

# Chapter 17

## Wood Flour-Reinforced Phenolic Foams (WFPF)



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### 1 Introduction

Global environmental, social and legal initiatives for sustainable development, circular economy, and climate neutrality are leading to development of renewable products for more sustainable materials. The introduction of more and more restrictive environmental regulations by the European Union and highly developed countries is leading to the growth of interest about wood polymer composites (WPCs) [1, 2]. Many branches of modern industries are interested in exchange of usage of inorganic fillers for natural, biodegradable, and renewable materials. This is due to the high consumption of high-density, expensive, and non-degradable fillers such as carbon and glass fibers. Moreover, the use of these materials is connected with high abrasive wear of machinery (expensive machines and their maintenance), harmful influence on the environment, and health of the workers. The most serious dangers from exposure to fibers for human are skin and eyes irradiation and respiratory system diseases. Recent research suggests the possible lung carcinogenicity of inhaled glass fibers. Nevertheless, 90% of produced polymer composites consist of glass fiber or/and carbon fiber [3].

In the last decades to overcome these problems, industry and scientists are trying to apply less expensive and less hazardous wood-based fillers. This interest can be observed in the increasing number of articles, books, and patents associated with incorporation of these materials. Looking at wood as an alternative option for other fillers, it is estimated that potential of wood origin fillers is huge. Global Forest Resources Assessment 2020 made by FAO reports that 31% of the total land area is covered by forests, what is equivalent to 0.52 ha per person. More than 54% of the world's forests are in five countries—Brazil, Canada, Russian Federation, China, and

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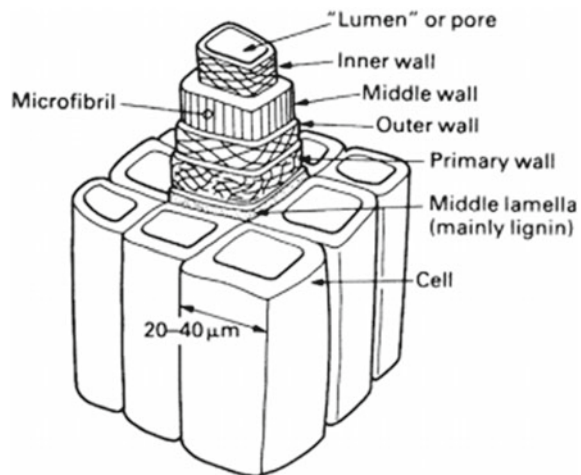
the United States [4]. Proper management of such a large amount of raw materials can lead to the development of a sustainable industry. It is necessary to process not only full-valuable products but also by-products. One of the most popular side product during wood processing is wood flour. About 50% of this waste is generated from processing of solid wood pieces in sawmills during production of wood panels, plywood, particle boards, and furniture [5]. Minimalization of the negative impact on the environment and human living can be caused by the implementation of effective utilization of this type of waste. In last years, a lot of researchers proposed effective methods of application of wooden wastes in a wide range of materials—especially in wood polymer composites [6].

## 2 Wood and Wooden Fillers

Wood is a material that has a huge impact on the social and economic life of human population all over the world. These materials played a huge role in the evolution of man and history of mankind. Wood is an orthotropic, natural composite (in micro and macroscopic levels) mainly composed of hemicellulose (15–25%), cellulose fibers (40–50%) forming cellular structures, which are connected by lignin (15–30%) forming middle lamella. As can be seen in Fig. 1, wood cell wall shows specific structure, which gives wood unique properties such as lightweight, good stability, elasticity, hardness, toughness, and high load-bearing capacity [7].

Due to the excellent mechanical properties, biodegradability and free availability of wood and products produced during the processing are widely used in building and constructions and manufacturing of household products (furniture, sports kit, paper, auto parts). The wood structure, chemical compositions, and acoustic, physical, mechanical, and thermal properties are different in various wood species even the

