

Article

Synthesis, Characterization of *sym*-2,4,6-trisubstituted-*s*-Triazine Derivatives and Their Effects on Flame Retardancy of Polypropylene Composites

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Abstract: Polypropylene (PP) is flammable material, which brings latent danger to the environment and human society. Therefore, developing new environmentally friendly and effective flame-retardant is one of the most important ways to improve the flame retardancy of PP and improve safety during its lifetime. Herein, we describe the synthesis of five *sym*-2,4,6-trisubstituted-*s*-triazine derivatives, namely, N^2,N^4,N^6 -triphenyl-1,3,5-triazine-2,4,6-triamine (TAT), N^2,N^4,N^6 -tris(4-bromophenyl)-1,3,5-triazine-2,4,6-triamine (TBAT), N^2,N^4,N^6 -tris(4-chlorophenyl)-1,3,5-triazine-2,4,6-triamine (TCAT), 4,4',4''-((1,3,5-triazine-2,4,6-triyl) tris(azanediyl)) triphenol (THAT), and N^2,N^4,N^6 -tris(4-methoxyphenyl)-1,3,5-triazine-2,4,6-triamine (TMAT), from the reaction of cyanuric chloride and *p*-substituted aniline employing conventional heating or microwave irradiation. The prepared compounds characterized by different techniques, such as Fourier-transform infrared (FTIR), Ultra-Violet and Visible (UV-Vis), Nuclear Magnetic Resonance spectroscopy (¹H-NMR and ¹³C-NMR), Thermogravimetric Analysis (TGA), and differential scanning calorimetry (DSC). The effect of substituent on the aniline moiety has great impact on its thermal stability, as observed from the TGA and DSC data. Based on the TGA and DSC results, three triazine derivatives TAT, TBAT, and TMAT were used as charring agents in the presence of different proportions of ammonium polyphosphate (APP) to form an intumescent flame-retardant (IFR) system, to improve the flame retardancy of PP. The flammability property of PP was investigated by a vertical burning test (UL94). The results of UL94 revealed that the TXAT/APP (IFR) system influence the PP and could improve the flame retardancy of PP. Best results were obtained with the mass ratio of APP and TXAT 2:1. When the IFR loading was 25 wt%, it displayed great influence and passed V-0 with TMAT, and V-1 with both TAT and TBAT in the UL94 test.

Keywords: trisubstituted triazine; thermal stability; flame retardant; polypropylene; UL94

1. Introduction

As one of the most widely used polymers, polypropylene (PP) plays a significant role in our daily lives, and is extensively used in numerous applications, such as in the electrical and insulation field, building materials, transportation aspects, etc. [1–5]. However, PP is also considered a flammable material, releasing smoke and toxic or corrosive gases, which brings latent danger to the environment and human society, and strongly limits its uses. Therefore, developing a new environmentally friendly and effective flame-retardant (FR) agent is one of the most important methods to improving the flame

retardancy of PP, and the safety during its lifetime. In addition, applying FR is needed to achieve excellent flame-retardant properties [1,6,7].

Based on that, and due to the flammability of PP, many researchers conducted intensive studies and came up with great efforts to improve the flame retardancy of PP. They suggested that adding flame-retardant agents into PP is one of the most effect methods to adapt its flammability and improve the safety during its uses [6–8].

The most common effective flame retardant agent is the one containing halogen (usually bromine) and antimony trioxide synergistic systems [7,9]. However, applying this type of FR agent is limited, since halogenated FR agent during burning produces large amounts of corrosive gases and smoke, which affects the environment and human life [10,11]. Alternative FR additives are metal oxides, such as magnesium hydroxide and aluminum hydroxide. However, to obtain the same level of halogenated FR, a high loading amount of metal oxide is required, which will destroy PP's mechanical properties remarkably [7–9,12,13].

In recent years, many researchers have focused on developing halogen-free flame-retardant agents, such as intumescent flame retardant (IFR) additives. IFR is considered a class of ecofriendly flame retardant additive with the effectiveness of isolating heat and oxygen transfer, cutting the release of smoke, being nontoxic, and avoiding dripping; it is considered to be one of the greatest capable candidates for its qualities, such as being low loading, protecting polymer matrix properties, being environmentally friendly, etc. [4,7,13].

