Addition of anti-flaming agents in castor oil based rigid polyurethane foams: studies on mechanical and flammable behaviour

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Abstract

The major drawback in the use of Rigid Polyurethane Foam (RPUF) is its high flammability which limits its industrial applications. In the presented studies, RPUF was incorporated with different anti-flaming agents such as Melamine (2,4,6-Triamino-1,3,5-triazine), Tris(1,3-dichloro-2-propylphosphate) (TDCPP) and Tris(2-chloroethyl) phosphate (TCP). Unlike the conventional RPUF, the foam developed here is derived from vegetable oil based polyol i.e. from Castor oil. Flammability of resulted RPUFs was tested according to UL 94 V test. The structure of the resulted foam samples was characterized by FTIR, XRD and SEM and their thermal properties were studied by TGA. The mechanical behaviour i.e. Tensile, compressive and flexural strength and hardness was examined by universal testing machine. The investigations made on flammability, mechanical and thermal properties of RPUFs incorporated with melamine, TCP, and TDCPP, suggested that, among all samples prepared, TDCPP incorporated RPUF rendered good thermal stability, mechanical and flame retardant properties. Results obtained from SEM analysis also revealed the reduction in the cell size in case of TDCPP based RPUFs.

Abbreviations

PU Polyurethane
MDI Methylenebis(4-phenylisocyanate)
RPUF Rigid Polyurethane Foam
TDCPP Tris(1,3-dichloro-2-propylphosphate)
TCP Tris(2-chloroethyl) phosphate
TGA Thermogravimetric analysis

1. Introduction

Rigid Polyurethane Foam (RPUF) is one of the best suitable material used extensively for the production of sandwiched construction panels, railway assemblies and in buildings for insulation purposes. Due to their light weight, excellent thermal insulation, good dimensional stability, easy processing, low density and high specific strength, they are one of the most widely used material in various industrial and engineering applications including false roofing, structural panels and for the thermal insulation of buildings and refrigerators etc. Moreover, the easy processing of RPUFs make them an ideal candidate for the fabrication of many nifty products which also help to enhance the aesthetic design of homes. However, the high combustibility of RPUF makes its use restricted in many important engineering applications. As per the experimental evidences, the pores of the foam entraps air which further aid in its combustion. This cellular material burns readily in the presence of oxygen and heat with a very high fire spread rate and a high smoke release rate [1–3]. The release of poisonous smoke and rapid reduction of oxygen concentration due to the combustion poses a threat to the
human health and environment [4–6]. Due to fire threats of RPUFs, special fire protocols have to make compulsory by regulatory bodies for their utilization in furniture and buildings [7–9]. The development of the fire behaviour of the RPUF has presently been a significant issue of many studies among the researchers as it hinders its practical applications [10]. Hence, the improvement of flame retardancy of RPUFs is one of the areas of prime importance and has attracted the attention of many researchers [11, 12]. The use of fire retardants in RPUFs to decrease its combustibility and smoke production has become a vital parameter during the design and development of their products. RPUFs can be made fireproof by the incorporation of halogens, nitrogen, phosphorus, inorganic metal oxides and hydroxides based flame retardants [13]. Nitrogen and phosphorous based fire retardants are less poisonous and eco-friendly being gases themselves and produce less toxic gases or vapours products during combustion [14, 15]. In contrast, another flame retardant melamine while combustion, grips the heat of the PU matrix and go through the advanced endothermic condensation with evolution of ammonia. Polyurethane/phosphate combinations are reported to form intumescent flame retardant systems [16]. The growth of flame retardants in industrial and engineering uses is motivated due to the increased consciousness towards the safety, among the consumers, and by the environment threats posed by the researchers [14, 17, 18]. Recent researches are focused on smart flame retardants such as halloysite nanotubes, which in addition to fire retardancy, also act as economic reinforcing materials for polymers [19] The present studies report the effects of different anti-flaming agents i.e. Melamine (2,4,6-Triamino-1,3,5-triazine), Tris(2-chloroethyl) phosphate (TCP) and Tris(1,3-dichloro-2-propylphosphate) (TDCPP) on the properties of RPUFs. The RPUFs developed in the given study have been derived from a plant source i.e. castor oil, the properties of which are studied and reported earlier by the some researchers [20–27] and other investigators and found to be comparable with commercial petrochemical based RPUFs.

