A review of the state-of-the-art on thermal insulation performance of polymeric foams

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Batch foaming
Extrusion foaming
Foam injection molding

ABSTRACT
Achieving the global energy sustainability plays a key role in the energy fields. Thermal insulation materials play a vital role on this sustainability. There are different potential thermal insulating materials such as cork, cellulose, mineral wools, vacuum insulation panels, aerogels and polymeric foams. Polymeric foams are one of the most promising thermal insulation materials with a bright outlook and widespread application range. In this review, a comparative analysis was performed using multi-criteria decision making methods between the prevalent insulating materials. It was concluded that the polymeric foams were the most promising thermal insulating materials for different applications. A theoretical model was developed using the literature data to predict the overall thermal conductivity based on the foam density and the cell size and was validated in comparison to the experimental results. The most valuable experimental achievements in the field of thermal insulation performance of the polymeric foams in recent years were reviewed.

1. Introduction
The total energy consumption is growing considerably. For instance, the U.S. Energy Information Administration (EIA) predicts that the total U.S. energy consumption is going to increase by 31% from 2017 through 2050 [1]. The energy consumption in the European Union (EU) in 2014 reached the lowest value over the 27-year period from 1990 to 2016 [2]. However, an increasing trend was observed from 2014 according to the report published by the Joint Research Centre (JRC), the European Commission’s science and knowledge service [2]. The final energy consumption in the EU-28 in 2016 was 1,107.8 Mtoe (millions of tonnes of oil equivalent). Transportation segment with consumption of 23.15% of this energy was the sector with the largest share of final energy consumption. In the second rank, residential consumed 25.71% of final energy.

Although heavy investments have been devoted to develop renewable energies to overcome the drawbacks of fossil fuels such as their polluting emissions [3], but their contribution still is very small in the total energy production [4]. For instance, the share of the wind, tidal, and solar energy was only 0.2% in Canada’s energy production between 2010 and 2014 [5]. Therefore, energy conservation is an efficacious method to achieve global energy sustainability [6]. In this regard, thermal insulation materials show an essential role in energy conservation [7].

Wang et al. [8] reviewed wall materials from the standpoints of cement reinforcement and recycled waste construction materials. They performed an overview on green construction materials for cement reinforcement and recycled construction. They did not focus on the thermal-insulation materials with cellular structures. Villasalim et al. [9] reviewed a parametric comparative study between the thermal insulation materials for thermal energy storage systems. They compared the advantages of different thermal insulation materials for different applications. Jelle [10] and Abu-Jdayil et al. [11] performed a comprehensive study on the applications of the thermal building insulation materials. Jelle [10] reviewed the advantages and disadvantages, limitations and possibilities, of the thermal insulation materials for different conditions. The focus of Abu-Jdayil et al. [11] was on the applications of renewable resources and wastes in the development of the thermal insulation materials. Baetens et al. [12] reviewed the properties and applications of aerogels as a thermal insulation material. The solid properties of silica aerogels such as optical and acoustic properties, thermal conductivity, fire behavior and safety features and their building applications were reviewed. There are also different reviews [13–16].

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on the properties, current applications, and future directions of vacuum insulation panels for thermal insulating applications. However, there is not a state-of-the-art review on the applications of polymeric foams as thermal insulation materials with a bright outlook. In the present review, firstly, the properties and challenges of thermal insulating materials including cork, cellulose, mineral wools, vacuum insulation panels, aerogels, and polymeric foams are discussed. A comparative analysis based on multi-criteria decision-making techniques is performed between the thermal insulating materials for different applications which give a novelty to this review. A comprehensive review is conducted on the recent progress in polymeric foams including the steps and methods for the production of polymeric foams using different approaches of batch, extrusion, and injection molding foaming processes. The most important studies achieving superior morphological properties in polymeric foams are reviewed in detail. As another novelty, a theoretical model is developed to predict the thermal conductivity of
polymeric foams based on the cell size and foam density utilizing the data available in the literature. The most important experimental achievements in the thermal insulation performance of polymeric foams in recent years are reviewed.

2. Thermal insulating materials

The need for reducing the greenhouse gas emission and potential influence of improving energy efficiency leads to an enormous requirement for enhancing the thermal insulation performance of buildings. The most widely used materials as the thermal insulating are cork, cellulose, mineral wools, vacuum insulation panels (VIPs), aerogels, and polymeric foams.

2.1. Cork

Cork is one of the thermal insulating materials prepared from the cork oak. Cork has the ability to be perforated, cut, and adjusted during the installation in the buildings without any deterioration of the insulation performance [10]. However, its thermal conductivity, typically in the range of 40 to 50 mW.m⁻¹.K⁻¹, is relatively high for the thermal insulation performances [11]. Although its compositions with different reinforcements such as gypsum [17] were introduced as a potential material for building applications, but their mechanical properties were poor. The thermal conductivity of the cork (41 mW.m⁻¹.K⁻¹) was increased to almost 68 mW.m⁻¹.K⁻¹ by locating between two wooden plates [18].

2.2. Cellulose

Polysaccharide, (C₆H₁₀O₅)ₙ, or cellulose is a product of recycled paper or wood fiber with a relatively good thermal insulation performance [19]. They can be used as fillers for cavities and spaces or as boards and mats. However, their thermal conductivity is relatively high ranging from 40 mW.m⁻¹.K⁻¹ to 50 mW.m⁻¹.K⁻¹ [20]. Also, its thermal insulation performance is significantly influenced by moisture and temperature variations. For instance, absorption of only 5 vol% of moisture increased the thermal conductivity of the cellulose from 40 mW.m⁻¹.K⁻¹ to 66 mW.m⁻¹.K⁻¹ [17].

