Chapter 18
Lignin Nanoparticle-Reinforced Phenolic Foams

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1 Introduction

Foams consist of two phases: a continuous solid phase (matrix) and a discontinuous gaseous phase (cells). For the formation of foams, gas bubbles diffuse in the matrix and make open and close cells. This process directly influences the properties of the final yields such as the cell size distribution, cell type, and density of foams [1, 2]. Foam preparation conditions, materials used in its preparation, and structural parameters are effective factors in the structure and characteristics as well as the final application of foams. Phenolic compounds are widely used for the preparation of various products, including adhesives and foams. Phenolic foams (PFs) are one of the most commonly used polymeric foams [3].

Polyurethane, polyvinyl chloride, or polystyrene foams compared to PFs have less brittleness and friability, higher density, and better thermal and mechanical properties. However, they have low heat resistance and generate toxic gases during combustion. These features limited their applications where fire resistance is critical so that PFs are suitable substitutions for industrial applications especially in the area of the insulating material. Therefore, PFs attracted more attention compared to the other commercial polymeric foams because of their advantageous properties such as low flammability and outstanding fire, chemical resistance, low fire propagation speed, low smoke density, nontoxicity, high thermal stability over a broad range of temperatures, low cost, and non-dripping during combustion [4–13]. Phenolic foam's specific features make them attractive for several applications such as insulation, decontamination, fire protection, packaging, structural and domestic elements, agriculture, horticulture, and energy absorption. Phenolic resins are produced by an exothermic reaction of phenol with formaldehyde. It is a polycondensation reaction and depends

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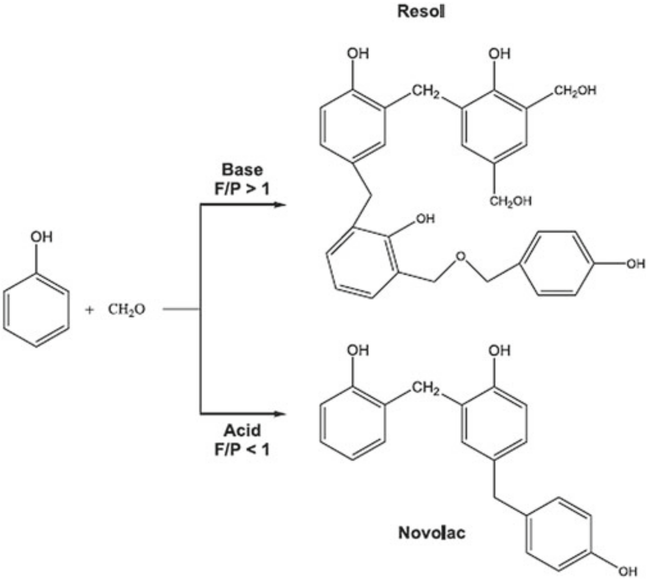

Fig. 1 Synthesis conditions for producing resol and novolac resins. Reproduced from [9] with permission from Springer

on the pH of the mixture, catalyzer, and reactant molar ratio. In the presence of acidic catalysts, two types of resin could be produced which depends on the ratio of formaldehyde to phenol (F/P, Fig. 1). If the molar ratio of F/P is less than one, it leads to the production of novolac-type resin, and if it is higher than one, it leads to the production of resol-type resin. Resol-type resins have methylol groups and they are the most used to produce foam [4, 9].

After preparing phenolic resins, the next necessary step in preparing PFs is the production of gases as an expansion agent. Gases can be obtained by evaporating a low boiling point solvent or by thermal decomposition of chemical blowing agents [9]. An emulsifier is also used to emulsify the expansion agent, and stabilize the forming foam. Other materials involved in the phenolic foam formation are a catalyst and optionally some additives for improving its final features [14].

It is noteworthy that the brittleness, friability, and pulverization tendencies are the weaknesses of PFs that restrict their applications [15]. Therefore, researchers have focused on improving the mechanical properties of PFs such as compressive strength, flexural strength, and friability, without deteriorating its excellent fire resistance. In recent years, the use of various fillers to improve the properties of phenolic foams has attracted much attention. On the other hand, the emphasis on producing the biocompatible products has led to investigate the effect of various bio-based reinforcements like inert natural filler (e.g., wood flour, lignin) and natural fibers (e.g., cellulose, kenaf) into the PFs [12, 16].

