# Chapter 19
# The Role of Polyurethane Chemistry on the Properties of Phenolic Foams Applied in the Thermal Insulation Industry

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## 1 Introduction

Phenolic foams (PFs) represent the material of choice whenever fire resistance is a fundamental design requirement. The combination of a very low-flame spread velocity, almost null smoke or toxic gas emissions, no liquid dripping when subjected to high temperatures, and high insulation value represent the key distinct properties that differentiate PF with respect to other insulation materials available in the industry [1, 2]. According to the European Phenolic Foam Association (EPFA), the main applications of PF are insulation, mining, and floral.

The use of urea–formaldehyde PF in housing and industrial structures was introduced in the 1960s in northern Europe [3, 4], while in the 1970s, Canada and the USA continued this path. However, the emissions of formaldehyde gas provoked by poor industrial application standards in the interior of residential houses caused a severe setback in the residential industry in Canada and the USA. Another issue was raised in the 1990s, where the application of PF in decking caused corrosion in metallic structures. Recent research programs led mostly by the Department of Energy of the USA [1] are aimed at the development of PF with a higher pH and improved adhesive as well as mechanical properties. The recent transition of the construction industry from traditional wet construction systems to industrialized building systems (IBS) will lead the way to increased growth of the PF industry in sandwich structures [5]. The main advantage of this approach is that the structural panel is manufactured continuously in an industrial environment. Due to the fact that it is possible to introduce high-quality standards and to maintain this in a localized manufacturing

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facility, future initiatives in the development of PF applied in sandwich construction will certainly pave the way to a new growth stage. One of the key issues to catalyze this growth is related to the highly friable nature of PF. The use of polyurethane chemistry is a key aspect to reduce the friability of PF without a simultaneous deleterious effect on flammability performance. To achieve this objective, reactive routes based on the use of isocyanate prepolymers represent the state-of-the-art. Other methodologies based on the use of composites and nanotechnology will also be discussed in this chapter, emphasizing the interplay between these strategies and the cure kinetics, friability, flammability, and environmental impact of PF and PUF.

Another relevant application of PF is in underground mining [1]. During normal operations, if mineworkers stumble into an unstable crumble rock face or lair, it is frequent to use foams so as to eliminate a plausible accident. To this effect, PF foams are usually sprayed in situ so as to increase structural stability. The main advantage of PF applied in this industry is related to the fact that when it is accidentally ignited, no volatile emissions are released. Finally, PF is also used for the growth of flowers and all sorts of floral arrangements. It is important to highlight that, due to the niche nature of these last applications, in this chapter our discussion will be centered on PF applied in thermal insulation.

In contrast to PF, polyurethane foams (PUF) also find widespread uses in industry, such as spray-up thermal insulation as well as structural panels [6, 7]. Even though both PF and PUF share a common chemical precursor, that is, benzene, initial R&D efforts were not focused on using both systems synergistically. This has led to the development of parallel industries known as the phenolic and polyurethane foam industries. Nowadays, the R&D efforts focus on the development of PF with improved toughness retaining as well as high fire resistance. To achieve this goal, it is important to apply a synergistic approach using polyurethane chemistry as an ally. For example, the introduction of isocyanate prepolymers and glycols in the molecular structure of PF can help to improve toughness without altering significantly other relevant properties.

The main objective of this chapter is to highlight how PF properties can be tailored using the flexibility of polyurethane chemistry. To this effect, Sect. 2 will deal with a brief introduction on polyurethane chemistry, emphasizing the principal concepts and ideas which are frequently used by polyurethane specialists. Due to the fact that this book is specialized in phenolic foams, the reader can consult specific aspects of PF chemistry in other chapters. The following section will focus on correlating the properties of PF and PUF, particularly on the areas of formulations, blowing agents, cure kinetics, friability, environmental impact, and flammability. Section 4 will deal with how reactive routes are applied in PF chemistry. The section starts laying out the main principles associated with the use of reactive routes and how those are related to polyurethane chemistry. Then, study cases are presented so as to illustrate the main application of those principles. Finally, the chapter finalizes with a conclusion section so as to emphasize the main concepts that were studied in this chapter.

## 2 A Brief Introduction to the Polyurethane Chemistry

The polyurethane chemistry was born when Dr. Otto Bayer, around the year 1938, reacted a diisocyanate with a natural polyester polyol, that is, castor oil [7]. Nowadays, the polyurethane industry represents one of the most relevant polymeric commodities and their applications range from flexible to rigid foams, coatings, thermoplastic and thermosetting polymers, adhesives, sealants, as well as other applications. This versatility is based mostly on the chemistry of the diisocyanate precursor, where its facile reaction with a wide range of functional groups has led to such different applications and uses.

Polyurethanes are obtained through the reaction of two main chemical precursors, diisocyanates (from now on isocyanates) and polyols. Blowing agents (BAs), catalysts, surfactants as well as other additives are usually employed and dispersed within the polyol component. In industry, both physical and chemical BAs are usually employed. The physical BAs rely on the evaporation of a low melting point liquid (such as a hydrocarbon) and the chemical BAs are based on the reaction of isocyanate with water, forming carbon dioxide during PUF cure [7]. Hence, polyurethane chemistry can be significantly altered mostly by chemical BAs, because the in situ formation of $CO_2(g)$ can compete with the chemical reactions of the polyol with the isocyanate precursor [6]. In PUFs, catalysts are usually employed to increase the gelling and blowing reactions [8]. In this regard, tin-based catalysts are frequently employed to increase the cure kinetics of reactions between isocyanates and hydroxides (polyol). On the other hand, amine-based catalysts are usually responsible to improve the kinetics of blowing reactions, such as the formation of $CO_2(g)$ from isocyanate and water. Typical formulations of PUFs usually employ both catalysts, whereas the specific concentrations are carefully determined so as to have the right balance between the gelling and blowing reactions. Surfactants are a key aspect for the development of a closed and homogeneous cell structure. These usually don't have a substantial effect on polyurethane chemistry, but instead, have a preponderant role in the formation of a PUF with a high content of closed cells.

From an industrial point of view, polyurethanes are usually two-component systems, where component A is usually a mixture of different types of isocyanates and component B represents the polyol and all the remaining additives and catalysts. The preferred isocyanate used for the thermal insulation industry is polymeric methylene diphenyl diisocyanate (pMDI). Due to the fact that MDI is solid at room temperature, eutectics are usually employed to obtain a pMDI with low viscosity, that is, within the range of 200–400 cp (at 25 °C). The main characteristic of pMDI is the isocyanate number ($NCO_{number}$), which is a measurement of how many isocyanate groups are available to react on a weight basis. This value should not be confused with the isocyanate index, which is referred to as the stoichiometric relationship between isocyanate and hydroxide (or other reactive) groups present in the component B. On the other hand, the polyol is usually a blend of a wide range of monomers characterized mainly by its molecular weight, functionality, and viscosity. A higher molecular weight polyol is usually employed to mitigate the effect of a highly crosslinked structure, which will inevitably lead to fragile material. This characteristic is of paramount importance for the reactive modification of PF precursors. Further details will be explained in Sect. 4. The functionality has also a relevant impact on the final properties of the material. Due to the fact that both PF and PUF are crosslinked polymers (thermosetting), polyols with functionality above 2.0 are mostly employed. The chemical nature of the functionality is also relevant; hydroxides being the main radical group that is used to react with the isocyanate moiety. Viscosity plays a fundamental role, particularly when processing technology is taken into account. In this regard, polyols with either low, medium, or high viscosities can be employed (200–4000 cp). A summary of the properties of the precursors frequently used for PUF systems is depicted in Table 1.

Polyurethanes can be prepared using the one-shot [9], quasi-prepolymer [10], and prepolymer techniques [11]. The distinction between these three types of techniques is fundamental, especially when PFs are taken into consideration. Further details about the relationship between these techniques and PF synthesis will be discussed in the next section. The one-shot technique [6] is usually employed for the preparation of either flexible or rigid polyurethane foams (RPUF). In this method, the precursors need to be of relatively low viscosity (<1000 cp) so as to achieve good physical mixing using conventional or high-pressure dosing equipment. The properties of a typical PUF precursor used for the one-shot technique are reported in Table 1. As it can be deduced, the isocyanate component (A) has a high $NCO_{number}$ (29.0%), which is an indication that no reaction has taken place so as to change the properties of this component. With respect to the polyol (B), in this case the hydroxide number (#OH) and functionality indicate that the polyol has been formulated for in situ spray foaming.

The quasi-prepolymer technique is based on the use of precursors which are the reaction products of a blend of polyols with a large excess of isocyanate. The term adduct is usually employed to identify this intermediate, which has a lower $NCO_{number}$, between 15 and 29 wt%. The main objective of this technique is to circumvent one of the great disadvantages of isocyanates, that is, the unstable nature of isocyanate moieties. These are prone to react with water, forming both carbon dioxide and polyamines. In addition, a reduced volatile organic content (VOC) can also be achieved, reducing the environmental impact of the formulation. Further details can be consulted in Table 1.