2.3. Mineral wools

Glass wool, rock wool, and slag wool are different types of mineral wools that can be utilized as the thermal insulating materials [21]. Mineral wools with different properties can be used for various applications. For instance, applications in frame houses and cavities need soft and light mineral wools. When the mineral wools are under loads such as applications in floors and roofs, they should be heavier and harder. Mineral wools have the thermal conductivity typically in the range of 30 to 50 mW.m⁻¹.K⁻¹. Glass wools have the thermal conductivity ranging from 30 to 46 mW.m⁻¹.K⁻¹ and the thermal conductivity of rock wools is in the range of 33 to 46 mW.m⁻¹.K⁻¹ [9]. One of the drawbacks of mineral wools is the huge influence of water uptake on its thermal insulating performance. The thermal conductivity of mineral wools increased from 37 mW.m⁻¹.K⁻¹ to 55 mW.m⁻¹.K⁻¹ by only 10 vol% increase in the moisture content [11]. On the other hand, skin and lung can be irritated in the direct contact with mineral wools that makes concerns about more serious problems.

2.4. Vacuum insulation panel (VIP)

Vacuum insulation panel (VIP) is a material with a sandwich structure containing a porous core covered by an envelope material. The porous core can be different materials such as fiberglass, expanded cork, fumed silica, precipitated silica and etc. [9,14]. Although the thermal conductivity of the core material is very low around 4 mW.m⁻¹.K⁻¹ [11], it is increased in long term. One of the major disadvantages of VIPs is the increment of the thermal conductivity as an inevitable phenomenon with elapsed time [16]. The envelope of VIPs can be easily damaged even by nails or similar reasons during installation. Their thermal conductivity is increased to 20 mW.m⁻¹.K⁻¹ by puncturing its envelope [10]. This drawback impedes its applications in buildings because they cannot be cut or perforated in adjusting at the building sites. Their application is limited to the refrigeration industry (60%) and transport boxes (30%) and only 10% of its application is in the building industry [15]. In comparison with the conventional thermal insulation materials, the VIPs require lower thickness for the thermal insulating purposes at the same required thermal resistance (R-value) [22]. Also, its thermal resistance is potentially 5–8 times larger than the conventional thermal insulation materials [23]. According to the model presented by Schwab et al. [24], the thermal conductivity is increased by 0.5 mW.m⁻¹.K⁻¹ per mass% of adsorbed water and 1 mW.m⁻¹.K⁻¹ per 30 mbar increments in the pressure of gas inside the VIP [25]. High cost and ability to be damaged during installation and development are other disadvantages of the VIPs [14].

The effects of the time on the thermal conductivity of different VIPs have been presented in Fig. 1. The results are for two different panels of 50 cm × 50 cm × 1 cm and 100 cm × 100 cm × 2 cm, respectively named VIP-50 and VIP-100. AF is a metal film envelope, MF1 is a two-layer metalized film, and MF2 is a three-layer metalized film. Fig. 1 indicates one of the major drawbacks of the VIPs i.e. increasing the thermal conductivity in long term.

2.5. Aerogel

Aerogels, firstly invented in 1931 [26–29], are derived from a gel. Its liquid phase is replaced by a gas resulting in a solid material having very small pores ranging from 2 to 50 nm and high porosity up to 90% [30–32]. As a result, the aerogels have stupendous properties such as very low thermal conductivity, dielectric constant, sound velocity, and refractive index [33–35]. These unique properties enable it to be used as a core for the VIPs [9,35]. However, the aerogels have several drawbacks which impede its wide-spread commercial applications. Their production is a very high-cost process [35,36,12] and they have very low mechanical strength [12].

Although aerogels have relatively good compression strength, but their tensile strength is very low and as a consequence, they are very fragile [37]. Incorporating carbon fiber increases their tensile strength [48]. Adding carbon black decreases the thermal conductivity of the aerogels as low as 4 mW.m⁻¹.K⁻¹ due to its radiation blocking performance [38]. However, the commercially aerogels available for building applications have higher thermal conductivities ranging from 13 mW.m⁻¹.K⁻¹ to 14 mW.m⁻¹.K⁻¹ [39,40]. The aerogels can be produced as opaque, translucent or transparent materials which endow them a very interesting aspect and a wide application ranges in building and specific applications such as space missions [10].

Fig. 1. Long term variation of thermal conductivity of VIPs [24,13].
Although aerogels can be produced from different materials such as alumina, tin oxide, carbon, and chromium, but silica aerogels are reliable and easier from the production viewpoint. Several types of researches have been conducted to produce the silica aerogels under ambient pressure \([12,41]\) to decrease its production costs due to the high pressure (5–10 MPa) and high temperature (250–270 °C) required for supercritical drying method of silica aerogel production. Solar collector covers, space industry, aerosol particle collector, shock absorption, window panes, building walls, attics, appliances, tank baffles, pharmacy, oxygen and humidity sensors, space mirror protectors, catalyst supports, and battery electrodes are different potential applications of the aerogels but all of these applications are limited by its high cost \([28,30,32,42–44]\).