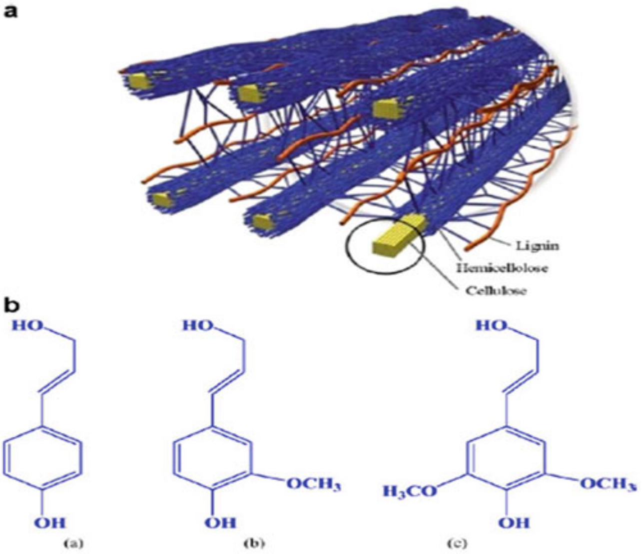

Fig. 2 **a** Cellulose strands surrounded by hemicellulose and lignin. **b** Monolignol monomer species: **a** p-coumaryl alcohol (4-hydroxyl phenyl), **b** coniferyl alcohol (guaiacyl), **c** sinapyl alcohol (syringyl). Reproduced from [22] with permission from Elsevier

In addition, the overconsumption of petroleum and other fossil fuels and also rising environmental concerns have led to increase efforts to find green and new sustainable raw material resources [17, 18]. It has been found that by biomass chemical substitution, the reduction in the use of phenol and the associated environmental pollution, and improvement in its performance can be observed [19]. Lignocellulosic biomass can be considered as one of the worldwide accessible substitutes for fossil fuels [20]. The cell walls of natural lignocellulosic biomass are composed of cellulose, hemicellulose, and lignin (Fig. 2). Researchers use lignocellulose directly or indirectly in the synthesis of foams. For example, in the synthesis of bio-foam, nanoparticles of lignin are directly added into the polymeric matrix to improve its mechanical behavior or they convert it to bio-polyols, which are used in the formation of foams [12, 21]. The amount of lignin used in the foams is less than 37% [3]. There are many phenolic hydroxyl groups in the lignin molecule, which leads to more activity of the C3 and C5 positions of guaiacol and p-hydroxyphenyl groups [6].

Lignin is the most available biopolymer, after cellulose [23, 24]. It is an amorphous polymer and is present in many different plants. The type of plant (hardwood/softwood/grass) and the extracting process affect its overall properties as well as its applications [25, 26]. Lignin is widely generated as by-products in different industries such as pulp and paper-making, ethanol production from biomass, etc. In the process of bioethanol production, the annual consumption of 225 million tons of dry biomass can produce 62 million tons of lignin [27]. Generally, the functional groups, elemental composition, and molecular weight of lignin isolated from various resources are different [28]. In recent years, only a small portion of industrial lignin is used for processes other than heat generation such as value-added products [29].

The similarity of lignin structure to phenol led researchers to study the substitution of phenol by lignin in the synthesis of lignin-based phenolic resins [30–32]. Lignin-based materials have more attractive properties compared to synthetic materials such as high abundance, low weight, inexpensive, eco-friendly, and reinforcing capability [33]. Some of the lignin-producing processes are, namely, Kraft, sulfite, soda, organ solve, hydrolysis, and steam explosion [3]. The insolubility of lignin in water limits its use in an industrial scale. Fortunately, it is now possible to prepare lignin nanoparticles dispersed in water. Researchers could successfully use the aqueous lignin nanoparticles as an improving agent in PFs [34–36]. The presence of different polar functional groups in lignin (alcohols, ketones, and aldehydes) is effective in their compatibility with the polymer matrixes [37]. The conversion of lignin into nanoparticles improves its properties compared to the raw material. Lignin nanoparticles have a higher surface area and more available functional groups (e.g., thiols, aliphatic hydroxyl, and phenolic). These features make it easier to modify the lignin surface and improve its blending properties. Also, they increase the potential applications of lignin in different fields [38].

