Synthesis a novel Schiff base and Chalcone derivatives compounds and using as flame retardant for unsaturated polyester and epoxy resins

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**Keyword:** Flame retardant; Flammability; Polyester resin; Unsaturated polyester resin; Epoxy resin; Schiff base; Chalcones; shiff base derivatives; chalcone derivatives.

Abstract

In this work, seven additives were used to reduced the flammability, namely:(1- (4-hydroxy-3-methoxyphenyl)-3-(2-hydroxy-5-(6-nitrobenzothiazoldiazenyl)phenyl)prop-2-en-1-one)(Add. I), (3-(2-hydroxy-5-(6-nitrobenzothiazoldiazenyl)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one)(Add. II), (3-(2-hydroxy-5-(6-nitrobenzothiazoldiazenyl)phenyl)-1-(4-methoxyphenyl)prop-2-en-1-one)(Add. III), 2-((2-hydroxy-4-methyl phenyl)limino)methyl)-4-(6-nitrobenzothiazoldiazenyl)phenol(Add. IV), 2-(6-methyl pyridin-2-yl)limino)methyl)-4-(6-nitrobenzothiazoldiazenyl)phenol(Add. V) and 2-(4-chlo rophenyl)limino)methyl)-4-(6-nitrobenzothiazol-2-yldiazenyl)phenol (Add. VI).

The effects of these additives on flammability of some types of the thermosetting polymers (unsaturated polyester and epoxy resins), have been studied. Sheets of the specimens (resins with different weight percentages of additives), in dimensions (150×150×3) mm were prepared. Two standard test methods used to measure the flame retardation which are: (ASTM: D-2863) and (ASTM: D-635).

Results are obtained from these tests indicated that, additive (Add. VI) has high efficiency as flame retardant, self–extinguishing (S.E.) at the percentage (0.1%) for unsaturated polyester and the epoxy resins. Also self- extinguishing (S.E.) at the percentage (0.1%) for additives (Add. I), (Add. IV) and (Add. V), in unsaturated polyester resin and non-burning occurs in (0.15%) with Additive (Add.VI) and (Add. V) in unsaturated polyester resin but it is occur in (0.2%) with additives (Add. VI) and (Add. V) in epoxy resin.

Introduction

The history of all polymer materials was traced by the success of their applications in replacing tradition materials like wood, leather and metals [1]. The rapidly expansion of combustion in courage many researches to used many additives to retard flammability of the polymers [3]; A large number of synthetic polymeric materials were used 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\cite{3,4}. Flame retardants are used to reduce flammability of polymeric materials, these chemical compounds are capable of imparting flame resistance to the materials and they can be classified into two general types\cite{5}, those which do not react chemically with the polymer and the other type which are those incorporated chemically in to the basic polymer structure. A good flame-retardant additive must meet following requirements\cite{6,7}, thermally stable up to the processing temperature of the polymer and stable to light, not interact with main chain of the polymer, should not be poisonous and should not inversely affect physical properties of polymer. Many inorganic compounds\cite{8,9}, were used as flame retardants, such as antimony, phosphorus and halogen compounds, but organic compounds were not used as flame retardants because they needed certain preparation conditions and their high efficacy was discouraged inhibition. In this work, the effectiveness of some organic aromatic shiff bases and chalcones compounds was studded.

Experimental part
1-Materials
A- All chemicals were used in this work analytical grade.
B- Preparation of flame-retardant additives

1- Preparation of (Add. I)\cite{10,11}

\(1-(4-hydroxy-3-methoxyphenyl)-3-(2-hydroxy-5-(6-nitrobenzodiazol diazenyl)phenyl)prop-2-en-1-one\)

This derivative was prepared by condensation (2.58 g, 0.006 mol.) of azo compound with(0.99g, 0.004mol.) of (4-hydroxy-3-methoxyacetophenone) in a 100 ml of round bottom flask by dissolved then it in 50 ml ethanol and stirred for 20 min.; A 10% sodium hydroxide solution was gradually added to the droplet for 2-3 min. under continuous stirring. The mixture was refluxed for 16 hr. and pH was equal to 7 by adding 10 ml of concentrated hydrochloric acid. The product was filtered and washed with distilled water and re-crystallization from ethanol. The reaction process was followed using TLC technique.

