Chapter 5
Fireproof Capability of Rigid Polyurethane Foam Based Composite Materials

Nazim Usta, Recep Yurtseven, Erkin Akdoğan, and Fatih Demiryuğuran

5.1 Introduction

Polyurethane foams are used in thermal insulation, automotive and furniture industries due to the best combination of performance and cost. There are mainly three different polyurethane foams used in different industries, namely rigid, semi rigid/integral and flexible polyurethane foams. The rigid polyurethane foams (PUR) that have closed cell structures and low thermal conductivity coefficients are preferred for thermal insulation applications. Semi rigid – integral polyurethane foams are used for production of some parts for automotive and furniture industries. The flexible polyurethane foams that have open cell structure are suitable for seating and bed applications in all kinds of industries.

The polyurethane foams are widely preferred because of their superior properties such as lightweight, thermal and electrical insulating, design flexibility, easy production, corrosion resistance etc. Nevertheless, the foams are flammable materials and this is an important disadvantage of the foams. During the ignition and the combustion of the foams, smoke, heat, toxic and corrosive compounds are released at different rates depending on the generic nature of the polyurethanes and the environmental conditions. The release rate of heat, smoke, toxic and corrosive compounds are responsible for generating both thermal and non-thermal hazards in fires. These hazards can be reduced by increasing fire resistance of the polyurethanes. Thus, the polyurethanes are modified by variety of techniques to increase their fire resistance. The most common technique is to use flame retardant materials and inorganic fillers (Gao et al. 2013, Jin et al. 2014, Kirpluks et al. 2014, Xu and Wang 2015, Lu et al. 2018, Qu et al. 2017, Kairytė et al. 2018, Shi et al. 2018,

N. Usta (✉) · R. Yurtseven · E. Akdoğan · F. Demiryuğuran
Mechanical Engineering Department, Pamukkale University, Denizli, Turkey
e-mail: n_usta@pau.edu.tr; ryurtseven@pau.edu.tr; eakdogan@pau.edu.tr;
fdemiryuguran@pau.edu.tr

S. Siddiquee et al. (eds.), *Composite Materials: Applications in Engineering, Biomedicine and Food Science*, https://doi.org/10.1007/978-3-030-45489-0_5

Chen et al. 2018). It should be taken in account the compatibilities of fillers and flame retardants with the polyol and the isocyanate components of the polyurethane foams and negative effects on the thermal and the mechanical properties (Usta 2012, Luo et al. 2015, Li et al. 2017). Furthermore, there are different studies related to the usage of glass fiber in rigid polyurethane foams (Latere Dwanisa et al. 2004, Kim et al. 2010, Han et al. 2010, Kumar and Kaur 2017) and in other polymers (Jiang et al. 2015, Hu et al. 2016).

In this chapter, the thermal, the combustion and the mechanical behaviors of the rigid polyurethane foams commonly used in thermal insulation, automotive and furniture industries were examined. New and effective fire-resistant polyurethane based composite foams were developed and tested in terms of the thermal, the combustion and the mechanical properties.

5.2 Rigid Polyurethane Foam (PUR)

Rigid polyurethane foams are produced by mixing of polyol and isocyanate components at certain ratios. After the mixing process, the foam rises, reaches a maximum point, and then slightly drops. Meanwhile some additives such as blowing agents, catalysts, surfactants, flame retardants and fillers are incorporated into the polyol component before mixing the isocyanate. Figure 5.1 shows an example for the foam formation and Fig. 5.2 shows the foam rising with respect to the time. The foam rising can be measured by using a special laser beam (Usta et al. 2011).

In general, low and high-pressure injection machines are used for mixing processes in industrial applications. The mixture is poured into special heated molds. The mixture expands and fills the inside of the mold. Figure 5.3 show a low-pressure polyurethane injection machine and process.

Rigid polyurethane foams have closed cell structure and low thermal conductivity coefficients. Figure 5.4 shows an example view of the cell structure that was taken by a microscope. In addition, they should withstand certain loads. The rigid polyurethane foams are mainly used in all thermal insulation applications. Density and thermal conductivity of the foams may change depending on the raw materials, the polyol/the isocyanate ratio and the production applications.

Fig. 5.1 The isocyanate, the polyol and the foam formation after mixing of them

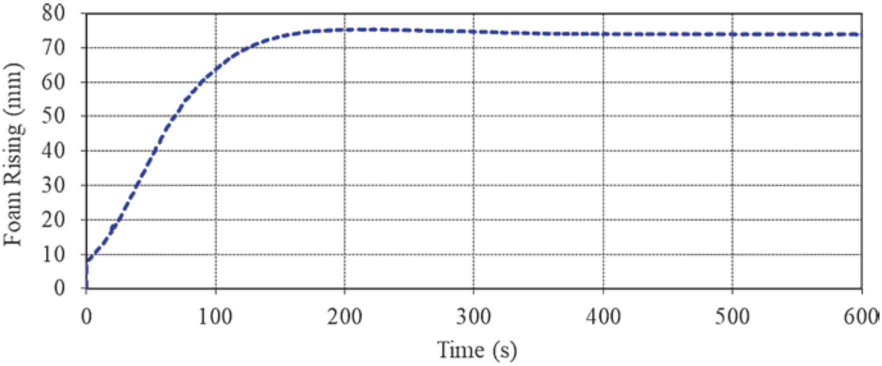


Fig. 5.2 Foam rising versus time after after mixing of the polyol and the isocyanate

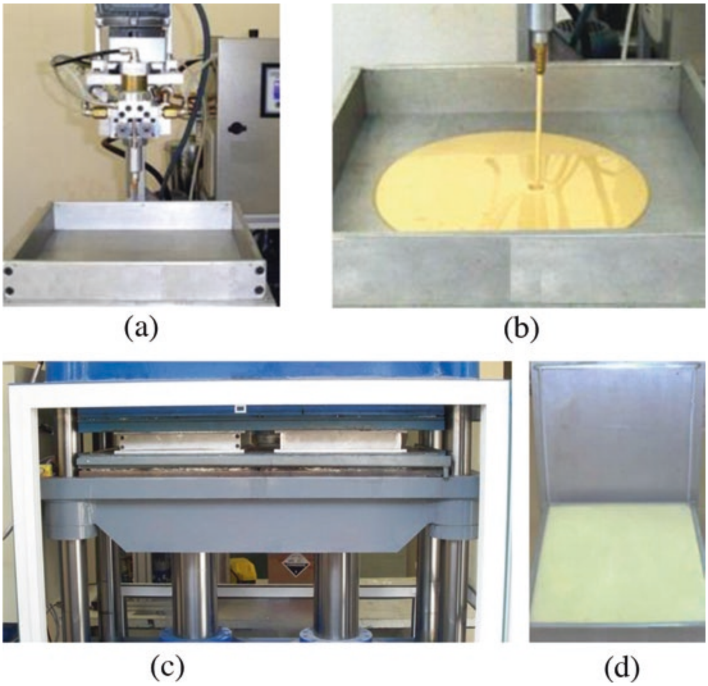


Fig. 5.3 (**a**) Low pressure injection machine, (**b**) Pouring of the polyol and the isocyanate mixture into the mold, (**c**) Curing process inside a heated press, (**d**) The rigid polyurethane foam

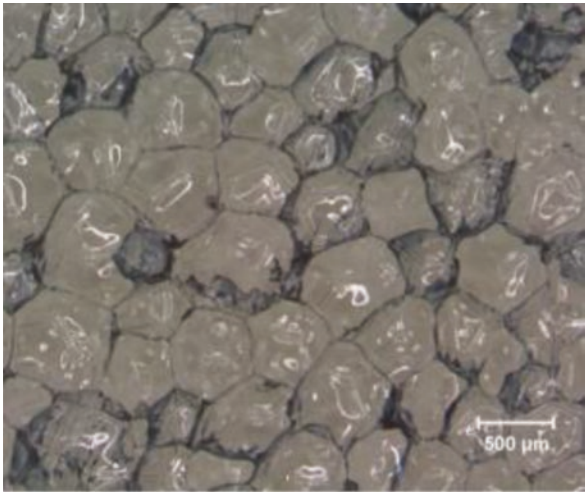


Fig. 5.4 Cell structure of PUR

5.3 Flame Retardancy and Intumescent Flame Retardant Systems

5.3.1 Flame Retardancy

Many studies have been performed to obtain fireproof rigid polyurethane foams. In general, different flame retardant materials and fillers are added into the polyol component and the doped polyol is mixed with the isocyanate component. Meanwhile it should be pointed out that the other properties of the foams should not be worsen. Otherwise, the foams cannot be used in the real life applications.

There are different studies related to the thermal decomposition, the combustion and the fire resistance of polyurethane foams in the literature. The thermal decomposition is very important step before start of combustion. Because solid materials do not burn directly. When a matter is exposed to a heat or a fire, some gases initially decompose from the solid matters and combustible gases can be ignited and burned easily. Meanwhile some liquid may appear before gasification. Then, the liquid / solid matters start to burn due to the generated heat. In general, the thermal decomposition of polyurethanes begins at thermally weakest links, namely allophanate and biuret, and the decomposition continue at ureas, urethanes, and isocyanurate group (Levchik and Weil 2004). In addition, the combustion of polyurethane foams were separated into two stages, namely solid and liquid pool combustions. In the solid phase combustion, the isocyanate component burns and yellow smoke is generated. Then the yellow smoke may decompose organic compounds and hydrogen cyanide, which partially results in nitrogen oxides. In the liquid pool phase combustion, the polyol component burns and heat, carbon monoxide and carbon dioxide are generated.

Flame retardants may be divided into two different groups as reactive and non-reactive (Singh and Jain 2009). It should be pointed out that the non-reactive flame retardants can be physically filled into the polyurethane foams and the reactive flame retardants can be incorporated chemically into the foams. Although the reactive flame retardants take part in the foaming reaction, the non-reactive flame reactants do not. Moreover, the reactive flame retardants essentially consist of phosphorus, nitrogen and halogen materials and they try to maintain the fire resistance of the foam by slowing down the decomposition of the foam (Tashev et al. 1992, Modesti and Simioni 1994, Prociak et al. 1997, Usta 2012). However, the flame retardants including the halogen produce hazardous poisonous gases and dense smoke during burning of the foam. Therefore, the flame retardants including halogens are not preferred and permitted in most of countries and many studies have been focused on halogen-free flame retardants. Flame retardants which consist of phosphorus and nitrogen can form char layer and decrease the generation of hazardous poisonous gases and dense smoke (Singh et al. 2008, Usta 2012).

Yang et al. (2015) studied on synthesis, mechanical properties and fire behaviors of rigid polyurethane foams with a reactive flame retardant including phosphazene and phosphate. They synthesized reactive flame retardant hexa-(phosphite-hydroxyl-methyl-phenoxyl)-cyclotriphosphazene (HPHPCP) by using hexachlorocyclotriphosphazene, diethyl phosphite and p-hydroxybenzaldehyde. It was reported that HPHPCP as a flame retardant inhibits foam collapse, pool-fire formation and restricted flame spread during burning.

The non-reactive flame retardants which may contain aluminum, boron, antimony, carbon, sulphur, phosphorus, nitrogen, halogens, and silicones etc., may be either compatible with the raw materials of the polyurethane foams acting as plasticizers, or not. The non-reactive flame retardants that are not compatible with the raw materials are evaluated as filler materials. The non-reactive flame retardants enhance fire resistance of the foam on weight basis. In general, the amounts of raw materials are decreased as the amounts of the fillers and this causes decreasing of the combustible decomposed gases (Lu and Hamerton 2002, Thirumal et al. 2009).

When the metal hydroxides as a part of the non-reactive flame retardants are added into the foams in high amount, namely more than 60 phr, the fire resistance of the foams may be significantly enhanced (Levchik and Weil 2004, Thirumal et al. 2010a, Lv et al. 2005, Zhang et al. 2004). However, the mechanical properties and the thermal insulation of the foams may be deteriorated (Bahattab et al. 2010, Liu et al. 2010). The deteriorations can be explained with inadequate interactions between the metal hydroxides and the foam materials (Thirumal et al. 2010b). In addition, the usage of the non-reactive and the reactive flame retardants together is also advised to generate synergistic effects for enhancing fire resistance of the foams (Zatorski et al. 2008, Bastin et al. 2003).

Akdogan et al. (2019) investigated the effects of triphenyl phosphate (TPhP), aluminum trihydrate (ATH), and zinc borate (ZnB) alone, as well as their binary blends on the thermal conductivity, the compressive strength and the flame retardancy of rigid polyurethane foams. The amounts of flame retardants were changed from 10 to 50% by polyol weight percentage. It was reported that there were no any negative effects on the thermal insulation and the compressive strength. The fire retardancy of the foams that were determined with limited oxygen index (LOI) and cone calorimeter tests were enhanced by the flame retardant additions.

Flame retardants may act either in the condensed phase or in the vapor phase of the combustion through physical and/or chemical mechanisms to delay and/or stop the combustion process consisting of heating, pyrolysis, ignition and flame spread stages. Jia et al. (2019) used imide and oxazolidinone, which were synthesized by using 3, 30, 4, 40-biphenyltetracarboxylic dianhydride (PTDA) and 9, 10-dihydro-9-oxa-(10-glycidoxypropylene)-10-phosphap-henanthrene-10-oxide (e-DOPO) as reactive flame retardants. They reported that the compressive strength and the thermal conductivity of the foams were improved with the flame retardant additions. The fire behaviors of the foams were investigated by using the limited oxygen index, cone calorimetry test, and smoke density test. They pointed out that the char layer of the foam including PTDA and e-DOPO achieved a stronger barrier to burning in the condensed-phase.

Red phosphorus (RP) and the coated RP with melamine formaldehyde resin (MFcP) were used in production of rigid polyurethane foam by Cao et al. (2017). The enhancement of fire resistance of the doped foam was determined with limiting oxygen index and UL 94 test. In addition, the results of the cone calorimeter test indicate that MFcP100 addition causes less heat, smoke and toxic gases than RP. In addition, it was reported that MFcP primarily takes effect in the condensed phase of the burning while RP is effective in the gaseous phase. This was explained with the wrap effect of graphitic carbon nitride generated from melamine.

