



Original Research Article

Preparation and Characterization of some Azo Phenolic Chlorinated Compounds and their Application as Flame Retardant with Polyurethane

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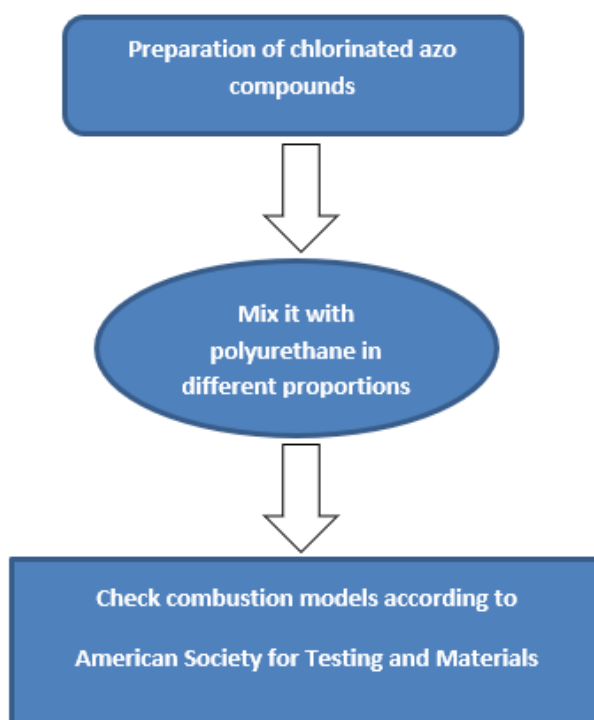
Azo phenolic chlorinated compounds

Polyurethane

ABSTRACT

This study involves preparing some of the azo phenolic chlorinated compounds and studying their properties as a fire retardant with commercial polyurethane according to ASTM (American Society Test of Materials), where the use of ratios is adding different from azo phenolic chlorinated compounds. Azo phenolic chlorinated compounds were developed as a flame retarding material by increasing the chlorine atoms. The azo phenolic chlorinated compounds with different numbers and places of substituted chlorine atoms were prepared. Fourier-transform infrared spectroscopy (FT-IR) predicted the chemical structure of the azo phenolic chlorinated compounds. In addition, the efficiency of the sample increases as an inhibitor of fire, by increasing the number of chlorine atoms and increasing the proportion of azo phenolic chlorinated compounds added.

GRAPHICAL ABSTRACT



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Introduction

Azo compounds, characterized by the presence of the -N=N- azo linkage, have attracted significant attention in various scientific fields due to their wide range of applications, including dyes, pharmaceuticals, and advanced materials. Among these, azo phenolic compounds, which combine the azo functional group with phenolic hydroxyl groups, have shown remarkable properties such as thermal stability, UV-absorption, and potential flame-retardant characteristics [1-7]. The introduction of chlorine atoms into the molecular structure further enhances these properties, providing increased resistance to combustion and degradation under heat. Flame retardants are crucial additives for improving the fire resistance of polymeric materials. Polyurethane (PU), a widely used polymer in industries such as construction, automotive, and furniture, is inherently flammable. Therefore, the development of efficient flame-retardant systems is essential to meet safety standards and protect lives and property. Traditionally, halogenated flame retardants, which rely on the action of chlorine and bromine, have been effective but raise environmental concerns due to the release of toxic gases upon combustion [8-13]. In recent years, there has been growing interest in the use of multifunctional flame retardants that not only improve fire resistance, but also enhance other properties of the polymer, such as mechanical strength and thermal stability. Azo phenolic compounds, particularly those chlorinated, represent an attractive class of flame retardants due to their ability to interact with the polymer matrix and inhibit the propagation of combustion. When incorporated into polyurethane, these compounds are expected to modify the thermal degradation pathways and char formation, improving flame-retardant performance [14-28]. This study focuses on the preparation and characterization of a series of

azo phenolic chlorinated compounds (Figure 1). The structural features, thermal stability, and flame-retardant properties of these compounds will be investigated in detail. Furthermore, their application as flame retardants in polyurethane systems will be evaluated, with an emphasis on their efficiency in reducing flammability and enhancing the overall fire resistance of the polymer material. By exploring the potential of these novel compounds, this study aims to contribute to the development of more effective and environmentally friendly flame-retardant solutions for polyurethane and other polymer systems.