Generally, IFR has three main constituents: (i) an acid source, such as ammonium polyphosphate (APP); (ii) a carbon source, such as a charring agent to form a charred layer, which acts as a physical barrier to reduce heat and mass transfer between gas and condensed phase over the creation of intumescent char cover. Finally, (iii), a blowing agent, such as nitrogen-containing material to produce abundant incombustible gases [8,14–16].

Mainly, APP is used as an acid catalyst and as a blowing agent because of its high contents of nitrogen and phosphorus. The charring agents, which presently used are generally small molecular compounds, such as *s*-triazine derivatives. These types of derivatives are highly nitrogen-containing compounds; during burning, they make multicellular swollen char on the polymer surface. The swollen char displays good adherence and offers an efficient barrier effect against the spread of the flame. In addition, it forms char, which can expand below the action of the blowing source to offer an intumescent char layer, to decrease heat transfer between the heat source and the polymer surface, and limit fuel transfer between polymer and the flame [4,8].

In recent years, various novel charring agents have been investigated and showed high flame retardant efficiency and stability, such as phenolic resin [17], polyamide [18,19], expandable graphite [20,21], etc. Recently, several *s*-triazine derivatives have been reported as charring agents due to their high nitrogen containing compounds, which can participate in the formation of a high efficiency, stable, char layer [22–26]. These types of derivatives performed excellent synergistic intumescent flame retardant effects with APP [27–31].

The ingredient cyanuric chloride [32–35] is the starting material used to prepare *s*-triazine derivatives via nucleophilic substitution reaction of the active chlorine atoms at the *s*-triazine ring with different nucleophiles [35–38]. Therefore, the structure of *s*-triazine derivatives are designed by controlling the substituent groups attached to the *s*-triazine ring at different temperatures [39].

By taking into account all of these aspects, the present work represents the synthesis and characterization of five *sym*-2,4,6-trisubstituted *s*-triazine derivatives (TXAT) based on the different substituent attached to the *s*-triazine ring. These derivatives containing aniline, *p*-bromoaniline, *p*-chloroaniline, *p*-hydroxyaniline, and *p*-methoxyaniline. The influence of substituent on their thermal stability were considered. Moreover, the prepared TXAT derivatives with higher limiting oxygen index (LOI) values were used together with APP at different weight ratios to improve the flame retardancy of PP. The UL94 V-0 rating was used to find out the flame retardancy properties of the reported compounds.

2. Materials

Polypropylene resin was provided from SABIC (PP 595A, Riyadh, Saudi Arabia). Ammonium polyphosphate commercial grade (phase II, the degree of polymerization ≥ 1000) was purchased from Hubei Jusheng Technology Co. Ltd. (Wuhan, China). Cyanuric chloride (98%), aniline derivatives, and all solvents were purchased from Sigma-Aldrich (Chemie GmbH, Taufkirchen, Germany). Hydrazine hydrate (80%) purchased from Alpha Chemika (Mumbai, India). FTIR (KBr, cm^{-1}) recorded on Shimadzu 8201 PC spectrophotometer (Shimadzu, Ltd., Kyoto, Japan). Nuclear Magnetic Resonance (NMR) spectrum (^1H and ^{13}C) recorded on JEOL-NMR (400 MHz) spectrometer (JEOL, Ltd., Tokyo, Japan). Elemental microanalysis (CHN) measured by using Perkin-Elmer 2400 CHNS/O Series II elemental analyzer (PerkinElmer, Inc., 940 Winter Street, Waltham, MA, USA).

3. Methods

3.1. General Method for the Synthesis of sym-2,4,6-trisubstituted-s-Triazine

For the synthesis of the target compounds, two methods were used, as follows:

Method A: conventional heating

Cyanuric chloride **1** (1.84 g, 10 mmol) in 100 mL acetonitrile was added dropwise to a mixture of aniline derivatives **2a–e** (30 mmol), K_2CO_3 (100 mmol) in acetonitrile (100 mL) at $0\text{ }^\circ\text{C}$. After complete addition, the reaction mixture stirred at $0\text{ }^\circ\text{C}$ for 1 h, then at room temperature for another 1 h, and finally refluxed for 16–18 h. The solvent was removed under vacuum and then excess of water was added. The final products were isolated by filtration, washed with ethanol-water, and then dried at room temperature to afford the pure products.

