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RESEARCH ARTICLE

Studying the Effect of Some Organic Sulfur Compounds as Flame Retardants for Polyester and Epoxy Resins

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Abstract

In this work, five additives were used, namely; Pentane -2,3,4-trione3-[(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)hydrazine])(Additive I). (5-[(z)-(5,6-diphenyl-6H-1,3,4-thiadiazin-2-yl)diazenyl]-4,6dimethyl-2H-1,3-thiazin-2-amine)(AdditiveII).((4Z,6E)-6-((Z)-(5,6-diphenyl-6H-1,3,4thiadiazin-2-yl)diazenyl)-5,7-dimethyl-2,3-dihydro-1,4-thiazepine-3carboxylicacid),(Additive III). (6-[(5,6-diphenyl-6H-1,3,4-thiadiazin-2yl)diaz enyl]-5,7dimethyl-1,3,4-thiadiazepin-2-amine)(Additive IV). (2,2-(1,4-phenylene)bis(4,5-dihydro1,thiazole-4-carboxylicacid) (Additive V).The effects of these additives on flammability of unsaturated polyester and epoxy resins have been studied. Sheets of the resins with weight percentages of (0.2, 0.4, 0.6 & 0.8 %) of the additives in dimensions (150×150×3) mmwere used.Two standard test methods used to measure the flame retardation are: (ASTM: D-2863) and (ASTM: D-635).Results are obtained from these tests indicated that, additive IV has high efficiency as flame retardant, self–extinguishing (S.E.)at the percentage (0.2 %) for unsaturated polyester resin and the percentage (0.4 %) for epoxy resin. Also self- extinguishing (S.E.) at the percentage (0.4%) for additives II in unsaturated polyester resin and the (0.6%) for additives II in epoxy resin Additive V show low effect on flammability in both resins

Keywords: *Sulfur compounds; Organic sulfur compounds; Additives; Flame retardants; Flammability; Unsaturated polyester resin; Epoxy resin; Thermosetting polymer.*

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 [2].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[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 [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 [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 [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 ring sulfur compounds.

Experimental

Materials

- All chemicals were used in this work analytical grade.
- Preparation of flame-retardant materials

Additive I [10]

Preparation the mixture by dissolve (2.67gm, 0.01mol) of compound ((5,6-diphenyl-6H-1,3,4-thiadiazin-2-amine)) in 5 ml and 10 ml of distilled water, the mixture was cooled at(0-5C°) and add (0.7gm ,0.01mole) of sodium nitrate($NaNO_3$) dissolve in 10 ml of distilled water with continuous stirring. Leave the solution to settle for 15 minutes.

Then add the diazonium solution with continuous stirring to a solution of (1.00gm, 0.01mole) of

(Acetyl acetone) dissolve in 50ml of absolute ethanol and 10 ml of sodium hydroxide 10%. The solution is colored in light orange and the precipitate was formed. The left to the following day and a precipitate formed that was filtered and recrystallized from absolute ethanol, the percentage of product was (84%), as the following equation, as in equation (1).

Additive II[11]

A mixture of compound (Additive I), (0.42gm, 0.001mol), absolute ethanol (50ml), thiourea (0.07612gm, 0.001mol) with continuous stirred and was add 5ml of concentrate sulfuric acid, the mixture was reflex for (4h) under 78C^o. The mixture was cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol, the percentage of product was (79%), as in equation (2).

Additive III [12]

A mixture of compound (Additive I), (0.42gm, 0.001mol), absolute ethanol (50ml), cysteine (0.121gm, 0.001mol) with continuous stirred and was add (5ml) of concentrate sulfuric acid, the mixture was reflex for (4h) under 78C^o, the mixture was cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol, the percentage of product (80%), as in equation (3).

Additive IV [11]

A mixture of compound (Additive I) (0.42g, 0.001mol), absolute ethanol (50ml), thiosemicarbized (0.09114gm, 0.001mol) with continuous stirred and was add (5ml) of concentrate sulfuric acid, the mixture was reflex for (4h) under 78C. The mixture was cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol ,the percentage of product was (80%) , as in equation (4).