### Table 1. Different formulations of foam (pbw).

| Samples | Flame retardants | Mpol | TEDA | n-Pentane | Silicon Oil | MDI |
|---------|------------------|------|------|-----------|-------------|-----|
| AF-00   | Neat             | 100  | 2    | 15        | 3           | 110 |
| AF-01   | Melamine         | 100  | 2    | 15        | 3           | 110 |
| AF-02   | TDCPP            | 100  | 2    | 15        | 3           | 110 |
| AF-03   | TCP              | 100  | 2    | 15        | 3           | 110 |

2. Experimental

2.1. Raw materials

Castor oil (AR Grade) and 4,4’-diphenylmethanediisocyanate (AR grade) were supplied by Shivathene Linopack Ltd Parwanoo, Himachal Pardesh. Triethylenediamine (TEDA) (99%), Melamine (2,4,6-Triamino-1,3,5-triazine), Tris(2-chloroethyl) phosphate (TCP) and Tris(1,3-dichloro-2-propylphosphate) (TDCPP) were bought from Standard Chemicals (ISO 9001:2008 certified), Tilak Bazar, New Delhi. Silicon oil (C-63148-62-9) and n-Pentane (C-109-66-0) were gotten from CDH(P) Ltd, New Delhi – 110022 (India) and Glycerol (99.9%) was purchased from Sisco Industries Pvt. Ltd

2.2. Preparation of foams

The foam formulations are as reported in table 1. A two-step process was used to prepare the anti-flammable RPUFs. Castor oil was modified by transesterification process in the first step to get polyol (Mpol) according to the procedure reported in prior studies [24–26]. Glycerol was used to enhance the hydroxyl value of castor oil by introducing more hydroxyl groups. The modification of the castor oil was performed under the inert atmosphere of nitrogen using 2:1 ratio of the castor oil to the glycerol at the temperature 180 °C–210 °C for 4–5 h, till a hydroxyl value of 390–410 mg KOH g⁻¹ is achieved. A schematic representation of the castor oil modification by transesterification process is as given in figure 1. In the subsequent step, all the constituents as per the table 1 were added to the reactor and stirred at 2200 rpm at room temperature. The resulted mixture was spread onto a metal mould (200 × 200 × 100 mm) and cured for 96 h. On complete curing (after 96 h), the foam was de-moulded, cut into standard dimensions and tested for its hardness, compressive, flexural and tensile strength, cell morphology and density. Dimensional finishing was achieved by rubbing with fine emery papers. FTIR, XRD and TGA were performed to find out structure and thermal stability of resulted RPUFs. Fire behaviour of the resulted RPUFs was confirmed by ULV-94 test.
3. Results and discussion

3.1. Density
Density of the resulted RPUFs considerably affect their surface and mechanical properties. The density of the resulted RPUFs samples was determined according to ASTM D 1622-03. The size of the specimen was taken as $30 \times 30 \times 30$ mm$^3$ and average result of four samples are reported. The density of all samples obtained from different formulations of flame retardants are as given in table 2. As per the results obtained, the density of the RPUFs incorporated with melamine flame retardant was observed to be decreased as compared to neat RPUFs. The reason for this might be the voids formation in the cell structures of the foam, which, also affected the density of the foam significantly. This result is similar to that already reported in previous literature study [13]. Unlike melamine, the density of RPUFs filled with TDCPP and TCP was found to be more than neat RPUFs which is due to the reduction in the average cell size and the development of uniform cell structure that is also evident from SEM analysis.