To conclude, high cost, process-ability issues including difficulty and time-consuming, the large amount of toxic substances involved in their fabrication and inherent fragile feature limit the aerogel applications \([13,12,45]\).

### 2.6. Polymeric foam

Cellular polymers or polymeric foams are one of the widely used thermal insulating materials especially in building applications \([46,47]\). These wide application ranges are due to their superior properties such as low thermal conductivity, low cost, easy handling and installation, and no water absorption \([48–52]\). The most commonly used polymeric foams for thermal insulation purposes, such as EPS and XPS, have low thermal conductivities between 30 and 40 mW.m\(^{-1}\).K\(^{-1}\) \([53]\). These thermal insulating materials will be reviewed in detail in the following sections.

### 3. Comparative analysis

In this section, a multi-criteria decision making (MCDM) analysis is performed. VIP, aerogel, glass wool, EPS, XPS, and PUR are considered as different alternatives for thermal insulation purposes. Thermal conductivity, density, maximum service temperature, compressive strength, specific cost, and required thickness are selected as different criteria.

**Table 1** shows the comparison results for the VIP, the aerogels, the glass wool, and the rock wool from the thermal conductivity \((\lambda)\), the density \((\rho)\), the maximum service temperature \((T\text{max})\), and the compressive strength \((\sigma_c)\) and specific cost and required thickness viewpoints. It should be noted that the thermal conductivity is at 20 °C and dry conditions. One of the most important criteria of the thermal insulating materials is their cost. Their cost is dependent on the required thickness for insulation purposes. Table 1 shows also the specific cost, the cost to area ratio, of VIP, aerogels, glass wool, and rock wool and their required thickness \((L_{\text{req}})\) for an R-value of 10 m².K.W\(^{-1}\). The mean values of the thermal conductivities presented in Table 1 have been used in \(L_{\text{req}}\) calculations. It should be noted that for VIP, its long term thermal conductivity i.e. 8 mW.m\(^{-1}\).K\(^{-1}\) has been considered. Specific cost and required thickness are not independent. However, the required thickness has a significant effect on the building volume occupied by the thermal insulating material. Therefore, they are considered as two different criteria in this section.

**Table 2** presents the properties of EPS, XPS, and PUR foams.

The mean values of the properties are considered for MCDM analysis.

<table>
<thead>
<tr>
<th>Insulating material</th>
<th>(\lambda) (mW.m(^{-1}).K(^{-1}))</th>
<th>(\rho) (kg.m(^{-3}))</th>
<th>(T\text{max}) (°C)</th>
<th>(\sigma_c) (kPa)</th>
<th>Specific cost (€.m(^{-2}))</th>
<th>(L_{\text{req}}) (cm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIP</td>
<td>4.8</td>
<td>65–300</td>
<td>90</td>
<td>45–120</td>
<td>247</td>
<td>7.9</td>
<td>([13,14,15,54–56,57–60])</td>
</tr>
<tr>
<td>Aerogel</td>
<td>4–20</td>
<td>3–350</td>
<td>750</td>
<td>0–5000</td>
<td>547</td>
<td>12.1</td>
<td>([13,16,54,55,57,58,61–63])</td>
</tr>
<tr>
<td>Glass wool</td>
<td>30–46</td>
<td>8–150</td>
<td>500</td>
<td>15–80</td>
<td>43</td>
<td>38.4</td>
<td>([54–56,64–69])</td>
</tr>
<tr>
<td>Rock wool</td>
<td>33–46</td>
<td>13–240</td>
<td>750</td>
<td>15–80</td>
<td>36</td>
<td>40.0</td>
<td>([56,64,65,67–72])</td>
</tr>
</tbody>
</table>

It should be noted that the long-term thermal conductivity of VIP is selected. In this regard, the decision matrix is as Table 3.

Criteria weighting is an important step in MCDM problems. There are several methods to weight different criteria. Some of these methods are based on the data \([77–81]\) and others are according to the designers’ or engineers’ experience and knowledge \([82–86]\). Different scenarios are assumed in the present study related to different conditions. These scenarios are tabulated in Table 4.

In the first scenario, the importance of thermal conductivity is considered slightly higher than other criteria. The other criteria are assumed to have equal weights. This procedure is repeated in the second, the third and the fourth scenarios for maximum working temperature, specific cost and density, respectively. In other words, it is assumed that the working temperature is slightly more important than the other criteria in the second scenario, the specific cost is slightly more important than other criteria in the third scenario while the density is assumed to be slightly more important in the fourth scenario. In scenario V, the weights of thermal conductivity and specific cost are considered as 0.25 and other criteria are assumed with equal weights. In other words, thermal conductivity and specific cost are simultaneously very important in scenario V. Thermal conductivity and density in scenario VI and density and specific cost in scenario VII are considered with a high importance level with the weights of 0.25.

The lowest values of thermal conductivity, density, specific cost, and required thickness are desirable. Therefore, these criteria are non-beneficial or smaller-better criteria. On the other hand, maximum service temperature and compressive strength are beneficial or larger-better criteria.

The alternative ranking is performed for different scenarios using technique for order preferences by similarity to ideal solution (TOPSIS) method.