Additive V [13]

A mixture of diethylterephthalate (0.222gm, 0.001mol), absoluteethanol (100ml), cysteine (0.242gm,0.002mol) with continuous stirred and was add (5ml) of concentrate sulfuric acid, the mixture was reflex for (4h) under 78 C^o, the mixture was cooled in the ice bath and a precipitate formed that was filtered and recrystallized from absolute ethanol,the percentage of product (82%), as in equation (5).

Polymers

- Epoxy resin, type (CY223), hardener type (HY 956), imported from Ciba-Geigy Co.
- Unsaturated polyester resin, hardener type (MEKP), imported from United Arab Emirate (U.A.E).

Standard Tests

ASTM: D-2863

The measurement of limiting Oxygen Index (LOI), is widely used for measuring flammability of polymers [14].

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].

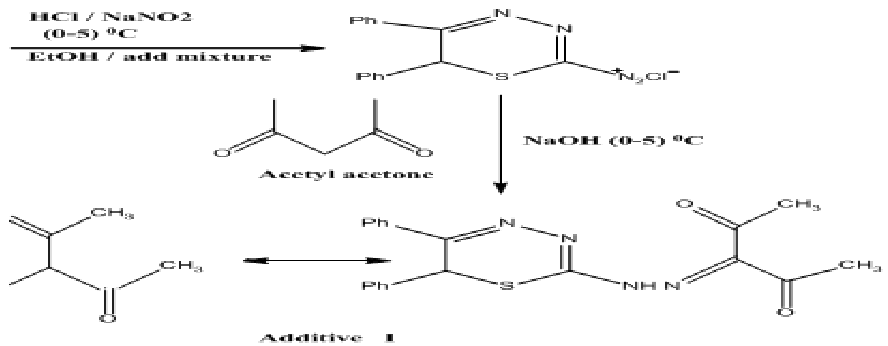
Preparation of Polymeric Specimens

The specimens of polymeric material containing additives were prepared in dimensions (150X 150X3) mm; three sheets were prepared from each percentage weight (0.2, 0.4, 0.6 & 0.8 %); 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

Measurement of LOI Using ASTM: D -2863

The limiting oxygen Index (LOI) for unsaturated polyester resin without additives is (20.4) [16] and for epoxy resin without additives is (19.7) [17]; Tables (1&2) and Figures (1&2) indicated that, Oxygen concentration required to support a candle–like in unsaturated polyester and epoxy



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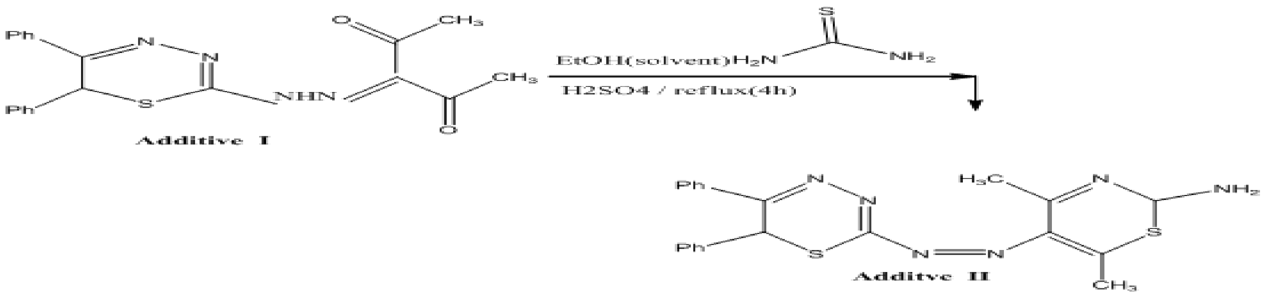