**Fig. 1** Molecular structure of a wood cell wall [3]



**Table 1** Chemical composition and properties of selected wood species from literature sources [5, 9, 10]

Wood species	Cellulose [%]	Hemicellulose [%]	Lignin [%]	Others [%]	Density [g/cm <sup>3</sup> ]	$\sigma_{\max}$ [MPa]	E [GPa]
<b>Softwood</b>							
<i>Pine</i>	44–46	25–28	27–29	4–5	0.35	12–27	0.1–0.5
<i>Spruce</i>	44–46	25–27	27–29	–	1.5	85	18–40
<i>Cedar</i>	37	19	34	3 0.35		12–27	0.1–0.5
<i>Fir</i>	41–46	27–35	28–30	2–3	0.33	78	14
<i>Larch</i>	38.5	27.2	21	–	0.56	100	11
<b>Hardwood</b>							
<i>Teak</i>	49	30	30	–			
<i>Maple</i>	47	30	21	2 0.54		108	9.58
<i>Beech</i>	44–46	30–35	21–23	–	0.56	86	9.5
<i>Poplar</i>	44–46	33–36	18–21	– 0.33		154	5.9
<i>Oak</i>	42–47	20–27	25–27	3–4 0.63		78	10.4
<i>Sal</i>	40–50	15–25	15–30	–	0.72	40	1.5
<i>Mango</i>	40	11.5	36	–	0.52	24	1.17
<i>Apple wood shell</i>	40	26	30	0.9 –		–	–
<i>Bamboo</i>	26–43	30	21–31	–	0.6–1.1	140–230	11–17
<i>Birch</i>	40	26	33	–	0.62	137	4.8

same species growing in different conditions [8]. Depending on the wood composition and anatomy, it can be divided into two groups—hardwood and softwood. Table 1 shows division into these two groups, chemical composition and properties of most popular wooden species [5, 9, 10].

## 2.1 Production of Wood Flour

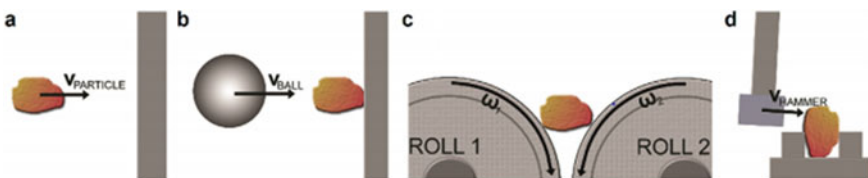
Wood flour is mostly generated from various scraps from wood processors. To obtain the high-quality wood flour, it has to be free from dirt, bark, and other impurities and should be composed of a specific species (or a mixture of species group) of wood. Availability of different kinds of wood flour depends on the continent, country, or even region of clean raw materials from the wooden industry. For example, in the

United States, the most commonly used wood flour is derived from pine, oak, and maple.

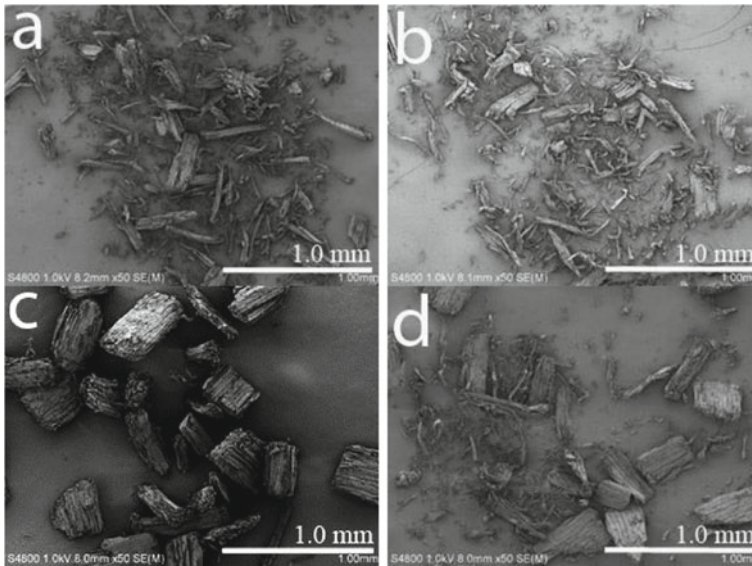
Nowadays, there is no standard method of producing wood flour, some general points can be discussed. The most important issues in this process are size reduction and size classification. Initial grinding of the larger raw materials may be conducted using equipment such as a hog, chipper, or hammer mill. Pre-grounded material can be pulverized by crushing in roller mill, beating with hammers, impactors or grinding in attrition mills. This process results in receiving particles containing fibers and their fragments [11].

Depending on the intended application, wood can be treated to obtain different shape and size of grain [12]. Grinding wood into small particles to form wood powder called wood flour is necessary for many applications. Depending on the energy, mechanism of grinding, and wood properties, it is possible to obtain wood flour with fine particle size, high specific surface area, various particle shapes, or even with low crystallinity. It has been proposed that wooden biomass is finely grinded when product size is less than  $100\eta\text{m}$ . On the other hand, in few studies, particles with size up to 1 mm is acceptable in further production of wood flour-reinforced composites. During wood grinding, a number of different stress types in wood structures occur. Most likely stress types are presented in Fig. 2 [10]. The process of size reduction of wood is a highly energy-consuming process. This is due to viscoelastic nature of wood. The amount of energy may be lowered by appropriate pretreatment of wood, selecting the appropriate grinding technique, and grinding medium.