Meanwhile, some flame retardants may act in the both condensed and the vapor phases (Weil and Levchik 2004, Lu and Hamerton 2002). Wang et al. (2018a) synthesized a novel reactive flame retardant triol (TDHTPP) based on a triazine and a phosphate structure for rigid polyurethane foams and the triol was chemically merged in the main chains of the foam as a chain-extender. They reported that TDHTPP retain both vapor phase and condensed phase flame retardant behaviors and only 5 wt % of TDHTPP addition results in V-0 rating (UL 94) for the foam.

Liu and Wang (2018) introduced a novel phosphorus and nitrogen-based flame retardant, zinc amino-tris-(methylenephosphonate) (Zn- AMP), into rigid polyurethane foam to improve the flame retardancy, the mechanical and the thermal properties. It was reported that 20 wt % Zn-AMP considerably increases the thermal stability of the foam and Zn-AMP acts in both the condensed and the gas phases of the burning. Zn-AMP can result in formation a stable char residue and releases of non-combustible nitrogen-containing gases diluting oxygen and flammable gases in the gas phase.

Xu et al. (2018) produced fire resistive rigid polyurethane foams by using tris (1-chloro-2-propyl) phosphate (TCPP) and modified aramid fiber (MAF). It was found that using TCPP and MAF together could decrease smoke and toxic emissions such as hydrogen cyanide and increase char residue compared to the using TCPP alone. In addition, nonflammable gases carbon dioxide and water were also decreased. It was reported that TCPP and MAF could generate the quench effect in the gaseous phase and barrier effect in the condensed phase.

In another study, effects of functionalized graphene oxide (fGO) on thermal degradation and the flame retardant mechanism of the rigid polyurethane foams were investigated by Chen et al. (2019). It was pointed out that only 0.25 g fGO addition could achieve 28.1% (LOI) and V-0 rating (UL 94) for the rigid polyurethane foam. In other words, the fGO can be considered effective flame retardant, which can increase the thermal stability and decrease the flammability of the foams.

Michałowski and Pielichowski (2018) physically modified polyurethane foams by two additive phosphorous flame retardants - phenol isobutylenated phosphate or phenol isopropylated phosphate, and chemically reinforced by functionalized 1, 2-propanediolizobutyl POSS (PHI-POSS). The analysis of micro calorimetry test revealed an enhancement of fire resistance of the foams including hybrid reactive (POSS)/additive (phosphate) flame retardant systems resulting reduced heat release rates.

Effect of environmentally-friendly flame retardants, such as ammonium polyphosphate, melamine pyrophosphate, triethyl phosphate, bentonite and expanded graphite on the fire resistance and the mechanical properties of rigid polyurethane foams were investigated by Czech-Polak et al. (2016). They classified the doped foams with flammability class V-0 (UL 94). It was reported that the addition of the flame retardants resulting V-0 rating does not considerably deteriorated the mechanical properties of the foams. Norzali and Badri (2016) developed palm-based polyurethane containing phosphate ester (PE) as a fire retardant. It was found that the lowest burning rate could be achieved with loading of 15 wt % PE.

In general, the researchers focused on intumescent flame retardant systems which form a char layer acting as an insulator/mass transfer barrier and enhance the fire resistance (Lv et al. 2005, Tuzcu 2010, Usta 2012, Hu and Wang 2013, Luo et al. 2017, Chen et al. 2017, Hu and Wang 2013, Xu et al. 2013, Wu et al. 2013a, Wu et al. 2013b, Wu et al. 2014, Gao et al. 2014, Li et al. 2019b, Sykam et al. 2019).

Effects of different size-modified expandable graphite (EG) and ammonium polyphosphate (APP) on the flame retardancy, the thermal stability, the physical and the mechanical properties of rigid polyurethane foams were investigated by Pang et al. (2019). It was reported that APP is more effective matter for forming the chemical char than EG. In addition, the size of EG is an important parameter for better thermal and fire resistance. As the size of EG increases, the heat release rate and the total heat released decrease.

Some fillers such as calcite, clay and fly ash are used in polyurethane foams for decreasing production costs (Alavi Nikje et al. 2006, Zatorski et al. 2008, Akdogan 2011, Yurtseven et al. 2013). In addition, the fillers may strengthen the char layer produced by the intumescent flame retardants. The uniform dispersion of the small sized fillers in the foam are very important for enhancement of all the properties (Gürü et al. 2009a, Gürü et al. 2009b, Mishra et al. 2005, Mishra and Shimpi 2007, Shimpi and Mishra 2010, Mishra et al. 2009).

Peng et al. (2018) investigated effects of hydrotalcite on different properties of rigid polyurethane foam including 10 wt % organic phosphate mixture as a commercial flame retardant. It was concluded that the hydrotalcite increases the char residue, retards the decomposition temperatures, improve the thermal stability, and enhance the sound absorption. In addition, it was reported that a small amount of hydrotalcite increases the compressive strength; however, excessive hydrotalcite negatively affects it. The optimum amount of hydrotalcite was mentioned as 5 wt % for most of the properties.

The effects of multi-walled carbon nanotubes and nanoscale titanium dioxide on the flammability and smoke emission of rigid polyurethane foams containing halogen-free fire retardants were examined by Salasinska et al. (2017). They reported a synergistic effect between the nano fillers and halogen-free flame retardants in terms of fire resistance of the foam. It was informed that generation of the carbonized coating on the surface of the foams restricting the access of fire into the unburned parts of the foam and inhibiting the formation of radicals enhanced the fire resistance of the foam.

Peng et al. (2019) investigated the effects of magnesium hydroxide and aluminum hydroxide additions on the flame retardancy, the thermal stability, the sound absorption and the mechanical properties of rigid polyurethane foam including an organic phosphate mixture as a commercial flame retardant. It was determined that aluminum hydroxide is more effective filler than magnesium hydroxide in terms of the flame retardancy of the foam.

Kuznia et al. (2019) reported that the incorporation of fluidized bed combustion fly ash as a filler enhances the thermal stability of rigid polyurethane foams due to the barrier effect of the fly ash preventing the release of gases from the foam. Furthermore, it was determined that the addition of the fly ash into the foam, up to 10 wt %, improves the mechanical performance of the foams. Cheng et al. (2018) investigated effects of flax fiber on improving performance of rigid polyurethane foams. Their results reveal that the fiber can enhance the mechanical properties and fire resistance of the foam.

As a different approach, Li et al. (2019a) decorated silica aerogels onto surfaces of rigid polyurethane foam to produce porous silica aerogel/polyurethane foam composites. It was reported that the introduction of silica aerogel increased the compressive strength and decreased the thermal conductivity of the foam. In addition, the fire resistance of the foam was enhanced with a compact silica-rich hybrid barrier preventing the thermal decomposition products and the heat transfer during burning. In addition, there are some studies, which are related to the fire protective coating on the surface of the foam (Liu et al. 2019).

5.3.2 Intumescent Flame Retardant (IFR) Systems

The intumescent flame retardant system is composed of mainly three components, namely acid source, blowing agent and carbonizing agent. There are different chemical matters for these components. In this study, ammonium polyphosphate (APP) as an acid source and blowing agent and pentaerythritol (PER) as a carbonizing agent were used to synthesize the intumescent flame retardant (Usta et al. 2011). APP and PER are generally mixed into the polyol component by using a mechanical

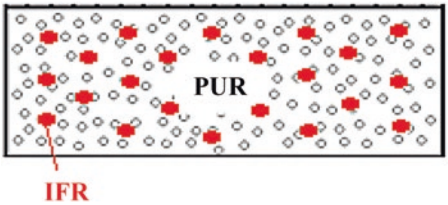


Fig. 5.5 PUR with IFR

mixer and a homogenizer. Then the doped polyol and the isocyanate are mixed by using a mechanical mixer. IFR (APP/PER) should be homogeneously distributed in the foam as shown in Fig. 5.5.

Since the thermal decomposition is an important step before the ignition of the foam, thermogravimetric analyses should be examined to investigate the fire retardant mechanism of IFR. The thermogravimetric analyses of ammonium polyphosphate (APP, Clariant - Exolit AP 423, n > 1000, Phase II, d_{50} = 8 µm) and pentaerythritol (PER, MKS Marmara Chemistry Company d < 75 below 75 µm) are shown in Fig. 5.6. The analyses were performed between 40 °C and 800 °C at a rate of 20 °C/min under nitrogen by using Perkin–Elmer Diamond thermogravimetric analysis (TG/DTA) equipment. Ceramic pans were used in the experiments. The decomposition of PER begins around 175 °C and ends completely around 345 °C. PER has only one decomposition process in which the maximum degradation temperature and the maximum rate of degradation were 334.9 °C and 53.3%/min, respectively. APP starts to decompose around 250 °C and there are three decomposition steps between 40 °C and 785 °C. The residual weight of APP is approximately 12%. Ammonia, water and polyphosphoric acid are evaluated between 300 °C and 450 °C and the polyphosphoric acid is evaporated and/or dehydrated to phosphorus oxides between 500 °C – 700 °C (Duquesne et al. 2000, Wu et al. 2008).

When the rigid polyurethane foam composed of the intumescent flame retardant is exposed to heat or fire, it swells, IFR decomposes and a char layer acting as an insulator and mass transfer barrier slowing down the escape of the combustible volatiles and enhancing the fire resistance of the foam is generated (Lu and Hamerton 2002, Wang and Chen 2005, Bian et al. 2008, Ni et al. 2009, Ni et al. 2010, Barikani et al. 2010, Wang et al. 2018b, Wang et al. 2018c). Figure 5.7 shows a simple view of the char layer.

The ratio of APP to PER is an important factor for effectiveness of IFR system. Four different ratios (APP/PER) which are 1:0, 3:1, 2:1 and 1:2 were investigated for the rigid polyurethane foam. In general, addition of additives and flame retardants may deteriorate the foam process and negatively affect the rising. The effects of IFR systems additions on the foam rising are shown in Fig. 5.8. It was determined that 10% IFR additions resulted in decreasing of foam rising between 7.2% and 9.1%.

There are different kinds of tests used for investigation of fire resistance of polymeric materials, like UL 94, LOI and cone calorimeter (Usta 2012, Gao et al. 2013, Luo et al. 2017). The fire resistance of PUR with and without IFR system, which was determined by using UL 94 test, are shown in Fig. 5.9. Although the flame

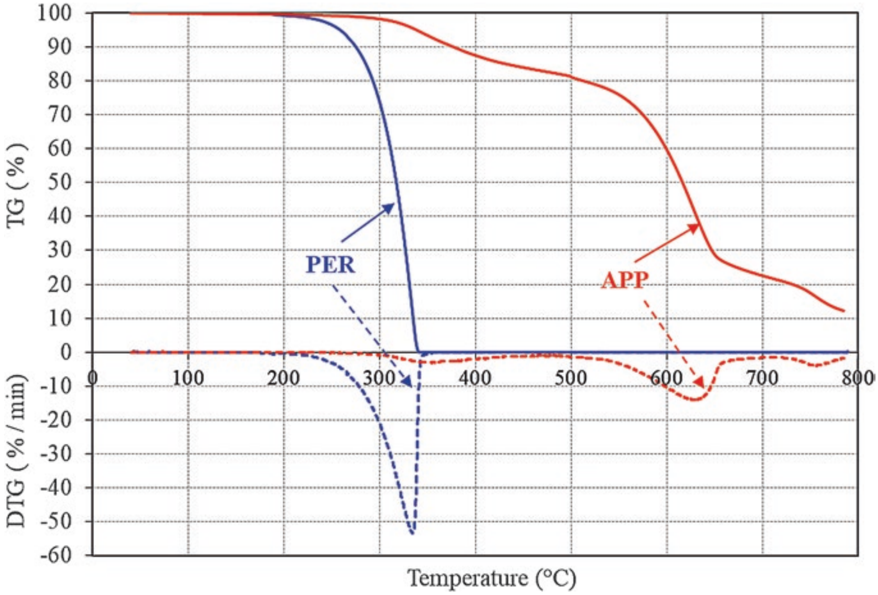
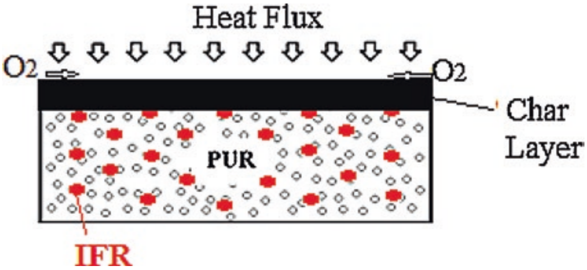


Fig. 5.6 Thermogravimetric analysis of APP and PER

Fig. 5.7 Simple view of intumescent flame retardant mechanism



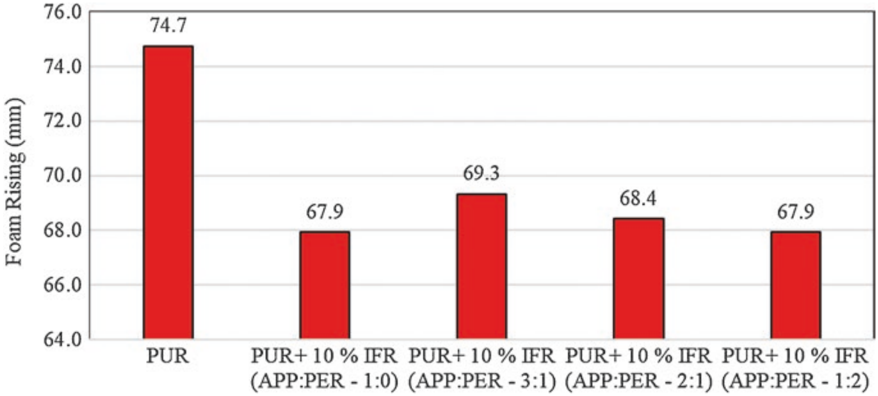


Fig. 5.8 The effects of IFR systems additions on the foam rising

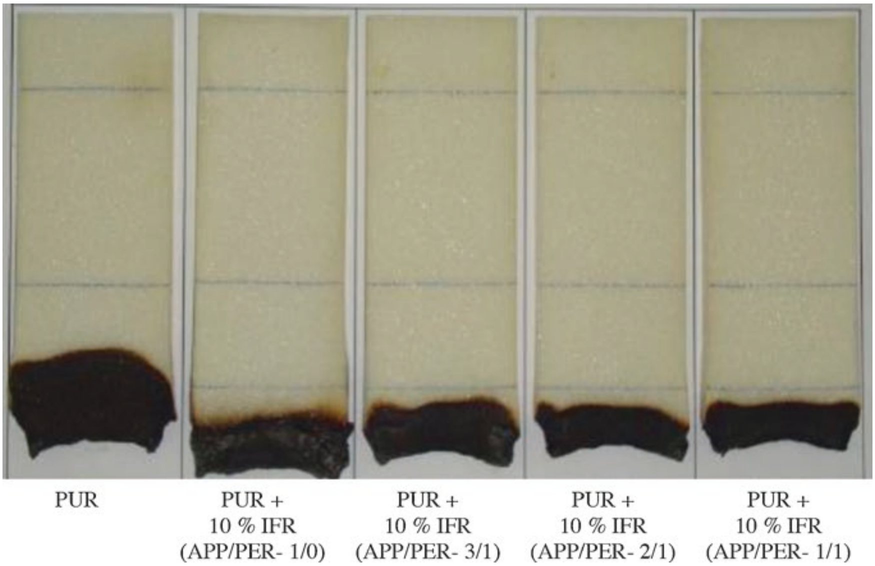


Fig. 5.9 The foam pictures after UL 94 tests

passed the first gauge mark in the pure PUR foam at the burning speed of 40 mm/min, IFR additions obviously enhanced the flammability resistance of the foams. All of the systems show similar effects, and the flame did not pass the first reference line.