Method B: microwave irradiation

Cyanuric chloride **1** (10 mmol) in 25 mL dioxane was slowly added to a mixture of aniline derivatives **2a–e** (30 mmol) and K_2CO_3 (30 mmol) in 20 mL dioxane at $0\text{ }^\circ\text{C}$. After complete addition, the reaction mixture was stirred at room temperature for 20 min and then irradiated in a microwave oven at 600 W for 20–25 min using a Galanz microwave oven, connected with a refluxing condenser. The solvent was removed under reduced pressure and the solid obtained was washed with water, dried, and then recrystallized to afford the pure product.

3.1.1. N^2,N^4,N^6 -triphenyl-1,3,5-triazine-2,4,6-triamine (TAT); **3a**

The product obtained as an off-white solid in 84% yield (**A**), 95% yield (**B**), mp $230\text{--}232\text{ }^\circ\text{C}$ (Lit. [40,41] $29\text{--}230\text{ }^\circ\text{C}$ (isopropanol); in 93 % yield); λ_{max} (nm) in MeOH: 275; FTIR (cm^{-1}): 3370 (NH), 1500 (C=N), 1620, 1495 (C=C), 1260 (C–N); $^1\text{H-NMR}$ (DMSO- d_6 , δ ppm): 6.8–8.0 (m, 15H, Ar–H), 9.3 (s, 3H, NH).

3.1.2. N^2,N^4,N^6 -tris(4-bromophenyl)-1,3,5-triazine-2,4,6-triamine (TBAT); **3b**

The product was obtained as a white solid in yield 84% (**A**), 98% (**B**); mp $268\text{--}270\text{ }^\circ\text{C}$; λ_{max} (nm) in MeOH: 283; FTIR (cm^{-1}): 3380 (N–H), 1550 (C=N), 1600, 1440 (C=C), 1250 (C–N), 620 (C–Br); $^1\text{H-NMR}$ (Supplementary Materials, DMSO- d_6 , δ ppm): 7.45 (d, $J = 8.8\text{ Hz}$, 6H, Ar), 7.76 (d, $J = 7.2\text{ Hz}$, 6H, Ar), 9.47 (s, 3H, NH). $^{13}\text{C-NMR}$ (Supplementary Materials, DMSO- d_6 , δ ppm): 113.8, 122.2, 131.1, 139.2, 163.9. Anal. Calc. for $\text{C}_{21}\text{H}_{15}\text{Br}_3\text{N}_6$ (587.89): C, 42.67; H, 2.56; N, 14.22. Found C, 42.88; H, 2.64; N, 14.41.

3.1.3. N^2,N^4,N^6 -tris(4-chlorophenyl)-1,3,5-triazine-2,4,6-triamine (TCAT); **3c**

The product was obtained as an off-white solid in yield 82% (**A**), 96% (**B**); mp $245\text{--}246\text{ }^\circ\text{C}$ (Lit. [42], mp $212\text{--}214\text{ }^\circ\text{C}$ in yield 22%); λ_{max} (nm) in MeOH: 280; FTIR (cm^{-1}): 3390 (NH), 1550 (C=N), 1630, 1420 (C=C), 1240 (C–N), 730 (C–Cl); $^1\text{H-NMR}$ (Supplementary Materials, DMSO- d_6 , δ ppm): 7.33 (d, $J = 8.8\text{ Hz}$, 6H, Ar), 7.82 (d, $J = 6.6\text{ Hz}$, 6H, Ar), 9.48 (s, 3H, NH); $^{13}\text{C-NMR}$ (Supplementary Materials, DMSO- d_6 , δ ppm): 121.9, 125.9, 128.2, 138.9, 164.0. Anal. Calc. for $\text{C}_{21}\text{H}_{15}\text{Cl}_3\text{N}_6$ (457.74): C, 55.10; H, 3.30; N, 18.36. Found C, 55.23; H, 3.42; N, 18.55.

3.1.4. 4,4',4''-((1,3,5-triazine-2,4,6-triyl) tris(azanediyl)) triphenol (THAT) **3d**

The product obtained as a white powder; in yield 89% (A), 97%(B), mp 285–287 °C (Lit. [43,44] yield 89%); λ_{\max} (nm) in MeOH: 275; FTIR (cm^{-1}): 3400 (NH), 1500 (C=N), 1630, 1430 (C=C), 1260 (C–N), 1050 (C–O); $^1\text{H-NMR}$ (Supplementary Materials, $\text{DMSO-}d_6$, δ ppm): 7.50 (d, 6H, $J = 6.8$ Hz, Ar), 7.88 (d, 6H, $J = 6.0$ Hz, Ar), 8.71 (s, 3H, NH); 9.03 (s, 3H, OH) ppm; $^{13}\text{C-NMR}$ (Supplementary Materials, $\text{DMSO-}d_6$, δ ppm): 115.0, 128.4, 131.6, 133.8, 161.5. Anal Calc for $\text{C}_{21}\text{H}_{18}\text{N}_6\text{O}_3$: C, 62.68; H, 4.51; N, 20.88. Found C, 62.81; H, 4.65; N, 21.01.