2 Preparation of Lignin Nanoparticle-Reinforced PFs

To prepare lignin nanoparticle-reinforced phenol–formaldehyde foams, first phenol–formaldehyde resins consisting of nano-lignin are synthesized and then they are converted into the foams by incorporating other components. Phenol and formaldehyde are reacted together in an acidic or alkaline medium to form phenolic resins. Also, lignin nanoparticles are mixed with the resol resin in this step. Phenolic resins act as a solid matrix in which gas diffuses into it. Other basic components that are used in this synthesis include a blowing agent, surfactant, catalyst, and curing agent [39, 40]. The blowing agent expands that its evaporation can form a cellular structure. Some of the blowing agents are n-pentane, cyclopentane [41], hexane [42], and petroleum ethers [10]. Having the lowest boiling point (36 °C), n-pentane is the most common blowing agent for the preparation of PFs [14, 43].

The curing agent affects the final density of the foam. Therefore, depending on the desired density, the blowing agent can be used with/without the curing agent. During the foam formation process, surfactants are also used to control the characteristics of the foam by making a stable and homogeneous emulsion between the phenolic matrix and the blowing agent. Tween 40 and Tween 80 are the most used surfactants [44–46]. Catalysts increase the curing process rate. Also, they reduce the gelation time and take part in the foam expansion. Recently, acids like p-toluene sulfonic acid [47] and phenol sulfonic acid [13], compared to sulfuric acid or hydrochloric acid [13] are more used. When all of the components are mixed, the mixture is poured into a mold and is held for 1 h in a pre-heated oven at 80 ºC and post-cured for 24 h at 105 °C [40].

3 Microstructure of Lignin Nanoparticle-Reinforced PFs

The foaming process basically consists of two main steps: (a) bubble nucleation and (b) bubble growth. In the nucleation process, a new phase (bubble phase) is generated from the initially homogeneous polymer–gas mixture. In the second process, the bubble nuclei grow into final bubbles. Both processes are affected by many physical properties such as viscosity, gas solubility, surface tension, and glass transition temperature. Therefore, a change in any of these factors can affect the foam-forming process, the microstructure, and properties of foams [48]. Considering nanoparticles, they can greatly alter the physical properties of the polymer mixture and also the microstructure and density of the foams. Therefore, gaining a clear understanding of these changes is critical to study the properties of the foams. Del Saz-Orozco et al. [39] investigated the effect of formulation parameters, namely, stirring speed and blowing agent content on the microstructure of unreinforced and lignin-reinforced PFs. As shown in Fig. 3, the cell size distribution of PFs (containing 2.5 wt.% blowing agent, without lignin nanoparticles) changes by altering the stirring speed. The SEM images revealed the increase in stirring speed results in finer cells in nanocomposite foam structure. Particularly, the mean cell size decreased from 0.103 to 0.07 mm when the stirring speed increased from 609 to 750 rpm. The authors stated that at elevated stirring speeds, the surface tension of the formulation mixture decreased which favors the nucleation of bubbles in the foaming process and decreased the mean cell size in the foam structure [49].

The SEM images also reveal that the effect of blowing agent content is not as significant as the stirring rate; however, when the blowing agent content was decreased, the mean cell size increased. The possible explanation could be the higher gas supply in the formulation mixture at higher blowing agent content [50].

As illustrated in Fig. 4, the mean size of the cells in the foam decreased as the lignin nanoparticle percentage decreased from 0.05 to 9.95 wt.%. It is reported that lignosulfonates can have surfactant properties decreasing the surface tension of the formulation mixture, which the same as stirring speed favors the nucleation of bubbles in the foaming process resulting in finer cell size [49, 51].

In another study conducted by the same group later in 2015 [52], the effect of hydrothermal aging (the samples were placed in an environmental chamber at 38 °C and 97% of relative humidity for 2 weeks) on the morphology and cell size distribution of unmodified PFs and lignin-modified PFs (8.5 wt.%) was investigated. The results suggested that hydrothermal aging did not affect cell size distribution. It can be seen in Fig. 5 that both unmodified and modified foams exhibited similar diameters before and after aging.