In addition, the effects of IFR systems additions on the compressive strength are shown in Fig. 5.10. The compressive tests were performed using an Instron 8801 computer controlled testing machine (model 8801) in accordance with the ASTM D1621- 04a (2004b) standard. As it is expected that IFR additions decreased the compressive strength of the foam. 10% IFR addition causes decreasing of the compressive strength in the range of 15.8 to 29.6%. However, it should be pointed out that all of them have the compressive strength more than 100 kPa, which is an acceptable value for most of the rigid polyurethane foam applications.

Thermal conductivity is an important property for rigid polyurethane foams. The effects of different IFR systems on the thermal conductivity that was measured using Kyoto QTM-500 are shown in Fig. 5.11. The addition of IFR system caused increasing of thermal conductivity of the foams in the range of 4.3 to 9.0%. The smallest increase was obtained with IFR (APP:PER – 2:1) as 4.3%.

In general, these results imply that effective fire resistance of the rigid polyurethane foam can be obtained by using the intumescent flame retardant including APP:PER in the mass ratio of 2:1 without significant increasing of thermal conductivity. Demir et al. (2005) also found the same ratio for fireproof polypropylene.

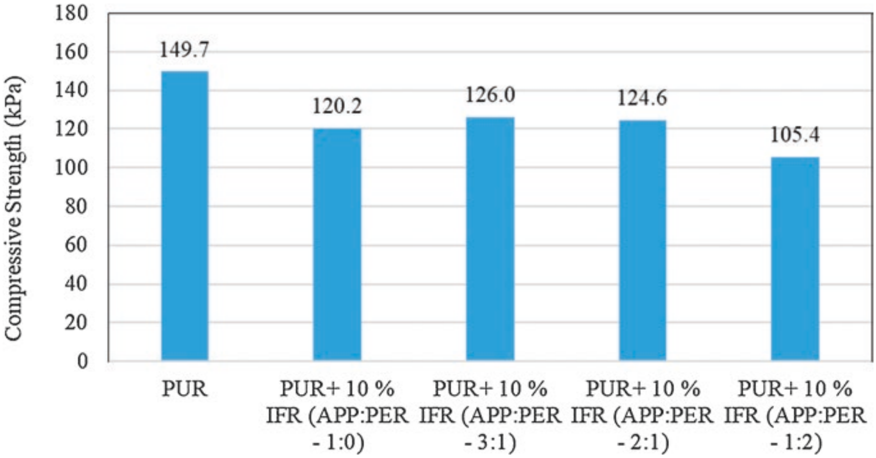


Fig. 5.10 Effects of different IFR systems on the Compressive Strength of the foams

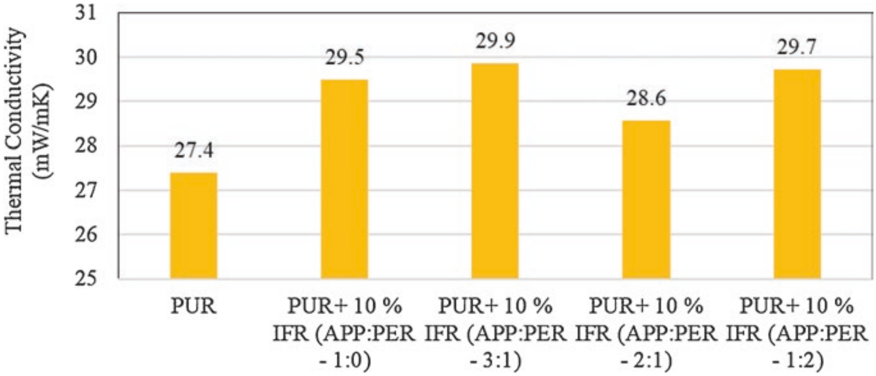


Fig. 5.11 Effects of different IFR systems on the thermal conductivity of the foams

5.4 Fireproof Rigid Polyurethane Foams

In this section, two different applications were presented for fireproof rigid polyurethane foams. The first one is halogen-free intumescent flame retardant (IFR) addition into the PUR and the second one is covering of the PUR with glass fiber fabric (GFf). In addition, these two approaches are compared at two different fire scenarios, namely medium sized and small sized fire scenarios.

5.4.1 Intumescent Flame Retardant (IFR) Application

The intumescent flame retardant containing ammonium polyphosphate (APP, 2 unit) as an acid source/blowing agent and pentaerythritol (PER, 1 unit) as a carbonific agent was used as a flame retardant for rigid polyurethane foams (Usta et al. 2011). "IFR" notation implies this combination of the intumescent flame retardant in the rest of the chapter. A laboratory-scale batch process was used to produce the rigid polyurethane foams (PUR) with and without IFR. The ratio of polyol and isocyanate was 1/1.18 and the amounts of the components were determined to get foams of 40 ± 0.5 kg/m^3 density. IFR was incorporated into the polyol in 5, 10, 15 and 20 wt % by using a mechanical homogenizer. The polyol/IFR and the isocyanate are mixed with a mechanical stirrer. Then the mixture was poured into a preheated aluminum mold. The samples were removed from the mold, which was kept under a press after the curing process completion. Effects of different amounts of IFR on the rising of the foam are shown in Fig. 5.12. IFR addition results in decreasing of the foam rising. However, the foam rising of PUR with 20% IFR addition is acceptable level. In addition, the density of the foam increases with IFR (Fig. 5.13).

In addition, the compressive strength and the thermal conductivity are very important properties for thermal insulation applications. The effects of IFR additions on these properties are shown in Figs. 5.14 and 5.15. IFR additions slightly enhanced the compressive strength of the foam. However, there was a slight increase in thermal conductivity. 20% IFR addition caused less than 5% increase in the thermal conductivity. Different factors, which are the cell size and orientation, the foam

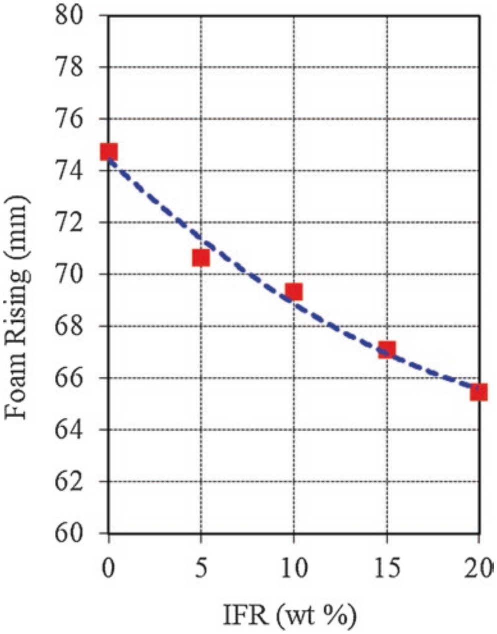


Fig. 5.12 Effects of different amounts of IFR systems on the rising of foam

Fig. 5.13 Effects of different amounts of IFR systems on the density of foam

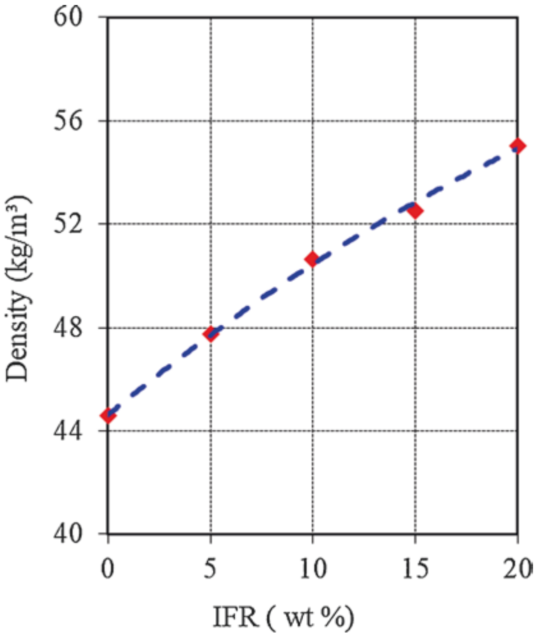
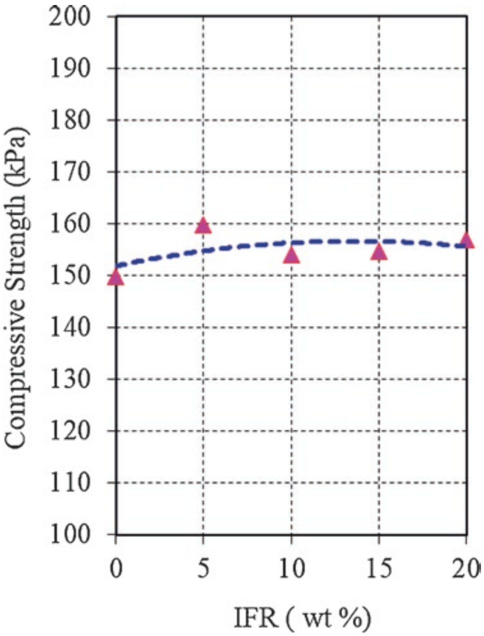


Fig. 5.14 Effects of different amounts of IFR systems on the compressive strength



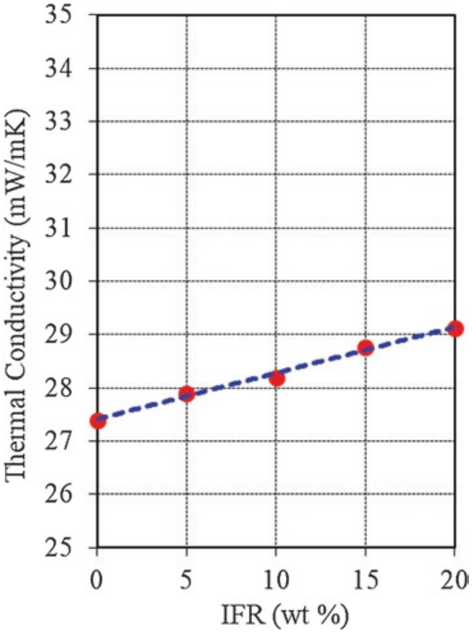


Fig. 5.15 Effects of different amounts of IFR systems on the thermal conductivity

density, the ratio of close to open cell and the thermal conductivity of the gases in the cells and the filling materials, affects the thermal conductivity of rigid polyurethane foam (Thirumal et al. 2010a). As a different description, the thermal conductivity of the foam is affected by three different parameters, namely, thermal conductivity of the gas inside the cells, thermal conductivity of the solid phase and the radiation across the cells (Modesti and Simioni 1994).

Scanning Electron Microscope (SEM) views of the foams are shown in Fig. 5.16. The shape of cells in PUR was approximately polyhedron. However, the addition of IFR into PUR slightly changed the shapes of the cells. There was slightly increasing in the mean diameters of the cells.

As it is known that investigation of the thermal degradation is very important to investigate the flammability, the burning, and the flame retardancy of polymer materials. The thermogravimetric analyses of the foams are shown in Fig. 5.17. The foams exhibited similar three decomposition processes. The thermal decomposition starts with evolving water (over 100 °C) and continued with the dissociation of the thermally weakest links, namely allophanate and biuret (Levchik and Weil 2004).

The incorporation of IFR accelerated the main decomposition processes and decreased the maximum degradation temperature (Duquesne et al. 2001). The early decomposition of PUR including IFR can be explained with the intumescent flame retardant. Because IFR quickly decomposes and produces a char layer. This char layer can partially slow down the decomposition of the foam. This results in enhancing of the thermal stability at high temperatures (Kulesza et al. 2006, Wu et al. 2008). Figure 5.18 shows the results of UL 94 flammability tests of the foams. As it is shown that 20% IFR addition provided the best fire resistance.