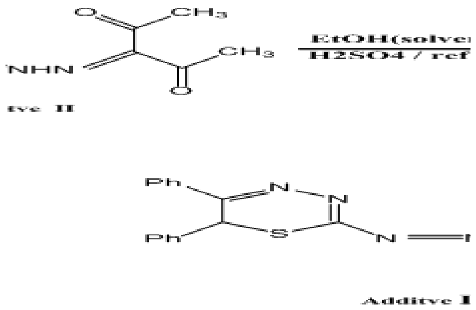

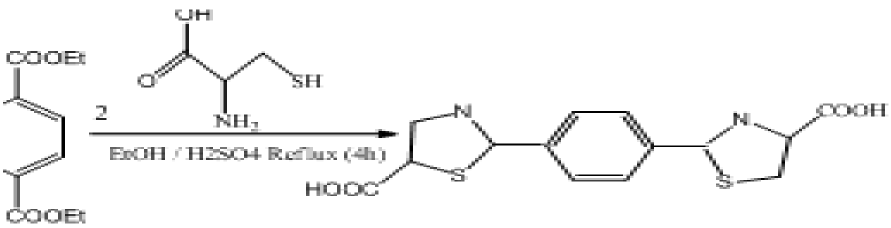

Additive V

Table 1: Limiting oxygen index for unsaturated polyester resin with different additives

LOI / Additives	LOI %				
	Non	0.2	0.4	0.6	0.8
I	20.6	21.72	22.45	22.97	23.62
II	20.6	22.84	23.53	24.38	25.14
III	20.6	21.98	22.70	23.25	23.96
IV	20.6	23.71	24.56	25.46	26.31
V	20.6	21.14	21.70	22.30	22.86

Table2:Limiting oxygen index for Epoxy resin with different additives

LOI / Additives	LOI %				
	Non	0.2	0.4	0.6	0.8
I	19.7	20.84	21.43	22.08	22.61
II	19.7	21.73	22.62	23.71	24.46
III	19.7	21.03	21.84	22.48	23.16
IV	19.7	22.17	23.41	24.63	25.28
V	19.7	20.32	20.91	21.48	22.03

Table 3: Rate of burning (R.B) for unsaturated polyester resin with different additives

Tests	**Additives %**					**Additives**
	Non	**0.2**	**0.4**	**0.6**	**0.8**	
AEB (cm.)	10	10	10	8.52	8.00	**I**
	10	10	8.12	7.52	-	**II**
	10	10	10	9.27	8.42	**III**

	10	5.79	-	-	-	**IV**
	10	10	9.16	7.93	7.37	**V**
ATB (Min.)	6.92	9.091	9.901	9.793	10.000	**I**
	6.92	10.990	9.442	10.444	-	**II**
	6.92	10.000	10.869	11.444	11.534	**III**
	6.92	9.524	10.628	11.614	11.040	**IV**
	6.92	8.333	8.178	8.092	8.189	**V**
R.B. (cm./ Min.)	1.44	1.10	1.01	0.87	0.80	**I**
	1.44	0.91	0.86	0.72	-	**II**
	1.44	1.00	0.92	0.81	0.73	**III**
	1.44	0.72	-	-	-	**IV**
	1.44	1.20	1.12	0.98	0.90	**V**
S.E	-	-	-	-	-	**I**
	-	-	yes	yes	yes	**II**
	-	-	-	-	yes	**III**
	-	yes	yes	yes	yes	**IV**
	-	-	-	-	-	**V**
N.B	-	-	-	-	-	**I**
	-	-	-	-	yes	**II**
	-	-	-	-	-	**III**
	-	-	yes	yes	yes	**IV**
	-	-	-	-	-	**V**