3.2. FTIR
A Fourier transform infrared (FTIR) spectrophotometer was employed to analyze the structure of the modified polyols, MDI and polyurethanes. On Nicolet 380 spectrometer, spectra were recorded in the range 400–4000 cm$^{-1}$. For analysis, powdered samples obtained by crushing the resulted foam were mixed with pure dried KBr to form transparent KBr pellets. Figure 2(a) shows the characteristic absorption peaks of polyols and MDI at 3402 cm$^{-1}$ (O-H stretching frequency), 2925–2851 cm$^{-1}$ (-CH$_2$ and -CH$_3$ stretching frequency), 2268 cm$^{-1}$ (NCO stretching frequency). Figure 2(b) shows the FTIR of the RPUFs incorporated with anti-flaming agents. It is evident from figures 1(a) and (b) that there is disappearance of absorption peaks at

| Formulation | Density ($\text{kg/m}^3$) |
|-------------|---------------------------|
| AF00        | 102                       |
| AF01        | 82                        |
| AF02        | 112                       |
| AF03        | 107                       |

Table 2. Density of RPUFs in different formulations.
2268 cm$^{-1}$ (NCO stretching frequency) in RPUF, AF01, AF02 and AF03 which confirm that MDI is completely reacted with a polyl to form polyurethane linkage.

3.3. XRD

XRD patterns for Formulations AF00, AF01, AF02 and AF03 were obtained using BRUKER D8 ADVANCE diffractometer by employing CuK$\alpha$ ($\lambda$=1.54056 Å) radiation. X-ray diffraction pattern of resulted RPUFs incorporated with anti-flaming agents are as shown in figure 3. From the figure, it is evident that the RPUF exhibit amorphous structure, having broad amorphous peak at 2$\theta$ = 20°. Foam samples incorporated with melamine shows slight shift towards crystalline behaviour due to its own crystalline structure.

3.4. Thermogravimetric Analysis (TGA)

TGA of the foam samples was conducted on universal V4.5 A, TA instrument using a heating rate of 10 °C min$^{-1}$ from 30 to 1000 °C under N$_2$ atmosphere. Testing of all foam samples was conducted using a gas flow rate of 30 mL min$^{-1}$. Continuous loss in mass was examined as a function of time and temperature. Figure 4 indicates the Thermogravimetric (TG) curves of the foam samples under investigation. The sample AF00 i.e. neat PU (without any flame retardant) clearly exhibit three degradation stages. In the first stage between 80 and 140 °C, there is a loss of weight because of the evaporation of water from the sample. Second degradation step is visible in the 70 to 240 °C temperature range, which is, probably due to the breaking of the urethane linkage. The third degradation step is due to decomposition of material occurring above 250 °C. Compared with the formulation AF00, the other formulations AF01 (Melamine), AF02 (TDCPP) and AF03 (TCP) have a
significantly similar decomposing trend. PU foams incorporated with TDCPP shows a higher thermal stability while PU foam with melamine composition shows the least stability.

3.5. Flammability
Flammability of the resulted RPUF samples was classified according to the UL-94 vertical burning standard test [28–30]. The flammability of RPUFs was tested as per the ASTM D 3014 standards. The specimens were mounted vertically on the stand and ignited with the help of a burner for 10 s. As a standard procedure, a 3/4th inch high blue flame was used for heating at the bottom of the sample for exactly 10 s and then withdrawn, and again applied for more 10 s time. The time of glowing and flaming was noted as the sample was extinguished. To examine the ignitability of dripping material, a layer of cotton was placed beneath sample, during the test period. A record of time of burning, flame height and weight loss of the samples was accounted and reported in table 3. From table 3, it is clear that for the sample with formulation AF00, the recorded flame height travelled is more and for AF02 flame height was found to be least. With AF00 formulation extinguishing time is higher thus shows continuous burning. The reason may be the irregular and improperly disturbed cells in neat PU, with entrapped air, that supports prolong burning. As more is the extinguishing time, more is the recorded weight loss in the samples. Anti-flaming properties of RPUFs were found to be significantly enhanced by the incorporation of flame retardants due to better homogenization of foam structure as per the reported literature [17]. TDCPP incorporated foam samples i.e. formulation AF02 exhibited the best anti-flammable behaviour among the all three formulations. Tris (1,3-dichloro-2-propylphosphate is a semi-volatile flame retardant having both
phosphate and chlorine, contributing towards the enhancement of anti-flammability of the foam. TDCPP shows two types of flame retardancy mechanisms i.e. char yield and gas phase from chlorine radical. The phosphate group promotes the char-forming property of the RPUF and the halogenated group i.e. chlorine act in the vapour phase by liberating the chlorine atoms into the flame where they disrupt the combustion reactions [19]. As, the flame retardancy depends upon the content of phosphorus and chlorine in the RPUF, this is the reason that AF02 show the best flame retardant material than AF00, AF01 and AF03.