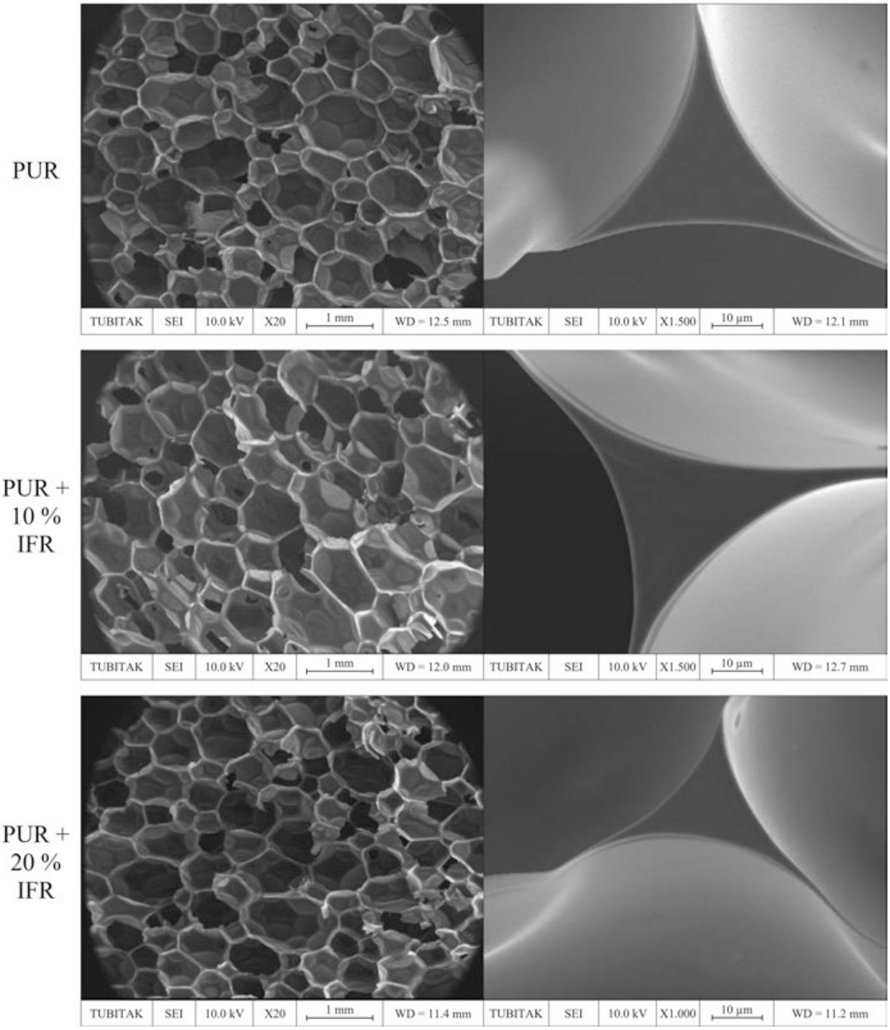


Fig. 5.16 SEM views of PUR and IFR added PUR

Cone calorimeter is a bench-scale equipment that can simulate real-world fire conditions (Morgan and Bundy 2007, Usta 2012). In addition, cone calorimeter test which is a combustion test for investigation of fire resistance of polymeric materials (Wu et al. 2008, Beyer 2007) can generate important parameters such as time to ignition (TTI), heat release rate (HRR), total heat released (THR), residual mass, smoke and CO/CO_2 release rates (Chung et al. 2009).

The fire behaviors of PUR, PUR+ 10% IFR and PUR+ 20% IFR were examined by a cone calorimeter according to ASTM E-1354 (2004a) and ISO-5660 (2002) standards. Figure 5.19 shows the pictures of the cone calorimeter. The foams (100 x

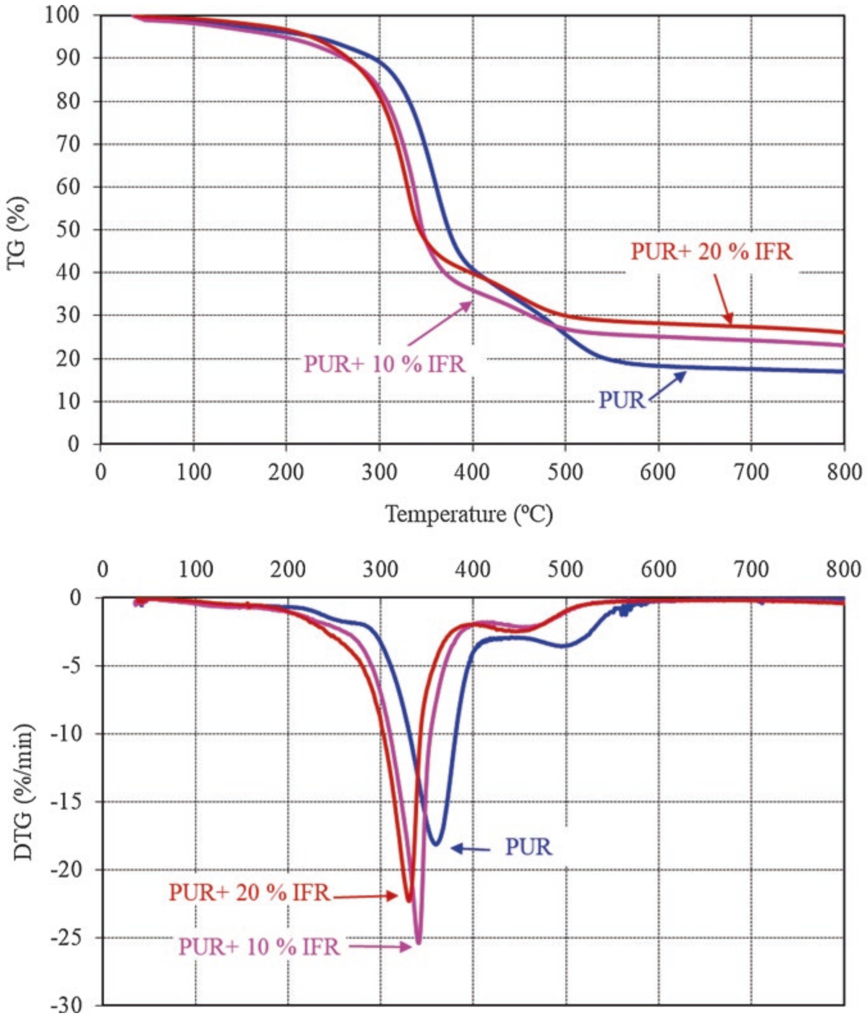


Fig. 5.17 Thermogravimetric analysis of PUR, PUR + 10% IFR and PUR + 20% IFR

100 x 50 mm) were exposed horizontally to a heat flux of 35 ± 1 kW/m^2 as shown in Fig. 5.20.

Heat release rate (HRR) is an important parameter to investigate fire resistance of polymer materials (Zhang et al. 2004). The heat release rates of PUR, PUR+ 10% IFR and PUR+ 20% IFR foams are given in Fig. 5.21. All of the foams presented similar characteristics of thermally thick charring samples. In other words, when the foams are exposed a heat flux, the heat release rate increases and then a char layer is generated, after that the thickness of the char layer increases resulting in decreases in the heat release rates (Schartel and Hull 2007, Lu et al. 2015, Wang et al. 2011, Usta 2012). However, IFR additions resulted in decreasing of peak heat release rates

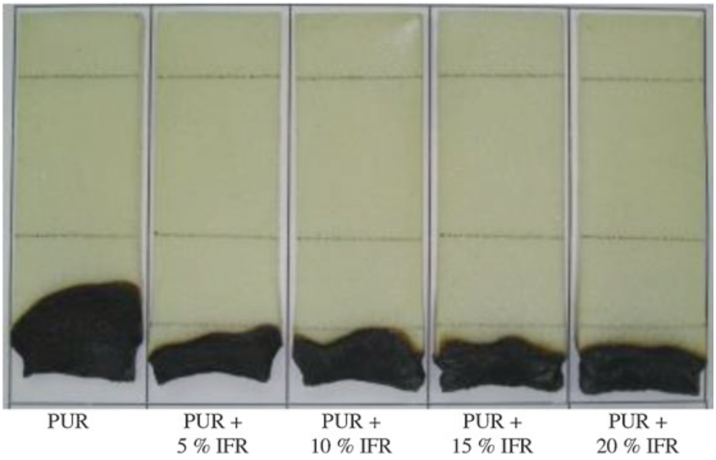


Fig. 5.18 Pictures of the foams after UL 94 Flammability Tests

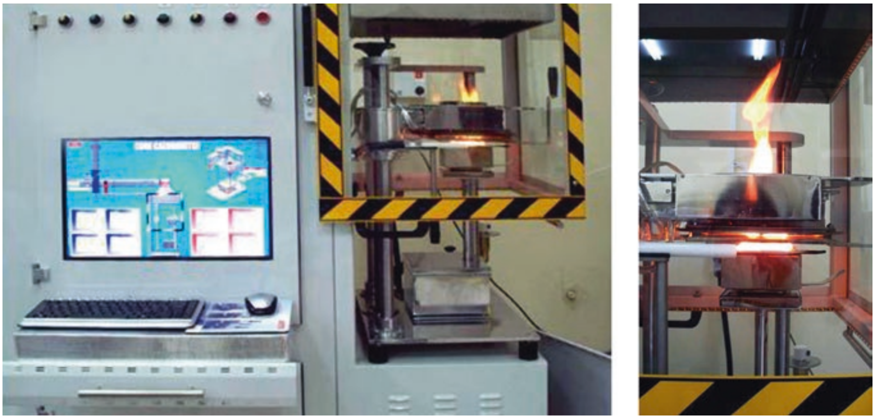


Fig. 5.19 Pictures of the cone calorimeter

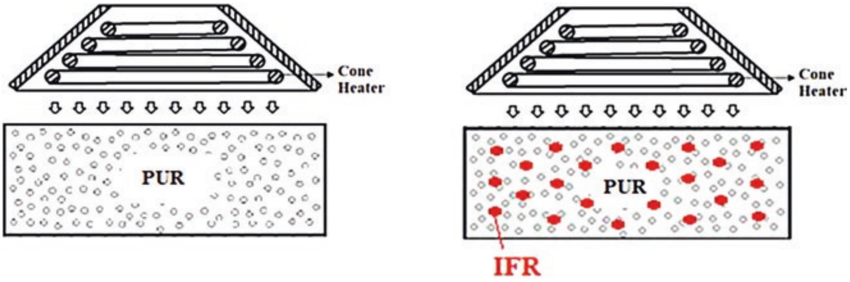


Fig. 5.20 Heat flux applications

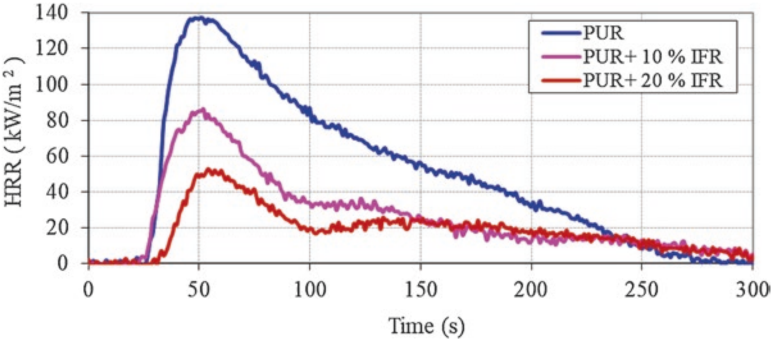


Fig. 5.21 The HRR variations of PUR, PUR+ 10% IFR and PUR+ 20% IFR

and extended the time to reach peak heat release rates. Furthermore, it should be pointed out that peak heat release rate (PHRR) is an important parameter indicating the intensity of fires (Chung et al. 2009). IFR decomposition accelerates the formation of a better char layer. This char layer slows down the decomposition of the foam and reduces the heat release rate (Usta 2012). Although 10% IFR did not increase the time to ignition significantly, 20% IFR delayed the ignition. It is desirable to have a long ignition time for the foams (Checchin et al. 1999). It can be said that PUR+ 20% IFR present better performance in terms of the fire resistance.

Figure 5.22 shows total heat released (THR) curves of PUR, PUR+ 10% IFR and PUR+ 20% IFR. It is obviously seen that IFR significantly reduced the THR values. The reductions are explained with the barrier effect of the char layer (Zhao et al. 2005, Konig et al. 2009). It is thought that 20% IFR addition results in a stronger and more effective char layer with respect to 10%IFR addition.

Smoke and carbon monoxide (CO) emissions are the most important toxic substances in fires of rigid polyurethane foams (Checchin et al. 1999). Smoke and CO emissions of PUR, PUR+ 10% IFR and PUR+ 20% IFR are given in Fig. 5.23 and Fig. 5.24, respectively. The strength of fire and the material properties affect the generation of smoke and CO, which are formed due to the incomplete combustion of the foam. The smoke and CO changes are similar. IFR additions considerably decreased the peak values of the smoke and CO. In addition, the effects of IFR continue, and smoke/CO generations decrease during the rest of burning times. Although the heat release rates reduced to nearly zero and there was no flame at the end of the burning time of 300 s, there were still some smoke and CO emissions because of the smoldering combustion of the foams at low intensity (Price et al. 2000).