Moreover, the same as their previous study, the cell size of the foam decrease from 0.085 to 0.061 mm after the addition of lignin nanoparticles.

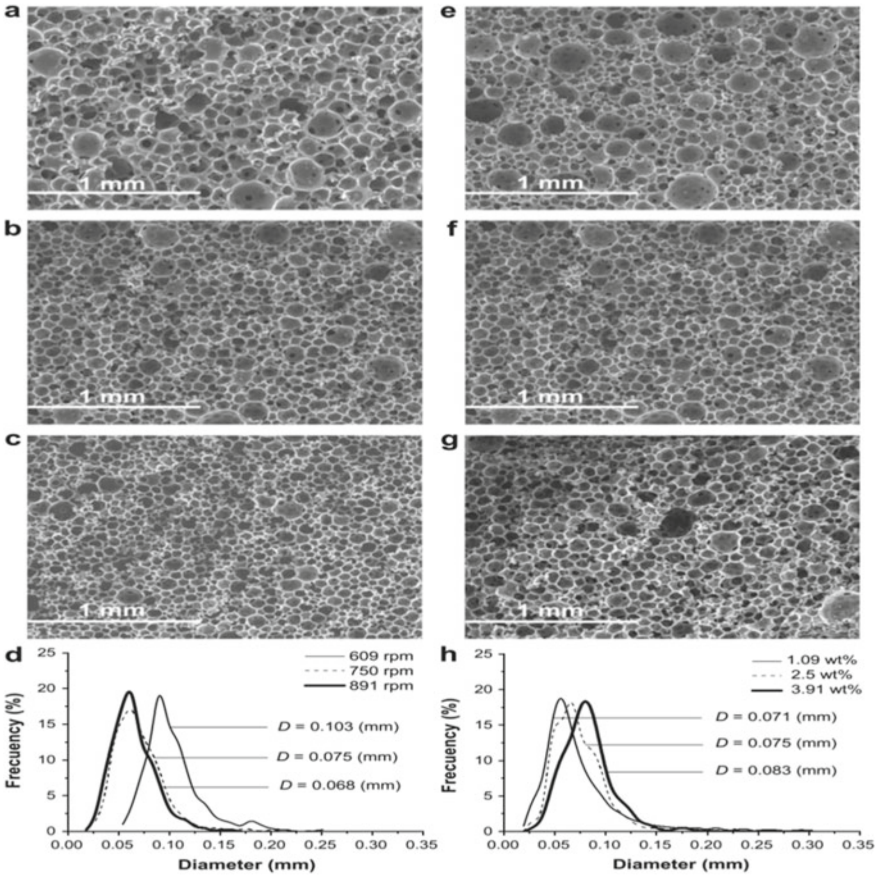

Fig. 3 SEM images of PFs formulated at stirring rate of **a** 609, **b** 750, **c** 891 rpm, and **d** their respective cell size distribution. SEM images of PFs formulated with **e** 1.09, **f** 2.5, **g** 3.91 wt.% blowing agent and stirring rate of 750 rpm and **h** their respective cell size distribution. Reproduced from [39] with permission from Elsevier

4 Physical Properties

4.1 Mechanical Properties and Friability

PFs are one of the best options to use in structural and insulating applications, especially when the fire resistance is crucial, mostly because of their high thermal stability, low thermal conductivity, and significant fire-resistant properties [53]. Nevertheless, as a severe drawback, the low mechanical properties of PFs compared to polymeric foams should be overcome to fabricate tougher PFs. The aromatic structure and rigidity of lignin nanoparticle make it an exceptional candidate to be used as a reinforcing component in polymer composites. In this context, Del Saz-Orozco et al.