Finally, the prepolymer is an isocyanate adduct with a lower $NCO_{number}$, between 1 and 14 wt%. These are usually synthesized by the slow addition of specific polyols to isocyanates in reactors under a controlled atmosphere (dry nitrogen gas) and temperature (around 60 °C). The resulting monomers are usually applied in urethane elastomers, coatings, adhesives, sealants as well as toughening agents of PF (Sect. 4). The main advantage of using this approach relies on the fact of a reduced cured exotherm, which leads to a widespread family of versatile polymers. These materials are also reacted with chain extenders, i.e., long aliphatic monomeric species which serve to increase molecular weight and to cause significant toughness improvements. In PF chemistry, it is usual to apply this technique, whereas the main disadvantage

**Table 1** Physical properties of typical PUF and PF systems

| Property | PUF (spray-up)[1] | | PUF prepolymer (elastomer)[2] | PUF (quasi-prepolymer)[3] | Phenolic foam[4] | |
|---|---|---|---|---|---|---|
| | CA (isocyanate) | CB (Polyol) | CA (isocyanate) | CA (polyol) | CA (phenolic resin) | Catalyst |
| $NCO_{number}$ (%) | 30–32.5 | – | 5–7 | 16.5–22.5 | – | – |
| HCl acidity (ppm) | <200 | <100 | <150 | <100 | – | – |
| Viscosity (cp) | 150–300 (25 °C) | 200–500 (25 °C) | 1000–4000 (50 °C) | 3000–10,000 (50 °C) | 2000–8000(25 °C) | <10 (25 °C) |
| Density ($g/m^3$) | 1.20–1.22 | 1.10–1.15 | 1.10–1.15 | 1.10–1.15 | 1.1–1.2 | 1.8–2.3 |
| #OH | – | 250–300 | – | – | – | – |
| Functionality | 2.1–2.9 | >3.0 | >2.5 | >3.0 | – | – |
| pH | – | – | – | – | 8.50–9.50 | <4.0 |
| Dry solid content (%) | >99.9 | >93 | >99.9 | >99.9 | 75–80 | Liquid |
| Free phenol (%) | 0 | 0 | 0 | 0 | 4.5–6.5 | 0 |
| Free formaldehyde (%) | 0 | 0 | 0 | 0 | <1.40 | 0 |

of using it relies on its impact on fire performance (Sect. 3). Specific details of an isocyanate prepolymer are reported in Table 1.

## 3 Correlating Cellular Structures Based on Polyurethane and Phenolic Chemistry

The phenolic chemistry is based on the chemical reaction of a phenol and formaldehyde in either acidic (Novolak) or basic conditions (resole). One of the key features is that the reaction can be performed either in acidic or basic conditions by changing the molar ratio of the phenol and formaldehyde precursors (P/F ratio). When the P/F ratio is less than 1, the molecular structure of the resulting phenolic resins is very stable (Novolak), whereas its subsequent use as a precursor for other materials is based solely on the use of catalysts. Taking into account the molecular structure (Fig. 1A) of the resulting precursor, Novolak resins can also be understood as low molecular weight and highly aromatic polyols [12], giving rise to a highly friable structure. Hence, the use of Novolak resins in the formulation of PF is not frequently employed, because it increases the crosslinking and aromatic content, giving rise to an extremely friable PF [1].

On the other hand, when the P/F ratio is higher than 1, the resulting molecular structure of the phenolic resin is not stable (resole), giving rise to resole-type precursors (commonly known in the industry as resins). The main reason associated with

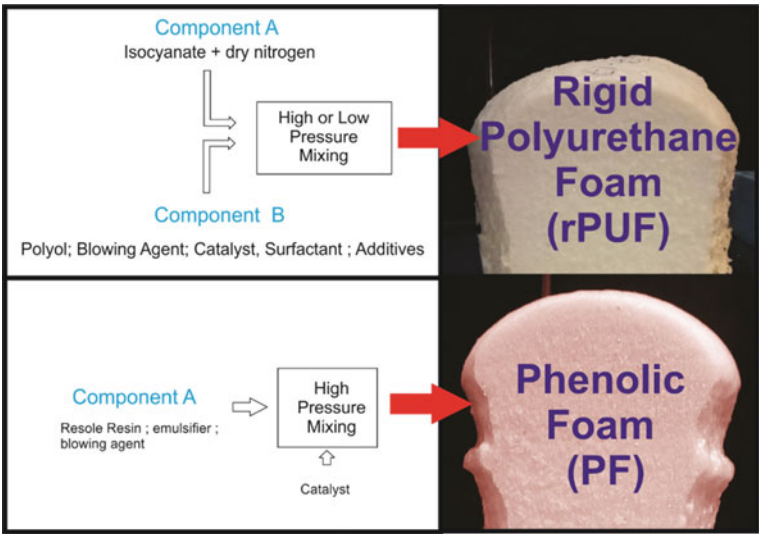

**Fig. 1** Rigid polyurethane foams (rPUF) and phenolic foams (PF) obtained from its chemical precursors

this characteristic is the presence of unstable methylol groups, which can further react without the addition of specific catalysts and those can crosslink solely by a slight temperature increase. This is a key feature for the plausibility of using this precursor for the preparation of phenolic foams (PFs). Taking into account that this precursor is the most relevant precursor of PF, the subsequent discussion will focus on resole precursors (resins). Further details can be consulted elsewhere [1].

The resins used for PF are mostly obtained from the resole chemistry. In this regard, the P/F lies within the range of 1:1.3 to 1:2.1 [1], and hydroxide salts are employed as catalysts so as to achieve a highly crosslinked network (Table 1). The typical viscosity of such resins lies within the range of 1500–12,000 cp. Hence, it can be understood that, from a processing point of view, PFs have precursors with a moderate to high viscosity. In contrast, polyurethane precursors used for spray foam applications have working viscosities well below those values (200–400 cp). It is important to notice that the solid content is a key aspect to consider to actually contrast polyurethane and PF precursors. Indeed, in both cases, processing viscosity can be effectively reduced by the use of non-reactive diluents [1, 6]. However, the use of such diluents has been a cause of severe critics, due to the fact that non-reactive diluents can be extremely toxic. Nowadays, strict emissions control enforced by the United Nations Environment Program (UNEP) is currently being deployed worldwide so as to reduce environmental impact.

## *3.1 Systems Based on PF and PUF Precursors*

The resulting monomers obtained from the synthesis of precursors used to manufacture either phenolic or polyurethane foams are usually not suitable by themselves to this effect. Then, blends of different components are usually employed so as to circumvent the disadvantages of each precursor and improve processing properties as well as reduce toxicity or emissions. These are denominated systems or formulations.

For the case of PFs, these are based on catalyzed one-component systems (Fig. 1). In this regard, a typical formulation is composed of the resole phenolic resin, an emulsifier, and a blowing agent (BA). The resin is inherently unstable, due to the presence of methylol groups which can react and crosslink the molecular structure of the precursor solely by temperature. The emulsifier is used to improve the miscibility of the BA and the resole resin and to avoid phase separation. Nowadays, the vast majority of PF are prepared using pentane as a BA and ethoxylated ricin-based emulsifiers which enhance emulsion stability [1]. When the manufacture of the PF is desired, an aqueous acid catalyst is added to this component and the temperature is raised in the mold so as to achieve higher cure conversions. Typical processing temperatures of PF are well above 60 °C, reaching in some cases up to 140 °C [1]. Even though higher amounts of catalysts can be added into the system to improve cure kinetics, most systems need much higher temperatures to achieve good conversions.

In contrast, PUF formulations are two-component systems (Fig. 1). One component is a mixture of isocyanates (A) while the second component is composed of one or more polyols, catalysts, blowing agents as well as surfactants and other additives (B). To manufacture the foam, the systems are usually formulated so that equals amounts (in volume) of component A are mixed with equal amounts of component B. The cure can be performed in a wide range of temperatures. It is possible to formulate the system so as to have a cure temperature as low as 5 °C, but most PUF systems cure at 20–25 °C. No post-cure is necessary to achieve the final mechanical properties.

### *3.2 Blowing Agents*

The cure reaction of both PF and PUF is exothermic, which gives rise to the possibility of using this energy for the volatilization of physical foaming agents. In contrast to PUF, the expansion of the polymeric mass during cure for PF is exclusively from the expansion of physical blowing agents (BAs). As already explained in Sect. 2, the isocyanate precursor has the capability of producing carbon dioxide gas through its chemical reaction with water. The boiling temperature of the BA must be slightly higher than 25 °C and the BA in the liquid state must have a suitable solubility with the precursor as well as low flammability and toxicity. The earlier adoption of BA based on chlorofluorocarbons (CFCs) has led, nowadays, to stringent worldwide regulations regarding the use of BAs with low ozone depletion potential (ODP) as well as low global warming potential (GWP). Then, the main difference between PF and PUF is that the former uses mostly physical BAs, whereas the latter can use either chemical or physical ones. Within the PF industry, the most common BA is pentane as well as liquid carbon dioxide. Even though it is known that pentane has a high explosive risk, the vast majority of industrial production of PF are performed under strict industrial conditions, particularly when pentane is used as the exclusive BA. In contrast, PUF is more flexible in this regard, whereas its application can be performed in situ (spray foam) as well as in industrial conditions.