TOPSIS is an alternative ranking method to select the best alternative that has the shortest and longest distances from the ideal and negative ideal solutions, respectively \([87]\). The steps of TOPSIS method after normalization of the decision matrix using Eq. (1) are as follows \([88–91]\):

\[
N_{ij} = \frac{X_{ij}}{\sqrt{\sum_{i=1}^{n} X_{ij}^2}}
\]

where \(X_{ij}\) indicates the performance value of the \(i\)th alternative to the \(j\)th criterion.

The weighted normalized matrix is obtained using Eq. (2):

\[
v_{ij} = N_{ij}^* w_j
\]

where \(v_{ij}\) is the weighted normalized value, \(N_{ij}\) is the normalized value, and \(w_j\) is the weight of each criterion.

The ideal \((P^+)^{\text{ideal}}\) and negative-ideal \((P^-)^{\text{ideal}}\) solutions are determined as follows:

\[
P^+ = \{v_1^+, \ldots, v_n^+\} = \{(\max, v_1^+)\text{beneficial criteria}, (\min, v_j^+)\text{non – beneficial criteria}\}
\]

\[
P^- = \{v_1^-, \ldots, v_n^-\} = \{(\min, v_1^-)\text{beneficial criteria}, (\max, v_j^-)\text{non – beneficial criteria}\}
\]
that aerogel is ranked the last in other scenarios. In other words, aerogel is in the priority only for some special applications and in other cases, its high density and considerably high specific cost (almost 12 times larger than polymeric foams) impede its applications. Mineral wools including rock wool and glass wool are ranked the next after the polymeric foams. Although they have good maximum service temperature, but their density is relatively high and they have low compressive strength. Their higher specific cost and larger required thickness in comparison with polymeric foams prevent their wide-spread application range. VIP is always ranked the last for different scenarios. They have the lowest values of thermal conductivities among the thermal insulating materials. However, their high specific cost, high density, low compressive strength, and low maximum service temperature significantly hinder its applications. Therefore, it is concluded in overall that polymeric foams are the most promising thermal insulating materials for different applications when considering all scenarios because they are ranked the first in some scenarios and are in the second rank in other scenarios where aerogel is ranked the first.

4. Polymeric foams

Special properties of polymers such as light weight, low cost, and flexibility have increased their usage in manufacturing systems [92]. One of the main needs in the plastic industry is decreasing the material consumption to lead a more cost-efficient production. This need is met by creating a cellular structure in polymers or in other words foaming [93–97]. Together with the weight and cost reduction, foaming enhances the thermal [98–101] and sound [102–106] insulation properties of polymeric parts. Statistically, polymeric foam production contains 19.1 million tons with a worth of 87 billion dollars up to 2018 which has increased to 25.1 million tons in 2019 [107]. Polymeric foams can have different characteristics based on their cell structure. For instance, there are open-cell and closed-cell foams (Fig. S.1. (available in Supplementary Information)) [108]. In closed-cell foams, gas cells are not connected throughout the polymeric matrix while in open-cell foams, the cells are connected all together inside the matrix letting the gas move among cells [109–112].

The structural properties of foams are formulated into two parameters named cell density and cell size. Cell density indicates the frequency of cells inside the polymer by calculating the number of cells in the unit of volume and cell size is the average size of the cells in the foam [113]. Foams are categorized into conventional (cell sizes larger than 100 µm and cell densities smaller than 106 cells/cm3), fine-cell (cell sizes ranging from 10 to 100 µm) and microcellular (cell sizes ranging from 1 to 10 µm and cell densities in the range of 106–109 cells/cm3), and noncellular (cell sizes

Table 2
Properties of EPS, XPS, and PUR foams.

<table>
<thead>
<tr>
<th>Insulating material</th>
<th>λ (mW.m⁻¹.K⁻¹)</th>
<th>ρ (kg.m⁻³)</th>
<th>T_max(°C)</th>
<th>σ_c(kPa)</th>
<th>Specific cost (€.m⁻³)</th>
<th>Lreq(cm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPS</td>
<td>29.41</td>
<td>10-50</td>
<td>80</td>
<td>60-260</td>
<td>32</td>
<td>35.1</td>
<td>[54,56,65,66,71,73,75]</td>
</tr>
<tr>
<td>XPS</td>
<td>25.35</td>
<td>20-80</td>
<td>75</td>
<td>150-700</td>
<td>46</td>
<td>32.8</td>
<td>[54,56,65,66,71,73,75]</td>
</tr>
<tr>
<td>PUR</td>
<td>19.30</td>
<td>25-100</td>
<td>120</td>
<td>100-500</td>
<td>59</td>
<td>24.6</td>
<td>[10,54,56,65,66,72,75,76]</td>
</tr>
</tbody>
</table>

Table 3
Decision matrix for MCDM analysis.