The obtained wood flour is characterized by different aspect ratios, especially length to diameter. Low aspect ratios allow wood flour to be more easily metered and fed than individual wood fibers, which tend to bridge. However, the low aspect ratio limits the reinforcing ability. After pulverization, the wood flour can be classified by size using vibrating, rotating, or oscillating screens. Moreover, separation of wood particles by air flow is also used, especially with finely ground wood flour. Separation by size can be described by the actual size of the powder or by mesh of the wire cloth sieves used to classify. The most popular manufactured wood flours used as fillers in thermoplastics are in the size range of 180–425  $\mu\text{m}$  (80–40 US standard mesh). Typical wood flour supplied for the further processing content between 4 and 8% of moisture and must be dried before use [11]. Figure 3 represents the scanning electron micrographs of different types of WFs—initial (00), dry pulverized at mill-plate gap 200  $\mu\text{m}$  (200), dry pulverized at mill-plate gap 350  $\mu\text{m}$  (350), wet pulverized at



**Fig. 2** Illustration of different stress types during grinding: **a** single impact, **b** double impact, **c** slow compression, **d** shearing impact [10]



**Fig. 3** Scanning electron microscopic images of short cypress flour (CWF<sub>S</sub>) and long cypress flour (CWF<sub>L</sub>), **a** CWF<sub>S</sub>00, **b** CWF<sub>S</sub>200w, **c** CWF<sub>L</sub>00, **d** CWF<sub>L</sub>200w [13]

mill-plate gap 200  $\mu\text{m}$  (200w), and wet pulverized at mill-plate gap 350  $\mu\text{m}$  (350w), respectively.

## 2.2 Impact of Wood Flour on Material Properties

Depending on the origin and type of processing, the types of wood flour may differ from each other with particle size, size distribution, chemical composition, and content of additives. Each parameter mentioned above could have a huge impact on the properties of the product. Very fine wood flours can cost more (increase of material price) and may increase melt viscosity more than coarser wood flour. On the other hand, composites made with smaller powders typically have a more uniform appearance and a smoother finish. If the filler is grounded too fine, the fiber bundles become wood dust. These fragments no longer resemble fiber or fiber bundles and may not cause such a significant enhancement.

Wood flour originating from the softwood has higher in comparison to the hardwood cellulose content, what leads to higher adhesion between two phases—wood particles and polymer matrix. On the other hand, materials with softwood filler have lower mechanical properties. Hardwood fillers with a lower cellulose content have poorer interfacial adhesion but better mechanical properties [14, 15].

### 3 Methods of Wood Flour Management

Before concern for the environment began, wood powder was a mainly waste stream from wood processing plants such as sawmills and furniture factories. In the last few decades, many common applications of wood flour have been found. Due to its unique properties and chemical composition, wood powder has a wide range of applications not only in material production.

One of the most popular applications of wood flour is combustion and co-firing. This process is conducted in specially designed boilers and furnaces, often with the addition of coal. Nowadays, 64% of wood and wood waste are subjected to this form of processing. Before combustion wood should be pulverized, which is a very energy-consuming process. In this process, the key parameters are particle size, shape, and density. Currently, the state-of-the-art for this method is obtaining wood pellets in the process of torrefaction. This process combined with pelletization changes wood properties to provide a better fuel quality for combustion and gasification applications. Torrefaction produces a relatively dry product, which reduces or eliminates its potential for organic decomposition. The possibility of replacing or supplementing coal with biomass in coal-based power plants with existing equipment is considered [16, 17]. Nevertheless, according to the normative acts about hierarchy in waste management, priority is given to preparing wastes for re-use and recycling than for energy recovery (Directive 2008/98/EC). Importantly, the opinion that energy recovery and reprocessing into materials to be used as fuels is a form of material disposal, not form of recycling, becomes more and more popular. For this reason, new methods of wood waste managing are being developed [18, 19].

Another management method of wood flour is the conversion to chemicals and biofuels. Liquefaction, saccharification, and gasification are the three most popular approaches to utilizing lignocellulosic biomass. These methods are based on thermal processing of wooden biomass under high pressure, generally with addition of auxiliary substances such as solvents, catalysts, mixture of gases, enzymes, or even bacteria [10]. This type of processing allows obtaining valuable intermediates in the production of synthetic chemicals. These products include conversion of biomass into simple sugars via acidic or enzymatic hydrolysis and further fermentation to methanol, ethanol, or butanol [20], preparation of bio-polyols [21] to production of bio-polyurethanes and their composites [22] or generation of syngas (mixture of hydrogen and carbon monoxide) during gasification [23]. The other uses of wood flour include lignophenol production [24], which is a valuable intermediate used for further production, obtaining absorbers and ion exchangers to remove organic pollutants and heavy metals from aqueous systems.