Table 4: Rate of burning (R.B) for epoxy resin with different additives

Tests	**Additives %**					**Additives**
	Non	**0.2**	**0.4**	**0.6**	**0.8**	
AEB (cm.)	10	10	10	8.7	8.1	**I**
	10	9.0	7.6	6.8	-	**II**
	10	10	9.0	8.3	7.6	**III**
	10	8.6	5.9	-	-	**IV**
	10	10	9.3	8.1	7.5	**V**
ATB (Min.)	5.12	6.810	7.194	6.960	7.297	**I**
	5.12	8.653	7.920	8,293	-	**II**
	5.12	7.576	7.317	7.477	7.917	**III**
	5.12	10.886	9.672	-	-	**IV**
	5.12	5.882	5.706	5.510	5.556	**V**
R.B. (cm./ Min.)	1.95	1.47	1.39	1.25	1.11	**I**
	1.95	1.04	0.96	0.82	-	**II**
	1.95	1.32	1.23	1.11	0.96	**III**
	1.95	0.79	0.61	-	-	**IV**
	1.95	1.70	1.63	1.47	1.35	**V**
S.E	-	-	-	-	-	**I**
	-	-	-	yes	yes	**II**
	-	-	-	-	-	**III**
	-	yes	yes	yes	yes	**IV**
	-	-	-	-	-	**V**

N.B	-	-	-	-	-	I
	-	-	-	-	yes	II
	-	-	-	-	-	III
	-	-	-	yes	yes	IV
	-	-	-	-	-	V

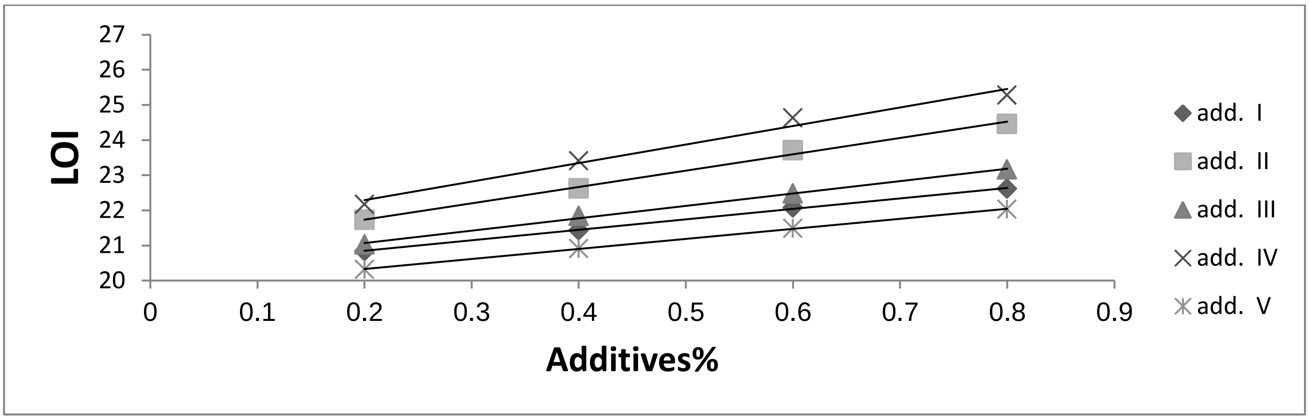

Figure 1: Limiting Oxygen Index (LOI) for unsaturated polyester resin with different weight percentage of additives