### *3.3 Cure Kinetics*

The underlying behavior of thermosetting polymers which undergo the cure process is mostly influenced by how the molecular structure of the precursors evolves to a final crosslinked network. In this regard, resole phenolics undergo both polyaddition and polycondensation reactions. However, it is important to highlight that temperature is a key variable that controls the preponderance of both reactions [1, 2, 13]. If the reaction evolves at temperatures below 60 °C, polyaddition of methylol groups will certainly be the most relevant reaction mechanism [1]. On the other hand, when the reaction temperature is higher than 60 °C, polycondensation might play a relevant role in cure kinetics. At the first sight, the occurrence of both phenomena might be intranscendental. However, it is important to highlight that polycondensation reactions in phenolic chemistry indicate the formation of a subproduct, which in this case is water. As already noticed in the previous section, the cure enthalpy is frequently employed to aid the volatilization of blowing agents, which, in turn, lead to the formation of a cellular structure. If the cure reaction generates liquid $H_2O$, the cure enthalpy will also be used to heat the liquid $H_2O$ produced in situ. This combined effect will lead to a decrease in the efficiency of the foaming process [1, 14]. In addition, if the PF main application is insulation, the high conductivity of liquid $H_2O$ will have a deleterious effect on the thermal properties of the final PF structure.

On the other hand, PUF chemistry is exclusively based on polyaddition kinetics. This indicates that the reaction between the precursors does not generate undesirable subproducts. However, as already noticed in the previous section, the volumetric expansion during cure is based on the use of both physical and chemical BAs. Indeed, small additions of water are intentionally added in the formulation of the polyol precursor so as to purposely cause the formation of carbon dioxide, which causes volumetric expansion. PUF cure kinetics is mainly dependent on temperature, polyol functionality, catalyst, filler content, and blowing agent [7]. An increase in temperature causes an overall increase of cure kinetics, but it is not frequent to use higher temperatures in this regard [6]. Instead, catalysts have the main role in PUF cure kinetics. The concentration added is specified according to the location of the manufacturing site as well as the desired final structure. For example, for spray-up PUFs, a higher content of tin-based catalysts is usually employed if the application is performed for temperatures in the range of 0–20 °C. On the other hand, the polyol functionality also has a fundamental role in PUF cure kinetics [15]. If a highly functional polyol is employed, cure kinetics will be certainly faster, and reduced amounts of catalysts will be employed to achieve the desired final mechanical properties. The BA can also have a role in PUF cure kinetics [16]. Due to the fact that physical BA relies on the absorption of heat to volatilize, a higher content of BA will certainly decrease the PUF cure kinetics. If this aspect is not taken into account, an incomplete cure will lead to an unstable PUF structure.

## 3.4 Friability

Polymeric cellular foams can be extremely fragile. In this regard, when the cell walls and struts do not have enough deformation to rupture, the overall cellular structure tends to break down into small pieces, forming dusty fragments after the application of small forces caused by handling or manipulation. This effect is usually noted as friability (brittleness, pulverization) and it is measured by the tumbling box technique following the guidelines of ASTM C421 [17]. However, it is frequent in the literature to evaluate foam pulverization using other tailored methods [10, 18, 19]. The main parameter measured is weight loss as a function of how the abrasion experiment is being performed (pulverization ratio). If a higher weight loss is measured, then the foam is said to have a higher friable or fragile nature.

Phenolic foams have always been extremely friable. The high aromatic content of the PF precursor (Fig. 2), its low molecular weight, and the highly crosslinked network after cure are the main causes of a very friable cellular structure. To circumvent this important issue, several strategies have been tested [14]. The first one is the reactive route, which is related to a change in the molecular structure of the PF precursor. However, the main drawback of this strategy has to do with the impact of such modification on the flammability of the resultant PF. Indeed, if conventional reactive routes are implemented, the flammability might be significantly reduced. Due to the relevance of this issue, further details on this will be discussed in Sect. 4. Another strategy is based on the development of particulate composites [20], whereas both granular particulates and fibers [19, 21–24] can be used in the precursor to reduce friability. This approach has been extensively studied in the literature and this chapter will focus mostly on the reactive route.

On the other hand, for the case of PUF, friability can always be modified through a change in the molecular structure of the polyol component. However, when it comes to polyurethane foams with high flame resistance, the polyisocyanurate foam (PIR) is widely employed (Table 1). The molecular structure of PIR is based on the trimerization of the isocyanate precursor, forming a highly crosslinked structure without the need of high weight content of polyol in the network [25]. The PIRs are known for being highly flame-retardant and heat-resistant [25]. However, the initial developments led to extraordinary friable foams which were of no practical or industrial use [25]. This changed after Ashida developed urethane-stabilized PIR foams. The first PIR foams were commercialized by Nisshinbo Inc. of Tokyo, Japan using the technology disclosed by the Ashida patent [26].

### *3.5 Environmental Impact and Renewable Content*

When it comes to the evaluation of the environmental impact of a product, it is important to perform a lifecycle analysis, which is the most comprehensive and suitable tool so as to evaluate the whole value chain of the product under analysis [27, 28]. Our discussion will only focus on the industrial production of the precursor, how it is processed in the industry to obtain a final product, and the properties of the final product by itself.

The industrial production of both PF and PUF chemical precursors shares a common origin. Indeed, both phenolic resins and isocyanates are obtained from the same hydrocarbon, benzene [7]. In addition, this chemical is obtained from crude oil, a non-renewable resource. The first aspect to notice is that for the case of phenolics, most of the weight content of the formulation is solely obtained from benzene using the cumene process [1]. Indeed, both phenol and acetone are synthesized from benzene and propylene using this path. Phenols are also obtained from renewable resources, such as coal tar or the liquid byproducts of gaseous processes. However, the main drawback of these renewable paths is that the phenols obtained are of low purity.

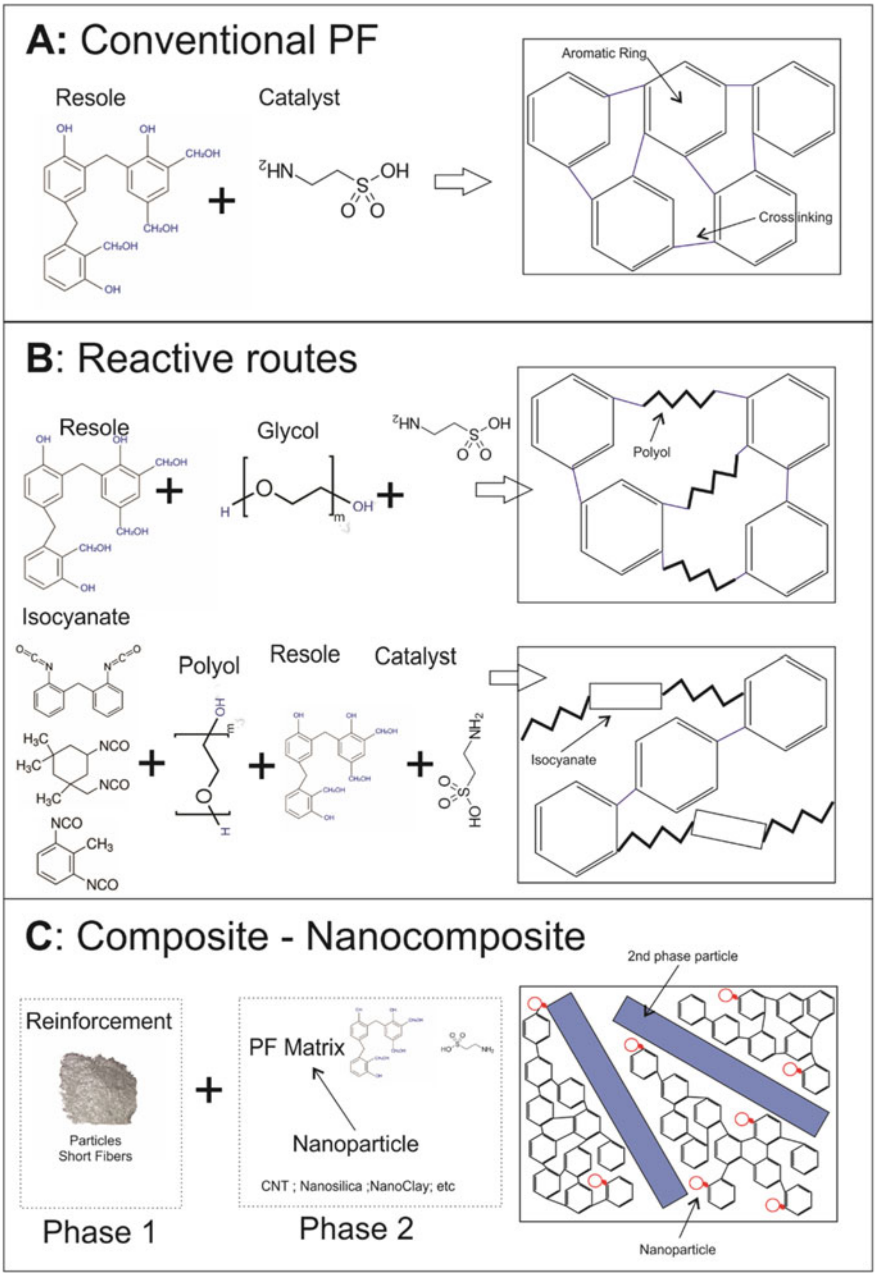

**Fig. 2** Conventional **A** PF route, reactive routes **B**, and composites and nanocomposite routes **C** used for the preparation of PF

Another relevant PF precursor is formaldehyde. As already noticed above, resoles are synthesized using a stoichiometric excess of formaldehyde. Even though the objective of the chemical process is to completely react the aldehyde, leaving only unreacted methylol groups, this is not usually the case and the PF precursors are usually characterized to evaluate its free formaldehyde content [29]. It is important to notice that formaldehyde has been classified by the Environmental Protection Agency (EPA, USA) as a "probable human carcinogen". This precursor is the main reason why PF participation in the thermal insulation market has been reduced significantly. Nowadays, formaldehyde is mainly produced from methanol, which is obtained from natural gas. Renewable resources, such as syngas, can be used to obtain methanol.