2- Preparation of (Add. II)\cite{10,11}

\(3-(2-hydroxy-5-(6-nitrobenzotiazoldiazylphenyl)phenyl)-1-(4-hydroxy phenyl)prop-2-en-1-one\)

This derivative was prepared by condensation (2.58 g, 0.006 mol.) of azo compound with(0.54g, 0.004mol.) of (4-hydroxy acetophenone) in a 100 ml of round bottom flask by dissolved then it in 50 ml ethanol and stirred for 20 min.; A 10% sodium hydroxide solution was gradually added to the droplet for 2-3 min. under continuous stirring. The mixture was refluxed for 16 hr. and pH was equal to 7 by adding 10 ml of concentrated hydrochloric acid (37 % M). The product was filtered and washed with distilled water and re-crystallization from ethanol. The reaction process was followed using TLC technique.

3- Preparation of (Add. III)\cite{10,11}

\(3-(2-hydroxy-5-(6-nitrobenzothiazoldiazylphenyl) phenyl)-1-(4-methoxy phenyl)prop-2-en-1-one\)

This derivative was prepared by condensation (2.58 g, 0.006 mol.) of azo compound with(0.6g, 0.004 mol.) of (4-methoxyacetophenone) in a 100 ml of round bottom flask by dissolved then it in 50 ml ethanol and stirred for 20 min.; A 10% sodium hydroxide solution was gradually added to the droplet for 2-3 min. under continuous stirring. The mixture was refluxed for 16 hr. and pH was equal to 7 by
adding 10 ml of concentrated hydrochloric acid. The product was filtered and washed with distilled water and re-crystallization from ethanol. The reaction process was followed using TLC technique.

4- Preparation of (Add. IV) \[12, 13\]

\[
2-((2\text{-hydroxy-4-methylphenyl})\text{imino})\text{methyl})-4-(6\text{-nitrobenzo thiazol diazenyl})\text{phenol}
\]

The derivative (Add. IV) was prepared by condensation of azo compound by dissolving (2.95 g, 0.009 mol.) in 20 ml of absolute ethanol in a round flask 100 ml and stirred for 10 min.. A solution of (0.42 g, 0.004 mol.) from 2- amino-5- methyl phenol which dissolved in 15 ml of ethanol was added and mixed, then added 3 drops from glacial acetic acid to solution that formed which be dark color after several minutes from stirring and leaving the reaction to 3 hr. with continues stirring. The reaction process was followed using TLC technique and kept the product 24 hr. then re-crystallize by using ethanol.

5- Preparation of (Add. V) \[12, 13\]

\[
4\text{-6-methylbenzothiazol-2-yl)diazenyl)-2-2-hydroxy-5-methylphenyl)imino})\text{methyl)phenol}
\]

The derivative(Add. V) was prepared by condensation of azo compound by dissolving (2.95 g, 0.009mol.) in 20 ml of absolute ethanol in a round flask (100 ml) and stirred for 10 min. A solution of (0.69 g, 0.004 mol.) from 2- amino-6- methyl pyridine which dissolved in 15 ml of ethanol was added and mixed, then added 3 drops from glacial acetic acid to solution that formed which be dark color after several minutes from stirring and leaving the reaction to 3 hr. with continues stirring. The reaction process was followed using TLC technique and kept the product 24 hr. then re-crystallize by using ethanol.

6- Preparation of (Add. VI) \[12, 13\]

\[
2-(4\text{-chlorophenyl})\text{imino})\text{methyl)-4-(6-nitrobenzothiazol-2-yl)diazenyl})\text{phenol}
\]

The derivative(Add. VI) was prepared by condensation of azo compound by dissolving (2.95 g, 0.009mol.) in 20 ml of absolute ethanol in a round flask (100 ml) and stirred for 10 min.. A solution of (0.51 g, 0.004 mol.) from 4-chloro aniline which dissolved in 15 ml of ethanol was added and mixed, then added 3 drops from glacial acetic acid to solution that formed which be dark color after several minutes from stirring and leaving the reaction to 3 hr. with continues stirring. The reaction process was followed using TLC technique and kept the product 24 hr. then re-crystallize by using ethanol.