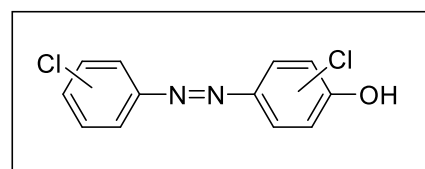


Figure 1. General chemical structure of azo phenolic chlorinated compounds.

Materials and Methods

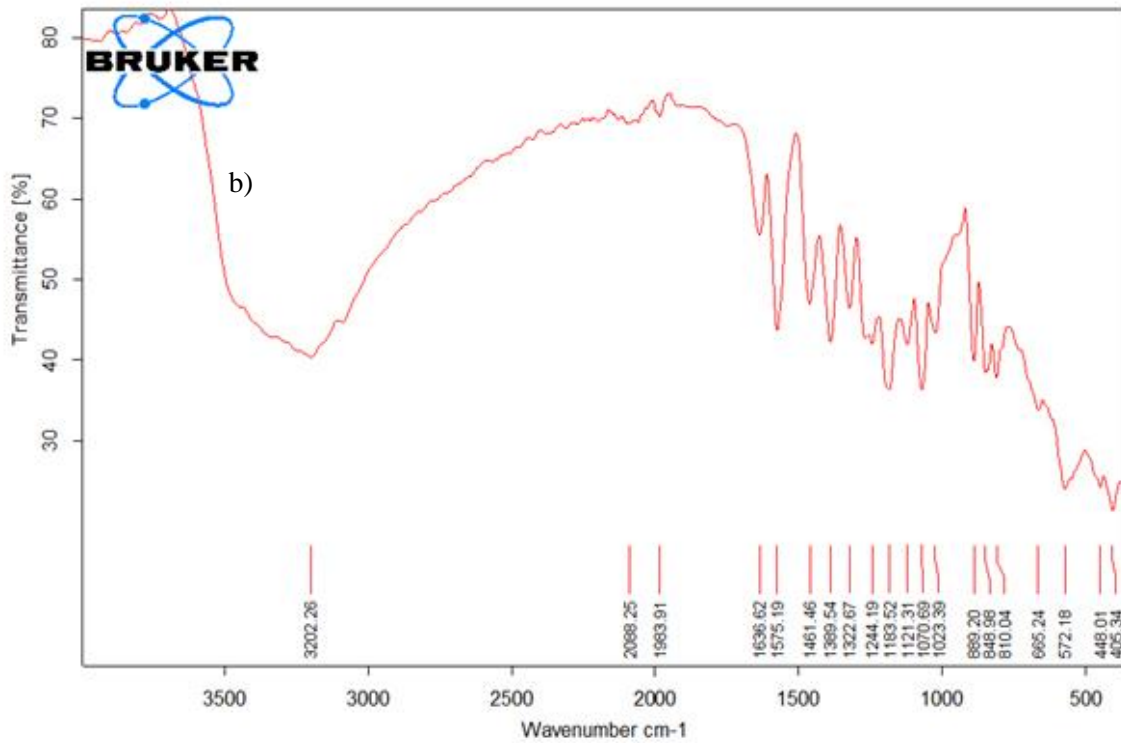
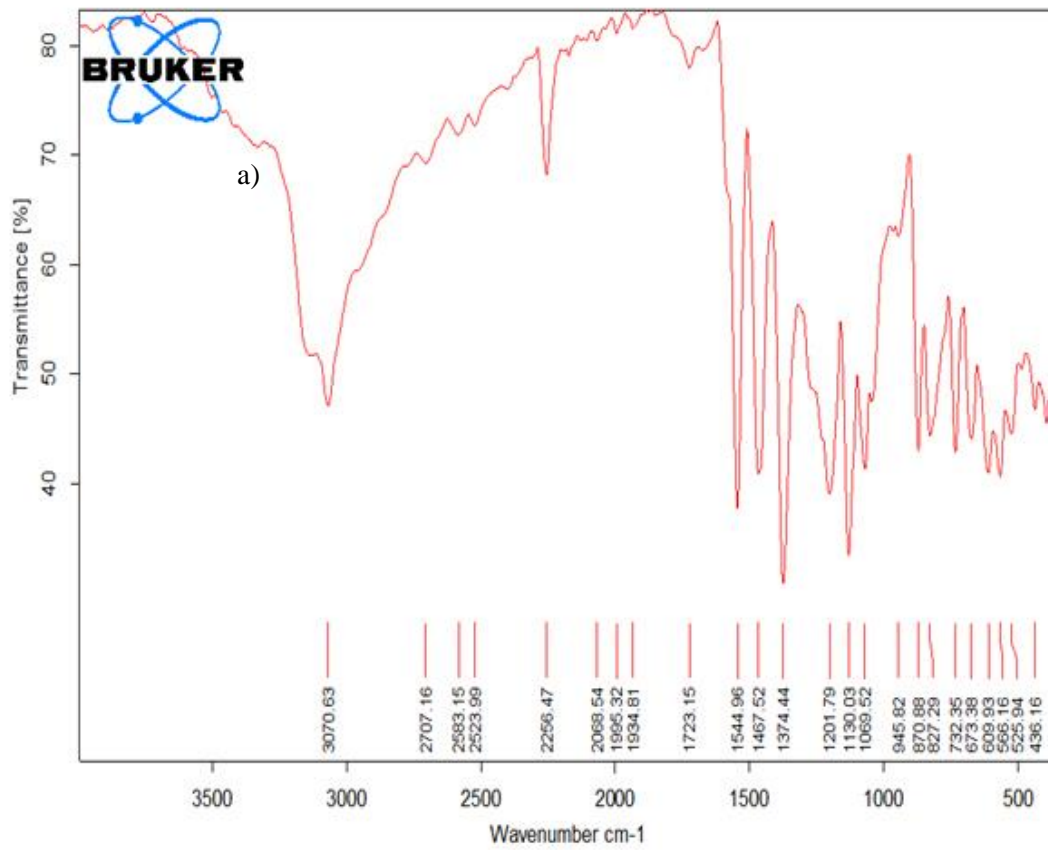
Materials and equipment