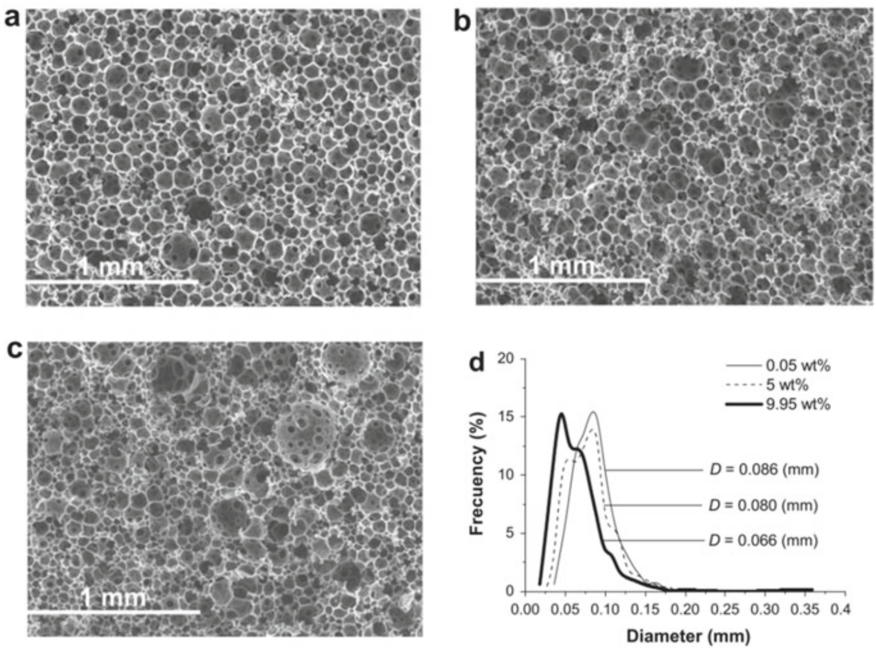

Fig. 4 SEM images of lignin nanoparticle-reinforced PF containing **a** 0.05, **b** 5, **c** 9.95 wt.% lignin, and **d** their respective cell size distribution. Reproduced from [39] with permission from Elsevier

[39] applied the ANOVA method to determine the influence of the formulation variables of lignin nanoparticle-reinforced phenolic foam (LRPF) such as stirring speed, blowing agent amount, and lignin nanoparticle percentage on the mechanical properties and density of the prepared foams. Based on the results of the experiments the modulus and strength of LRPFs were enhanced compared to pure PFs up to 128% and 174%, respectively. Moreover, the amount of needed blowing agents reduced by 31% with the use of lignin nanoparticles as a reinforcing agent, which reduced the used chemicals and fabrication costs.

In their next work, Del Saz-Orozco et al. [52] studied the effect of LRPF and wood flour-reinforced phenolic foam (WRPF) on the friability of PFs, and the effect of hydrothermal aging on mechanical properties. Friability is of great importance as it indicates the capacity of being easily disintegrated in small particles, and materials with high friability can generate a considerable amount of dust during work which is dangerous for human health.

The values of mass loss for the PF and LRPF and WRPF (reinforced with 8.5 wt. %) were measured to be 32.2%, 22.2%, and 42.8%, respectively. Besides, PF/8.5 wt.% LFPF and 8.5 wt.% WRPF before and after the friability test are shown in Fig. 6. The presence of lignin particles decreased mass loss of the phenolic foam which can be due to the agglutinating properties of lignin nanoparticles, which increases the toughness of the material [22]. Interestingly, wood flour adversely affects the