3.1.5. N^2, N^4, N^6 -tris(4-methoxyphenyl)-1,3,5-triazine-2,4,6-triamine (TMAT); **3e**

The product was obtained as a grey solid in yield 83% (A), 96% (B); mp 215–217 °C (Lit. [42], mp 212–214 °C in yield 22%); λ_{\max} (nm) in MeOH: 278; FTIR (cm^{-1}): 3400 (NH), 1500 (C=N), 1640, 1450 (C=C), 1260 (C–N), 1040 (C–O); $^1\text{H-NMR}$ (Supplementary Materials, CDCl_3 , δ ppm): 3.78 (9H, s, OCH_3), 6.81 (d, $J = 9.6$ Hz, 6H, Ar), 7.04 (brs, 3H, NH), 7.38 (d, $J = 9.6$ Hz, 6H, Ar); $^{13}\text{C-NMR}$ (Supplementary Materials, CDCl_3 , δ ppm): 55.5, 113.9, 122.8, 131.6, 155.9, 164.5. Anal. Calc. for $\text{C}_{24}\text{H}_{24}\text{N}_6\text{O}_3$ (444.19): C, 64.85; H, 5.44; N, 18.91. Found C, 65.01; H, 5.68; N, 18.73.

3.2. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

The TGA performed on a TA Q500 thermal analyzer (Waters LLC, New Castle, DE, USA) with flow rate of 60 mL/min, starting from room temperature to 800 °C. Around 6 mg of sample was placed in an alumina crucible and heated from 25 °C to 800 °C with the heating rate of 10 °C/min under N_2 atmosphere; data were collected in Table 1.

Differential scanning calorimetry (DSC) was conducted on TA Instruments DSC Q1000 (Waters LLC, New Castle, DE, USA) in the range between 80 °C and 400 °C under nitrogen atmosphere. The 5–8 mg samples were placed in the aluminum pans and measured under N_2 at the heating rate of 10 °C/min. Each sample was analyzed three times and readings were averaged.

Table 1. FTIR (cm^{-1}) and Ultra-Violet and Visible (UV)-Visible (λ_{\max} nm) data for compounds **3a–e**.

Compound	FT-IR (cm^{-1})	λ_{\max} (nm)
TAT; 3a	3370 (NH), 1500 (C=N), 1620, 1495 (C=C), 1260 (C-N)	275
TBAT; 3b	3380 (NH), 1550 (C=N), 1600, 1440 (C=C), 1250 (C-N)	283
TCAT; 3c	3390 (NH), 1550 (C=N), 1630, 1420 (C=C), 1240 (C-N)	280
THAT; 3d	3400 (NH), 1500 (C=N), 1630, 1430 (C=C), 1260 (C-N)	275
TMAT; 3e	3400 (NH), 1500 (C=N), 1640, 1450 (C=C), 1260 (C-N)	278

3.3. Flammability Test UL94

The vertical burning test was investigated according to the UL94 test standard with the sample dimension of $130 \times 13 \times 3.2$ mm. Before mixing PP, all additives were dried in vacuum oven at 70 °C for 24 h. All samples were prepared by mixing PP with different proportions of APP and TXAT using a two-roll mill mixing (Rheomixer XSS-300, Shanghai Ke Chuang, Shanghai, China) at a temperature range of 170 °C–180 °C for 10 min, and the roll speed was maintained 100 rpm. The formulations of prepared composites in the shape of vertical bars are listed in Table 2.