## 4 Wood Plastic Composites

Polymer composites reinforced with wood fiber or flour are generally known as wood plastic composite—WPC. These composites are made of wood fibers/flour (or other cellulose-based fillers, such as bamboo, peanut hulls) and preferably waste plastics. As the material of matrix, the most frequently used plastics are polyvinyl chloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS). The search for more environmentally friendly solutions led to the gain in importance of biodegradable plastics produced from renewable resources. Examples of such materials include polylactic acid (PLA), starch acetate, non-biodegradable bioplastics such as bio-derived PE and polyamide [25]. The plastics mentioned above are chosen due to their low temperature of processing, which is between 150 and 220 °C, what prevents wood from decomposition during processing. While temperature arises over 200 °C, wooden materials are starting to release volatile products [26]. Degradation of the least stable ingredients of wood (hemicellulose and extractives) starts at 210 °C [27]. Cellulose and lignin have more stable structure and starts to degrade over 270 °C. Processing of the composites filled with these substances over 220 °C leads to the generation of volatile degradation products. This effect causes foaming of product and decrease of material properties [28]. Moreover, both materials before processing should be dried and kept sealed, because more than 1% of moisture in material could lead to foaming of the product. The presence of water may cause generation of micro voids and lead to porous structure with irregular shapes, what will result in deterioration of mechanical properties of the product [29].

Nowadays, the most popular method of production of WPC is two-step extrusion. First, the prepared blend is subjected to pelletizing, and then obtained pellets are used to extrude into a final product. Pelletized material is more homogeneous and it is easier to control moisture content. In order to facilitate the production, installations enabling the processing of untreated wood in a single-stage process were developed. The main ingredients in the composition of WPC are wood flour and plastic matrix. In commercial WPC products, the addition of wood flour reaches up to 70%. This amount varies due to material of matrix, application and required appearance. Moreover, to enhance properties, extend product life, improve processing, or facilitate material maintenance, a number of different types of additives are used during processing. The most popular additives during processing are coupling agents, which can improve the dispersion of the wood inside matrices, bonding on the matrix/reinforcement border and reduces the rate of water uptake. Due to possible incompatibility between matrix and reinforcement, coupling agents should work as a connection of their surfaces. The most popular coupling agents are: silanes, titanites, and functionalized polymers (e.g. polyolefins). Other additions include lubricants, foaming agents, pigments, fire retardants, antioxidants, biocides, and UV stabilizers. It should be remembered that the addition of these substances may be associated with an increase in the price of the received material [29].

## 4.1 Properties of WPC

Due to subjection of WPCs to the thermal and mechanical loadings, this kind of material should be characterized by appropriate flexural, impact and compressive strength, hardness, resistance to aging, and thermal stability. Listed properties greatly depend on the type of matrix and type of reinforcement. The most important properties of wood flour that affect are content of wood flour, aspect ratio, geometry of filler, type of wood (softwood/hardwood), and interfacial properties between phases.

The major advantage of wood polymer composite over wood is the possibility of forming composite to every projected shape. Designed properties of WPCs hardly depend on their predicted application. Unlike wood, this material needs no application of additional preservatives on surface, what makes it environmentally friendly and material requires less maintenance. The addition of filler also provides WPCs excellent resistance to splitting and cracking. Moreover, it looks and behaves like wood but it does not have the same rigidity as wood.

The use of waste from the wood industry in these materials may reduce the rate of deforestation due to obtaining full value products with possibility of modification of material properties by modification of composition. The right mix and proportions of wood, matrix, and additives can lead to receiving materials with the better or equivalent properties to wood. Unfortunately, due to the addition of non-biodegradable plastic binder of wood (phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins, polyurethane), these materials are only partially biodegradable. To obtain fully biodegradable materials, it is suggested to use plastics such as PLA or thermoplastic starch.

## 5 Reinforced Phenolic Foams

Phenolic foams are getting more and more popular material all over the world. Nowadays, scientists are looking for materials that will meet more restrictive requirements. Due to unique combination of properties, phenolic foams (PF) have a number of engineering applications. These materials are used in energy adsorption, insulation, fire protection, and lightening of structures. The most important advantages of this material include high thermal stability, low thermal conductivity, and tremendous fire resistance. Moreover, generation of toxic gases during combustion process is very low and material shows no dripping behavior. Unfortunately, phenolic foams have a number of disadvantages such as brittleness and tendency to pulverization, what limits wider application. In order to solve this problem, scientists in their research present methods to improve the properties of these materials [30].