The carbon dioxide (CO_2) emissions are shown in Fig. 5.25. CO_2 emissions of PUR+ 10% IFR and PUR+ 20% IFR were lower than that of PUR. The CO_2 emissions of the foams revealed similar changes with the HRR curves (Bustamante Valencia et al. 2009). The CO_2 emissions of PUR+ 10% IFR and PUR+ 20% IFR decreased because of the char layer formation generated by IFR. It is thought that

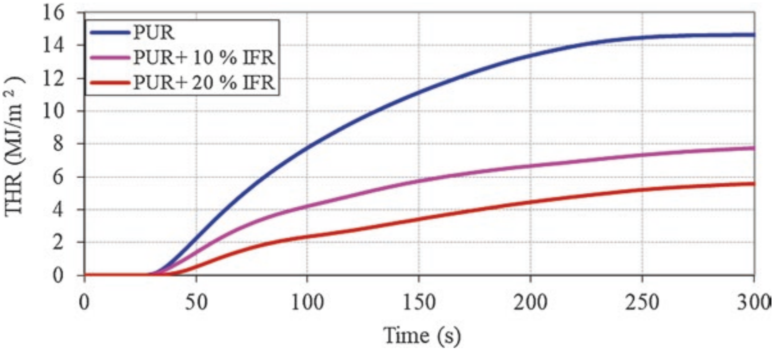


Fig. 5.22 The THR variations of PUR, PUR+ 10% IFR and PUR+ 20% IFR

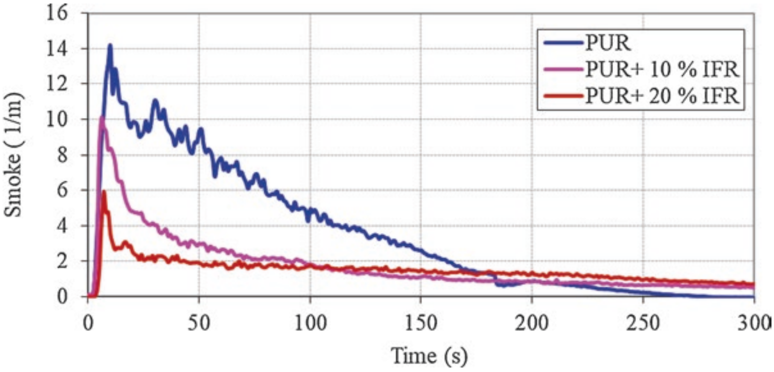


Fig. 5.23 Smoke emissions of PUR, PUR+ 10% IFR and PUR+ 20% IFR

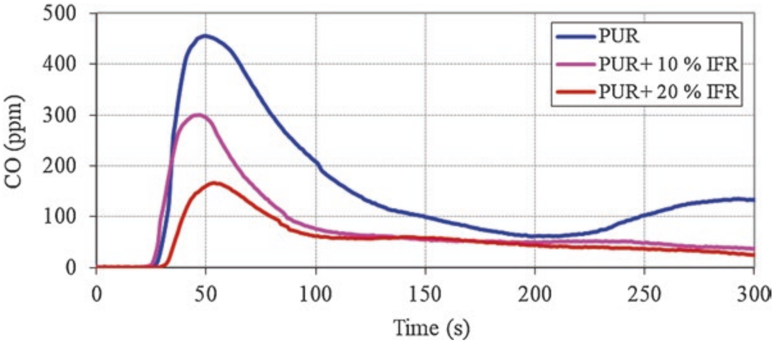


Fig. 5.24 CO emissions of PUR, PUR+ 10% IFR and PUR+ 20% IFR

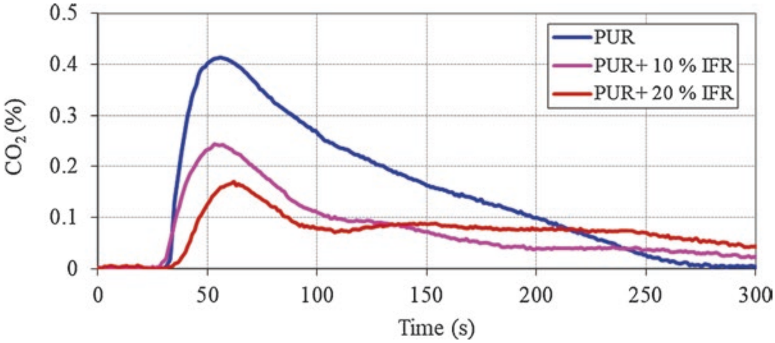


Fig. 5.25 CO_2 emissions of PUR, PUR+ 10% IFR and PUR+ 20% IFR

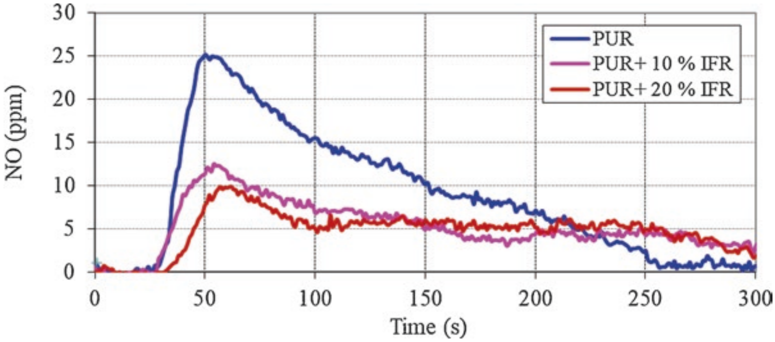


Fig. 5.26 Nitrogen oxides of PUR, PUR + 10% IFR and PUR + 20% IFR

the char layer protects the underlying foam from further burning (Duquesne et al. 2000, Wu et al. 2008).

Bustamante Valencia et al. (2009) reported that the quantities of nitrogen gas species (NO_2, HCN, N_2O, NH_3) are less than 2 ppm in gas products emitted during burning of the polyurethane foams at different heat applications. Since even the small amount of NO emission is considerably harmful, it is useful to examine NO emission. There are mainly two reasons for the formation of NO emission from the polyurethane foam burning, namely the high temperature and the nitrogen in the foam. Figure 5.26 shows NO emissions of PUR, PUR+ 10% IFR and PUR+ 20% IFR. IFR additions decreased NO emissions. This situation can be explained with the lower HRR values of PUR+ 10% IFR and PUR+ 20% IFR. Twenty percent IFR addition reduced NO emission below 10 ppm.

The char structure may reveal the burning behavior of the foams. The effective char layer formation prevents the heat transfer and the oxygen between the burning foam and the flame zone. Meantime the layer retards the decomposition of the foam and retains the underlying foam from further burning (Lv et al. 2005). Pictures of PUR, PUR+ 10% IFR and PUR+ 20% IFR after cone calorimeter tests are shown in Fig. 5.27. It is obviously seen that the char layer of PUR + 20% IFR is better than that of PUR+ 10% IFR. In addition, the residual mass of PUR+ 20% IFR is more than that of PUR + 10% IFR.

5.4.2 Glass Fiber Fabric (GFf) Application

A laboratory-scale batch process is used to produce the rigid polyurethane foams (PUR) as mentioned previous section. Similar procedure was applied to produce the rigid polyurethane foam covered with glass fiber fabric (PUR + GFf) (Demiryuguran 2015). However, the glass fiber fabric, which was supplied from Cam Elyaf Corporation (Turkey), was placed at the bottom of the mold and under the cover of the mold as shown in Fig. 5.28. The schematic of PUR with GFf is shown in Fig. 5.29.

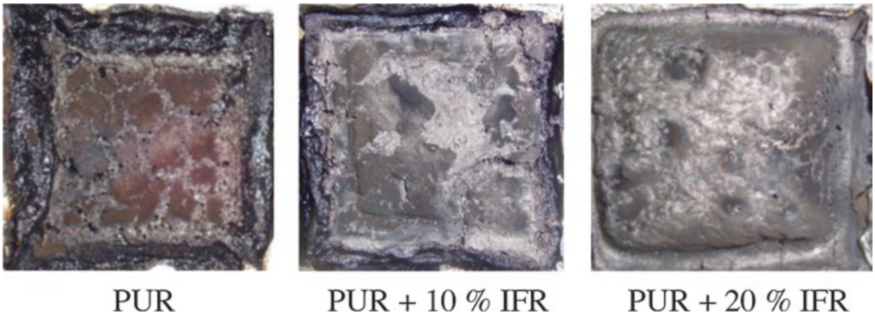


Fig. 5.27 Pictures of PUR, PUR+ 10% IFR and PUR+ 20% IFR after cone calorimeter tests

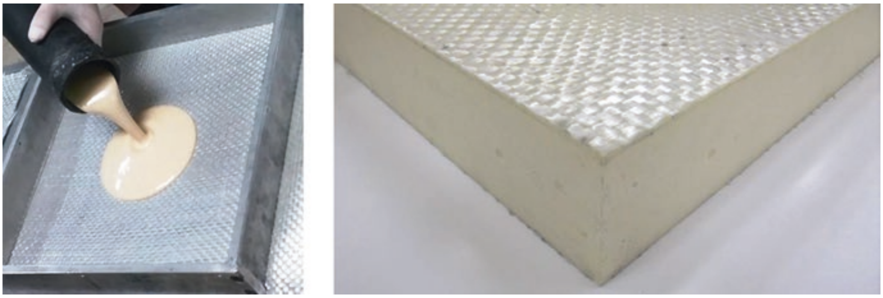
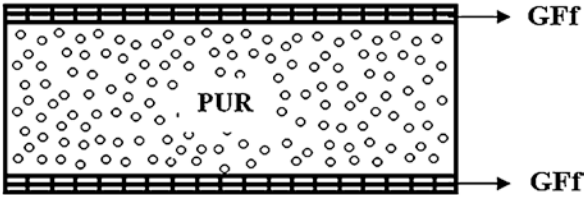


Fig. 5.28 Pouring of polyol and isocyanate mixture over GFf and PUR with GFf

Fig. 5.29 Schematic of PUR with GFf



The thermogravimetric analysis of the glass fiber fabric, which is an E-glass woven fabric (0°/90°) with areal weight of 500 g/m^2, is shown in Fig. 5.30. As it is shown that GFf does not decompose up to 950 °C.

PUR and PUR+GFf were tested in the cone calorimeter at different heat fluxes, namely 15 kW/m^2 and 35 kW/m^2 in the horizontal position as shown in Fig. 5.31 to simulate small and medium sized fires, respectively.

5.4.2.1 Medium-Sized Fire Simulation (35 kW/m^2)

The HRR values of PUR+ GFf are compared with those of PUR and PUR+ 20% IFR at heat flux of 35 kW/m^2 in Fig. 5.32. Although GFf does not considerably affect the ignition behavior of the foam, the peak heat release rate was slightly decreased with GFf. However, PUR+ GFf cannot satisfy the fire resistance as much as PUR + 20% IFR addition. Meanwhile, the effect of GFf on the total heat released (THR) is shown in Fig. 5.33. There is only 26% reduction was occurred in 300 s with GFf.

Figures 5.34 and 5.35 show smoke and CO generations of PUR, PUR+ GFf and PUR+ 20% IFR, respectively. GFf retards the smoke generation and results in lower smoke than that of PUR. However, GFf cannot decrease the smoke as much as 20% IFR addition. Meanwhile, GFf causes reduction in CO emissions and the general trend of PUR+ GFf is very similar to that of PUR+ 20% IFR. CO emission of PUR foam increases after approximately 230 s implying smoldering combustion of the foam. Again, GFf and 20% IFR reduces the smoldering combustion intensity of the foam. CO_2 emissions of PUR, PUR+ 20% IFR and PUR+ GFf are shown in Fig. 5.36. Since the CO_2 formation is directly related to burning mass of the foam, CO_2 emissions are very similar to the HRR values. NO emissions of the foams are compared in Fig. 5.37. GFf coverage does not change NO emission of PUR. Figure 5.38 shows the pictures of the foams after cone calorimeter test. The glass fiber fabric can be seen clearly, but the foam under the glass fiber fabric was burned.

5.4.2.2 Small-Sized Fire Simulation (15 kW/m^2)

When the foams were exposed to the heat flux of 15 kW/m^2, there were obvious differences in burning characteristics and the fire resistances of the foams. Although PUR+ 20% IFR shows similar trend with PUR, PUR+ GFf shows different characteristics

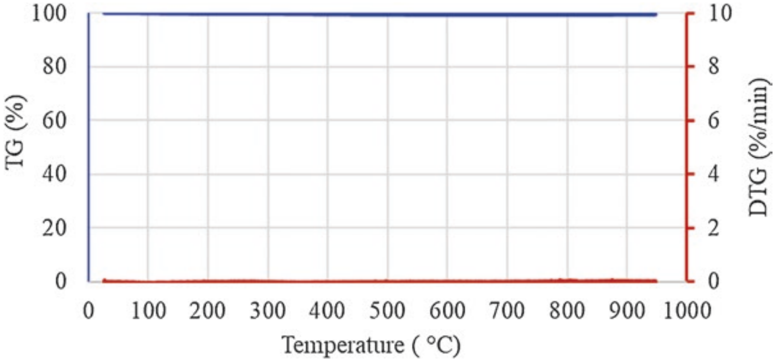
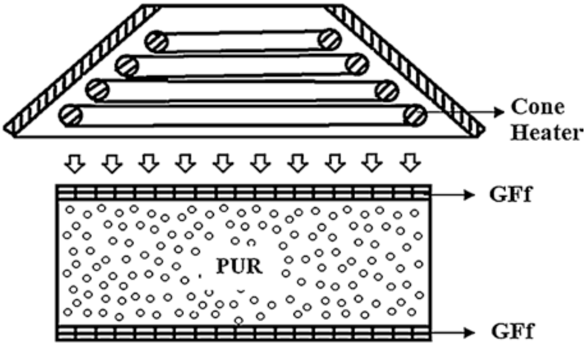


Fig. 5.30 Thermogravimetric analysis of GFf

Fig. 5.31 Heat Flux application on PUR + GFf



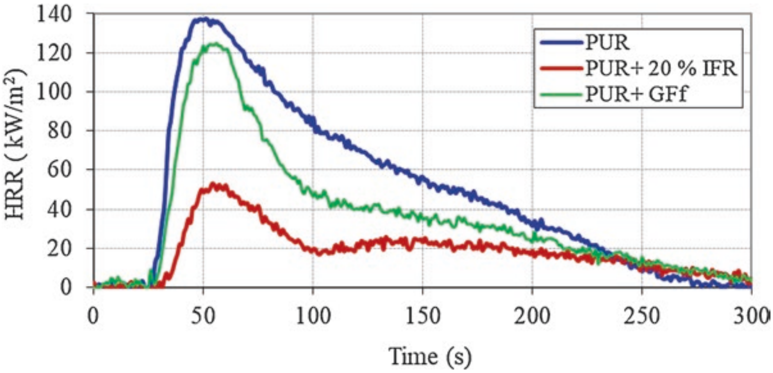


Fig. 5.32 HRR variations of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 35 kW/m^2