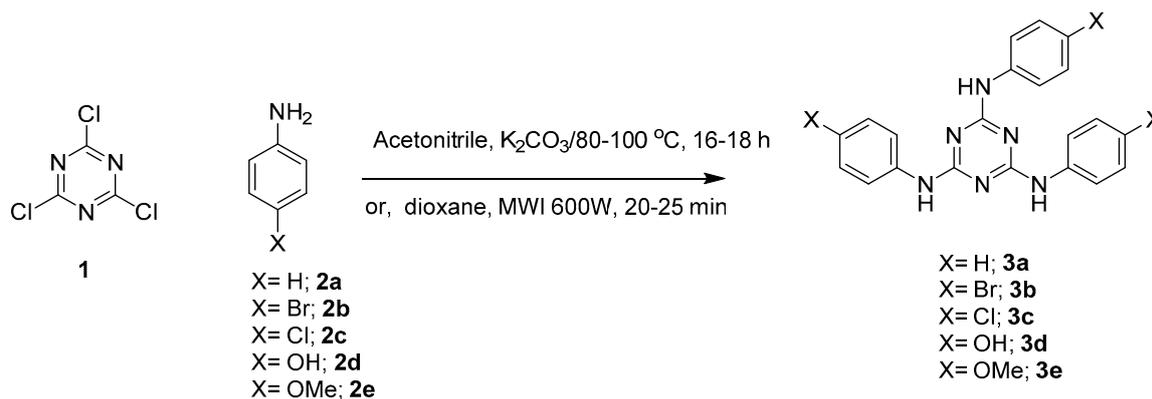
Table 2. Thermal degradation parameters for **3a–e**.

Sample ID	Temperature Range (°C)	Mass Loss (%)	T _g (°C)	CR at 600 °C	LOI at 600 °C	CR at 800 °C	LOI at 800 °C
TAT	320–440	50	145	29	29.1	20	25.5
TBAT	330–440	60	140	35	31.5	22	26.3
TCAT	240–340	80	143	15	23.5	6	19.9
THAT	330–450	50	143	45	35.5	35	31.5
TMAT	350–450	50	141	45	35.5	36	31.9

4. Results and Discussion

4.1. Synthesis of *sym*-2,4,6-trisubstituted-*s*-triazine Derivatives

The preparation of the target compounds were performed in one step reaction using conventional heating or microwave irradiation, as shown in Scheme 1. First, the reaction was carried out at 0 °C, due to the high reactivity of the first substitution, and then heated gradually to 80–100 °C, or irradiated by microwave at 600 W. Microwave irradiation always afforded the products in shorter reaction times (Section 3.1) with high yields and purities, as observed from their spectral data (Supplementary Materials).



Scheme 1. Synthesis of *sym*-2,4,6-trisubstituted-*s*-triazine derivatives.

4.2. Characterization of the Target Products

4.2.1. FTIR Spectroscopy

The FTIR spectrum for compounds **3a–e** illustrated in Table 1 and Supplementary Materials showed absorption peaks in the range 3370–3400 cm^{-1} , and were attributed to N-H bond and characteristic peaks in the range 2850–2930 cm^{-1} related to C-H sp^3 and sp^2 . The absorption peaks at 1569 and 1550 cm^{-1} were attributed to C=N bond of the *s*-triazine ring. The absorption peaks at 1642, 1495, and 1430 cm^{-1} were attributed to C=C of the phenyl ring, while the absorption peaks in the range 1240–1260 cm^{-1} attributed to C-N bond (Table 1).

4.2.2. UV-Vis Spectra

The UV-Vis spectroscopies of the prepared compounds **3a–e** were measured in methanol (Figure 1). The results showed that the prepared compounds have λ_{max} in range at 275–283 nm, depending on the type of substituent attached to the aniline moiety, as shown in Table 1 (Figure 1). The substituent effects had a clear impact on the λ_{max} as shown in Table 1, where the electron-withdrawing substituents, such as chloro (Cl) and bromo (Br), shifts λ_{max} to longer wavelength (Bathochromic shift) than electron-donating substituents, such as hydroxyl (OH) and methoxy (OMe) group. This behavior can be explained by considering that, the *p*-position favors the extension of *p*-conjugation and the formation of highly delocalized in the excited state [45].

4.2.3. Thermogravimetric Analysis (TGA)

The thermal parameters of the prepared compounds **3a–e** (TAT, TBAT, TCAT, THAT, and TMAT, respectively) were evaluated using the thermogravimetric technique (TGA). Degradation curves of **3a–e** are shown in Figure 2 and summarized in Table 2. The results from thermal degradation data of **3a–e** showed that all compounds have good thermal stability and started to degrade in range 240–350 °C, which is expected to have good char residue [27].