Two methods of improving the properties of these materials have been distinguished. The first one relies on the appropriate choice of method of production. For example, free rise/closed mold method will influence on homogeneity and density of obtained foam. The second one is based on the modification of formulation of



foam to improve properties of the product. Such methods include modification of the foam composition, which affects its chemical and physical structure and includes the addition of other components to the material to improve their properties. The most common modifications include addition of fillers (fibers, particles, etc.) to the materials to improve flexural and compressive strength of material, addition of nucleating agents to increase density of the material, or addition of flame retardants [30].

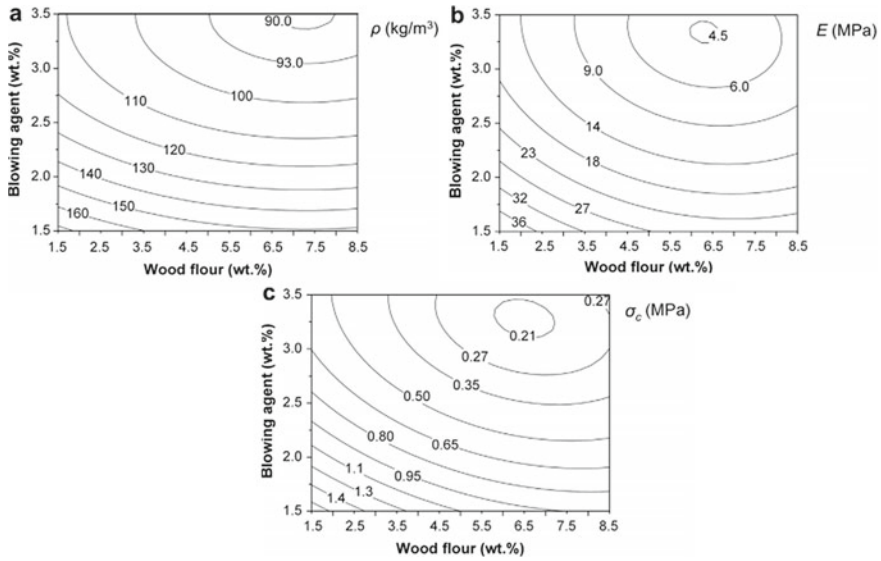
Moreover, fillers are not only added to increase mechanical properties but also for reduction of material price. In the case of phenolic foams, the main purpose of addition of fillers is to increase compressive strength and decrease excessive friability. The most popular additives are glass fiber, aramid fiber, multiwall carbon nanotubes, and other organic and inorganic fillers intentionally added to the material. Recently, scientists are interested in preparation of phenolic foams using common and natural fillers such as wood flour, cellulose fiber, or even lignin. Addition of these substances is associated with a slight decrease in thermal stability and fire resistance, improvement of mechanical properties, and increase of viscosity.

## 6 Wood Flour Reinforced Phenolic Foams

Currently, there are only a few studies describing the influence of wood flour on the properties of phenolic foams. However, due to the unique properties of PF filled with wood flour, there is a possibility that this material will become more popular in the near future.

In some research [31], wood flour derived from *Pinus Radiata* was incorporated in phenolic foam matrix. Wood flour was obtained by milling wooden chips in a mill and then sieved to a size lower than 0.15 mm. To obtain phenolic foams, the authors used a petrochemical system with addition of hardener (ACE 1035), catalyst (phenol-4-sulfonic acid), and blowing agents (Tween® and n-pentane). The ratio of phenolic:surfactant:catalyst:blowing and agent:hardener was 100:2:4:1.1 and 3.9:20 (by weight). Selected substances were mixed with mechanical stirrer and then obtained mixture was poured into a mold. Material was cured for 1 h at 80 °C and then further post-cured for 24 h at 105 °C. To study the influence of variables on the reinforced PF properties, the author changed the weight fraction of wood flour (1.5–8.5 wt.%) and blowing agent amount (1.5–3.5 wt.%) in the composition.