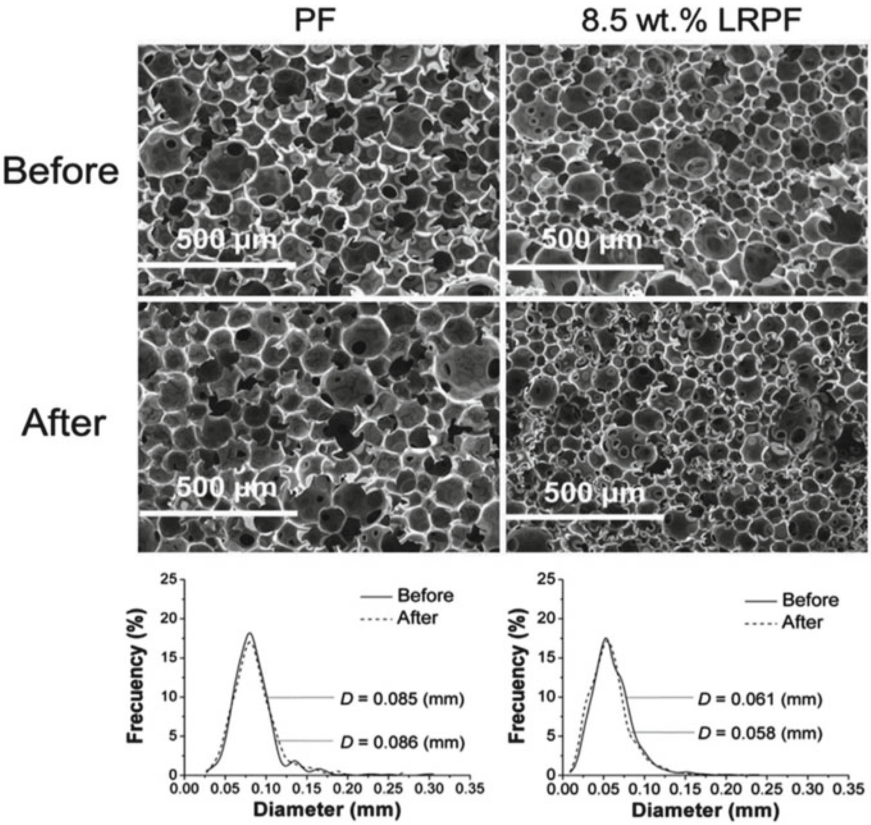

Fig. 5 SEM images and cell size distribution of pure PF and lignin-reinforced PF before and after hydrothermal aging. Reproduced from [52] with permission from Elsevier

friability and increased by 30% concerning PF. This could be a result of defects in the material such as cracks, which can favor the mass loss of the foam during the friability test.

To make sure that PFs are the right choice to use in the insulating application, investigating their behavior under moister and pressure is essential. The strain–stress curves of unreinforced and 8.5 wt.% lignin nanoparticle-reinforced PFs, before and after the hydrothermal aging, are shown in Fig. 7.

The LRPF and PF transformed from rigid brittle foams to plastic foams after hydrothermal aging as it is evident from strain–stress curves [54]. This change in behavior could be the result of the plasticizing effect of water on polymeric materials [55]. It can be seen that the mechanical properties for both modified and unmodified PFs decreased after hydrothermal aging. In particular, the change in compressive modulus after hydrothermal aging was 61% and 69% for PF and LRPF, respectively. The reduction of stress values after hydrothermal aging in LRPF was also due to a weakened interface of matrix reinforcement as a result of the interaction

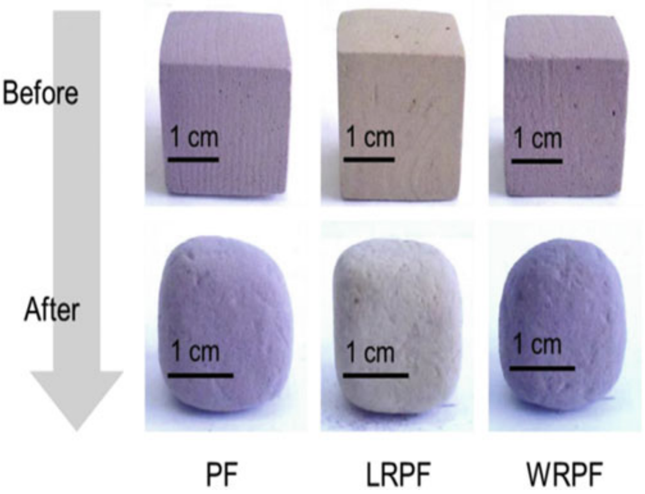

Fig. 6 Friability test of PF and reinforced PF containing 8.5 wt% lignin nanoparticle and wood flour. Reproduced from [52] with permission from Elsevier