<table>
<thead>
<tr>
<th>Alternatives</th>
<th>Criteria</th>
<th>λ (mW.m⁻¹.K⁻¹)</th>
<th>ρ (kg.m⁻³)</th>
<th>T_max(°C)</th>
<th>σ_c(kPa)</th>
<th>Specific cost (€.m⁻³)</th>
<th>Lreq(cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIP</td>
<td></td>
<td>8</td>
<td>182.5</td>
<td>90</td>
<td>82.5</td>
<td>247</td>
<td>7.9</td>
</tr>
<tr>
<td>Aerogel</td>
<td></td>
<td>12</td>
<td>176.5</td>
<td>750</td>
<td>2500</td>
<td>547</td>
<td>12.1</td>
</tr>
<tr>
<td>Glass wool</td>
<td></td>
<td>38</td>
<td>79</td>
<td>500</td>
<td>47.5</td>
<td>43</td>
<td>38.4</td>
</tr>
<tr>
<td>Rock wool</td>
<td></td>
<td>39.5</td>
<td>126.5</td>
<td>750</td>
<td>47.5</td>
<td>36</td>
<td>40.0</td>
</tr>
<tr>
<td>EPS</td>
<td></td>
<td>35</td>
<td>30</td>
<td>80</td>
<td>160</td>
<td>32</td>
<td>35.1</td>
</tr>
<tr>
<td>XPS</td>
<td></td>
<td>30</td>
<td>50</td>
<td>75</td>
<td>425</td>
<td>46</td>
<td>32.8</td>
</tr>
<tr>
<td>PUR</td>
<td></td>
<td>24.5</td>
<td>62.5</td>
<td>120</td>
<td>300</td>
<td>59</td>
<td>24.6</td>
</tr>
</tbody>
</table>

Eq. (5) and (6) are employed to calculate the distance of each alternative from positive (D⁺) and negative (D⁻) ideal solutions, respectively:

$$D^+_i = \sqrt{\sum_{i=1}^{n} (v_i - v^*_i)^2}$$  \hspace{1cm} (5)

$$D^-_i = \sqrt{\sum_{i=1}^{n} (v_i - v^-_i)^2}$$  \hspace{1cm} (6)

Finally, the closeness coefficient (C) for each alternative is determined as follows:

$$C = \frac{D^-_i}{D^+_i + D^-_i}$$  \hspace{1cm} (7)

The ranking of the alternatives is based on the higher values of C.

It should be noted that the TOPSIS analysis is performed in TOPSIS software. The MCDM analysis in different scenarios was performed using TOPSIS software. The alternative ranking has been presented in Fig. 2. Table 5 indicates the results of the closeness coefficient for different scenarios.

The most valuable results for different scenarios have been summarized in section S.1 (available in Supplementary Information).

To conclude, polymeric foams in some scenarios are ranked the first. Their relatively low thermal conductivity, low density, high compressive strength, and low specific cost are different advantages of polymeric foams. These advantages give them the first rank in most scenarios. In other scenarios, they are ranked the second after aerogel. Aerogel is ranked the first in some scenarios especially when the thermal conductivity is very important. Its considerably high compressive strength and maximum service temperature besides low thermal conductivity are the reasons for this rank of aerogels in some scenarios. It should be noted

Table 4
Different scenarios for criteria weighting of MCDM analysis.

<table>
<thead>
<tr>
<th>Alternatives</th>
<th>Weights</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scenario I</td>
</tr>
<tr>
<td>λ</td>
<td>0.250</td>
</tr>
<tr>
<td>ρ</td>
<td>0.150</td>
</tr>
<tr>
<td>T_max</td>
<td>0.150</td>
</tr>
<tr>
<td>σ_c</td>
<td>0.150</td>
</tr>
<tr>
<td>Specific cost</td>
<td>0.150</td>
</tr>
<tr>
<td>Lreq</td>
<td>0.150</td>
</tr>
</tbody>
</table>
smaller than 1 μm and cell densities larger than $10^{12}$ cells/cm$^3$) with respect to cell size and cell density [114]. For instance, conventional polystyrene (PS) foams had sizes larger than 100 μm [115]. However, due to developments in manufacturing methods such as batch foaming, producing foams with cell sizes smaller than 100 μm became possible in the 1980s [108].

Researchers have attempted to improve the properties of foams using two different strategies, first, enhancing the homogeneity of cell size distribution [116] and second, reduction of cell size [117]. Achieving nano cellular structures with cell sizes smaller than 1 μm activates the Knudsen effect and results in super thermal insulation [118,119].

Another key improvement in nano cellular structures is outstanding

![Alternative ranking of MCDM analysis.](image)