Author has shown a decrease of density of WRPF with an increase in amount of wood flour and blowing agent. This can be due to the performance of wood flour as a nucleating agent, which promotes generation of bubbles in the foam. Moreover, a greater addition of blowing agent caused an increase in the quantity of gas. This effect caused a decrease in the density of foams. This effect was also observed when lignin nanoparticles were added to the matrix [32]. On the other hand, the addition of glass or aramid fibers in phenolic foams did not show this effect but some works showed that it is necessary to add more blowing agents to maintain previous density [33]. It is also shown that with an increase in amount of blowing agent and wood flour, compressive strength and modulus decrease. Contour maps of change of properties



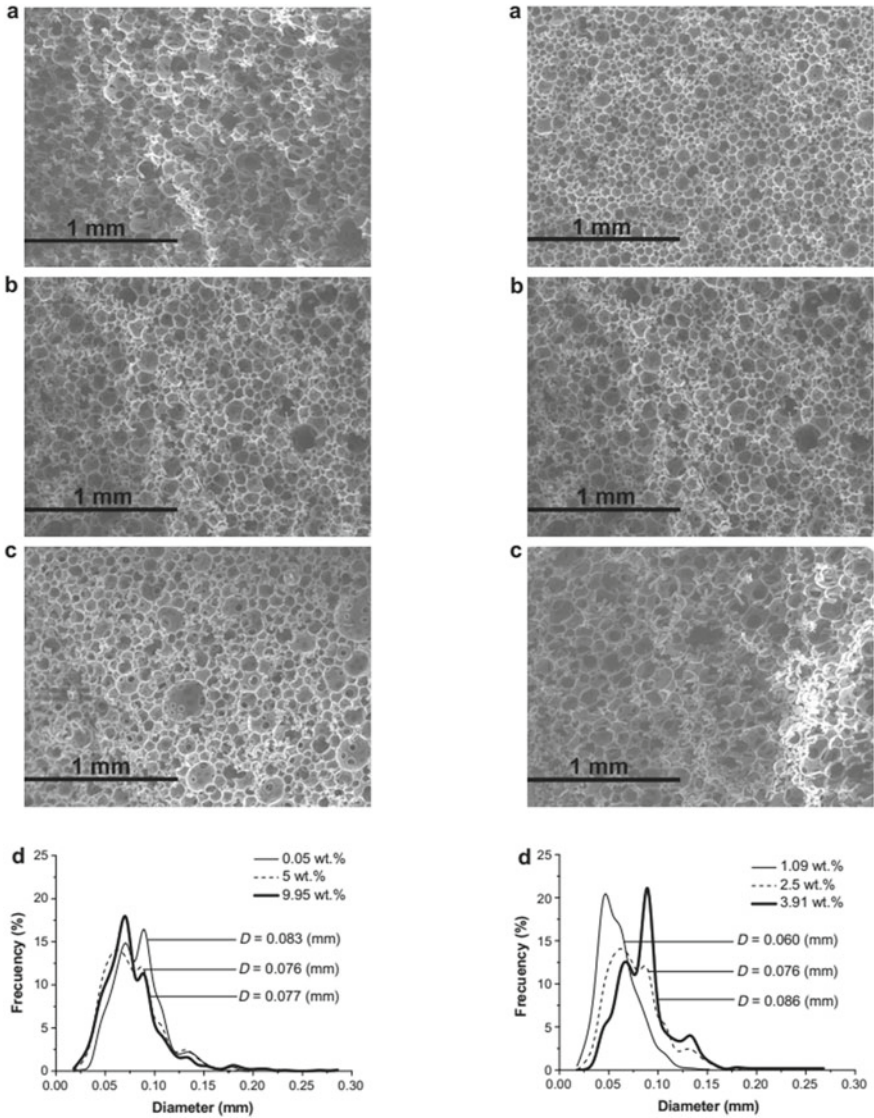
**Fig. 4** Contour maps for WRPF **a** apparent density ( $\text{kg/m}^3$ ), **b** compressive modulus (MPa), and **c** compressive strength (MPa) [31]

with different amount of filler and blowing agent are shown in Fig. 4. Author noticed that changes in mechanical properties of obtained composites are differed depending on the material density. This can be caused by change of cell wall thickness, which can be responsible for reinforcing effect of fiber.

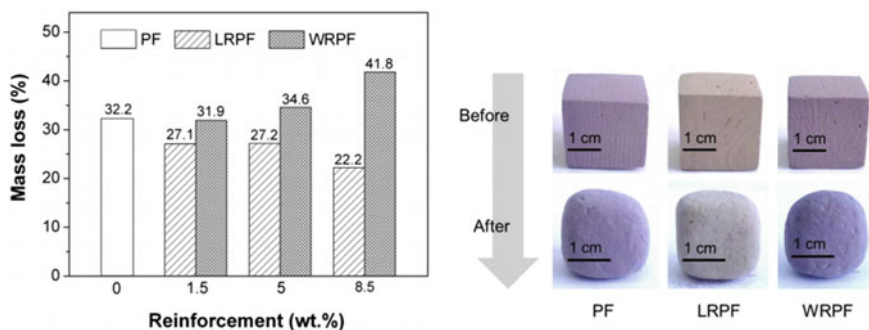
The microstructure of these materials has been determined using scanning electron microscopy. It was noticed that wood flour can be found inside cell walls and among cells. Due to the hydrophilic nature of wood and phenolic foam, the compatibility between these two phases is very good. This is confirmed by the absence of voids in the obtained material. Moreover, observation of the cellular structure of the obtained composites with different addition of reinforcement and blowing agent showed that mean cell size decreases with lower addition of wood flour (0.05–5 wt.%). Higher addition (5–9.95 wt.%) of wood flour barely changes the cell size distribution. On the other hand, the addition of more blowing agent is associated with a continual increase in cell size. SEM images for WRPFs formulated with the addition of blowing agent and wood flour are shown in Fig. 5.