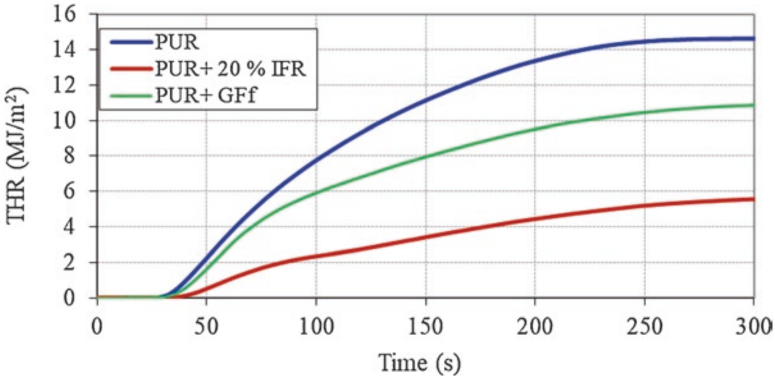


Fig. 5.33 THR variations of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 35 kW/m^2

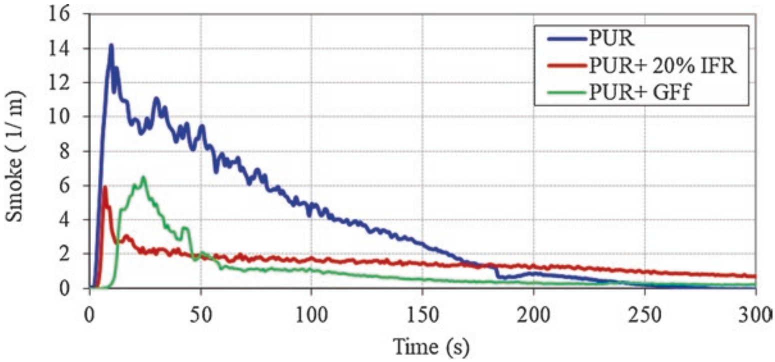


Fig. 5.34 Smoke emissions of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 35 kW/m^2

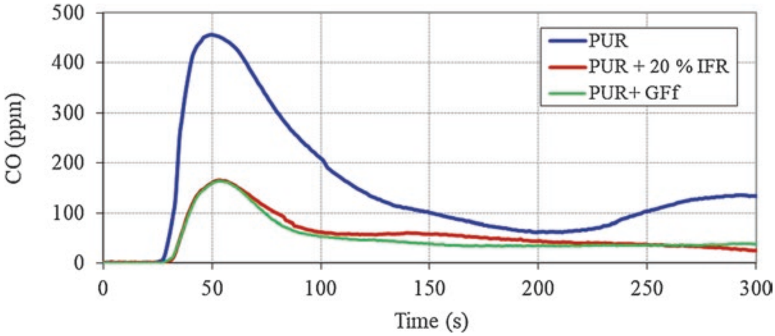


Fig. 5.35 CO emissions of PUR, PUR + 20% IFR and PUR + GFf at heat flux of 35 kW/m^2

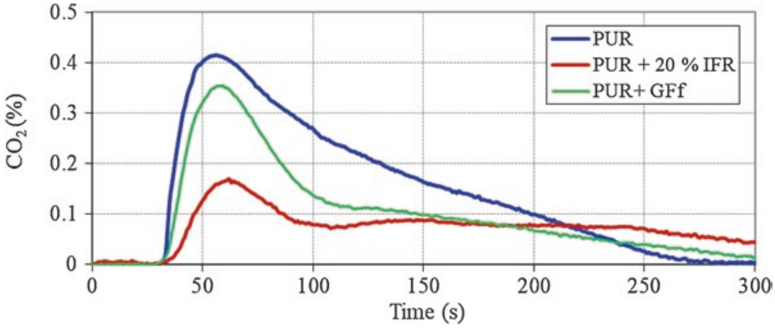


Fig. 5.36 CO$_2$ emissions of PUR, PUR + 20% IFR and PUR+ GFf at heat flux of 35 kW/m^2

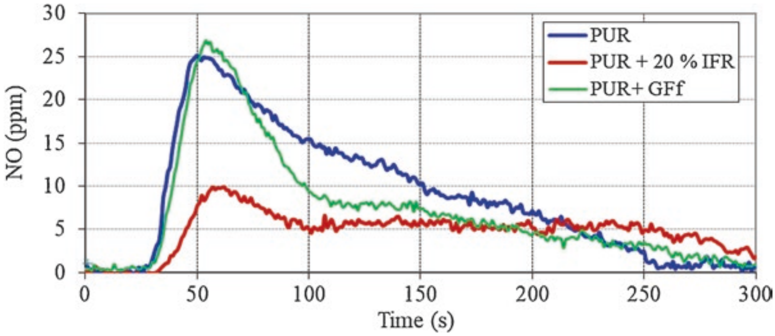


Fig. 5.37 NO emissions of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 35 kW/m^2

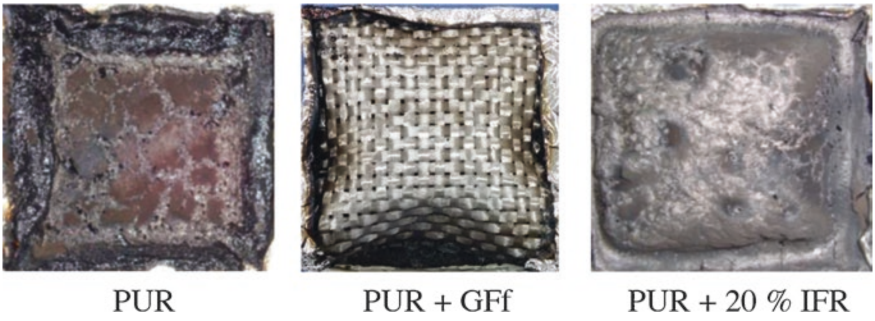


Fig. 5.38 Pictures of PUR, PUR+ 20% IFR and PUR+ GFf after cone calorimeter tests (35 kW/m^2)

(Fig. 5.39). The time to ignition increased with GFf and the peak heat release rate increased sharply, but it decreased quickly. The flame diminished early than others. In addition, the difference can be seen clearly in THR values shown in Fig. 5.40. GFf can achieve better fire resistance than 20% IFR addition at the heat flux of 15 kW/m^2.

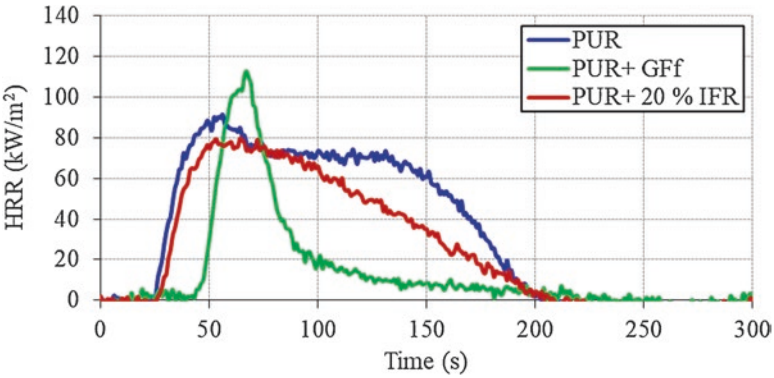


Fig. 5.39 HRR variations of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 15 kW/m^2

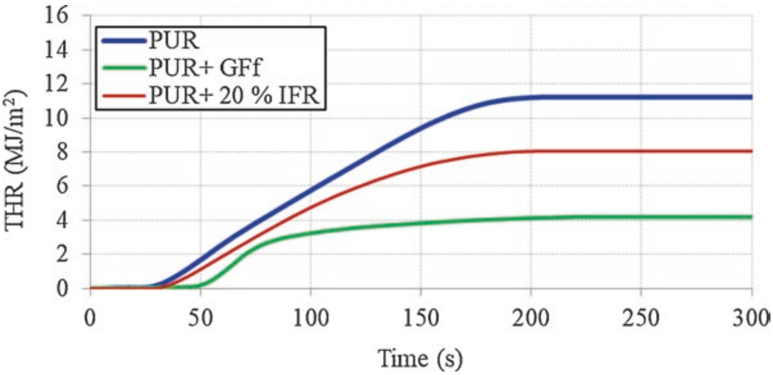


Fig. 5.40 THR variations of PUR, PUR+ 20% IFR and PUR + GFf at heat flux of 15 kW/m^2

Smoke emissions are shown in Fig. 5.41. The smoke generations were reduced with decreasing of the heat flux. The smoke generations of PUR and PUR+ 20% IFR are very close each other. However, GFf retarded the smoke emissions and again resulted in lower smoke emissions in shorter time range.

CO emissions are presented in Fig. 5.42. There is a strange changing at the heat flux of 15 kW/m^2. PUR+ 20% IFR generate more CO emissions than PUR. However, GFf retarded CO emissions and resulted in lower CO emissions.

CO_2 emissions of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 15 kW/m^2 are shown in Fig. 5.43. Since the CO_2 formation is directly related to burning mass of the foam, CO_2 emissions are very similar to the HRR values. NO emissions of the foams are compared in Fig. 5.44. GFf retarded NO emission and generation of NO occurred in a short time. Figure 5.45 shows the pictures of the foams after cone calorimeter test. The positive effect of the glass fiber fabric can be seen clearly.

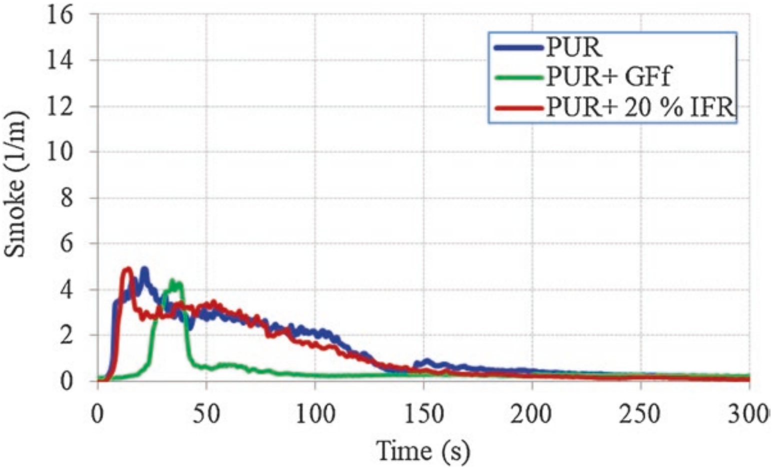


Fig. 5.41 Smoke emissions of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 15 kW/m^2

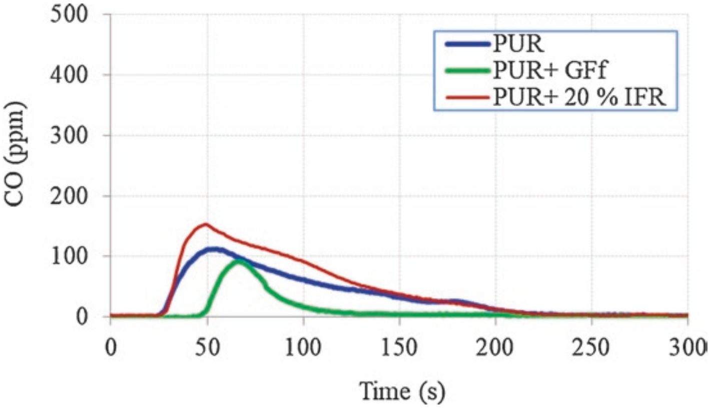


Fig. 5.42 CO emissions of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 15 kW/m^2

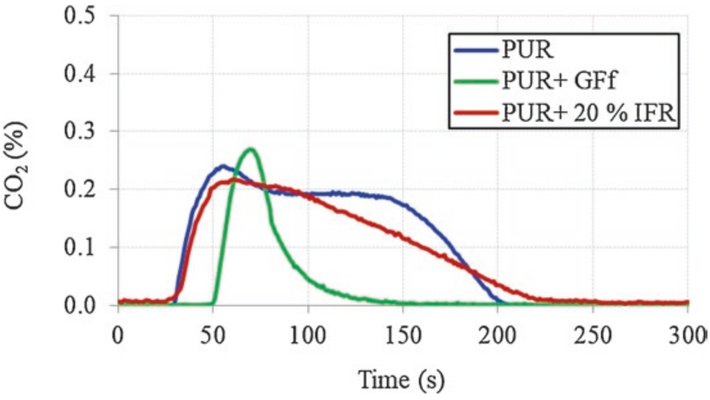


Fig. 5.43 CO$_2$ emissions of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 15 kW/m^2

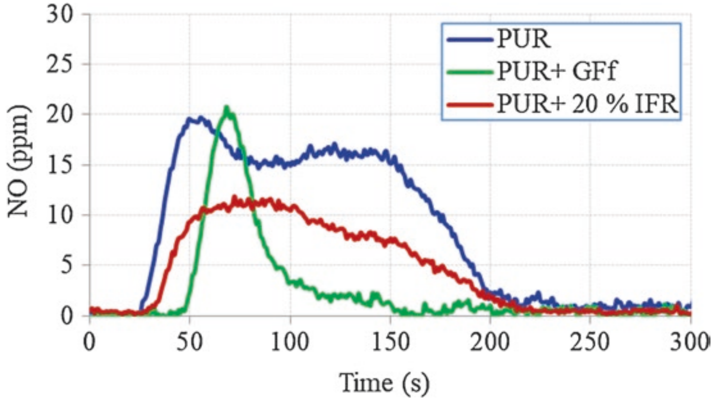


Fig. 5.44 NO emissions of PUR, PUR+ 20% IFR and PUR+ GFf at heat flux of 15 kW/m^2

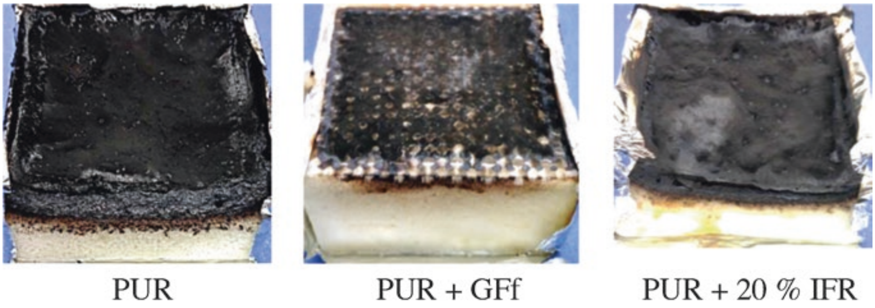


Fig. 5.45 Pictures of PUR, PUR+ 20% IFR and PUR+ GFf after cone calorimeter tests (15 kW/m^2)

5.5 Conclusions

In this chapter, the information about different studies that were performed to enhance the fireproof capability of rigid polyurethane foams are presented briefly. In this context, the flame retardants and their effects on the fire resistance of the foams are introduced. Among them, the intumescent flame retardants as halogen-free flame retardants have been found to stand out because of better performance. Therefore, extensive studies were conducted on the intumescent flame retardants for providing fireproof rigid polyurethane foams.