For the case of PUF, the development of isocyanates from renewable resources has not been studied extensively either in academia or in the industry [5]. In this regard, a non-isocyanate route [30–32] to polyurethanes has emerged as a possible substitute for the use of the isocyanate moiety as an intermediate in the manufacture of polyurethane foams. On the other hand, the polyol component can be completely obtained from renewable resources, such as soybean, sunflower, castor, and other natural oils [5, 33–36].

When it comes to the environmental impact of insulation applied in residential structures, it is important to highlight the history of insulation materials used in this field. One of the first insulation foams applied in residential buildings was the urea–formaldehyde foam (UFFI). The initial development of UFFI goes back to 1933 [3, 4, 37, 38]. The residential use in northern Europe flourished during the 1960s and, then, in the USA during the 1970s. The UFFI is based on the in situ application of a mixture of urea, formaldehyde, and aqueous acid catalysts. Due to the highly unstable nature of formaldehyde and to the lack of stringent industrial application standards, the application of UFFI inside residential homes in the 1970s led to the release of a significant amount of that gas in household environments. In turn, this led to an increasing health impact on house owners. The increasing relationship between health issues and UFFI led to the banning of the use of UFFI in Canada and the USA in 1980 and 1982, respectively.

One of the most relevant aspects regarding the use of PF and PUF is the processing technologies involved in the transformation of the liquid polymer into foam. Even though the use of industrialized building systems (IBS) has led to the development of sandwich structures using either PF or PUF as a core material, the in situ application of foams still remains a convenient way to insulate either commercial, industrial, or residential buildings. The processing technology used to apply foams in situ has evolved significantly from the initial application of sprayed foams in the 1930s. The main concept behind this technology is the atomization of two components that are simultaneously sprayed onto the surface which needs to be insulated. The main advantage of this technology is that it can be applied to any surface, improving its insulation properties dramatically and also generating a sealed environment, which reduces convective air circulation from the outside atmosphere. All these improvements can be obtained at a low cost, which can be amortized through an increase in energy efficiency. However, the main drawback of this technology has to do with the fact the unreacted precursors are sprayed on the surface and it is generally assumed that those precursors will react completely forming either PF or PUF foams. This is certainly not the case and external auditors are needed to control that no toxic emissions are present after the application of the foam. For example, the use of spray foam polyurethane (SPF) insulation in residential houses in the USA usually involves the fact that the owners have to leave their residency for at least a couple of days so as to perform the foam application. Due to the fact that the formulation of PUF systems involves the use of amines as catalysts, it has been reported that if the application of SPF is not performed under standard procedures, then the toxic amines or unreacted isocyanates might remain in the atmosphere of the house. This has led to several complaints of house owners, and in some cases, a complete removal of the insulation material had to be performed.

## *3.6 Flammability or Fire Resistance*

Fire propagation is a key aspect when cellular foams are applied in infrastructural applications. The performance evaluation tests are strongly related to regulations imposed by each country or state. For example, in the UK, phenolic insulation foams must be tested according to the BS476 standard. In the USA, the Ohio State University (OSU) 65/65 heat release standard is usually employed, and in Argentina, the DIN4012B2 is required by state law. Nonetheless, all these methods share a common scientific basis. The key aspect is to quantify the amount of heat released over time of a material subjected to a specific ignition or burning scheme. For example, the DIN4012 standard involves suspending the sample vertically and igniting it at the lower end. The speed at which the flame propagates is estimated and the emission of toxic gases as well as the dripping of burned material can also be quantified. All these measurements must comply with the specific regulation of each country and it is common to test not only the foam by itself but to analyze how the material behaves in real applications, where the foam can be combined in a sandwich structure with composite or steel facings.

Nowadays, PF is still the highest performance material whenever flammability is taken into account. Its use in infrastructure is highly associated with local regulations. As a matter of fact, the UK applies the highest standards in the world regarding foam flammability requirements. Hence, PF has found widespread application in that country. However, in the rest of the world, PIR foams or even conventional PUR foams with anti-flame additives are also widely used. To aid the worldwide development in this field, limiting oxygen index (LOI) and UL94 experiments are frequently reported in the literature. The LOI experiments are obtained following the guidelines of ISO 4589. In this analysis, a long sample is tested vertically and it is located inside a tight glass container. The atmosphere of the container is controlled by changing the volume mixture of nitrogen and oxygen gases. The LOI index is then obtained for the minimum oxygen concentration within the chamber which sustains the combustion of the polymeric foam. An LOI index below 21% is a characteristic of flammable material, and flame-retardant materials usually have indexes above approximately 27% [1].

## 4 Synergistic Reactive Routes to Improve the Properties of PF Using the Polyurethane Chemistry

When it comes to analyzing how to improve the properties of PF, it is important to establish benchmark parameters. Taking into account that our discussion is centered on thermal insulation panels applied to IBS, the minimum properties of the foam shall be deduced from the requirements associated with that application.

The first important properties are obtained from compressive and flexural mechanical tests. The compressive strength ($\sigma_c$) of foamed materials is measured following the guidelines of ASTM 1621. In a typical compressive mechanical test, the stress–strain curve presents three stages. The initial is a linear-elastic response followed by a plateau regime, finalizing with a densification stage at higher deformations [39]. This measurement is usually performed at 25 °C and the sample is oriented at the direction of cell growth. It is important to highlight that foams are anisotropic materials whereas the principal direction is oriented parallel to cell growth. To obtain the compressive strength, two methods are usually employed. The first one is to use directly the peak stress measured when the linear-elastic response finalizes and the second one is to report the stress at 10% deformation. Taking into account this last definition, foam cores for thermal insulation should have compressive strengths above $1.0 \times 10^{-1}$ MPa [40]. Another frequently employed mechanical test is three-point bending [14]. The most relevant parameter obtained from this test is flexural strength, which is the stress associated with the yielding point of the stress–deformation curve. A higher flexural strength indicates that the foam will be able to tolerate higher loads within its linear-elastic regime. In addition, the flexural strain at break is also an indication of the maximum deformation that the foam will be able to tolerate before rupture. Even though several research groups have studied the flexural properties of the foams, it is important to highlight that the foams are mostly applied in sandwich construction. Hence, the evaluation of the flexural properties of the foam alone is not as relevant as to evaluating the sandwich structure. Another important factor in this test is the span to length ratio (SLR). In order to compare the results of one work with another, it is important to use similar SLR values. A low SLR value will cause a relative increase of shear stress with respect to applied flexural bending stress [41]. Comparison of mechanical properties deduced from this mechanical test should be based upon similar SLR values.

With respect to flammability performance, the results of both UL94 and limiting oxygen index (LOI) experiments are usually reported. As a reminder, flame-retardant materials need to have LOI values above 27%. The higher the LOI value, the better the material will behave with respect to flame propagation. It is important to highlight that the minimum requirements of this property are strictly related to state regulations.

The final decision associated with the use of the foam in the industry is related to the approval of certified tests performed by third-party institutes specialized in this area. However, in R&D studies, the LOI technique is usually employed so as to compare the results obtained from laboratories all around the world. The heat release rate measured with the cone calorimeter test is also widely employed; however, this chapter will focus only on LOI indexes.

With respect to friability, even though the standard experiment is the tumbling box, this technique is not frequently employed in R&D studies. Indeed, most of the researchers perform different experiments to assess the friability of a specific foam, which is based on erosion caused by a specific cyclic state of stress. The pulverization ratio, which is a weight relationship describing the weight loss associated with that experiment, is usually regarded as the friability indicator. Hence, it is difficult to establish a benchmark in this particular measurement, and the analysis will be centered on relative measurements.

One of the most relevant properties of PF applied in thermal insulation applications is their insulation value. The cellular nature of polymeric foams has the advantage of generating a microstructure will small and closed cells, such as the ones depicted in Fig. 3. This structure is composed of struts and cell walls, and within each cell, gases are entrapped, preventing convective among the whole volume of the foam. The thermal conductivity ($\lambda$) is defined and measured as the heat energy passing through a plate of standard dimensions. In polymeric foams, the thermal conductivity has the contribution [7] of radiate, solid, gas, and convective heat transfer. The most relevant value is the gas conductivity ($\lambda_{gas}$) and its value defines the overall conductivity of a polymeric foam [5]. Hence, the composition of the gas within the cell is a key aspect to take into account. In addition, if the gas within the cell diffuses or permeates outside the cell, a change of thermal conductivity will be measured (aging effect).