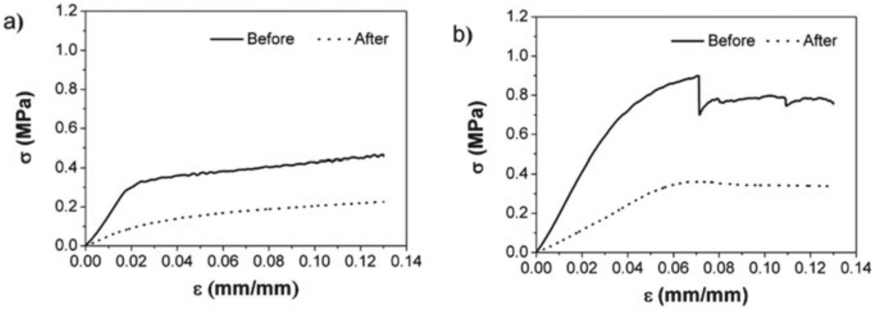

Fig. 7 Strain–stress curves of **a** PF and **b** LRPF before and after hydrothermal aging. Reproduced from [52] with permission from Elsevier

between water molecules and the lignin particles. Although the reduction in mechanical properties of lignin-reinforced foams was higher than for the unreinforced foam after hydrothermal aging, modulus and strength of the reinforced foams were significantly improved after the addition of lignin nanoparticle. The modulus and the strength of 5.72 and 0.388 MPa were achieved for LRPF which were considerably improved compared to PF with modulus and strength of 4.95 and 0.256 MPa. The best overall performance before and after hydrothermal aging was obtained when 8.5 wt.% of lignin particles were incorporated in PFs.

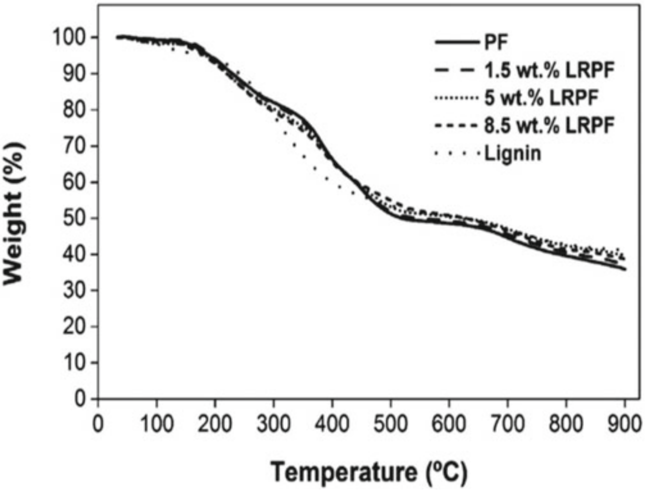

Fig. 8 Thermograms of PF and LRPF with different weight fractions. Reproduced from [52] with permission from Elsevier

4.2 *Thermal Stability and Degradation*

As mentioned before, PFs are mainly used in insulating applications. Therefore, thermal stability in a broad range of temperature and fire-resistance properties are important features to study [52]. Del Saz-Orozco et al. [52]studied the thermograms of PF and LRPFs containing several reinforcement weight fractions as shown in Fig. 8. The similarity thermograms of both foams are because they have similar polyphenolic chemical structure [56]. It can be seen that thermal degradation happens in three steps. The first step occurs at temperature below 150 °C and corresponds to the loss of volatile compounds and moisture.

The second step which takes place between 150 and 500 °C is due to the degradation of the polymer, cleavage of weak polymer bonds, and the release of water. And last the release of carbonaceous substances which happens [7, 40]. Moreover, T5%, T25%, and Ash 900 °C of PF were measured, and in the temperature range between 250 and 500 °C, LRPF degrades significantly faster than PF. In short, it was noted that lignin nanoparticles did not significantly influence the thermal stability, except for the range of 250–500 °C.

5 Conclusion

In this study, the developments and general views concerning the fabrication of lignin/PF nanocomposites and the influence of nanoparticles on mechanical, thermal, and structural properties of PFs have been discussed in detail. It can be concluded from the above studies that the use of lignin nanoparticles as an improving agent in the PF structure can significantly increase their mechanical and thermal stabilities, compared to the pure PFs. In addition, the microstructure of the PFs improves with an increase of lignin nanoparticle loading. It can be explained by the good dispersion of lignin nanoparticles in PF matrix and creating the strong crosslink between nanoparticles and resin.

Briefly, the lignin nanoparticles/PF composites present both serious challenges and excellent potential, so it can be considered as a research field for years to come. Moreover, the outstanding progress in the applications and improvement of these foams will strongly depend on how we can solve the challenges.

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