### 3.6. Mechanical properties

Tensile, compressive and flexural properties of the resulted foams were measured using Instron (Model No.: 3369) universal testing machine as per ASTM D 638, ASTM D 695 and ASTM D 790, respectively. Hardness (Shore D) was determined by using ASTM D 2240 method. The results obtained are as given in figure 5. As seen in the figure, the neat RPUF (AF00) showed an average value of tensile, compressive and flexural strength and average hardness equal to 0.82 MPa, 6.87 MPa, 3.80 MPa and 45 (Shore D) respectively. Average tensile strength of the RPUF (AF01), (AF02), (AF03) is equal to 0.69 MPa, 2.02 MPa, 1.10 MPa, respectively. The average compressive strength of RPUF (AF01), (AF02), (AF03) was recorded to be 7.24 MPa, 9.12 MPa, 7.42 MPa, respectively. The average flexural strength of RPUF (AF01), (AF02), (AF03) was observed to be 6.30 MPa, 12.02 MPa, 8.42 MPa, respectively and average hardness achieved was 48, 53, 48 (Shore D) respectively. Almost linear increment in the said properties (except tensile strength in case of formulation AF01) up to formulation AF02 indicates a good distribution of anti-flamming agents in the PU matrix, leading to appropriate adhesion. From AF02 to AF03 formulation, the observed mechanical properties were decreased. The decrease in tensile strength in case of the AF01 formulation is due to involvement of melamine in the polyurethane matrix that weakens the cellular structure. Higher particles size of the melamine results in collapsing of cellular structure during the formation of foam [31].

### Table 3. Flammability Testing of RPUFs with different formulations.

| Formulation | Flame height (mm) | Extinguishing time (sec) | Loss of weight (grams) | UL—94 ratings |
|-------------|-------------------|--------------------------|------------------------|---------------|
| AF00        | 35                | Continuously burn        | 5.2                    | No ratings    |
| AF01        | 28                | 82                       | 3.1                    | V1            |
| AF02        | 22                | 55                       | 2.8                    | V1            |
| AF03        | 25                | 62                       | 2.9                    | V1            |

### Figure 5. Mechanical properties of different formulations of RPUFs.
observed as a result of homogenized dispersal of TDCPP into the polyol. Uniform cell morphology and small pore size of resulted RPUFs with formulation AF02 further support the enhancement in mechanical properties.

3.7. SEM micrograph

The morphologies of RPUFs were observed using scanning electron microscopy (SEM, Hitachi S3700) with an accelerating voltage of 15 kV. Prior to testing, samples were gold coated to make them conducting. Figure 6 shows the micrographs of the castor oil based rigid polyurethane foams with different formulations. As observed from figure 6 that the shape of the cells is almost spherical. For the formulations AF00, AF01, AF02 and AF03, the average pore size is equal to 305.25 μm, 266 μm, 225.71 μm and 263.2 μm, respectively. There is a significant reduction in pore size from AF00 to AF02 and then size increase occurs in formulation AF03. The reduced pore size for the formulation AF02 indicated that the 3D structure of the foam was more packed than AF00, AF01 and AF03. The further increase in pore size AF03 is may be due to collapsing of cells. A graph of cell size versus different formulations of RPUFs is as shown in figure 7. The best results were obtained for mechanical properties for AF02 formulation i.e. RPUF incorporated with Tris (1,3-dichloro-2-propylphosphate) (TDCPP).