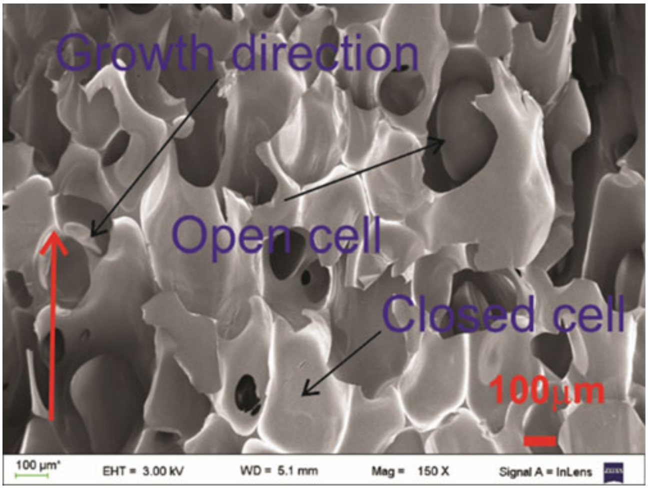

Fig. 3 Typical geometry of PUF polymeric cellular structures

Indeed, the most relevant features of thermal insulation foams are their initial λ value and variation as a function of time (thermal aging). Typical values of thermal conductivity for either PF or PUF are reported in Table 2. For the benchmark, a λ value less than 25 mW $m^{-1}$ $K^{-1}$ should be achieved. Another relevant property is closed-cell content. In order to achieve a negligible increase of thermal conductivity as a function of time (thermal aging), the cells need to be closed. If the processing technology or the system creates a foam with a high content of open cells, the internal gases will tend to migrate and generate convective flow, reducing significantly the thermal insulation value of the foam. Higher closed-cell contents of around 85% can achieve this requirement [7].

The strategies that are used in the literature to improve the previously mentioned properties are based mostly on changing the molecular structure of the polymer (also known as reactive routes) and through the preparation of composites (Fig. 2). The reactive route is the main scope of this chapter (Fig. 2b). Hence, further details of this technique will be discussed below. The other route is related to the composite field (Fig. 2c). Composites are a class of materials that have the main purpose of using polymers, ceramics, and metals synergistically [42]. The constituents of a composite material are reinforcement, matrix, and interface. The three main families of composites materials are based on the structure of the matrix constituent. Polymeric matrix composites (PMC), ceramic matrix composites (CMC), and metal matrix composites (MMC) are the three main families associated with polymeric, ceramic, and metallic matrices, respectively. In phenolic and polyurethane foams, the matrix is then polymeric. On the other hand, the reinforcement can be either particles or short fibers with different aspect ratios [19, 21–23, 43–60]. Another relevant possibility relies on the use of nanotechnology (Fig. 2c). Any constituent can be nanostructured using a wide range of nanoparticles, which gives rise to the nanocomposites field [61, 62]. It is important to emphasize that any constituent can be nanostructured; hence, when the term nanocomposite is used, either the reinforcement or the matrix could be nanostructured. Another important aspect relies on the type of nanoparticles employed. If the surface functionality of the nanoparticle alters the chemistry of the matrix being studied (phenolic or polyurethane), then the nanoparticle will be treated as a reactive route because the molecular structure of the polymer is being changed by the incorporation of nanoparticles. Several articles have been published on this topic [63–74] and further details of this approach will be discussed below.

### *4.1 Principles Associated with the Development of Synergistic Routes*

First, it is important to emphasize the most relevant aspects of the PF and PUF chemistry and how those can be combined synergistically. As already noticed in the previous section, the resole PF is solely based on the polyaddition and condensation of methylol groups. In this regard, the chemical properties of this PF precursor are

**Table 2** Summary of physical properties of the study cased developed in this work

| System | Route | Toughener concentration (wt. %) | Apparent density (kg $m^{-3}$) | Compressive strength (MPa) | Friability (pulverization ratio, %) | LOI index (%) | Thermal conductivity (mW $m^{-1}$ $K^{-1}$) | Closed cell content (%) |
|---|---|---|---|---|---|---|---|---|
| rPUF [5] | In situ | 0 | 25–35 | >0.3 | <2.0 | <20 [83, 84] | 24–28 $0.10^{-3}$ | >90 |
| rPIR [5] | In situ | 0 | 35–40 | >0.3 | <2.0 | <25 [84] | 24–28 $0.10^{-3}$ | >90 |
| PF-PEG; MW 600–400 [76] | Reactive | 0–4 | 60–70 | 0.10–0.15 | 2.2–5.8 | 25–31 | N.M | 30–80 |
| PF BPEG; MW 200–600 [18] | Reactive | 0–6 | 25 | 0.05–0.11 | 2.1–3.5 | 35.5–39.0 | N.M | N.M |
| PF-PPEG; MW 400–600 [75] | Reactive | 3–10 | 36.5–45 | 0.11–0.15 | N.M | 40–51 | N.M | N.M |
| PF-PSIP [11] | Reactive prepolymer | 2–5 | 32.6–60.2 | 0.12–0.35 | 1.75–5.0 | 43–47 | N.M | N.M |
| PF-GF-PTDI [44] | Reactive prepolymer composite | 0–10 | 47.7–58.2 | 0.15–0.28 | N.M | 41–52 | N.M | N.M |
| PF-GO-LDH [65] | Reactive nano | 0–1.5 | 40 | 0.05–0.08 | 6–14 | 38–39.5 | N.M | N.M |
| PF-NSi-GO [66] | Reactive nano | 0–2 | 16 | 0.06–0.07 | 1.5–5.5 | 38–41.0 | N.M | N.M |
| PF-Bio-oil MMT [69] | Reactive nano renewable | 0–8 | 55.5–62.5 | 0.14–0.17 | 5–9 | 29.8–39.7 | N.M | N.M |
| PF-CNT [81] | Reactive nano | 0–2.0 | 48.7–103.2 | 0.11–0.24 | N.M | N.M | 57–91 | N.M |
| PF-RGO [82] | Nano | 0.08–0.15 | 58.8–70.0 | N.M | N.M | N.M | 89–113 | N.M |

much more similar to the structure of a polyol rather than an isocyanate. Indeed, the resole precursor can be understood as a highly aromatic polyol with a tailored molecular weight. The high specific content of benzene rings and the highly crosslinked nature of the resulting PF are the main reasons why PFs are highly friable (fragile). From this argument, the simplest reactive route can be deduced. That is, to decrease the aromatic content and increase molecular weight by adding an aliphatic chain into the molecular structure of the resole precursor (toughening). This route is straightforward and it might severely affect flammability performance, altering one of the key design features of PF. One of the most applied techniques has been the use of aliphatic monomers [13, 18, 75, 76], such as polyethylene glycol (PEG), incorporated directly in the formulation of resole PF. In order to attenuate a poor flammability performance, boron and phosphorous have been incorporated into the molecular structure of those aliphatic monomers [18]. This approach can be considered simple and straightforward, not having substantial changes in the chemistry of the resole precursor. Finally, let's compare this approach using the principles of polyurethane systems. In polyurethanes, the main contributor to aromatic content is the isocyanate precursor (hard segment), while in some exceptional cases aromatic polyols are also the source. The molecular structure which has the highest aromatic content is polyisocyanurate foams (PIR), where the isocyanate precursor trimerizes, obtaining highly crosslinked and friable materials [25]. In this case, if a reduction in friability is desired, the common strategy is associated with a change in the molecular structure of the polyol. As it can be understood from these statements, in both systems, PF and PUF, similar chemical strategies are implemented so as to reduce friability. Another example of this strategy involves the use of either epoxy, phenoxy, and dicyandiamide [77] groups.

A second strategy employed by several researchers is to exploit the versatility of isocyanate chemistry so as to achieve complex molecular structures. In literature, the term prepolymer or quasi-prepolymer is usually used to identify this path. The main idea of this route is related to the reaction of any isocyanate precursor with other monomers so as to create a tailored molecular structure. Finally, this tailored molecule is inserted within the PF resole precursor, and the crosslinking reaction proceeds using similar cure procedures. The first important aspect to consider is the type of isocyanate being used. Two main types of isocyanates are available: aliphatic and aromatic [6]. The aliphatic isocyanate, such as isophorone diisocyanate, is the best choice because it does not have aromatic rings; hence, it is unlikely to increase the fragile nature of the PF matrix. However, the main drawbacks rely on its high cost and low reactivity. Aromatic isocyanates, such as pMDI or toluene diisocyanate (TDI), are frequently employed in the literature as a starting point for the development of molecular structures which can improve the properties of PF. The main drawback of this isocyanate is its high aromatic content, which means that the use of aliphatic polyols with medium or high molecular weight and low functionality is mandatory. Otherwise, the properties of the final material will not be improved. It is important to highlight that the use of TDI as a starting material might generate an increase in the volatile organic content (VOC) of the PF precursor. In this regard, only prepolymers are suitable to achieve this objective. As already noticed earlier, quasi-prepolymers have a high $NCO_{number}$, then higher VOCs should be expected (Table 1).