All chemicals and reagents are purchased from Fluka and used as received without purification. Fourier-transform infrared spectroscopy (FT IR) was accomplished using a Bruker FT-IR Infrared Spectrophotometer.

Synthetic route

Azo phenolic chlorinated compounds were prepared according to the following general method [29]:

0.01 mol of aniline or its derivatives were dissolved in 10 mL of concentrated hydrochloric acid at -10 °C. An aqueous solution of 0.01 M of sodium nitride was added drop wise with stirring at -10 °C for 30 minutes. Phenol compound (0.01 mol) was dissolved in 10 mL of sodium hydroxide solution (%10) and added to the



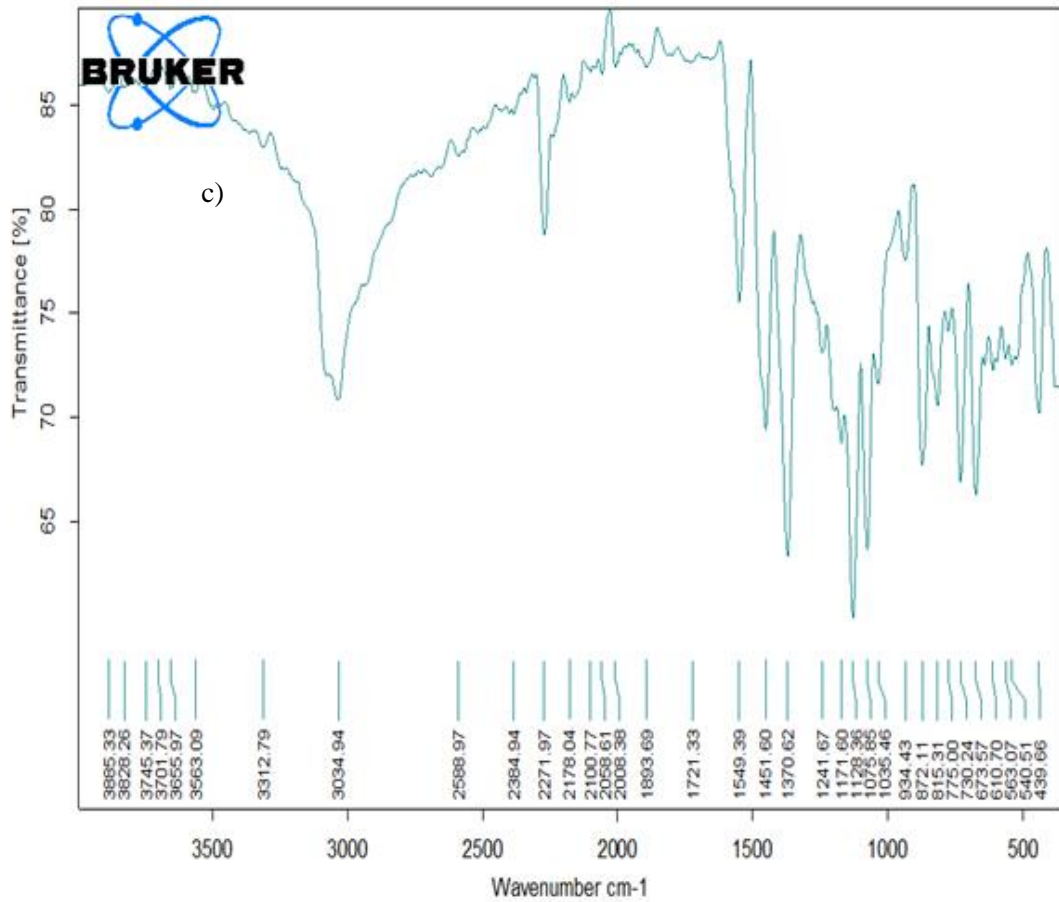


Figure 2. FT-IR spectra of azo phenolic chlorinated compounds a) A1, b) A2, and c) A3

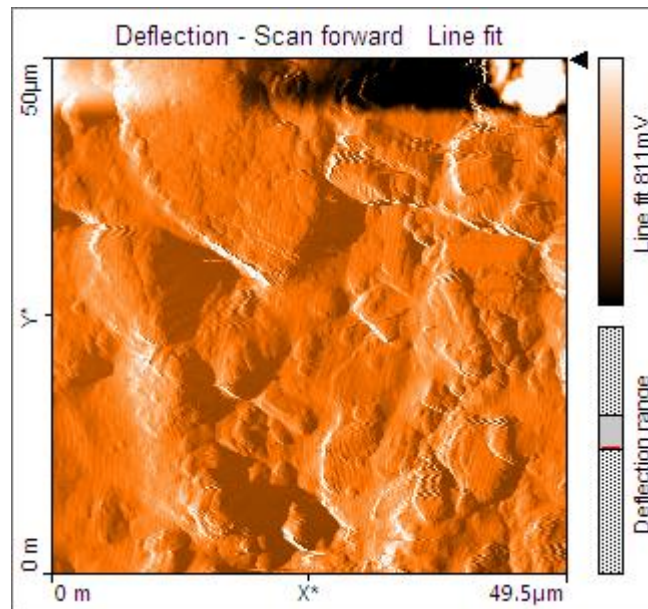


Figure 3. AFM of mixing Polyurethane with azo phenolic chlorinated compound A1 ratio %5

The homogeneity of the constructional polyurethane with azo phenolic chlorinated compounds was conducted by the atomic force microscope (AFM) measurement (Figure 3).

Through the measurement of burning time and other variables in Tables 2a, 2b, 2c, 2d, and 2e, we noted that the increase number of chlorine atoms in the azo phenolic chlorinated compounds operates to increase efficiency the models as fire retardant and increase of the plus % added from azo phenolic chlorinated compounds to the polyurethane, the efficiency the models as a fire retardant. It is also increasing, the percentage %5 gave the best resistance flammable.

This test was accomplished according to method ASTM E 285-80 for all azo phenolic chlorinated compounds with commercial polyurethane [32]. The mixing percentage was %1, %2, %3, %4, and %5. The properties of

flame retarding were calculated as following: (a) Insulation index (I.I) was recorded according to Equation (1):

$$I.I = B.T \text{ (sec)}/4 \text{ mm} \quad (1)$$

Where, B.T = Burning Time/sec, 4 mm = Sample thick; Erosion rate (E.R) was calculated according to Equation (2):

$$E.R = 4 \text{ mm}/B.T \text{ sec} \quad (2)$$

The percentage of residual weight of combustion was calculated according to Equation (3):

$$\%RWR = ((W1-W2) / W1) * 100 \quad (3)$$

Where, W1 = Sample Weight before Burning (gm) and W2 = Weight of the missing material (gm).