4. Conclusion

Though RPUF being one of the industrially important material construction material, it suffers from the drawbacks of its high flammability, formation of dark smoke with the irritating smell and with release of toxic gases on burning. Significant enhancement in the thermal and anti-flaming properties of RPUFs was observed with the addition of anti-flaming agents such as Melamine (2,4,6-Triamino-1,3,5-triazine), Tris(1,3-dichloro-2-propylphosphate) (TDCPP) and Tris (2-chloroethyl) phosphate (TCP). RPUF incorporated with TDCPP was found to have exhibited best anti-flaming behaviour due to well homogenization of flame retardant into the polyol. Tensile, compressive & flexural strength and Hardness (Shore D) of RPUFs are found to be improved with TDCPP addition because of uniform cell structure and decreased in pore size of resulted RPUFs. Tensile strength was found to be poor with melamine based RPUFs as embedment of melamine in the polyurethane matrix weakens the structure due to the formation of inconsistent structure. The resulted foams incorporated with different antiflaming agents with their improved mechanical, thermal and anti-flammable properties are
expected to be much suitable for the new generation anti-flammable lightweight materials for different engineering and industrial applications especially in the field of construction and building materials.

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Conflict of interest

This study has been conducted for the research purpose only and there is no conflict of interest is involved.

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References

[1] Yang R, Hu W, Xu L, Song Y and Li J 2015 Synthesis, mechanical properties and fire behaviours of rigid polyurethane foam with a reactive flame retardant containing phosphazene and phosphate Polym. Degrad. Stab. 122 102–9
[2] Hatakeyama H, Matsumura H and Hatakeyama T 2013 Glass transition and thermal degradation of rigid polyurethane foams derived from castor oil-molasses polyols J. Therm. Anal. Calorim. 111 1545–52
[3] Luo F, Wu K, Lu M, Nie. S and Guan X 2015 Thermal degradation and flame retardancy of microencapsulated ammonium polyphosphate in rigid polyurethane foam J. Therm. Anal. Calorim. 120 1327–35
[4] Levchik S V and Weil E D 2004 Thermal decomposition, combustion and fire-retardancy of polyurethanes—a review of the recent literature Polym. Int. 53 1585–610
[5] Almeida Pinto U, Visconte L L Y, Gallo J and Nunes R C R 2000 Flame retardancy in thermoplastic polyurethane elastomers (TPU) with mica and aluminium trihydrate (ATH) Polym. Degrad. Stab. 69 257–60
[6] Guo H, Gao Q, Ouyang C, Zheng K and Xu W 2015 Research on properties of rigid polyurethane foam with heteroaromatic and brominated benzyl polyols J. Appl. Polyms. Sci. 132 1–8
[7] Zatorski W, Brzozowski Z K and Kolbrecki A 2008 New developments in chemical modification of fire-safe rigid polyurethane foams Polym. Degrad. Stab. 93 2071–6
[8] Zhu H, Peng Z, Chen Y, Li G, Wang L, Tang Y, Pang R, Khan Z U H and Wan P 2014 Preparation and characterization of flame retardant polyurethane foams containing phosphorus-nitrogen-functionalized lignin RSC Adv. 4 55271–9
[9] Qian L, Peng F and Tang S 2014 Bi-phase flame-retardant effect of hexa-phenoxy-cyclotriphosphazene on rigid polyurethane foams containing expandable graphite Polym. (United Kingdom). 55 95–101
[10] Ye L, Meng X Y, Ji X, Li Z M and Tang J H 2009 Synthesis and characterization of expandable graphite-poly(methyl methacrylate) composite particles and their application to flame retardation of rigid polyurethane foams Polym. Degrad. Stab. 94 971–9