**Table 5**
Closeness coefficient ($C$) of TOPSIS analysis.

<table>
<thead>
<tr>
<th>Material</th>
<th>Scenario I</th>
<th>Material</th>
<th>C</th>
<th>Material</th>
<th>C</th>
<th>Material</th>
<th>C</th>
<th>Material</th>
<th>C</th>
<th>Material</th>
<th>C</th>
<th>Material</th>
<th>C</th>
<th>Material</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerogel</td>
<td>0.5730</td>
<td>Aerogel</td>
<td>0.5960</td>
<td>XPS</td>
<td>0.5739</td>
<td>Aerogel</td>
<td>0.5121</td>
<td>PUR</td>
<td>0.6032</td>
<td>Aerogel</td>
<td>0.5166</td>
<td>XPS</td>
<td>0.6328</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PUR</td>
<td>0.4705</td>
<td>Rock wool</td>
<td>0.5241</td>
<td>PUR</td>
<td>0.5729</td>
<td>XPS</td>
<td>0.5071</td>
<td>XPS</td>
<td>0.5927</td>
<td>PUR</td>
<td>0.5148</td>
<td>PUR</td>
<td>0.6266</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XPS</td>
<td>0.4582</td>
<td>Glass wool</td>
<td>0.4791</td>
<td>Rock wool</td>
<td>0.5671</td>
<td>EPS</td>
<td>0.5016</td>
<td>EPS</td>
<td>0.5714</td>
<td>XPS</td>
<td>0.5079</td>
<td>EPS</td>
<td>0.6247</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rock wool</td>
<td>0.4454</td>
<td>PUR</td>
<td>0.4249</td>
<td>Glass wool</td>
<td>0.5635</td>
<td>PUR</td>
<td>0.5014</td>
<td>Rock wool</td>
<td>0.5672</td>
<td>EPS</td>
<td>0.4973</td>
<td>Glass wool</td>
<td>0.6095</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPS</td>
<td>0.4379</td>
<td>XPS</td>
<td>0.4197</td>
<td>EPS</td>
<td>0.5593</td>
<td>Glass wool</td>
<td>0.4794</td>
<td>Glass wool</td>
<td>0.5669</td>
<td>Glass wool</td>
<td>0.4553</td>
<td>Rock wool</td>
<td>0.5853</td>
<td></td>
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<tr>
<td>Glass wool</td>
<td>0.4358</td>
<td>EPS</td>
<td>0.4133</td>
<td>Aerogel</td>
<td>0.4504</td>
<td>Rock wool</td>
<td>0.4616</td>
<td>VIP</td>
<td>0.4907</td>
<td>Rock wool</td>
<td>0.4238</td>
<td>VIP</td>
<td>0.4107</td>
<td></td>
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</tr>
<tr>
<td>VIP</td>
<td>0.4271</td>
<td>VIP</td>
<td>0.3428</td>
<td>VIP</td>
<td>0.4286</td>
<td>VIP</td>
<td>0.3487</td>
<td>Aerogel</td>
<td>0.4372</td>
<td>VIP</td>
<td>0.4057</td>
<td>Aerogel</td>
<td>0.3859</td>
<td></td>
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</tr>
</tbody>
</table>
Absorption of the gas in the polymer is the first step of the foaming process. Then, reaching a single-phase polymer/gas mixture is necessary, which is achieved mainly through mixing and diffusion using screw rotation or static mixers with proper die resistance in extrusion, through mixing and diffusion while maintaining a high barrel pressure with proper gas injection control in injection molding, or by enough gas-diffusion time in the batch foaming process. In the next step, by applying a thermodynamic instability through temperature rise and/or pressure drop, cell nucleation occurs. The generated cells grow larger resulting in expanded foams [125]. Finally, the grown cells need to be stabilized inside the polymer matrix. Different process and material parameters affect the foaming procedure, hence choosing the parameter levels is important. Fig. 3 shows the schematic of the foaming process.

The main processes used for foam making are batch, extrusion, and injection molding.

### 4.1. Batch foaming process

This foaming method can be performed in two different ways called one-step and two-step batch foaming processes. In one-step batch foaming, the sample is placed in a heated chamber filled with high-pressure gas which leads to diffusion of gas into the polymer, and then, by a sudden decrease of the pressure of the chamber to atmosphere pressure, cell nucleation occurs in the sample due to the thermodynamic instability. In the two-step method, the sample is first saturated with high-pressure gas inside a chamber with lower temperatures. After completion of diffusion, the samples are drenched in a high-temperature bath, letting the cells nucleate and consequently grow, and finally, the foam is cooled in water or other liquids to make the cells stable. The schematic of this process is demonstrated in Fig. 4. The bath temperature (i.e., the foaming temperature) and the soaking time (i.e., the foaming time) of the samples are two important parameters in the batch process.

### 4.2. Extrusion foaming process

The extrusion foaming method is implemented using both physical and chemical blowing agents. In the physical extrusion foaming, the gas is directly injected into the molten polymer. The shear forces inside the extrusion cylinder make a uniform solution of polymer and gas under a high pressure created by the high resistance of the die lip; in the extrusion die the pressure drop leads to cell nucleation and growth. The stabilization of cells is performed by cooling the polymeric foam either by water or air [126–128]. The physical extrusion foaming is depicted in Fig. 5. In the chemical extrusion foaming process, the polymer and chemical blowing agent are mixed in specified percentages. The mixture is heated inside the extrusion barrel which leads to the melting of polymer and later, at a specified temperature, the chemical blowing agent is decomposed to release gas inside the molten polymer. After the dissolution of gas inside the polymer, the thermodynamic instability caused by the pressure drop in the die exit leads to the expansion of the foam. In chemical foaming, temperature adjustment is of high importance, because it controls the decomposition of the blowing agent and prevents the agglomeration of these particles in the polymeric foam, which is undesirable [125].

### 4.3. Foam injection molding (FIM) process

This foaming method is categorized as high-pressure foam injection molding (HPFIM) and low-pressure foam injection molding (LPFIM) [129,130]. In the LPFIM method, schematically shown in Fig. S.2 (available in Supplementary Information), the shot size is considered smaller than the cavity capacity normally 65–80% of it. After injection of the polymer/gas mixture inside the mold cavity, the foam expansion occurs due to pressure drop, filling the empty part of the cavity [131]. However, the foams obtained in the LPFIM process may have larger cell sizes due to cell coalescence occurring along the long aspect ratio cavity channel, and therefore the mechanical properties are somehow sacrificed [132–134]. Also, the cell density of these foams is in general between 10 to 10³ cells/cm³ including a non-uniform structure [133]. This is why HPFIM is suggested for engineering applications.