C. Polymers

1-Unsaturated polyester resin, hardener type (MEKP), imported from United Arab Emirate (U.A.E).

2-Epoxy resin, type (CY223), hardener type (HY 956), imported from Ciba-Geigy Co.

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. ) \[15\].
3- Preparation of polymeric specimens

The specimens of polymeric material containing additives were prepared in dimensions (150×150×3) mm; three sheets were prepared from each percentage weight (0.1, 0.15, 0.2, 0.25 & 0.3 %); of flame retardant materials (as additives) and using the hardener for each resin. These sheets were cut as samples according to ASTM standard were used in this work.

Results and Discussion

1- Preparation of (Add. I); Figure(1), The spectrum of the FT-IR of the derivative (Add. I); showed, the band appearance at (3381) cm⁻¹ to the stretching (OH), the band at (3099) cm⁻¹ belong to the stretching (=CH )aromatic in the ring, the band at frequency (1658) cm⁻¹ is due to (C=O) ketone, and the band at (1290) cm⁻¹ indicates the presence of amine (C-N) and the frequency band at (1655) cm⁻¹ of the (C=N), we also note that there are two band due to the presence of the azo group at (1519, 1575) cm⁻¹.

Figure (2), The spectrum of 'H-NMR of the derivative (Add. I); showed, Singlet at (10.6, 10.4) ppm is belong to the proton of phenolic hydroxyl to two group of the ring, the other single signal at displacement (3.3) ppm belong to the proton in the (OCH₃) group, and two double signal at the displacement (6.86, 6.87) ppm of the alkenes group (CH=CH), and another multiple signal at (7.3-8.6) ppm of the protons aromatic group. The spectrum of ¹³C-NMR of the derivative(Add. I); showed, Figure (3); Signals at (201) ppm belong to C16, signal at (60) ppm belong to C23 and signal at (177) ppm belong to C1, signal also at displacement (163) ppm belong to C20, , signal also at displacement (157) ppm belong to C11, signal also at displacement (152) ppm belong to C5, signal also at displacement (145) ppm belong to C2,signal also at displacement (136) ppm belong to C7, signals at displacement at (116,120,121,122,127,128,133) ppm belong to aromatic carbon. Equation (1), represent this reaction.

2- Preparation of (Add. II); Figure (4), the spectrum of the FT-IR of the derivative (Add. II); showed; The band appearance at (3456) cm⁻¹ to the stretching (OH), the band at (3062) cm⁻¹ belong to the stretching(=CH )aromatic in the ring, the band at frequency (1668) cm⁻¹ is due to (C=O) ketone, and the band at (1296) cm⁻¹ indicates the presence of amine (C-N) and the frequency band at (1650) cm⁻¹ of the (C=N), the frequency band at (1456) cm⁻¹ of the (NO₂); we also note that band due to the presence of the azo group at (1450) cm⁻¹. Figure (5), the spectrum of "H-NMR of the derivative (Add. II); showed, Single signal at (10.58, 11.07) ppm is belong to the proton of phenolic hydroxyl to two group of the ring, the other single at the displacement (7, 7.02) ppm of the alkenes group (CH=CH), and another multiple signal at (7.3-8.6) ppm of the protons aromatic group. The spectrum of ¹³CNMR of the derivative (Add. II); showed Figure (6); Signals at (196) ppm belong to C16, signal at (171) ppm belong to C1 and signal at (163) ppm belong to C20, signal also at displacement (158) ppm belong to C11, signal at (140) ppm belong to C5, signal at (131) ppm belong to C2, signal at (130) ppm belong to C7 signals at displacement at (113,116,117,121,129) ppm belong to aromatic carbon. Equation (2), represent this reaction.