Another aspect to consider with respect to this route is that the tailored molecule which is synthesized has to be hydrophilic or at least with a high hydrophilic character. Otherwise, even though after using surfactants or emulsifiers, the resulting PF precursor might not be a colloidal stable dispersion, leading to phase separation and to the impossibility of producing PF with suitable thermomechanical properties. This characteristic is not easy to achieve, because the isocyanate precursor is highly hydrophobic. Hence, the synthesis path will have to involve the formation of hydrogen liable groups so as to reduce its hydrophobic character.

Finally, it is important to discuss the role that nanotechnology can have in the change of molecular structure of PF. There are several nanoparticles that can be applied in this field so as to obtain substantial improvements of either mechanical properties, flammability, or insulation value [5, 63, 65–69]. One important feature of nanoparticles is their geometry. Spherical nanoparticles, such as nanosilica, have diameters within the orders of 5–10 nm and are frequently dispersed in the matrix as aggregates (tactoids) [78]. Nanoclays are lamellar nanostructures that have a thickness of around 0.1–0.5 nm and usually conglomerate into a layered structure that needs to be exfoliated in the matrix being reinforced. Finally, carbon nanotubes (CNT) are tubular structures with diameters ranging in the order of 10 nm with variable lengths [79]. However, the most relevant feature that needs to be considered when using nanoparticles is surface functionality. The extremely high area per unit weight of nanoparticles indicates that the interface will have a fundamental role when it comes to analyzing the performance of a nanoparticle as a reinforcement. Hence, taking into account the previous analysis, it can be inferred that nanoparticles that have a suitable surface functionality (such as hydroxide groups) can be considered as an alternative reactive route toward the synthesis of nanostructured PF. On the other hand, if the nanoparticle does not have any surface functionality which cannot covalently react forming a network, then the nanoparticle will behave as a second phase (Fig. 2c).

## *4.2 Study Cases*

The reactive route based on the incorporation of aliphatic chains using PEG was studied by Hu et al. [76] for the development of urea–formaldehyde PF (Table 2). The main scope of the study was centered on evaluating the effect of PEG molecular weight (from 600 to 4000) and concentration (up to 4 wt%). The reported apparent density fell within the range of 60–70 kg $m^{-3}$, whereas its variation followed a non-monotonous increase as a function of PEG weight content. The compressive strength of the pristine PF was superior to the benchmark (Sect. 4.1) and it reached a maximum with a PEG concentration of 2 wt% and a molecular weight of 1000. This reflected the presence of a compromise relationship between this property, PEG weight content, and molecular weight. Intermediate values of these properties were the most appropriate to increase compressive strength. A similar trend was also deduced from friability measurements (pulverization ratio). This ratio decreased as a function of PEG weight content and molecular weight, with a minimum located at a PEG content of 2 wt% and a 1000 molecular weight. The LOI indexes showed clearly how the gradual increase of PEG content in the PF caused a deterioration of the fire performance of the foam. Comparing the reported values with the benchmark, it can be deduced that for PEG contents higher than 2 wt%, the LOI index fell below the benchmark value (27%). These results clearly reflect the compromised relationship between adding aliphatic chains into the PF molecular structure and its concomitant reduction of flammability performance. A summary of the properties of this work and all the others reported in this section can be consulted in Table 2.

Liu et al. [18] studied the incorporation of a borate PEG into a resole PF precursor (Fig. 2a). Starting with a PEG monomer, boric-acid-assisted esterification was implemented so as to introduce boron into the molecular chain of the aliphatic monomer (borate-PEG). Then, the strategy was based on the reduction of the aromatic content of the resole PF precursor so as to reduce friability as well as the incorporation of boron backbones so as to attenuate the concomitant flammability reduction. The reported compressive strength of the pure PF was 0.06 MPa (apparent density 25 kg $m^{-3}$), which was significantly lower than the minimum required by the benchmark. The incorporation of PEG with a molecular weight of 200, 400, and 600 proved to increase that value, but only for the case of a borate-PEG with a molecular weight of 400, the compressive strength accomplished the minimum established by the benchmark. Friability measurements indicated that the incorporation of PEG and borate-PEG in the molecular structure contributed to a reduction of the pulverization ratio. LOI and UL94 tests were performed and in all cases, the values were higher than the benchmark.

Yang et al. [75] studied the incorporation of phosphorous-functionalized PEG (PPEG) monomers using phenyl dichlorophosphate as the precursor. The reported PF had apparent densities which varied in the range of 36–46 kg $m^{-3}$ as a function of increasing PPEG weight content (0–10 wt%). The compressive strength of all the PF prepared in this work surpassed the value established by the benchmark, proving also that an increase of PPEG also caused significant improvements. LOI and UL94 tests corroborated that both the pristine PF and the PPEG-PF foams achieved and surpassed the minimum requirements of the benchmark. Comparing the results obtained in this work and those obtained by Liu et al. [18], it is important to mention that in this last case, the foam density was fixed at 25 kg $m^{-3}$.

Another work of the same group [11] reported the implementation of a reactive route exploiting the chemistry of polyurethane systems (Fig. 2b). A prepolymer obtained from TDI and the reaction of phosphorus and silicon-containing polydimethylsiloxanes (PSPUP) was incorporated in a PF system with the objective of improving its compressive strength, pulverization ratio, and fire performance. The apparent density of the PF ranged from 32.6 kg $m^{-3}$ for the pristine PF to 60.2 kg $m^{-3}$ for the PF modified with 5 wt% of PSPUP. In all cases, the compressive strength of the foams surpassed the minimum established by the benchmark. It is important to emphasize that the incorporation of the polyurethane prepolymer caused substantial improvements in both the compressive and the specific compressive strength. As already noticed by Lobos et al. [80], the comparison of different foams is valid only when specific properties are reported. An additional advantage of this approach was associated with the dramatic reduction of the pulverization ratio, whereas its reduction was proportional to the PSPUP weight content. Finally, in all cases, the LOI indexes were much higher than the benchmark, indicating that the prepolymer route did not adversely affect fire performance.

A synergistic approach combining the polyurethane prepolymer (Fig. 2b) reactive route and the composite one (Fig. 2c) using chopped fiberglass as reinforcement was studied by Yuan et al. [44]. Due to the fact that chemical flame retardants usually have a highly aromatic structure, it is important to increase their molecular weight so as to avoid further embrittlement of the PF matrix. In this regard, the study presented the preparation of a polyurethane prepolymer (DOPU) reacting a phosphaphenanthrene oxide (DOPO-BQ) with isophorone diisocyanate (IPDI). The isocyanate moieties of IPDI reacted with the hydroxyl functionalities of the DOPO-BQ, producing a precursor with increased molecular weight and reduced aromatic content. On the other hand, chopped fiberglass (GF) was used to combine both an increase of compressive strength and fire performance. A fixed concentration of GF (0.5 wt%) was implemented for all the synthesized foam and the effect of increasing amounts of DOPU (up to 10 wt%) was the main variable under scrutiny. Under these conditions, the reported density ranged between 47.7 and 58.2 kg $m^{-3}$, increasing as a function of higher DOPU content. With respect to the compressive strength, all the foams analyzed in this work had values that were better than the benchmark. The incorporation of both GF and DOPU up to 10 wt% caused a monotonous increase of the compressive strength. Even though the specific compressive strength was not reported, our calculations based on the experimental results indicated that the specific compressive strength increased significantly as a function of DOPU content. LOI tests indicated that for all the foams prepared in this work, the values were much higher than the benchmark, even for the case of no incorporation of DOPU into the molecular structure of the PF. This suggested that the small addition of GF had a relevant effect on the fire performance of the PF.

A reactive route based on the use of nanotechnology was studied by Wang et al. [65]. The approach was centered on the use of a nanohybrid based on graphene oxide (GO) immobilized with layered double hydroxides (CoAl-LDH/GO). The functionalization of GO with the LDH helped to create a reactive route as well as to avoid the poor fire performance of GO. The PF was synthesized with a fixed apparent density of 40 kg $m^{-3}$. The reported compressive strength presented improvements as a function of increasing weight content of the CoAl-LDH/GO, reaching a peak value at 0.9 wt%. Comparing the results with the benchmark, it can be deduced that, in all cases, the reported values were inferior to the minimum established by the benchmark. On the other hand, the reported pulverization ratio was significantly reduced as a function of increasing CoAl-LDH/G weight content, indicating that the reactive path produced a less friable PF. Finally, all the reported LOI indexes showed values well above the benchmark, indicating that all the PF developed in this work had excellent fire performance. Similar results were also obtained in another work published by the same group using nanosilica instead of LDH [66].