Table 2. Shows the results of the burning test for azo phenolic chlorinated compounds with Polyurethane

a) Addition ratio %1 of azo phenolic chlorinated compounds with polyurethane

N. B	S. E	RWR %	W2 gm	W1 gm	AEB cm	H cm	E.R mm/sec	I.I sec/mm	B. T sec	No. S
-	-	10	5.3	6	15	8.0	0.011	90.5	362	P.U*
-	Yes	66	2.0	6	7.5	4.0	0.023	42.5	170	P.U: A1
-	Yes	68	2.2	6	9.1	4.0	0.0218	45.75	183	P.U: A2
-	Yes	68	1.4	6	7.3	3.5	0.0239	41.75	167	P.U: A3

b) Addition ratio %2 of azo phenolic chlorinated compounds with polyurethane

N. B	S. E	RWR %	W2 gm	W1 gm	AEB cm	H cm	E.R mm/sec	I. I sec/mm	B. T sec	No. S
-	-	10	5.3	6	15	8.0	0.011	90.5	362	P.U*
-	Yes	73	1.6	6	3.2	4.0	0.029	33.5	134	P.U: A1
-	Yes	72	1.7	6	4.6	4.0	0.028	35.5	142	P.U: A2
-	Yes	80	1.2	6	3.3	3.5	0.030	33.0	132	P.U: A3

c) Addition ratio %3 of azo phenolic chlorinated compounds with polyurethane

N. B	S. E	RWR %	W2 gm	W1 gm	AEB cm	H cm	E.R mm/sec	I. I sec/mm	B. T sec	No. S
-	-	10	5.3	6	15	8.0	0.011	90.5	362	P.U*
-	Yes	80	1.2	6	3.5	3.5	0.023	42.5	109	P.U: A1
-	Yes	76	1.4	6	4.7	3.5	0.0218	45.75	122	P.U: A2
-	Yes	83	1.0	6	3.6	3.0	0.0239	41.75	104	P.U: A3

d) Addition ratio %4 of azo phenolic chlorinated compounds with polyurethane

N. B	S. E	RWR %	W2 gm	W1 gm	AEB cm	H cm	E.R mm/sec	I. I sec/mm	B. T sec	No. S
-	-	10	5.3	6	15	8.0	0.011	90.5	362	P.U*
-	Yes	83	1.0	6	3.5	3.0	0.023	42.5	94	P.U: A1
-	Yes	82	1.1	6	4.1	3.5	0.0218	45.75	102	P.U: A2
-	Yes	86	0.8	6	3.3	2.5	0.0239	41.75	90	P.U: A3

e) Addition ratio %5 of azo phenolic chlorinated compounds with polyurethane

S. E	RWR %	W2 gm	W1 gm	AEB cm	H cm	E.R mm/sec	I. I sec/mm	B. T sec	No. S
-	10	5.3	6	15	8.0	0.011	90.5	362	P.U*
Yes	88	0.7	6	2.0	2.5	0.023	42.5	79	P.U: A1
Yes	86	0.8	6	2.2	2.5	0.0218	45.75	97	P.U: A2
Yes	90	0.6	6	1.5	2.0	0.0239	41.75	76	P.U: A3

Where,

B.T = Burning Time (sec).

I.I = Insulation Index (sec/mm).

E.R = Erosion Rate (mm/sec).

H = High flame (cm).

A.E.B = Average extent of burning (cm).

W1 = Sample weight before burning (gm).

W2 = Weight of the missing material (gm).

RWR = Percentage of residual weight after combustion (%).

E.S = Self-Extinguishing.

N.B = Non-Burning.

P.U* = Only Polyurethane without Azo phenolic compounds.

Conclusion

In this study, a series of azo phenolic chlorinated compounds were successfully


synthesized and characterized for their potential application as flame retardants in commercial polyurethane. The incorporation of chlorine atoms into the azo phenolic structure enhanced the flame-retardant properties of the compounds, with increasing numbers and positions of chlorine substitutions proving particularly effective in improving thermal stability and fire resistance. The chemical structures of these compounds were confirmed using Fourier-transform infrared spectroscopy (FTIR), further validating their composition. The flame-retardant efficiency of these azo phenolic chlorinated compounds was evaluated according to ASTM standards, showing a clear correlation between the increased chlorine content and enhanced flame retardancy. Higher concentrations of these compounds in the polyurethane matrix led to a significant

reduction in flammability, demonstrating their effectiveness as fire inhibitors. These findings suggest that azo phenolic chlorinated compounds, with their tunable structure and halogenation, offer a promising route for developing more effective flame retardants for polyurethane and other polymeric materials. This study contributes to the ongoing search for improved fire safety solutions in commercial applications, offering both scientific insight and practical implications for polymer materials.

Conflict of Interest

The authors declares that there is no conflict of interest in this study.

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