3- Preparation of (Add. III); Figure (7), the spectrum of the FT-IR of the derivative (Add. III) showed, the band appearance at (3452) cm⁻¹ to the stretching (OH), the band at (3062) cm⁻¹ belong to the stretching(=CH )aromatic in the ring, the band at frequency (1678) cm⁻¹ is due to (C=O) ketone, and the band at (1257) cm⁻¹ indicates
the presence of amine (C-N) and the frequency band at (1631) cm⁻¹ of the (C=N), we also note that there are band due to the presence of the azo group at (1442)cm⁻¹.

Figure (8), the spectrum of ¹H-NMR of the derivative (Add. III); showed singlet at (10.7) ppm is to the proton of phenolic hydroxyl group of the ring, the other singlet at the displacement (4.5-6.5) ppm of (C=C-H), and two doublet at displacement (7.0, 7.02) ppm belong to (CH=CH), and another multiplet at (7.2-8.01) ppm of the protons aromatic group. The spectrum of ¹³CNMR of the derivative (Add. III); showed Figure (9); signal at (21) ppm belong to C21, and signal at (159) ppm belong to C11, signal also at displacement (172.2) ppm belong to C1, and (172.3) belong to C14, signal at (141) ppm belong to C16 , signal at (132) ppm belong to C5, signal at (122) ppm belong to C5, signals at displacement at (116,117,118,120,130) ppm belong to aromatic carbon. Equation (3), represent this reaction.

4- Preparation of (Add. IV); Figure (10),The spectrum of the FT-IR of the derivative (Add. IV) showed, the band appearance at (3402) cm⁻¹ to the stretching (OH), the peak at (3078) cm⁻¹ belong to the stretching(=CH ) aromatic in the ring, and the band at (1288) cm⁻¹ indicates the presence of amine (C-N) and the frequency band at (1627) cm⁻¹ of the (C=N), the frequency band at (1527) cm⁻¹ of the (NO₂) we also note that there is band due to the presence of the azo group at (1450) cm⁻¹. Figure (11), the spectrum of ¹H-NMR of the derivative (Add. IV) showed, Singlet at (9.9) ppm is belong to the proton of hydroxyl group of the ring, the other singlet at the displacement (1.8) ppm belong to (CH₃), singlet at displacement (6.2) ppm belong to (CH=N), and another multiplet at (7.3-8.6) ppm of the protons aromatic group. The spectrum of ¹³CNMR of the derivative (Add. IV) showed, Figure (12), Signals at (21) ppm belong to C20, signal at (172) ppm belong to C1and C14, and signal at (159) ppm belong to C11, signal also at displacement (141) ppm belong to C16, signal at (132) ppm belong to C5 ,signal at (122) ppm belong to C15, signals at displacement at (116,117,118,120) ppm belong to aromatic carbon. Equation (4), represent this reaction.

5- Preparation of (Add. V); Figure (13), the spectrum of the FT-IR of the derivative (Add. V) showed; The band appearance at (3462) cm⁻¹ to the stretching (OH), the band at (3078) cm⁻¹ belong to the stretching(=CH ) aromatic in the ring, and the band at frequency (2962) cm⁻¹, and the band at (1122) cm⁻¹ indicates the presence of amine (C-N) and the frequency band at (1654) cm⁻¹ of the (C=N), we also note that there is band due to the presence of the azo group at (1492) cm⁻¹. Figure (14), the spectrum of ¹H-NMR of the derivative (Add. V); showed, a Singlet at (9.17) ppm is belong to the proton of the ring, the other singlet at the displacement (1.89) ppm belong to (CH₃), singlet at displacement (5.9) ppm belong to (CH=N) , and another multiplet at (6.2-8.6) ppm of the protons aromatic group. The spectrum of ¹³CNMR showed, Figure (15); Signal at (23) ppm belong to C20, signal at (172.4) ppm belong to C1and(172.3) belong to C14, and signal at (159.3) ppm belong to C15, signal also at displacement (159) ppm belong to C19, signal at (155) ppm belong to C5 , signal at (141) ppm belong to C11, signal at (138) ppm belong to C2, signal at (132) ppm belong to C7, signals at displacement at (105,111,117,118,122) ppm belong to aromatic carbon. Equation (5), represent this reaction.