A reactive route based on the use of nanotechnology and renewable resources was recently published by Xu et al. [69]. The strategy of this work was centered on an increase of the renewable content of the PF precursor through the use of biomass obtained from the pyrolysis of Larix gmelinii. In addition, montmorillonite (MMT) lamellar nanoparticles were also used in the PF system. Taking into account that the MMT nanoparticles had hydroxyl functionality, the strategy used by the researchers can be classified as a reactive route. Indeed, the authors corroborated that the MMT was covalently bonded to the PF matrix. The reported apparent density ranged between 55 and 62.5 kg m$^{-3}$ and its variation was mainly due to the incorporation of MMT in the PF system (up to 8 wt%). The compressive strength of the foams prepared in this work was higher than the benchmark, and a substantial increase of the specific compressive strength was found as a function of increasing MMT content, peaking at a 4 wt%. The friability analysis revealed that small contents of MMT (<4 wt%) caused a decrease in the pulverization ratio. On the other hand, higher MMT loadings caused a significant increase of this property, increasing friability above benchmark values. The LOI index showed that in the PF prepared in this work, the reported values were better than the benchmark. In addition, the LOI index reached a plateau of approximately 37% even for a low MMT concentration (2 wt%).

The properties of PF foams nanostructured with multi-wall carbon nanotubes (MWCNT) or graphene were studied by Song et al. [81]. The reported apparent density ranged between 48.7 and 103.2 kg m$^{-3}$ and its variation was a strong function of nanoparticle type and content. The highest density was attained when MWCNT was used at 2 wt%, while the lowest density was measured at MWCNT of 0.5 wt%. The incorporation of graphene in the PF matrix caused a similar apparent density variation, whereas the lowest apparent density was measured at 1 wt%. The reported compressive strength of all the foams studied in this work was higher than the benchmark. In addition, the incorporation of nanoparticles caused an increase of the compressive strength, however, reducing significantly the specific compressive strength of the resulting foam. This work also highlighted the measurements of processing viscosity and final thermal conductivity of the PF. In this regard, it is important to emphasize that the incorporation of nanoparticles caused a significant reduction in thermal conductivity. However, the reported $\lambda$ values are still high compared to other PF foams available in the industry.

A recent work applying nanotechnology to produce nanocomposite foams based on PF precursors was performed by Sandhya et al. [82]. To avoid the use of poisonous reducing agents, such as hydrazine, the starch potato was used to chemically reduce graphene oxide (GO). The reported apparent density ranged from 58.8 to 70.0 kg m$^{-3}$, whereas its variation changed non-monotonously as a function of reduced graphene oxide (RGO) content (from 0.08 up to 0.15 wt%). The reported thermal conductivity ranged between 0.089 and 0.113 W m$^{-1}$ K$^{-1}$. The incorporation of RGO into the microstructure permitted a change in thermal conductivity so as to produce foams with tailored electrical properties.

## 5 Conclusions

The path to the new generation of PF is based on synergistic strategies using the tools that have been laid out in this chapter. To achieve a PF with improved friability (reduced pulverization rate), it is crucial to use the polyurethane chemistry for the development of additives that can be incorporated into the PF precursor, decreasing the overall degree of aromatic content of the final polymeric network without affecting other properties. Several study cases have been analyzed which emphasize how it is possible to increase specific compressive strength, attain a high fire performance, and reduce friability significantly by the use of reactive routes based on the versatility of the isocyanate chemistry. Combining this reactive route with the use of composite and nanocomposite technology can give rise to PF with outstanding properties. These aspects have been emphasized by establishing a benchmark and by comparing the results available in the state-of-the-art with respect to the benchmark.

Even though substantial R&D efforts have been devoted to study the thermomechanical properties, fire performance, thermal degradation, and friability, it is important that future efforts should focus on how to increase the thermal insulation value of PF. To this effect, further studies should deal with the new safe blowing agents with low ODP as well as GWP values. In addition, further aging studies which reflect the performance of PF as a function of time should also be conducted. New materials based on PF precursors should have a higher solid content so as to achieve a decrease of organic volatile emissions in the manufacturing process. Finally, the change from using precursors obtained mostly from oil and gas has already been taking place and future PF precursors will certainly contain a higher content of renewable resources, leading the way to a sustainable industry.

## References

1. Pilato L (2010) Phenolic resins: a century of progress, 10th edn. Springer, New York
2. Asim M, Saba N et al (2018) A review on phenolic resin and its composites. Curr Ann Chem 3:185–197
3. Norman G R, Pengelly LD, et al (1986) Respiratory function of children in homes insulated with urea formaldehyde foam insulation. CMAJ: Can Med Assoc J 10:1135–1146
4. Harris JC, Rumack BH et al (1981) Toxicology of urea formaldehyde and polyurethane foam insulation. JAMA 3:243–246
5. Chiacchiarelli L (2019) Sustainable, nanostructured, and bio-based polyurethanes for energy-efficient sandwich structures applied to the construction industry. In: Verma, D (ed) Biomass, biopolymer-based materials, and bioenergy,1st edn. Elsevier, United Kingdom, pp 135–160
6. Szycher M (1999) Szycher's handbook of polyurethanes, 2nd edn. CRC Press, New York
7. Randall D, Lee S (2003) The polyurethanes book, 2nd edn. Wiley, New Jersey
8. Chiacchiarelli LM, Puri I et al (2012) Cure kinetics of a highly reactive silica–polyurethane nanocomposite. Therm Acta 3:172–178
9. Gimenez RB, Leonardi L et al (2017) Improved specific thermomechanical properties of polyurethane nanocomposite foams based on castor oil and bacterial nanocellulose. J Appl Polym Sci 25:730–746

10. Ding H, Wang J et al (2015) Preparation and properties of a novel flame retardant polyurethane quasi-prepolymer for toughening phenolic foam. J Appl Polym Sci 35:324–333
11. Yang H, Wang X et al (2013) A novel polyurethane prepolymer as toughening agent: preparation, characterization, and its influence on mechanical and flame retardant properties of phenolic foam. J Appl Polym Sci 5:2720–2728
12. Ionescu M (2005) Chemistry and technology of polyols for polyurethanes, 1st edn. Rapra Technology Limited, United Kingdom
13. Wang FY, Ma CM et al (2001) Kinetic parameters of thermal degradation of polyethylene glycol-toughened novolac-type phenolic resin. J Appl Polym Sci 2:188–196
14. Mougel C, Garnier T et al (2019) Phenolic foams: a review of mechanical properties, fire resistance and new trends in phenol substitution. Polymer 1:86–117
15. Herrán R, Amalvy JI et al (2019) Highly functional lactic acid ring-opened soybean polyols applied to rigid polyurethane foams. J Appl Polym Sci 4:59–65
16. Park S-B, Choi S-W et al (2016) Effect of the blowing agent on the low-temperature mechanical properties of CO2-and HFC-245fa-blown glass-fiber-reinforced polyurethane foams. Comp Part B: Eng 3:317–327
17. Zieleniewska M, Leszczyński MK et al (2016) Development and applicational evaluation of the rigid polyurethane foam composites with egg shell waste. Polym Degrad Stab 2:78–86
18. Liu L, Fu M et al (2015) Synthesis of boron-containing toughening agents and their application in phenolic foams. Ind Eng Chem Res 7:1962–1970
19. Yang C, Zhuang ZH et al (2014) Pulverized polyurethane foam particles reinforced rigid polyurethane foam and phenolic foam. J Appl Polym Sci 1:342–356
20. Mallick P (2007) Fiber-reinforced composites: materials, manufacturing, and design, 3rd edn. CRC Press, New York
21. Shen H, Nutt S (2003) Mechanical characterization of short fiber reinforced phenolic foam. Comp Part A: Appl Sci Manfact 9:899–906
22. Huang YJ, Wang CH et al (2010) Enhancing specific strength and stiffness of phenolic microsphere syntactic foams through carbon fiber reinforcement. Polym Compos 2:256–262
23. Kaynak C, Cagatay O (2006) Rubber toughening of phenolic resin by using nitrile rubber and amino silane. Polym Test 3:296–305
24. Desai A, Auad ML et al (2008) Mechanical behavior of hybrid composite phenolic foam. J Cell Plast 1:15–36
25. Ashida K (2006) Polyurethane and related foams: chemistry and technology, 1st edn. CRC Press, New York
26. Ashida K, Yagi T (1996) French Patent 1,511,865
27. Tingley DD, Hathway A et al (2017) The environmental impact of phenolic foam insulation boards. Proc Inst Civ Mat 2:91–103
28. Kylili A, Seduikyte L, et al (2018) Life cycle analysis of polyurethane foam wastes. In: Harson J (ed) Recycling of polyurethane foams, 1st edn. Elsevier, pp 97–113
29. Li W, Lin Q et al (2003) Reducing the contents of free phenol and formaldehyde in phenolic foam. J Appl Polym Sci 9:2333–2336
30. Guan J, Song Y et al (2011) Progress in study of non-isocyanate polyurethane. Ind Eng Chem Res 11:6517–6527
31. Kathalewar MS, Joshi PB et al (2013) Non-isocyanate polyurethanes: from chemistry to applications. RSC Adv 13:4110–4129
32. Delebecq E, Pascault J-P et al (2013) On the versatility of urethane/urea bonds: reversibility, blocked isocyanate, and non-isocyanate polyurethane. Chem Rev 1:80–118
33. Lligadas G, Ronda JC et al (2010) Plant oils as platform chemicals for polyurethane synthesis: current state-of-the-art. Biomacromol 11:2825–2835
34. Meier MA, Metzger JO et al (2007) Plant oil renewable resources as green alternatives in polymer science. Chem Soc Rev 11:1788–1802
35. Mosiewicki MA, Aranguren MI (2013) A short review on novel biocomposites based on plant oil precursors. Eur Polym J 6:1243–1256