[11] Agrawal A, Kaur R and Walia R S 2019 Flame retardancy of ceramic based rigid polyurethane foam composites J. Appl. Polyms. Sci. 136 48250
[12] Agrawal A, Kaur R and Walia R S 2019 Investigation on flammability of rigid polyurethane foam–mineral fillers composite Fire Mater. 43 917–27
[13] Thirumal M, Khashigir D, Nando G B, Naik Y P and Singha N K 2010 Halogen-free flame retardant PUF: effect of melamine compounds on mechanical, thermal and flame retardant properties Polym. Degrad. Stab. 95 1138–45
[14] Lu S Y and Hamerton I 2002 Recent developments in the chemistry of halogen-free flame retardant polymers Prog. Polym. Sci. 27 1661–712
[15] Horacek H and Grabner R 1996 Advantages of flame retardants based on nitrogen compounds Polym. Degrad. Stab. 54 205–15
[16] Wu K, Song L, Wang Z and Hu Y 2009 Preparation and characterization of double shell microencapsulated ammonium polyphosphate and its flame retardance in polypropylene J. Polym. Res. 16 283–94
[17] Czeck-polak J, Heneczkowski M, Przybyszewski B, Gzulak A and Gude M 2016 Effect of environmentally-friendly flame retardants on fire resistance and mechanical properties of rigid polyurethane foams Polymers/Polymers 61 113–6
[18] Rao R V and Manujesh B J 2013 Burning behaviour of polyurethane foam cored/E-glass reinforced/vinylester sandwich composites: Effect of core density and fibre architecture European Journal of Applied Engineering and Scientific Research 2 1–8 www.scholarsresearchlibrary.com
[19] Goda E S, Yoon K R, El-Sayed S H and Hong S E 2018 Halloysite nanotubes as smart flame retardant and economic reinforcing materials: a review Thermochim. Acta 669 173–84
[20] Malik M and Kaur R 2018 Synthesis of NIPU by the carbonation of canola oil using highly efficient 5,10,15-tris(pentafluorophenyl) corrolato-manganese(III) complex as novel catalyst Polym. Adv. Tech. 29 1078–85
[21] Aggarwal A, Kaur R and Walia R S 2017 PU foam derived from renewable sources: perspective on properties enhancement: an overview Europ. Polym. J 95 255–74
[22] Kumar M and Kaur R 2017 Glass fiber reinforced rigid polyurethane foam: synthesis and characterization e-Polymers 7 517–21
[23] Malik M and Kaur R 2018 Influence of aliphatic and aromatic isocyanates on the properties of polyether–ester polyol based PU adhesive system Polym. Eng. Sci. 58 112–7
[24] Malik M and Kaur R 2018 Mechanical and thermal properties of castor oil–based polyurethane adhesive: effect of TiO2 filler Adv. Polym. Tech. 37 24–30
[25] Kaur R and Kumar M 2013 Function of silicon oil in the castor oil based rigid polyurethane foams’ Jl. Polym. Eng. 33 857–61
[26] Kumar M and Kaur R 2013 Effect of different formulations of MDI on rigid polyurethane foams based on castor oil Int. Jl. Sci. Res. Review. 2 Special Issue April—May 29–42
[27] Agrawal A, Kaur R and Walia R S 2019 Vegetable oil based conducting rigid PU foam e-Poly. 19 411–20
[28] Tirri T, Aubert M, Wilen C E, Pfandmner R and Hoppe H 2012 Novel tetrapotassium azo diphophonate (INAZO) as flame retardant for polyurethane adhesives Polym. Degrad. Stab. 97 375–82
[29] Wang Y and Zhang J 2013 Thermal stabilities of drops of burning thermoplastics under the UL 94 vertical test conditions J. Hazard. Mater. 246-2 47 103–9
[30] Wu H, Lee M, Wu Y, Su Y and Ma C M 1996 Pultruded fiber-reinforced polyurethane–toughened phenolic resin II. Mechanical properties, thermal properties, and flame resistance J. Appl. Polym. Sci. 62 227–34
[31] Kong A, Fehrenbacher U, Hirth T and Kroke E 2008 Flexible polyurethane foam with the flame-retardant melamine J. Cell. Plast. 44 69–80