The effects of intumescent flame retardant (IFR) systems which are composed of ammonium polyphosphate (APP) as an acid source/blowing agent and pentaerythritol (PER) as a carbonific agent on the fire resistance, the thermal stability, the thermal conductivity and the mechanical properties of the rigid polyurethane foams were investigated. 20 wt % IFR (APP:PER – 2:1) addition into the rigid polyurethane foam can effectively enhance the fire resistance of the foam at medium sized fire condition (heat flux of 35 kW/m^2) without deterioration of the mechanical properties, the thermal stability and the thermal conductivity. Furthermore, it was determined that IFR additions can decrease toxic emissions namely CO, smoke and NO, during the burning.

Additionally, a different approach, which is the coverage of rigid polyurethane foams with glass fiber fabric (GFf), is introduced to enhance the fireproof capability of the foams in this chapter. Although the coverage of the foam with GFf can provide limited fire resistance at the medium sized fires (heat flux of 35 kW/m^2), it can achieve very good fire resistance at small sized fire conditions (heat flux of 15 kW/m^2), even better than 20 wt % IFR addition. Moreover, GFf can significantly inhibit CO, smoke and NO emissions at the small sized fire conditions.

Acknowledgments The authors would like to thank TÜBİTAK (The Scientific and Technological Research Council of Turkey) supporting this study under project contract no. 108T246. In addition, the authors would like to Pamukkale University for providing necessary facilities to complete this study.

References

Akdogan E (2011) Farklı Katkı Maddelerinin Poliüretan Malzemelerin Mekanik Özellikleri Üzerine Etkileri (in Turkish)., MSc Thesis. Pamukkale University

Akdogan E, Erdem M, Ureyen ME, Kaya M (2019) Rigid polyurethane foams with halogen-free flame retardants: thermal insulation, mechanical, and flame retardant properties. J Appl Polym Sci 47611:47611. https://doi.org/10.1002/app.47611

Alavi Nikje MM, Garmarudi AB, Haghshenas M (2006) Effect of talc filler on physical properties of polyurethane rigid foams. Polym Plast Technol Eng 45:1213–1217. https://doi.org/10.1080/03602550600887541

ASTM (2004a) E-1354-04a standard test method for heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter. An American National Standard. https://doi.org/10.1520/E1354-04A

ASTM (2004b) D-1621-04a, standard test method for compressive properties of rigid cellular plastics, ASTM international. An American National Standard. https://doi.org/10.1520/D1621-04A

Bahattab MA, Mosnáček J, Basfar AA, Shukri TM (2010) Cross-linked poly(ethylene vinyl acetate) (EVA)/lowdensity polyethylene (LDPE)/metal hydroxides composites for wire and cable applications. Polym Bull 64:569–580. https://doi.org/10.1007/s00289-009-0194-0

Barikani M, Askari F, Barmar M (2010) A comparison of the effect of different flame retardants on the compressive strength and fire behaviour of rigid polyurethane foams. Cell Polym 29:343–358. https://doi.org/10.1177/026248931002900602

Bastin B, Paleja R, Lefebvre J (2003) Fire behavior of polyurethane foams. J Cell Plast 39:323–340. https://doi.org/10.1177/0021955X03039004005

Beyer G (2007) Flame Retardancy of thermoplastic polyurethane and polyvinyl chloride by organoclays. J Fire Sci 25:65–78. https://doi.org/10.1177/0734904107064602

Bian X-C, Tang J-H, Li Z-M (2008) Flame retardancy of hollow glass microsphere/rigid polyurethane foams in the presence of expandable graphite. J Appl Polym Sci 109:1935–1943. https://doi.org/10.1002/app.27786

Bustamante Valencia L, Rogaume T, Guillaume E et al (2009) Analysis of principal gas products during combustion of polyether polyurethane foam at different irradiance levels. Fire Saf J 44:933–940. https://doi.org/10.1016/j.firesaf.2009.05.003

Cao ZJ, Dong X, Fu T et al (2017) Coated vs. naked red phosphorus: a comparative study on their fire retardancy and smoke suppression for rigid polyurethane foams. Polym Degrad Stab 136:103–111. https://doi.org/10.1016/j.polymdegradstab.2016.12.004

Checchin M, Cecchini C, Cellarosi B, Sam F (1999) Use of cone calorimeter for evaluating fire performances of polyurethane foams. Polym Degrad Stab 64:573–576. https://doi.org/10.1016/S0141-3910(98)00131-1

Chen X, Li J, Gao M (2019) Thermal degradation and flame retardant mechanism of the rigid polyurethane foam including functionalized graphene oxide. Polymers (Basel):11. https://doi.org/10.3390/polym11010078

Chen Y, Li L, Qian L (2018) The pyrolysis behaviors of phosphorus-containing organosilicon compound modified ammonium polyphosphate with different phosphorus-containing groups, and their different flame-retardant mechanisms in polyurethane foam. RSC Adv 8:27470–27480. https://doi.org/10.1039/c8ra04439b

Chen Y, Li L, Wang W, Qian L (2017) Preparation and characterization of surface-modified ammonium polyphosphate and its effect on the flame retardancy of rigid polyurethane foam. J Appl Polym Sci 134:1–9. https://doi.org/10.1002/app.45369

Cheng JJ, Qu WJ, Sun SH (2018) Effects of flame-retardant flax-fiber on enhancing performance of the rigid polyurethane foams. J Appl Polym Sci 135:1–10. https://doi.org/10.1002/app.46436

Chung YJ, Kim Y, Kim S (2009) Flame retardant properties of polyurethane produced by the addition of phosphorous containing polyurethane oligomers (II). J Ind Eng Chem 15:888–893. https://doi.org/10.1016/j.jiec.2009.09.018

Czech-Polak J, Przybyszewski B, Heneczkowski M et al (2016) Effect of environmentally-friendly flame retardants on fire resistance and mechanical properties of rigid polyurethane foams. Polimery/Polymers 61:113–116. https://doi.org/10.14314/polimery.2016.113

Demir H, Arkış E, Balköse D, Ülkü S (2005) Synergistic effect of natural zeolites on flame retardant additives. Polym Degrad Stab 89:478–483. https://doi.org/10.1016/j.polymdegradstab.2005.01.028

Demiryuğuran F (2015) Cam Elyaf, Karbon Elyaf ve Organik Madde Takviyeli Kompozit Poliüretan Köpük Malzemelerin Isıl Bozunma ve Yanma Davranışlarının İncelenmesi (in Turkish)., MSc Thesis. Pamukkale University

Duquesne S, Le Bras M, Bourbigot S et al (2000) Analysis of fire gases released from polyurethane and fire-retarded polyurethane coatings. J Fire Sci 18:456–482. https://doi.org/10.1106/6CRG-Q8VD-PV3G-ELDD

Duquesne S, Le Bras M, Bourbigot S et al (2001) Mechanism of fire retardancy of polyurethanes using ammonium polyphosphate. J Appl Polym Sci 82:3262–3274. https://doi.org/10.1002/app.2185

Gao L, Zheng G, Zhou Y et al (2013) Synergistic effect of expandable graphite, melamine polyphosphate and layered double hydroxide on improving the fire behavior of rosin-based rigid polyurethane foam. Ind Crop Prod 50:638–647. https://doi.org/10.1016/j.indcrop.2013.07.050

Gao M, Wu W, Liu S et al (2014) Thermal degradation and flame retardancy of rigid polyurethane foams containing a novel intumescent flame retardant. J Therm Anal Calorim 117:1419–1425. https://doi.org/10.1007/s10973-014-3856-6

Gürü M, Aruntaş Y, Tüzün FN, Bilici I (2009a) Processing of urea-formaldehyde-based particleboard from hazelnut shell and improvement of its fire and water resistance. Fire Mater 33:413–419. https://doi.org/10.1002/fam.1011

Gürü M, Şahin M, Tekeli S, Tokgöz H (2009b) Production of polymer matrix composite particleboard from pistachio shells and improvement of its fire resistance by Fly ash. High Temp Mater Process 28:191–195. https://doi.org/10.1515/HTMP.2009.28.3.191

Han DS, Park IB, Kim MH et al (2010) The effects of glass fiber reinforcement on the mechanical behavior of polyurethane foam. J Mech Sci Technol 24:263–266. https://doi.org/10.1007/s12206-009-1136-3

Hu X, Cheng W, Nie W, Wang D (2016) Flame retardant, thermal, and mechanical properties of glass fiber/nanoclay reinforced phenol–urea–formaldehyde foam. Polym Compos 37:2323–2332. https://doi.org/10.1002/pc.23411

Hu XM, Wang DM (2013) Enhanced fire behavior of rigid polyurethane foam by intumescent flame retardants. J Appl Polym Sci 129:238–246. https://doi.org/10.1002/app.38722

ISO (2002) ISO 5660-1 Reaction-to-fire tests — Heat release, smoke production and mass loss rate - Part 1: Heat release rate (cone calorimeter method). International Standard. 1–8

Jia D, Hu J, He J, Yang R (2019) Properties of a novel inherently flame-retardant rigid polyurethane foam composite bearing imide and oxazolidinone. J Appl Polym Sci 136:1–12. https://doi.org/10.1002/app.47943

Jiang J, Cheng Y, Liu Y et al (2015) Intergrowth charring for flame-retardant glass fabric-reinforced epoxy resin composites. J Mater Chem A 3:4284–4290. https://doi.org/10.1039/c4ta06486k

Jin J, Dong QX, Shu ZJ et al (2014) Flame retardant properties of polyurethane/expandable praphite composites. Procedia Eng 71:304–309. https://doi.org/10.1016/j.proeng.2014.04.044

Kairytė A, Kirpluks M, Ivdre A et al (2018) Cleaner production of polyurethane foam: replacement of conventional raw materials, assessment of fire resistance and environmental impact. J Clean Prod 183:760–771. https://doi.org/10.1016/j.jclepro.2018.02.164

Kim SH, Park HC, Jeong HM, Kim BK (2010) Glass fiber reinforced rigid polyurethane foams. J Mater Sci 45:2675–2680. https://doi.org/10.1007/s10853-010-4248-3

Kirpluks M, Cabulis U, Zeltins V et al (2014) Rigid polyurethane foam thermal insulation protected with mineral intumescent mat. Autex Res J 14:259–269. https://doi.org/10.2478/aut-2014-0026

König A, Fehrenbacher U, Kroke E, Hirth T (2009) Thermal decomposition behavior of the flame retardant melamine in slabstock flexible polyurethane foams. J Fire Sci 27:187–211. https://doi.org/10.1177/0734904108099329

Kulesza K, Pielichowski K, German K (2006) Thermal decomposition of bisphenol A-based polyetherurethanes blown with pentane: Part i - Thermal and pyrolytical studies. J Anal Appl Pyrolysis 76:243–248. https://doi.org/10.1016/j.jaap.2005.12.002

Kumar M, Kaur R (2017) Glass fiber reinforced rigid polyurethane foam: synthesis and characterization. E-Polymers 17:517–521. https://doi.org/10.1515/epoly-2017-0072

Kuźnia M, Magiera A, Pielichowska K et al (2019) Fluidized bed combustion fly ash as filler in composite polyurethane materials. Waste Manag 92:115–123. https://doi.org/10.1016/j.wasman.2019.05.012

Latere Dwan'isa JP, Mohanty AK, Misra M et al (2004) Biobased polyurethane and its composite with glass fiber. J Mater Sci 39:2081–2087. https://doi.org/10.1023/B:JMSC.0000017770.55430.fb

Levchik SV, Weil ED (2004) Thermal decomposition, combustion and fire-retardancy of polyurethanes - a review of the recent literature. Polym Int 53:1585–1610. https://doi.org/10.1002/pi.1314

Li J, Mo X, Li Y et al (2017) Effect of zeolites on morphology and properties of water-blown semi-rigid ammonium polyphosphate intumescent flame-retarding polyurethane foam. J Polym Res 24:1–10. https://doi.org/10.1007/s10965-017-1306-4

Li ME, Wang SX, Han LX et al (2019a) Hierarchically porous SiO_2/polyurethane foam composites towards excellent thermal insulating, flame-retardant and smoke-suppressant performances. J Hazard Mater 375:61–69. https://doi.org/10.1016/j.jhazmat.2019.04.065

Li Q, Wang J, Chen L et al (2019b) Ammonium polyphosphate modified with β-cyclodextrin crosslinking rigid polyurethane foam: enhancing thermal stability and suppressing flame spread. Polym Degrad Stab 161:166–174. https://doi.org/10.1016/j.polymdegradstab.2019.01.024

Liu H, Yang H, Chen M et al (2019) An effective approach to reducing fire hazards of rigid polyurethane foam: fire protective coating. J Coatings Technol Res 16:257–261. https://doi.org/10.1007/s11998-018-0149-1

