. 14	8. 83	11. 20	-	IV
	7. 35	7. 70	10. 34	-	-	V
R. B (Cm/Min.)	1. 36	1. 13	1. 02	0. 85	0. 54	I
	1. 36	1. 09	0. 95	0. 80	0. 48	II
	1. 36	1. 05	0. 81	0. 72	-	III
	1. 36	1. 01	0. 77	0. 50	-	IV
	1. 36	0. 91	0. 58	-	-	V
S. E	-	-	-	yes	yes	I
	-	-	-	yes	yes	II
	-	-	yes	yes	yes	III
	-	-	yes	yes	yes	IV
	-	-	yes	yes	yes	V
N. B	-	-	-	-	-	I
	-	-	-	-	-	II
	-	-	-	-	yes	III
	-	-	-	-	yes	IV
	-	-	-	yes	yes	V

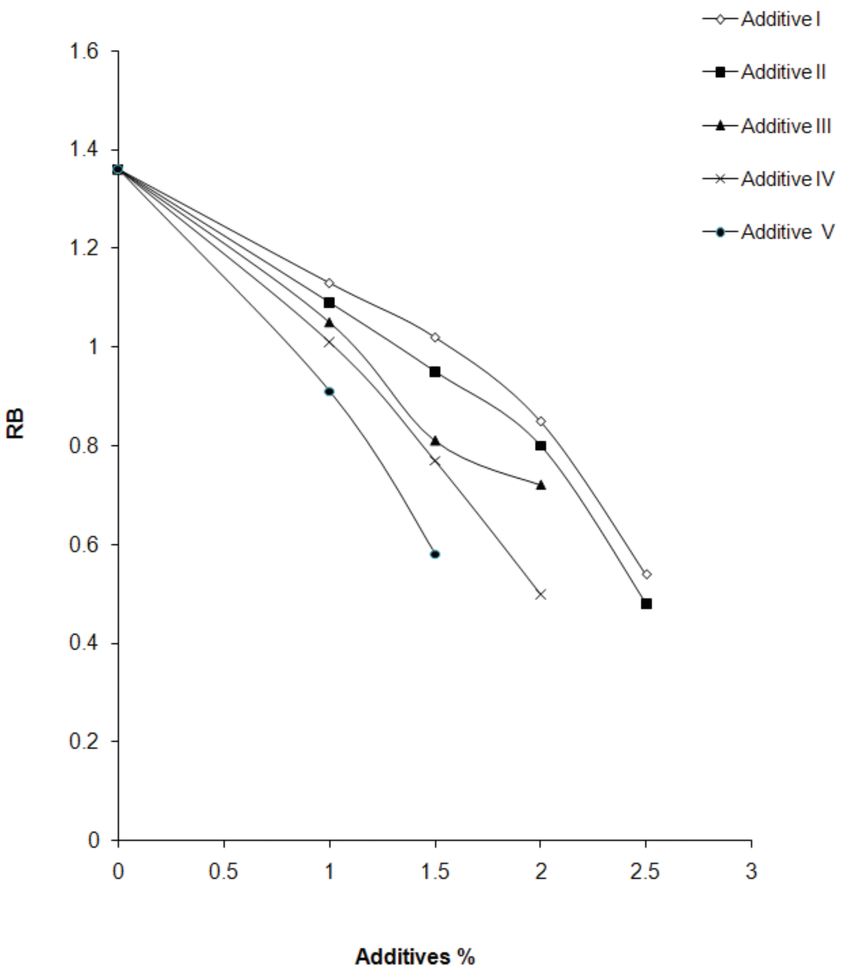


Fig. (7): Rate of burning (R. B.) of the prepared resin with additives.

Conclusions

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

1. The efficiency of the flame retardation for additives was in the following order:

   V >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 V has high effect on retard combustion for the composite, but it reduces the mechanical properties.

4. Additive I showed low effect on retard combustion for the composite, and it showed little effect on the values of mechanical properties comparing with additive V.

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