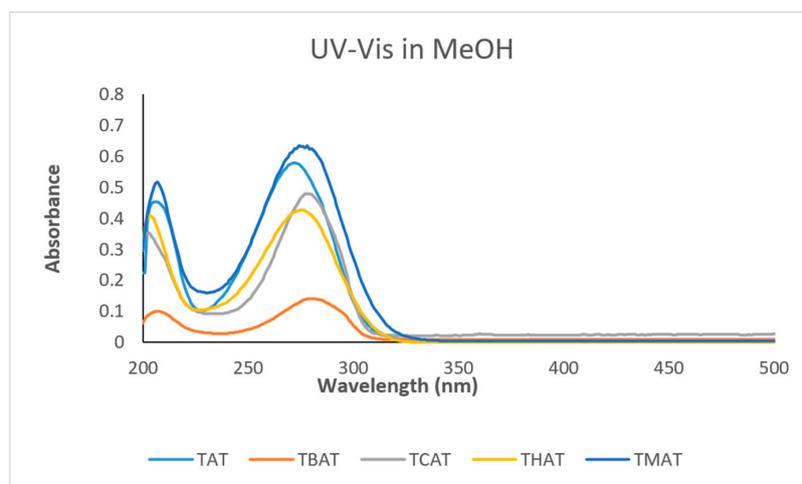


Figure 1. UV-Vis spectrum of *sym*-2,4,6-trisubstituted *s*-triazine derivatives (TXAT) in methanol.

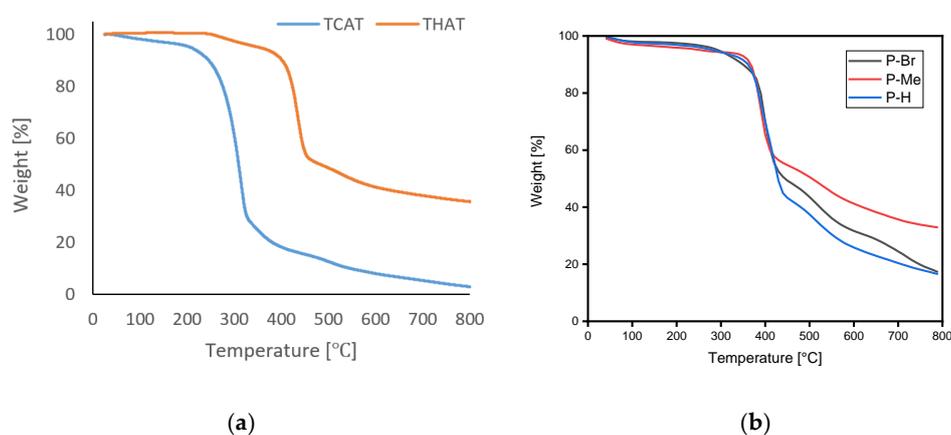


Figure 2. Thermogravimetric Analysis (TGA) degradation curves for (a) TCAT, THAT; (b) TBAT (p-Br), TAT (p-H), TMAT (p-MeO) derivatives.

As shown in Table 2 the compounds (TAT, TBAT, TCAT, THAT, and TMAT) have one main degradation steps in a range of 320–440 °C (TAT), 330–440 °C (TBAT), 240–340 °C (TCAT), 330–450 °C (THAT) and 350–450 °C (TMAT), with mass loss 5% (TAT, THAT & TMAT), 6% (TBAT) and 80% (TCAT).

The results in Table 2 indicated that TMAT and THAT are thermally more stable and have higher char residue (CR) than TAT, TBAT, and TCAT. This attributed to the type of substituent at the aniline ring attached to the *s*-triazine moiety, where compounds with an electron-donating group, such as methoxy group in TMAT and hydroxy group in THAT showed higher CR at 600 °C and 800 °C (45 and 35, respectively). On the other hand, compounds with a weak electron-withdrawing group, such as bromine in TBAT and chlorine in TCAT showed lower CR, as shown in Table 2. The bromo derivative TBAT showed higher CR at 600 °C and 800 °C (35 and 22, respectively); compared to its analogs of the chloro derivative TCAT at the same temperatures (15 and 6, respectively); this might be due to the difference in the electronegativity property. While, the unsubstituted derivative TAT was in the middle, as shown in Table 2.