Liu L, Wang Z (2018) High performance nano-zinc amino-tris-(methylenephosphonate) in rigid polyurethane foam with improved mechanical strength, thermal stability and flame retardancy. Polym Degrad Stab 154:62–72. https://doi.org/10.1016/j.polymdegradstab.2018.05.023

Liu SM, Huang JY, Jiang ZJ et al (2010) Flame retardance and mechanical properties of a polyamide 6/polyethylene/surface-modified metal hydroxide ternary composite via a master-batch method. J Appl Polym Sci 117:3370–3378. https://doi.org/10.1002/app.32086

Lu C, Liu L, Chen N et al (2015) Influence of clay dispersion on flame retardancy of ABS/PA6/APP blends. Polym Degrad Stab 114:16–29. https://doi.org/10.1016/j.polymdegradstab.2015.01.024

Lu S-Y, Hamerton I (2002) Recent developments in the chemistry of halogen-free flame retardant polymers. Prog Polym Sci 27:1661–1712. https://doi.org/10.1016/S0079-6700(02)00018-7

Lu W, Li Q, Zhang Y et al (2018) Lignosulfonate/APP IFR and its flame retardancy in lignosulfonate-based rigid polyurethane foams. J Wood Sci 64:287–293. https://doi.org/10.1007/s10086-018-1701-4

Luo F, Wu K, Guo H et al (2015) Effect of cellulose whisker and ammonium polyphosphate on thermal properties and flammability performance of rigid polyurethane foam. J Therm Anal Calorim 122:717–723. https://doi.org/10.1007/s10973-015-4766-y

Luo F, Wu K, Li D et al (2017) A novel intumescent flame retardant with nanocellulose as charring agent and its flame retardancy in polyurethane foam. Polym Compos 38:2762–2770. https://doi.org/10.1002/pc.23874

Lv P, Wang Z, Hu K, Fan W (2005) Flammability and thermal degradation of flame retarded polypropylene composites containing melamine phosphate and pentaerythritol derivatives. Polym Degrad Stab 90:523–534. https://doi.org/10.1016/j.polymdegradstab.2005.04.003

Michałowski S, Pielichowski K (2018) 1,2-Propanediolizobutyl POSS as a co-flame retardant for rigid polyurethane foams. J Therm Anal Calorim 134:1351–1358. https://doi.org/10.1007/s10973-018-7537-8

Mishra S, Patil UD, Shimpi NG (2009) Synthesis of mineral nanofiller using solution spray method and its influence on mechanical and thermal properties of EPDM nanocomposites. Polym Plast Technol Eng 48:1078–1083. https://doi.org/10.1080/03602550903092492

Mishra S, Shimpi NG (2007) Studies on mechanical, thermal, and flame retarding properties of Polybutadiene rubber (PBR) Nanocomposites. Polym Plast Technol Eng 47:72–81. https://doi.org/10.1080/03602550701580987

Mishra S, Sonawane SH, Badgujar N et al (2005) Comparative study of the mechanical and flame-retarding properties of polybutadiene rubber filled with nanoparticles and fly ash. J Appl Polym Sci 96:6–9. https://doi.org/10.1002/app.21114

Morgan AB, Bundy M (2007) Cone calorimeter analysis of UL-94 V-rated plastics. Fire Mater 31:257–283. https://doi.org/10.1002/fam.937

Modesti M, Simioni F (1994) Effect of phospho-halogenated polyether polyol on fire behavior of rigid polyurethane foams blown with various agents. Cell Polym 13:277–291

Ni J, Song L, Hu Y et al (2009) Preparation and characterization of microencapsulated ammonium polyphosphate with polyurethane shell by in situ polymerization and its flame retardance in polyurethane. Polym Adv Technol 20:999–1005. https://doi.org/10.1002/pat.1354

Ni J, Tai Q, Lu H et al (2010) Microencapsulated ammonium polyphosphate with polyurethane shell: preparation, characterization, and its flame retardance in polyurethane. Polym Adv Technol 21:392–400. https://doi.org/10.1002/pat.1441

Norzali NRA, Badri KH (2016) The role of phosphate ester as a fire retardant in the palm-based rigid polyurethane foam. Polym Polym Compos 24:711–718. https://doi.org/10.1177/096739111602400906

Pang XY, Xin YP, Shi XZ, Xu JZ (2019) Effect of different size-modified expandable graphite and ammonium polyphosphate on the flame retardancy, thermal stability, physical, and mechanical properties of rigid polyurethane foam. Polym Eng Sci. https://doi.org/10.1002/pen.25123

Peng HK, Wang XX, Li TT et al (2018) Effects of hydrotalcite on rigid polyurethane foam composites containing a fire retarding agent: compressive stress, combustion resistance, sound absorption, and electromagnetic shielding effectiveness. RSC Adv 8:33542–33550. https://doi.org/10.1039/C8RA06361C

Peng HK, Wang XX, Li TT et al (2019) Mechanical properties, thermal stability, sound absorption, and flame retardancy of rigid PU foam composites containing a fire-retarding agent: effect of magnesium hydroxide and aluminum hydroxide. Polym Adv Technol:2045–2055. https://doi.org/10.1002/pat.4637

Price D, Liu Y, Hull TR et al (2000) Burning behaviour of fabric/polyurethane foam combinations in the cone calorimeter. Polym Int 49:1153–1157. https://doi.org/10.1002/1097-0126(200010)49:10<1153::AID-PI551>3.0.CO;2-S

Prociak A, Pielichowski J, Modesti M, Simioni F (1997) Influence of different flame retardants on fire behaviour of rigid polyurethane foams blown with n-pentane. Cell Polym 16:284–295

Qu H, Fan R, Yuan J et al (2017) Preparation and performance of a P–N containing intumescent flame retardant based on hydrolyzed starch. Polym Plast Technol Eng 56:1760–1771. https://doi.org/10.1080/03602559.2017.1289405

Salasinska K, Borucka M, Leszczyńska M et al (2017) Analysis of flammability and smoke emission of rigid polyurethane foams modified with nanoparticles and halogen-free fire retardants. J Therm Anal Calorim 130:131–141. https://doi.org/10.1007/s10973-017-6294-4

Schartel B, Hull TR (2007) Development of fire-retarded materials—interpretation of cone calorimeter data. Fire Mater 31:327–354. https://doi.org/10.1002/fam.949

Shi X, Jiang S, Zhu J et al (2018) Establishment of a highly efficient flame-retardant system for rigid polyurethane foams based on bi-phase flame-retardant actions. RSC Adv 8:9985–9995. https://doi.org/10.1039/c7ra13315d

Shimpi NG, Mishra S (2010) Synthesis of nanoparticles and its effect on properties of elastomeric nanocomposites. J Nanopart Res 12:2093–2099. https://doi.org/10.1007/s11051-009-9768-x

Singh H, Jain AK (2009) Ignition, combustion, toxicity, and fire retardancy of polyurethane foams: a comprehensive review. J Appl Polym Sci 111:1115–1143. https://doi.org/10.1002/app.29131

Singh H, Jain AK, Sharma TP (2008) Effect of phosphorus-nitrogen additives on fire retardancy of rigid polyurethane foams. J Appl Polym Sci 109:2718–2728. https://doi.org/10.1002/app.28324

Sykam K, Meka KKR, Donempudi S (2019) Intumescent phosphorus and triazole-based flame-retardant polyurethane foams from castor oil. ACS Omega 4:1086–1094. https://doi.org/10.1021/acsomega.8b02968

Tashev E, Zabski L, Shenkov S, Borissov G (1992) Phosphorus-containing rigid polyurethane foams-II. Modifiers based on trimethyl phosphate. Eur Polym J 28:689–693. https://doi.org/10.1016/0014-3057(92)90044-3

Thirumal M, Khastgir D, Nando GB et al (2010a) Halogen-free flame retardant PUF: effect of melamine compounds on mechanical, thermal and flame retardant properties. Polym Degrad Stab 95:1138–1145. https://doi.org/10.1016/j.polymdegradstab.2010.01.035

Thirumal M, Khastgir D, Singha NK et al (2009) Effect of a nanoclay on the mechanical, thermal and flame retardant properties of rigid polyurethane foam. J Macromol Sci Part A 46:704–712. https://doi.org/10.1080/10601320902939101

Thirumal M, Singha NK, Khastgir D et al (2010b) Halogen-free flame-retardant rigid polyurethane foams: effect of alumina trihydrate and triphenylphosphate on the properties of polyurethane foams. J Appl Polym Sci 116:2260–2268. https://doi.org/10.1002/app.31626

Tuzcu H (2010) Isı yalıtımı ve otomotiv endüstrilerinde kullanılan yanmaya dirençli poliüretan esaslı malzemelerin tutuşma ve yanma karakteristiklerinin deneysel incelenmesi (in Turkish)., MSc Thesis. Pamukkale University

Usta N (2012) Investigation of fire behavior of rigid polyurethane foams containing fly ash and intumescent flame retardant by using a cone calorimeter. J Appl Polym Sci 124:3372–3382. https://doi.org/10.1002/app.35352

Usta N, Deda Altan B, Yurtseven R, Akdogan E, Tuzcu H (2011) Otomotiv ve Isı Yalıtım Endüstrileri İçin Yeni Yanmaya Dirençli Poliüretan Esaslı Malzeme Geliştirilmesi ve Bu Malzemelerin Isıl Bozulma ve Yanma Davranışlarının Deneysel ve Teorik İncelenmesi (in Turkish). Report 108T246, The Scientific and Technological Research Council of Turkey

Wang C, Wu Y, Li Y et al (2018c) Flame-retardant rigid polyurethane foam with a phosphorus-nitrogen single intumescent flame retardant. Polym Adv Technol 29:668–676. https://doi.org/10.1002/pat.4105

Wang J, Chen Y (2005) Flame-retardant mechanism resulting from an intumescent system. J Fire Sci 23:55–74. https://doi.org/10.1177/0734904105044266

Wang L, Wu X, Wu C et al (2011) Study on the flame retardancy of EVM/magnesium hydroxide composites optimized with a flame retardant containing phosphorus and silicon. J Appl Polym Sci 121:68–77. https://doi.org/10.1002/app.33226

Wang SX, Zhao HB, Rao WH et al (2018a) Inherently flame-retardant rigid polyurethane foams with excellent thermal insulation and mechanical properties. Polymer (Guildf) 153:616–625. https://doi.org/10.1016/j.polymer.2018.08.068

Wang Y, Wang F, Dong Q et al (2018b) Expandable graphite encapsulated by magnesium hydroxide nanosheets as an intumescent flame retardant for rigid polyurethane foams. J Appl Polym Sci 135:1–9. https://doi.org/10.1002/app.46749

Weil ED, Levchik SV (2004) Commercial flame retardancy of polyurethanes. J Fire Sci 22:183–210. https://doi.org/10.1177/0734904104040259

Wu K, Wang Z, Hu Y (2008) Microencapsulated ammonium polyphosphate with urea-melamine-formaldehyde shell: preparation, characterization, and its flame retardance in polypropylene. Polym Adv Technol 19:1118–1125. https://doi.org/10.1002/pat.1095

Wu D, Zhao P, Liu Y (2013a) Flame retardant property of novel intumescent flame retardant rigid polyurethane foams. Polym Eng Sci 53:2478–2485. https://doi.org/10.1002/pen.23710

Wu D, Zhao P, Zhang M, Liu Y (2013b) Preparation and properties of flame retardant rigid polyurethane foam with phosphorus-nitrogen intumescent flame retardant. High Perform Polym 25:868–875. https://doi.org/10.1177/0954008313489997

Wu DH, Zhao PH, Liu YQ et al (2014) Halogen free flame retardant rigid polyurethane foam with a novel phosphorus-nitrogen intumescent flame retardant. J Appl Polym Sci 131. https://doi.org/10.1002/app.39581

Xu D, Yu K, Qian K (2018) Thermal degradation study of rigid polyurethane foams containing tris(1-chloro-2-propyl)phosphate and modified aramid fiber. Polym Test 67:159–168. https://doi.org/10.1016/j.polymertesting.2018.01.034

Xu D-M, Hao J-W, Liu G-S, Xie S-M (2013) Thermal degradation and smoke production during combustion for intumescent flame retardant rigid polyurethane foams. Acta Polym Sin:832–840. https://doi.org/10.3724/SP.J.1105.2013.12264

Xu W, Wang G (2015) Synthesis of polyhydric alcohol/ethanol phosphate flame retardant and its application in PU rigid foams. J Appl Polym Sci 132:1–9. https://doi.org/10.1002/app.42298

Yang R, Hu W, Xu L et al (2015) Synthesis, mechanical properties and fire behaviors of rigid polyurethane foam with a reactive flame retardant containing phosphazene and phosphate. Polym Degrad Stab 122:102–109. https://doi.org/10.1016/j.polymdegradstab.2015.10.007

Yurtseven R, Tarakcılar AR, Topcu M (2013) Dolgu Maddesi Olarak Kullanılan Farklı Uçucu Küllerin Sert Poliüretan Köpük Malzemelerin Mekanik Özellikleri İle Isıl Ve Yanma Davranışları Üzerine Etkileri (in Turkish). J Fac Eng Archit Gazi Univ 28:841–853

Zatorski W, Brzozowski ZK, Kolbrecki A (2008) New developments in chemical modification of fire-safe rigid polyurethane foams. Polym Degrad Stab 93:2071–2076. https://doi.org/10.1016/j.polymdegradstab.2008.05.032

Zhang J, Wang X, Zhang F, Richard Horrocks A (2004) Estimation of heat release rate for polymer-filler composites by cone calorimetry. Polym Test 23:225–230. https://doi.org/10.1016/S0142-9418(03)00098-9

Zhao C, Qin H, Gong F et al (2005) Mechanical, thermal and flammability properties of polyethylene/clay nanocomposites. Polym Degrad Stab 87:183–189. https://doi.org/10.1016/j.polymdegradstab.2004.08.005