6- Preparation of (Add. VI); Figure (16), the spectrum of the FT-IR of this derivative showed, the band appearance at (3408) cm⁻¹ to the stretching (OH), the band at (3091) cm⁻¹ belong to the stretching(=CH ) aromatic in the ring, and the band at (1288) cm⁻¹ indicates the presence of amine (C-N), the band at (750) cm⁻¹ belong to
the (C-Cl), and the frequency band at (1620) cm\(^{-1}\) of the (C=N), we also note that there is band due to the presence of the azo group at (1492) cm\(^{-1}\). **Figure (17),** The spectrum of \(^1\)H-NMR showed, a signal at (11.3) ppm is belong to the proton of phenolic hydroxyl group of the ring, the other singlet at the displacement (1.9) ppm belong to (CH\(_3\)) and another multiple signal at (6.6-8.6) ppm of the protons aromatic group. **Figure (18),** the spectrum of \(^{13}\)CNMR showed, Signal at (21) ppm belong to C18, signal at (141) ppm belong to C11and (159) belong to C15, and signal at (172.2) ppm belong to C14, and (172.4) belong to C1 signals at displacement at (116, 117, 118, 120, 122, 123, 124, 133) ppm belong to aromatic carbon. **Equation (6),** represent this reaction. **Table (1)** showed the physical properties of synthesis compounds.

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

The limiting oxygen Index (LOI) for unsaturated polyester resin without additives is (20.6)\[^{16}\] and for epoxy resin without additives is (19.54)\[^{17}\]; **Tables (2&3) and Figures (19&20)** respectively, indicated that, Oxygen concentration required to support a candle–like in unsaturated polyester and epoxy resins samples were increased with increasing the weight percentage of additives. The efficiency of additives studied was in the following order:

\[ \text{VI} > \text{V} > \text{IV} > \text{I} > \text{III} > \text{II} \]

3-Measurement of rate of burning (R.B) using ASTM: D-635:

The rate of burning (R.B) for unsaturated polyester resin without additives is (1.44)\[^{16}\] and for epoxy resin without additives is (1.95)\[^{19}\]; Results obtained from these tests showed that the rate of burning (R.B) of these resins with additives are of inversely proportional with the percentage weight of additives, as indicated in **Tables (4&5), Figures (21&22)** respectively, showed the flame speed curves of flame retardation for the resins. The results obtained from these measurements correspond to the results obtained from the limiting oxygen index measurements. The efficiency of additives studied was in the following order:

\[ \text{VI} > \text{V} > \text{IV} > \text{I} > \text{III} > \text{II} \]

Conclusion

The results obtained can be summarized that, the limiting oxygen index (LOI) increased with increasing the weight percentages of the additives, as well as, the rate of burning (R.B), decreased with increasing the weight percentages of the additives. The flame retarding efficiency of the additives has the following order:

\[ \text{VI} > \text{V} > \text{IV} > \text{I} > \text{III} > \text{II} \]

Apparently, the action of these additives due to by the formation of char as result of removing the hydrogen atoms from the polymer chain with formed the inert compounds. Finally, the combustion products like; free radicals, char…etc., will form allayer to prevent burning and displacing oxygen that help continues burning of polymers.

The results showed that shiff base rules were better than chalcone in inhibition of flame of resins and using relatively low percentages compared to inorganic additives were used in previous research.
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\[
\begin{align*}
\text{Equation (1): Synthesis of additive I (Chalcone)}
\end{align*}
\]

\[
\begin{align*}
\text{Equation (2): Synthesis of additive II (Chalcone)}
\end{align*}
\]
Equation (3): Synthesis of additive III (Chalcone)

$$\text{p-methoxyacetophenone} \quad \xrightarrow{\text{Ethanol refluxing for 8-16 hr. NaOH / heating 35 C}} \quad 3 \text{ C}$$

Equation (4): Synthesis of additive IV (shiff base)

$$\text{C} \quad \xrightarrow{\text{refluxing for 3 hr. CH3COOH}} \quad 4 \text{ C}$$

Equation (5): Synthesis of additive V (shiff base)

$$\text{C} \quad \xrightarrow{\text{refluxing for 3 hr. CH3COOH}} \quad 4 \text{ C}$$

Equation (6): Synthesis of additive VI (shiff base)