36. Mosiewicki MA, Aranguren MI (2016) Recent developments in plant oil based functional materials. Polym Int 1:28–38
37. Thun MJ, Lakat MF et al (1982) Symptom survey of residents of homes insulated with urea-formaldehyde foam. Environ Res 2:320–334
38. Frigos E, Filley WV et al (1981) Asthma induced by dust from urea-formaldehyde foam insulating material. Chest 6:706–707
39. Chiacchiarelli LM, Cerrutti P et al (2019) Compressive behavior of rigid polyurethane foams nanostructured with bacterial nanocellulose at low and intermediate strain rates. J Appl Polym Sci 137:20–32
40. Davies JM (2008) Lightweight sandwich construction, 1st edn. John Wiley & Sons, New York
41. Chiacchiarelli LM, Escobar MM et al (2015) The role of the interphase on the shear induced failure of multiwall carbon nanotubes reinforced epoxy nanocomposites. J Appl Polym Sci 4:23–37
42. Mazumdar S (2001) Composites manufacturing: materials, product, and process engineering, 1st edn. CRC Press, New York
43. Shen H, Lavoie AJ et al (2003) Enhanced peel resistance of fiber reinforced phenolic foams. Comp Part A: Appl Sci Manufact 10:941–948
44. Yuan H, Xing W et al (2013) Mechanical and thermal properties of phenolic/glass fiber foam modified with phosphorus-containing polyurethane prepolymer. Polym Int 2:273–279
45. Huang Y-J, Vaikhanski L et al (2006) 3D long fiber-reinforced syntactic foam based on hollow polymeric microspheres. Comp Part A: Appl Sci Manufact 3:488–496
46. Huang Y-J (2009) Fiber-reinforced syntactic foams, 1st edn. University of Southern California, United States
47. Liu J, Li X et al (2018) Mechanical and thermal properties of modified red mud-reinforced phenolic foams. Polym Int 5:528–534
48. Xiao W, Huang Z et al (2017) The mechanical and thermal characteristics of phenolic foam reinforced with kaolin powder and glass fiber fabric. Mater Sci Eng 274:120–134
49. Zuluaga CL, Du J et al (2018) Lignin modifications and perspectives towards applications of phenolic foams: a review. BioResources 4:9158–9179
50. Zhuang XW, Li SH et al (2011) Preparation and characterization of lignin-phenolic foam. Adv Mater Res 4:1014–1018
51. Del Saz-Orozco B, Alonso MV et al (2015) Mechanical, thermal and morphological characterization of cellulose fiber-reinforced phenolic foams. Comp Part B: Eng 13:367–372
52. Li C, Ma H et al (2020) Preparation and properties of melamine-formaldehyde rigid closed-cell foam toughened by ethylene glycol/carbon fiber. Cell Polym 5:1234–1340
53. Sreekala M, Czigány T et al (2003) Investigation of oil palm and pineapple fiber reinforced phenol formaldehyde composites by acoustic emission technique. Polym Polym Compos 1:9–18
54. Balakrishnan P, Geethamma V, et al (2018) Polymeric biomaterials: state-of-the-art and new challenges. In: Martin N (ed) Fundamental biomaterials: polymers, 1st edn. Elsevier, pp 1–20
55. Sreekala M, Kumaran M et al (2004) Environmental effects in oil palm fiber reinforced phenol formaldehyde composites: Studies on thermal, biological, moisture and high energy radiation effects. Adv Compos Mater 34:171–197
56. Sreekala M, Thomas S et al (2005) Dynamic mechanical properties of oil palm fiber/phenol formaldehyde and oil palm fiber/glass hybrid phenol formaldehyde composites. Polym Compos 3:388–400
57. Sreekala M, Kumaran M et al (2000) Oil palm fibre reinforced phenol formaldehyde composites: influence of fibre surface modifications on the mechanical performance. Appl Compos Mater 5–6:295–329
58. Sreekala M, George J et al (2002) The mechanical performance of hybrid phenol-formaldehyde-based composites reinforced with glass and oil palm fibres. Compos Sci Technol 3:339–353
59. Joseph S, Sreekala M et al (2002) A comparison of the mechanical properties of phenol formaldehyde composites reinforced with banana fibres and glass fibres. Compos Sci Technol 14:1857–1868

60. Castillo-Lara JF, Flores-Johnson EA et al (2020) Mechanical Properties of Natural Fiber Reinforced Foamed Concrete. Materials 14:3060
61. Agarwal R, Saxena N et al (2000) Effect of different treatments on the thermal behavior of reinforced phenol–formaldehyde polymer composites. J Appl Polym Sci 3:603–608
62. Chiacchiarelli LM, Cerrutti P et al (2020) Compressive behavior of rigid polyurethane foams nanostructured with bacterial nanocellulose at low and intermediate strain rates. J Appl Polym Sci 20:48701–48711
63. Rangari VK, Hassan TA et al (2007) Cloisite clay-infused phenolic foam nanocomposites. J Appl Polym Sci 1:308–314
64. FortunatiE YW et al (2016) Lignocellulosic nanostructures as reinforcement in extruded and solvent casted polymeric nanocomposites: an overview. Eur Polym J 13:295–316
65. Wang Z, Li X (2018) Synthesis of CoAl-layered double hydroxide/graphene oxide nanohybrid and its reinforcing effect in phenolic foams. High Perform Polym 6:688–698
66. Li X, Wang Z et al (2015) Preparation of a silica nanospheres/graphene oxide hybrid and its application in phenolic foams with improved mechanical strengths, friability and flame retardancy. RSC Adv 121:99907–99913
67. Auad M, Nutt S et al (2007) Synthesis and properties of epoxy-phenolic clay nanocomposites. Exp Polym Lett 13:346–355
68. Hu X, Cheng W et al (2016) Flame retardant, thermal, and mechanical properties of glass fiber/nanoclay reinforced phenol–urea–formaldehyde foam. Polym Compos 8:2323–2332
69. Xu P, Yu Y et al (2019) Preparation and characterization of bio-oil phenolic foam reinforced with montmorillonite. Polymers 9:1471–1483
70. Zhu Y, Wang Z (2016) Phenolic foams, modified by nano-metallic oxides, improved in mechanical strengths and friability. Iran Polym J 7:579–587
71. Zhou J, Yao Z et al (2014) Fabrication and mechanical properties of phenolic foam reinforced with graphene oxide. Polym Compos 3:581–586
72. Li Q, Chen L et al (2016) Effect of multi-walled carbon nanotubes on mechanical, thermal and electrical properties of phenolic foam via in-situ polymerization. Comp Part A: Appl Sci Manufact 14:214–225
73. Yang Z, Yuan L et al (2013) Improvement in mechanical and thermal properties of phenolic foam reinforced with multiwalled carbon nanotubes. J Appl Polym Sci 3:1479–1488
74. Li X, Wang Z et al (2016) One-step in situ synthesis of a novel α-zirconium phosphate/graphene oxide hybrid and its application in phenolic foam with enhanced mechanical strength, flame retardancy and thermal stability. RSC Adv 78:74903–74912
75. Yang H, Wang X et al (2012) Fire performance and mechanical properties of phenolic foams modified by phosphorus-containing polyethers. J Polym Res 3:9831–9845
76. Hu X, Wang D et al (2014) Effect of polyethylene glycol on the mechanical property, microstructure, thermal stability, and flame resistance of phenol–urea–formaldehyde foams. J Mater Sci 4:1556–1565
77. Gao M, Wu W et al (2016) Phenolic foam modified with dicyandiamide as toughening agent. J Therm Anal Calorim 1:189–195
78. Kenny JM, Torre L et al (2015) The effect of processing routes on the thermal and mechanical properties of poly (urethane-isocyanurate) nanocomposites. J Appl Polym Sci 45:243–272
79. Hussain F, Hojjati M et al (2006) Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. J Compos Mater 17:1511–1575
80. Lobos J, Velankar S (2016) How much do nanoparticle fillers improve the modulus and strength of polymer foams? J Cell Plast 1:57–88
81. Song SA, Chung YS et al (2014) The mechanical and thermal characteristics of phenolic foams reinforced with carbon nanoparticles. Compos Sci Technol 3:85–93
82. Sandhya P, Sreekala M et al (2020) Thermal and electrical properties of phenol formaldehyde foams reinforcing with reduced graphene oxide. Polym Compos 10:4329–4339

83. Modesti M, Lorenzetti A (2002) Flame retardancy of polyisocyanurate–polyurethane foams: use of different charring agents. Polym Degrad Stab 2:341–347
84. Günther M, Lorenzetti A et al (2018) Fire phenomena of rigid polyurethane foams. Polymers 10:1166–1173