The other work [34] compared the effects of wood flour and lignin particles on the friability, thermal stability, and effect of hygrothermal aging on structure and properties of material.

High friability is one of the biggest disadvantages of phenolic foams. Literature indicates that average friability varies between 15 and 40% depending on chemical structure and used additives. In this work, it is shown that the addition of small amount of wood flour does not significantly influence on friability but higher addition is associated with strong increase of this parameter. This effect is caused by generation



**Fig. 5** SEM images for WRPFs formulated with 2.5 wt.% of blowing agent and **a** 0.05, **b** 5, and **c** 9.95 wt.% of wood flour and **d** cell size distributions, SEM images for 5 wt.% WRPFs formulated with **a** 1.09, **b** 2.5, and **c** 3.91 wt.% of blowing agent and **d** cell size distributions [31]

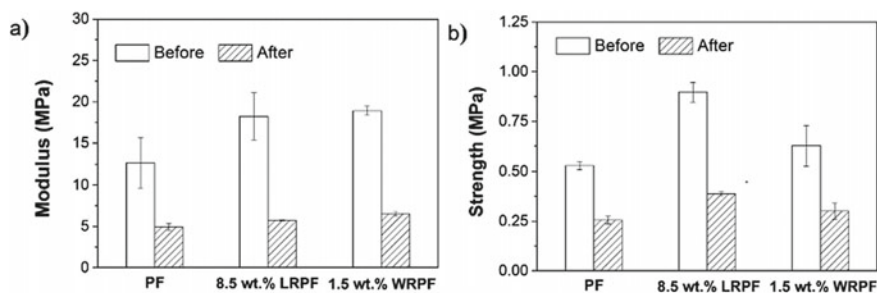


**Fig. 6** a Mass loss during friability test for unreinforced and reinforced phenolic foams, b Friability test specimens of unreinforced phenolic foam, 8.5 wt.% lignin particle and 8.5 wt.% wood flour-reinforced phenolic foams [34]

of defects (cracks etc.) and modification of crack propagation, which favors higher wear of material during friability tests. On the other hand, the addition of lignin particles caused a decrease in friability. The observed change of parameters may be caused by the modification of the cell edge thickness and cell size of the foam cells caused by the addition of fillers. The values of weight loss for these materials are shown in Fig. 6.

Thermal stability of the material was studied by thermogravimetry (TGA). Obtained thermograms were characterized by a three-stage course. The first step (below 150 °C) is related to the moisture and volatile products (formaldehyde, phenols, etc.) losses. The second step (between 150 and 500 °C) is associated with degradation of the polymer, while polymer bonds break and formaldehyde and water particles are generated. During the last step of degradation at temperatures over 500 °C, generation and release of carbonaceous substances occur. It was also shown that addition of lignin particles negligibly changed  $T_{5\%}$  and ash content ( $ASH_{900^{\circ}C}$ ), however,  $T_{25\%}$  decreased. Authors observed that wood flour reinforced foams had higher  $T_{5\%}$  and ash content but  $T_{25\%}$  has been significantly lowered. Although both substances modified thermal stability of materials, significant reinforcement effect is visible only in the temperature range of 250–500 °C in which wood flour particles and lignin decompose faster than phenolic foam.

Regarding hygrothermal aging, authors noted that strain–stress curves of the materials after aging were more similar to the plastic foams but unaged materials showed the nature of brittle foams. It can be concluded that water shows a plasticizing effect on polymeric material. This effect is confirmed by decrease in mechanical properties of the materials after aging in comparison to the unaged materials. Compressive modulus and strength before and after hygrothermal aging for PF, 8.5 wt.% LRPF and 1.5 wt.% WRPF are shown in Fig. 7. For reinforced materials, a greater decrease in properties is observed, but still, these samples have better properties than an aged material without any filler. SEM micrograms of samples subjected to the



**Fig. 7** Compressive mechanical properties for unreinforced and reinforced phenolic foams before and after hygrothermal aging: **a** Modulus, **b** Strength [34]

hygrothermal aging showed that all foams maintained similar cell size to the unaged materials.