In the HPFIM method, a uniform cell structure is achievable because of the expansion in the thickness direction and this uniform structure is the advantage of HPFIM compared to LPFIM. However, without mold opening, the expansion of the foam is limited in this method and is equal to the shrinkage of the polymeric part. HPFIM is preferred when the dimensional accuracy of the parts is important. The schematic of this method is demonstrated in Fig. S.3 (available in Supplementary Information).

As discussed earlier, a more desirable cellular structure is obtained in the HPFIM method; however, a high expansion ratio is not easily achievable. Different former studies attest to this. Peinado et al. [135] and Pantani et al. [136] studied the HPFIM process for polylactic acid (PLA). The maximum reported expansion ratio was limited. Therefore, some solutions were considered to overcome this disadvantage. One of these solutions is to use mold-opening technology [137–140]. The first stages of mold-opening foaming are identical to HPFIM, premature cells
nucleate at the gate, they collapse and the gas is dissolved in the melt again. In this step, the mold opens in the thickness direction, causing a meaningful pressure drop rate, and also providing space for foam expansion. Hence, a highly expanded, uniform foam structure is obtained. A schematic of this process is depicted in Fig. S.4 (available in Supplementary Information).

The main achievements in the field of polymeric foams fabricated by batch, extrusion and injection molding processes are discussed in Sections S.2, S.3. and S.4. (available in Supplementary Information) covering references [141–182].

5. Theoretical background

In this section, a theoretical model is developed to predict the overall thermal conductivity based on the foam density and the cell size. In the following, the developed model is validated against the experimental results.

5.1. Modeling

The overall thermal conductivity of polymeric foams ($\lambda_t$) consists of four different mechanisms including the thermal conductivity by convection within the cells ($\lambda_c$), the thermal conductivity through the solid phase ($\lambda_s$), the thermal conductivity through the gaseous phase ($\lambda_r$), and the thermal conductivity by radiation ($\lambda_r$). Different studies have shown that the thermal conductivity by convection within the cells can be neglected in microcellular polymeric foams [183,184]. Therefore [185]:

$$\lambda_t = \lambda_c + \lambda_s + \lambda_r$$  

Different models have been presented in the literature to predict the thermal conductivity of the polymeric foams. Two different cases have been considered: i) uniform cell size distribution and ii) non-uniform cell size distribution. In most cases, the models have been developed for the uniform cell size distribution and an average cell size has been considered [119,186]. Yaling He and co-workers [30,187–192] developed desirable models for predicting the thermal conductivity of silica aerogels in both micro- and nano-scales. They studied theoretically and numerically the thermal conductivity of silica aerogel composites containing different particles and fibers [187,188]. They proposed a fractal-intersecting sphere model for the nano-porous silica aerogel and a Roselland approximation and a mixing model for micro-porous silica aerogel [187]. A coupled structure reconstruction and numerical method was utilized to predict the thermal conductivity of silica aerogel composite [188]. The structure reconstruction problem was solved using random-number-based algorithms. The radiative transfer and the energy equations were solved using discrete ordinate and finite volume methods, respectively.

Several models have been developed for bimodal structures to accommodate the non-uniform cell size distribution [193,194]. Gong et al. [193] developed advanced bimodal PS/MWCNT nanocomposite foams with a superior thermal insulation performance. The radiative thermal conductivity was significantly decreased by adding MWCNT because of its high infrared absorption capability. They also developed a theoretical model to predict the thermal conductivity of the bimodal nanocomposite foams. They used the thermal resistance equations to predict the thermal conductivities through the solid and gas phases. The thermal conductivity by radiation was predicted using Rosseland theory. Bernardo et al. [194] developed a novel model to predict the thermal conductivity due to the solid and gas conduction of bimodal nanocellular PMMA foams with micro and nanometric cell sizes.

In this section, a theoretical model is developed to predict the thermal conductivity of polymeric foam with a uniform cell size distribution by considering an average cell size.

5.1.1. Thermal conductivity through solid phase

The thermal conductivity through the solid phase is calculated as follows [195]:

$$\lambda_s = (1 - \varepsilon) \cdot \left( \frac{2}{3} \cdot \varepsilon \right) \cdot \lambda_s'$$  

where $\lambda_s'$ is the thermal conductivity of the solid polymer and $\varepsilon$ is the void fraction of polymeric foam and is defined as follows:

$$\varepsilon = 1 - \frac{\rho_F}{\rho_P}$$  

where $\rho_F$ and $\rho_P$ are the foam density and polymer density, respectively. $f_c$ is the strut fraction of the polymeric foams and is expressed as follows:

$$f_c = \frac{V_{struts}}{V_{struts} + V_{walls}}$$  

where $V_{struts}$ and $V_{walls}$ are the volumetric fraction of struts and walls, respectively. Two different structural models including Placido [196] and Kaemmerlen [197] are utilized to calculate the $V_{struts}$ and $V_{walls}$. These quantities are calculated in the Placido model as follows [196]:

$$V_{struts} = \frac{\varepsilon}{0.348\rho_F^2\phi_c - 2.8\rho_F^2\phi_r + 3.93\rho_F^2}$$  

$$V_{walls} = \frac{1.3143\rho_F^2 - 7.367\rho_F\phi_r + 10.323\rho_F^2}{\phi_c}$$  

where $\phi_c$ and $\phi_r$ are the strut size and cell size, respectively.