The CR could be utilized for the limiting oxygen index (LOI) evaluation. To find out the correlation between the CR and LOI, the van Krevelen equation indicated below was used [46,47].

$$LOI = 17.5 + 0.4 (CR)$$

LOI, defined as the minimum concentration of O₂, supports the combustion to sustain in a mixture of O₂ and N₂ [43,44]. Materials displaying LOI values greater than 26 are classified as self-extinguishing material, while compounds with lower LOI than 26 are considered flammable material [47]. The LOI for TAT, TBAT, TCAT, THAT, and TMAT were calculated at 800 °C (Table 2). The results showed that the type of substituent has a clear effect on LOI values, where the chloro derivative TCAT showed the least LOI at 800 °C (19.9) compared to its analogs of the bromo derivative TBAT (26.3). On the other hand, the methoxy TMAT and the hydroxy derivatives showed the highest LOI values, while the unsubstituted was in the middle, as shown in Table 2.

4.2.4. Differential Scanning Calorimetry (DSC)

The thermal transitions of **3a–e** was studied using differential scanning calorimetry technique under nitrogen atmosphere. The DSC data were collected from the second run, as all samples were heated first to 100 °C to confirm the removal of any trace of solvent, then cooled down with the same rate to 30 °C. Then the second run was heated from 30 °C to 300 °C at a scan rate of 10 °C/min to determine the glass transition temperatures (T_g).

The results summarized in Table 2 and shown in Figure 3, reveals that the T_g of the tested compounds **3a–e** were in the range of 140–145 °C and are slightly similar to each other.

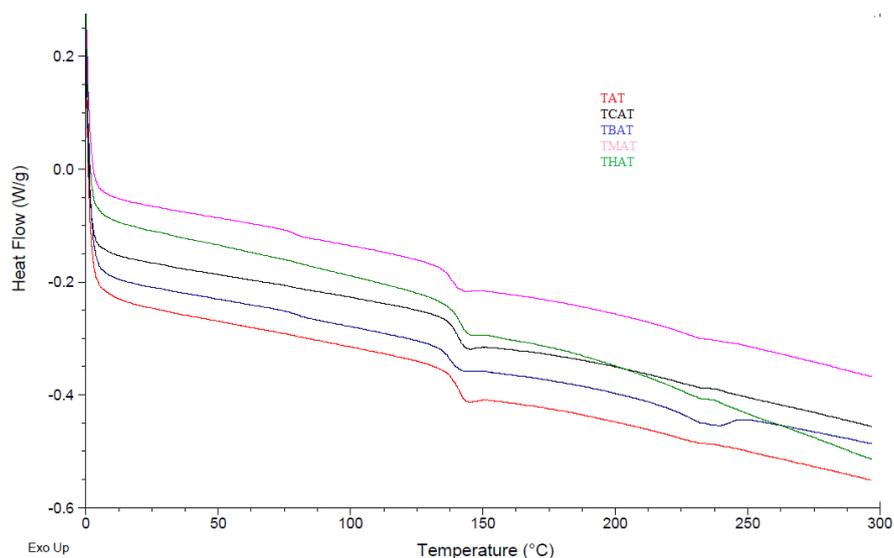


Figure 3. DSC (Differential Scanning Calorimetry) curves for *sym*-2,4,6-trisubstituted *s*-triazine derivatives (TXAT).

4.2.5. Flammability of PP and Its Composites UL-94

Based on the CR and LOI data, three derivatives TAT **3a**, TBAT **3b**, and TMAT **3e** were selected and mixed with APP in different weight ratios to afford several IFRs. These mixtures were used in PP to yield PP/IFRs composites. The UL94 test was used to evaluate the flame retardant performance of neat PP, PP/**3a**, PP/**3b**, or PP/**3e** and PP/IFRs to provide a qualitative classification of the samples used in this work (Table 3). Pure PP is highly combustible, and cannot pass the UL94 test. When the weight ratio was 25 wt% of the TAT **3a**, TBAT **3b** or TMAT **3e** and 75 wt% PP, the composite (PP_x, PP_y, and PP_z, respectively, Table 3) did not pass the UL94 rating. However, there was a remarkable enhancement of UL-4 rating of IFR-PP composite when APP was added to the TXAT/PP composite. When the weight ratio of APP to TAT was 1:1 and the IFR loading was 25 wt % (PP_a), the UL94 rating was V-2. The same rating was noticed with the same ratio of TBAT/APP (PP_b) and TMAT/APP (PP_c), as shown in Table 3. For further increase of the weight ratio of TXAT: APP (1:2) and using loading 25 wt% with 75 wt% PP, the UL94 rating remarkably improved and the char layer formed during combing could be observed obviously, which is unlike from that in neat PP and other PP composites. When