Table (1): Physical properties of synthesis compound

| No. | Compound | M.wt g.mol⁻¹ | m.p °C | Yield % | Color          | R_f |
|-----|----------|--------------|-------|---------|----------------|-----|
| 1   | I        | 476.08       | 158   | 76      | Dark brown     | 0.5 |
| 2   | II       | 446.07       | 194   | 75      | Dark brown     | 0.6 |
| 3   | III      | 433.08       | 149   | 74      | Dark brown     | 0.3 |
| 4   | IV       | 433.44       | 196   | 80      | Dark brown     | 0.5 |
| 5   | V        | 418.38       | 150   | 91      | Dark brown     | 0.4 |
| 6   | VI       | 437.86       | 153   | 86      | Dark green     | 0.4 |

Table (2): (LOI) for unsaturated polyester resin with additives

| Additives | LOI %   |
|-----------|---------|
|           | Non  0.1 | 0.15 0.2 | 0.25 0.3 |
| I         | 20.60    | 22.34 23.05 | 23.85 24.55 | 25.00 |
| II        | 20.60    | 21.74 22.63 | 23.10 23.71 | 24.25 |
| III       | 20.60    | 21.89 22.72 | 23.27 23.88 | 24.36 |
| IV        | 20.60    | 23.32 24.11 | 24.87 25.68 | 25.93 |
| V         | 20.60    | 23.63 24.48 | 25.38 26.15 | 26.67 |
| VI        | 20.60    | 23.88 24.74 | 25.74 26.86 | 27.25 |
Table (3): (LOI) for epoxy resin with additives

| Additives | LOI | LOI % |
|-----------|-----|-------|
| Non       | 0.1 | 0.15  |
| I         | 19.54 | 21.62 |
| II        | 19.54 | 21.76 |
| III       | 19.54 | 21.21 |
| IV        | 19.54 | 21.92 |
| V         | 19.54 | 22.08 |
| VI        | 19.54 | 22.33 |

Table (4): Rate of burning (R.B) for unsaturated polyester resin with additives

| Tests | Additives % | Additives |
|-------|-------------|-----------|
| Non   | 0.1 | 0.15 | 0.2 | 0.25 | 0.3 |
| AEB   | 10   | 9.3  | 8.6  | 7.1  | 5.7  | 5.0  | I  |
|       | 10   | 10   | 9.4  | 7.9  | 7.1  | I   |
|       | 10   | 10   | 8.7  | 6.6  | 5.8  | III |
|       | 10   | 8.4  | 6.8  | 5.2  | -    | IV  |
|       | 10   | 6.5  | 5.0  | -    | -    | V   |
|       | 10   | 4.7  | 2.8  | -    | -    | VI  |
| ATB   | 6.92 | 9.89 | 11.02 | 13.39 | 13.90 | 14.70 | I  |
|       | 6.92 | 7.40 | 7.87  | 7.89  | 6.99  | 6.69  | II |
|       | 6.92 | 8.62 | 9.09  | 8.87  | 7.25  | 7.07  | III |
|       | 6.92 | 9.88 | 10.79 | 12.68 | -     | -     | IV  |
|       | 6.92 | 9.56 | 11.90 | -     | -     | -     | V   |
|       | 6.92 | 13.43| 12.17 | -     | -     | -     | VI  |
| R.B   | 1.44 | 0.94 | 0.78  | 0.53  | 0.41  | 0.34  | I  |
|       | 1.44 | 1.35 | 1.27  | 1.19  | 1.13  | 1.06  | II |
|       | 1.44 | 1.16 | 1.10  | 0.98  | 0.91  | 0.82  | III |
|       | 1.44 | 0.85 | 0.63  | 0.41  | -     | -     | IV  |
|       | 1.44 | 0.68 | 0.42  | -     | -     | -     | V   |
|       | 1.44 | 0.35 | 0.23  | -     | -     | -     | VI  |
| S.E   | -    | -    | Yes   | Yes   | yes   | yes   | I  |
|       | -    | -    | -     | Yes   | yes   | I   |
|       | -    | -    | -     | -     | -     | -    |
|       | -    | yes | Yes   | yes   | yes   | yes   | IV |
|       | -    | yes | Yes   | yes   | yes   | yes   | V  |
|       | -    | yes | Yes   | yes   | yes   | yes   | VI |
| N.B   | -    | -    | -     | -     | -     | -     | I  |
|       | -    | -    | -     | -     | -     | -     | II |
|       | -    | -    | -     | -     | -     | -     | III |
|       | -    | -    | -     | yes   | yes   | IV  |
|       | -    | -    | Yes   | yes   | yes   | V   |
|       | -    | -    | Yes   | yes   | yes   | VI  |
Table (5): Rate of burning (R.B) for epoxy with additives