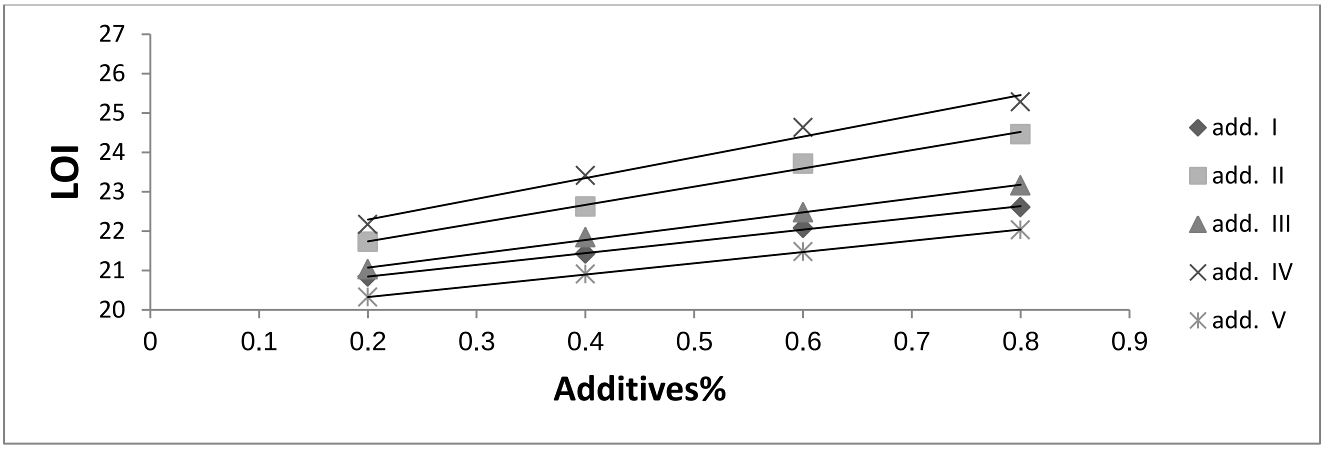

Figure 2: Limiting Oxygen Index (LOI) for Epoxy resin with different percentage of additives

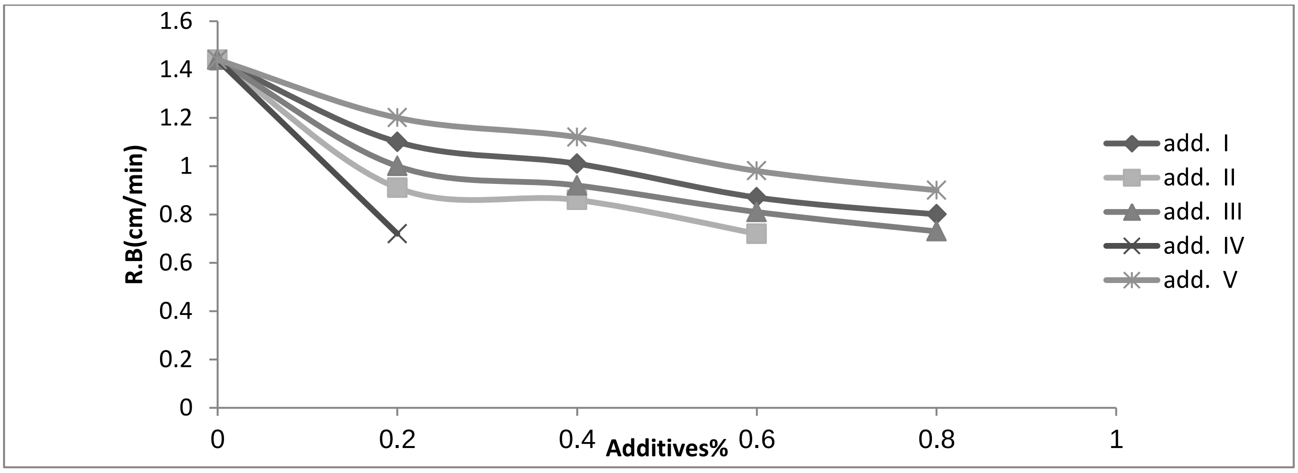

Figure 3: Rate of burning (R.B) for unsaturated polyester with different weight percentage of additives