the weight ratio of APP to TAT was 2:1 and when the IFR loading was 25 wt% (PP1), the UL94 rating improved and reached the V-1 rating of the UL94 tests, which is better than pure TXAT/PP with the same ratio (PP, PPx and PPa, Table 3). As for APP with TBAT (PP2) with the same weight ratio of 2:1, the UL94 rating also improved and reached the V-1 rating of the UL94 test, which is better than pure PP, TBAT/PP (PPy) and TBAT/APP (1:1)/PP (PPb). As for APP with TMAT (PP3) with the same weight ratio of 2:1, the UL94 rating also improved and reached the V-0 rating of the UL94 test, which is better than pure PP, TMAT/PP (PPz) and TMAP/APP (1:1)/PP (PPc).

Table 3. Flammability test of the prepared polypropylene (PP) composite.

Sample ID	PP (wt%)	APP (wt%)	FR (wt%)	UL94	Drip
PP neat	100	0	0	N/R	Yes
PPz	75	0	25	N/R	Yes
PPx	75	0	25	N/R	Yes
PPy	75	0	25	N/R	Yes
PPc	75	12.5	12.5	V-2 ^a	Yes
PPa	75	12.5	12.5	V-2 ^a	Yes
PPb	75	12.5	12.5	V-2 ^a	Yes
PP3	75	16.66	8.33	V-0 ^b	No
PP1	75	16.66	8.33	V-1 ^c	No
PP2	75	16.66	8.33	V-1 ^c	No

^a V-2 allows flaming drips; ^b V-0 rating is the highest flame-retardant rating for materials; ^c V-1 rating allows non-flaming drips.

Moreover, PP3 sample even reaches UL94 V-0 rating without dripping, while other flame retardant samples reach UL94 V-1 rating. This showed that PPc composite is highly efficient in improving the flame retardancy of PP among all PP composites.

These results demonstrated that the combination of TXAT and APP would cause huge enhancement of flame retardant performance of PP, especially with TMAT derivative. These results agreed with the results obtained in Table 2.

Photographs of PP1, PP2, and PP3 specimens after UL94 tests are shown in Figure 4, it shows that neat PP is in a melted form without obvious char residues; however, char residues were observed for PP1, PP2, and PP3 specimens.



Figure 4. PP1, PP2, and PP3 specimens after UL94 tests.

5. Conclusions

The *sym*-2,4,6-trisubstituted triazine derivatives **3a–e** were prepared, characterized, and used as charring agents along with ammonium polyphosphate (as acid source) to construct intumescent flame-retardant systems, which could enhance the flame retardant performance of polypropylene.

The char residue (CR) and limiting oxygen index (LOI) values were calculated from the thermogravimetric analysis (TGA) data. The results showed that TMAT (**3e**) and THAT (**3d**) have CR 31.5% and 31.9%, respectively, at 800 °C with LOI (35 and 36, respectively); while the unsubstituted aniline TAT and the halogenated derivatives TBAT, and TCAT showed CR (20%, 22%, 6%, respectively) with LOI (25.5%, 26.3%, 19.9%, respectively). Accordingly, the three derivatives with highest LOI values (TAT, TBAT, and TMAT) were selected and mixed with ammonium polyphosphate (APP) in different weight ratio to construct the IFR system. Combustion behavior showed that PP/IFR blends could acquire significant LOI values, and pass the UL94 V-0 rating. The PP/IFR blends achieve the UL94 V-0, indicating the flame-retardant efficiency is improved. When the components mass ratio of APP: TXAT in the IFR system was (2:1, respectively), the IFR offered the most effective flame retardancy in PP. When the mass ratio of APP and TXAT is 1: 1, the PP/IFR has a UL94 V-2 rating with high dripping. This has satisfactorily proved that IFR is very effective in PP.

Finally, the electron-donating group on the aniline residue attached to the *s*-triazine ring has a great effect on the thermal stability and intumescent flame retardant behaviors, as observed from TGA data and UL94 V-0.

Efforts on the synthesis and characterization of different generation of *sym*-trisubstituted *s*-triazine derivatives are in progress in our lab, which might have special interest as flame retardant agents in the industrial field.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2227-9717/8/5/581/s1>, Figure S1: FTIR for TXAT derivatives, and Figures S2–S5: ¹H-NMR and ¹³C-NMR of **3b–3e**.

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