| Tests   | Additives | 0.1 | 0.15 | 0.2 | 0.25 | 0.3 |
|---------|-----------|-----|------|-----|------|-----|
| AEB (cm.) | Non       | 10  | 9.6  | 8.4 | 7.0  | 5.3 | 4.6 |
|         | 0.1       | 10  | 10   | 9.4 | 8.2  | 7.3 | 7.3 |
|         | 0.15      | 10  | 10   | 9.2 | 8.7  | 7.4 | 6.8 |
|         | 0.2       | 10  | 8.5  | 7.4 | 6.1  | 4.6 | 3.3 |
|         | 0.25      | 10  | 5.7  | 4.9 | 3.3  | -   | -   |
|         | 0.3       | 10  | 5.0  | 4.2 | -    | -   | -   |

| ATB (Min.) | 5.12 | 7.38 | 6.77 | 6.36 | 5.52 | 5.47 |
|            | 5.12 | 6.45 | 6.89 | 7.17 | 6.95 | 6.64 |
|            | 5.12 | 7.29 | 7.07 | 7.37 | 6.98 | 7.23 |
|            | 5.12 | 7.79 | 7.18 | 6.35 | 6.21 | 5.69 |
|            | 5.12 | 6.06 | 6.81 | 6.23 | -    | -    |
|            | 5.12 | 7.04 | 7.50 | -    | -    | -    |

| R.B. (cm./ Min.) | 1.95 | 1.30 | 1.24 | 1.10 | 0.96 | 0.84 |
|                  | 1.95 | 1.55 | 1.45 | 1.31 | 1.18 | 1.10 |
|                  | 1.95 | 1.37 | 1.30 | 1.18 | 1.06 | 0.94 |
|                  | 1.95 | 1.09 | 1.03 | 0.96 | 0.74 | 0.58 |
|                  | 1.95 | 0.94 | 0.72 | 0.53 | -    | -    |
|                  | 1.95 | 0.71 | 0.56 | -    | -    | -    |

| S.E                  | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |

| N.B                  | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |
|                      | -    | -    | -    | -    | -    | -    |

Figure (1): The FT-IR spectrum of additive I
Figure (2): The $^1$H-NMR spectrum of additive I

Figure (3): The $^{13}$C-NMR spectrum of additive I

Figure (4): The FT-IR spectrum of additive II

Figure (5): The $^1$H-NMR spectrum of additive II
Figure (6): The $^{13}$C-NMR spectrum of additive II

Figure (7): The FT-IR spectrum of additive III

Figure (8): The $^1$H-NMR spectrum of additive III

Figure (9): The $^{13}$C-NMR spectrum of additive III
Figure (10): The FT-IR spectrum of additive IV

Figure (11): The $^1$H-NMR spectrum of additive IV

Figure (12): The $^{13}$C-NMR spectrum of additive IV

Figure (13): The $^1$H-NMR spectrum of additive V

Figure (14): The $^1$H-NMR spectrum of additive V
Figure (15): The $^{13}$C-NMR spectrum of additive V

Figure (16): The FT-IR spectrum of additive VI

Figure (17): The $^1$H-NMR spectrum of additive VI

Figure (18): The $^{13}$C-NMR spectrum of additive VI
Figure (19): (LOI) for unsaturated polyester resin with additives

Figure (20): (LOI) for epoxy resin with additives

Figure (21): (R.B) for unsaturated polyester resin with additives

Figure (22): (R.B) for epoxy resin with additives