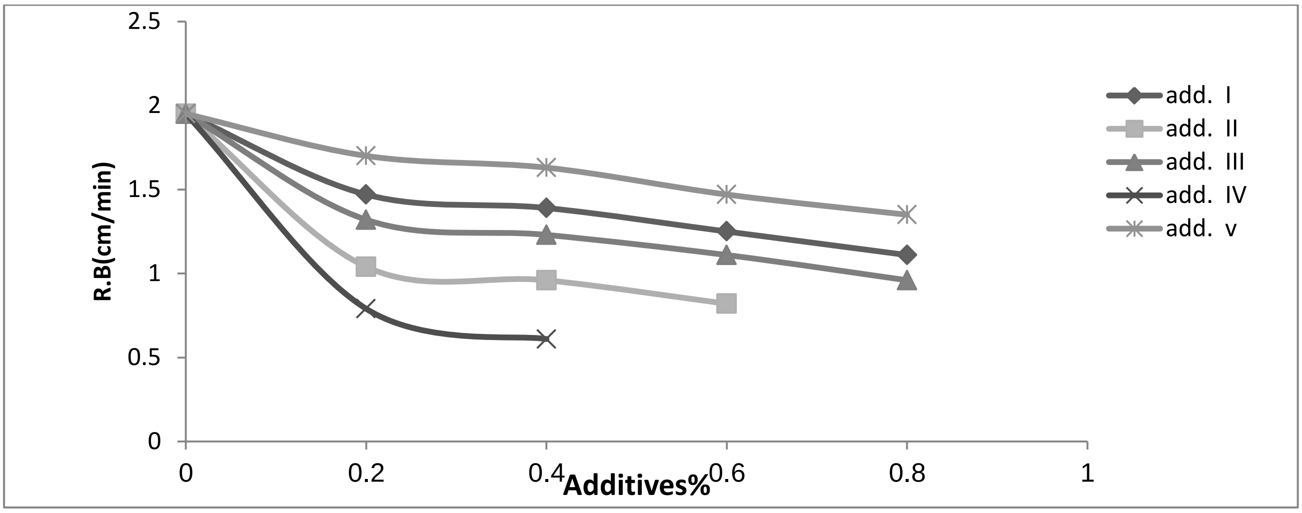

Figure 4: Rate of burning (R.B) for epoxy Resin with different weight percentage of additives

resins samples were increased with increasing the weight percentage of additives. The efficiency of additives studied was in the following order: IV > II > III > I > V

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) [18] 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 (3&4), Figures(3&4) 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: IV > II > III > I > V

Conclusion

The results obtained can be summarized the limiting oxygen index(LOI) increased with increasing the weight percentages of the additives, 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:

IV > II > III > I > V

And 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, chare…etc., will form allayer to prevent burning and displacing oxygen that help continues burning of polymers.

References

1. Hollingbery L, Hull T (2012)J. Polym. Degra. Dstab. 97(4):504.
2. Vander Veen I, de Boer J(2012)Chemosphere. J., 88(10):1119.
3. Shaw S, Blum A, Weber R, Kannan K, Rich D, Lucas D (2010) Rev. on Envi. Heal. 25(4):261.
4. Bastiurea M, Rodeanu M, Dima D, Murarescu M, Andrei G (2015) Digest J.Nanomaterials and Biostructures; 10:521.
5. Weil ED, Levchik SV (2015)Flame Retardants for Plastics and Textiles: Practical Applications; Carl Hanser Verlag; Munich 97.
6. Liu J, Zheng X, Tang K(2013) Rev. Adv.Mater. Sci.; 33:428.
7. Ugal J (2015)Chem. Sci. Trans.; 4(2):516.
8. Reddy C, Swamy B(2011)Inter. J. Phar. and Pharmacy. Sci.; 3(1):215.
9. Xu L, Jioo K, Zhang S, Kuang S(2002) Bull-Korean Chem. Soc.; 23:12.
10. NadiaA,Turk J (2008)Chem.; 32; 229.
11. Nachiket S, suraj B, prajakta R, amol S, Santosh S, Santosh D (2015)Int. J. pharm. chem.; 5(2); 31.
12. Marwa T, ALJamali N, Qasim K (2014) J. Res. Chem.; 7; 8.
13. Bijo M., Jerad A., Githa E., Shayam S.& Kuma S., (2001), Int. J.Chem. tech. Res.; 3(1): 364.
14. Annual Book of ASTM Standard, 08, 01, (1986).
15. Annual Book of ASTM Standard, Part-35, (1981).

16. AL-Baiati M., (2017), J. Global Pharmacy. Techn. 05(9); 01.

17. Butt C, Wang D, Stapleton HM (2011)Toxicological Sciences, 124 (2); 339.

18. Watkins D, McClean M, Fraser A, Weinberg J, Stapleton H, Sjodin A, Webster T (2012)Environ. Sci. &Tech., 46 (2);1192,

19. Besis A, Samara C (2012)Environ. Pollu, 169 217.