The other paper [35] investigated the thermal stability, changes in chemical structure during thermal degradation, and the kinetics of thermal degradation of a wood flour reinforced phenolic foam.

Changes in chemical structure during thermal degradation were studied by FTIR analysis. The tests of phenolic foams, reinforced foams, and reinforcement have been conducted in room temperature, 225 °C, 375 °C, 500 °C, and 800 °C. For the phenolic foam, the spectrum obtained at room temperature was similar to the spectrum at 225 °C, indicating that the foam did not undergo changes in its chemical structure below 225 °C. Significant differences were noticed at 375 °C, when intensity of band at 1200  $\text{cm}^{-1}$  was reduced. This can be due to pyrolysis of phenolic structures present in obtained materials. Furthermore, band at 800  $\text{cm}^{-1}$  fully disappeared, which indicates consumption of low molecular weight structures and phenolic monomers. At 500 °C, it was noticed that band at 1200  $\text{cm}^{-1}$  fully disappeared, which is associated with fully degradation of phenolic structures, and the intensity of band at 1581  $\text{cm}^{-1}$  was significantly reduced. It was noticed that the FTIR spectrum of the wood reinforced material was similar to the spectrum of the PF foam. This indicates that the amount of wood flour was not high enough to cause significant structural changes during the pyrolysis process.

The thermal stability and degradation process of reinforced foams and wood flour were analyzed using the thermogravimetric analysis (TGA). For the wood flour, the study proved degradation of each component at different temperature ranges. Obtained thermograms showed that hemicellulose degrades first (between 250 and 300 °C), then degradation cellulose (between 300 and 400 °C). The third main component of wood flour—lignin degrades between 250 and 450 °C and shows a maximum degradation rate at approximately 350 °C.

The study showed that the phenolic and reinforced phenolic foams degrade differently. Again, it was confirmed that three peaks found in the DTG curve for temperatures less than 900 °C indicate three different degradation stages of the samples. Due to moisture release during measurement, results below 150 °C have been removed

from all the thermograms. The results of previous studies about degradation of unreinforced and reinforced phenolic foams have been confirmed. Again, the first degradation stage occurred between 150 and 250 °C, and it is attributed to the volatilization of molecules of low molecular weight; however, it was added that responsible for this phenomenon is emission of monomeric phenol and formaldehyde, present in the structure of the foam during the curing/manufacturing process.

In the second stage of degradation, it was added that the mass loss that occurred during this stage is mainly due to the release of formaldehyde and water. It is caused by bond breaking (mostly methylene ether) and conversion into more stable structures. In this stage, the authors conclude that the mass loss could be associated with the decomposition of the material and transformation into carbonaceous structures and products low molecular products, such as water, carbon monoxide, carbon dioxide, methane, and phenol. The generation of CO<sub>2</sub> can be attributed to the breaking of the bridges connecting phenolic rings and of the bond joining the hydroxyl radical to the aromatic ring. It is considered that these reactions can take place at high temperatures (>500 °C) under an inert atmosphere. The radicals generated during these reactions can react with each other, leading to the formation of compounds whose functional groups are oxidized and giving rise to aldehyde groups, which can also easily oxidize carboxyl groups [36, 37].

Obtained by MFK methods, the values of activation energies are in a range of 110–170 kJ/mol. For almost all conversion ranges, the activation energies obtained for the reinforcement are constant and are about 162 kJ/mol. The results obtained using Flynn-Wall-Ozawa MFK and Kissinger–Akahira–Sunose methods showed high correlation coefficients when compared to the data. Research has also shown that the 2-Gaussian DAEM model is suitable for thermal degradation of manufactured phenolic foams and activation energy values vary between 108.6 and 175.6 kJ/mol.

## 7 Conclusions

Phenolic foams can be very useful materials; however, their common use is limited by disadvantages such as their high friability and low mechanical properties. A way to reduce or eliminate the drawbacks of this material may be the addition of particle reinforcement, especially wood flour. The use of this type of reinforcement not only has a pro-ecological character but also, as proved in the studies described above, has the potential to obtain materials with the desired characteristics. With this type of treatment, it is possible to obtain a material with increased compressive strength and Young modulus, reduced amount of foaming agent, and modified abrasion. It should also be remembered that the addition of wood flour increases the density of the material, which may limit its use. There is also a high possibility of an increase in the flammability of the obtained materials. Change of this parameter has not been extensively examined and requires attention in future research. Moreover, there is a lack of studies describing the biodegradability, decomposition of this material, and the effect of aging (UV, thermal, etc.) on the properties of this type of material.

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