The relationship between the structural properties is presented by the Placido model as follows [196]:

$$d_w = \frac{\frac{x_c}{2}}{\frac{\rho_F^2}{1.3143\rho_F^2 - 7.367\rho_F\phi_r + 10.323\rho_F^2} + \frac{4.639\rho_F}{1.3143\rho_F^2 - 7.367\rho_F\phi_r + 10.323\rho_F^2}}$$  

where $d_w$ is the cell wall thickness. $V_{struts}$ and $V_{walls}$ are defined in the Kaemmerlen model as follows [197]:

$$V_{struts} = \frac{2.805\rho_F^2\phi_r}{\frac{4.639\rho_F}{1.3143\rho_F^2 - 7.367\rho_F\phi_r + 10.323\rho_F^2}}$$  

$$V_{walls} = \frac{1.317\rho_F^2 - 13.4284\rho_F\phi_r + 34.2374\rho_F^2}{\phi_c}$$

Eq. (10) shows the relationship between the structural properties based on the Kaemmerlen model [197]:

$$d_w = \frac{-x_2 + \sqrt{x_2^2 - 4x_1x_3}}{2x_1}$$  

where:

$$x_1 = 4.639\phi_r - 17.976\phi_c$$  

$$x_2 = 1.317\phi_r - 13.4284\phi_r + 34.2374\phi_r^2$$  

$$x_3 = 2.805\phi_r\phi_r^2 - 0.549\frac{\rho_F}{\rho_P} \cdot \phi_c$$  

It should be noted that in both models, cells are considered like regular pentagonal dodecahedrons and walls are considered like thin platelets. The struts are supposed to have a circular cross-section with an area equivalent to the strut cross-sectional one. The strut and wall thicknesses are neglected with respect to the cell diameter in the Placido model while they are considered in the Kaemmerlen model.

Expansion ratio ($\phi$) is defined as the ratio of the foam volume ($V_F$) to the solid polymer volume ($V_P$). The foam volume consists of solid polymer volume and gaseous phase volume ($V_c$). Therefore:
\[ \frac{V_g}{V_P} = \frac{V_g + V_P}{V_P} \]  

(21)

The expansion ratio is calculated as Eq. (22) by neglecting the mass of the gaseous phase in comparison with the mass of polymer phase:

\[ \varphi = \frac{\rho_P}{\rho_P} \]  

(22)

Eq. (21) can be rewritten for a unit of polymer volume as Eq. (23):

\[ V_p = \varphi - 1 \]  

(23)

The cell nucleation density of polymeric foams is defined as follows:

\[ N = \frac{n_i}{\varphi} \]  

(24)

where \( N \) is the cell nucleation density and \( n_i \) is the cell number in an area equal to \( A \).

The gas volume can be calculated by multiplying the cell number with a volume of a cell. This quantity is obtained for a cell shape of cubical \( (\varphi_c(V_{c1})) \) and spherical with a diameter length of \( \varphi_c(V_{c2}) \) as Eqs. (25) and (26), respectively:

\[ V_{c1} = N \cdot \varphi_c^3 \]  

(25)

\[ V_{c2} = N \cdot \frac{\pi}{6} \varphi_c^3 \]  

(26)

Therefore, the cell size can be extracted for cubical \( (\varphi_{c1}) \) and spherical \( (\varphi_{c2}) \) cell shapes as follows:

\[ \varphi_{c1} = \left[ \frac{V_C}{N} \right]^{\frac{1}{3}} \]  

(27)

\[ \varphi_{c2} = \left[ V_C \cdot \frac{6}{\pi N} \right]^{\frac{1}{3}} \]  

(28)

By replacing Eq. (23) in Eqs. (27) and (28), the following equations are extracted:

\[ \varphi_{c1} = \left[ \frac{\varphi - 1}{N} \right]^{\frac{1}{3}} \]  

(29)

\[ \varphi_{c2} = \left[ \frac{\varphi - 1}{6N} \right]^{\frac{1}{3}} \]  

(30)

The difference between Eqs. (29) and (30) is \( \left[ \frac{2}{3} \right]^{\frac{1}{3}} \) which has a value equal to 1.241. Therefore, the cell nucleation density could be considered as Eq. (31), regardless of the cell shape:

\[ N = \frac{6(\varphi - 1)}{\pi \varphi_c^2} \]  

(31)

By considering a cell shape with a cell size of \( \varphi_c \) and a cell wall thickness of \( d_w \), the expansion ratio can be re-written as follows:

\[ \varphi = \left( \frac{\varphi_c + d_w}{\varphi_c + d_w} \right)^{\frac{3}{2}} \]  

(32)

By replacing Eq. (31) in Eq. (32):

\[ d_w = \left( \frac{\varphi}{\varphi - 1} - 1 \right) \left( \frac{\varphi - 1}{N} \right)^{\frac{1}{3}} \]  

(33)

Mathematical description of solution methodology is as following:

- Calculation of expansion ratio (Eq. (10))
- Calculation of cell density (Eq. (31))
- Calculation of cell wall thickness (Eq. (33))
- Calculation of strut diameter (Eqs. (14) or (17))

It is noteworthy that the structural model of Placido (Eq. (14)) is in order of three respects to \( \varphi_c \) but has one acceptable root. Also the structural model of Kaemmerlen (Eq. (17)) is in order of two respects to \( \varphi_c \) and has two acceptable roots. Therefore, the thermal conductivity through the solid phase is obtained through three roots including the Placido model’s root, the first Kaemmerlen model’s root, and the second Kaemmerlen model’s root. These three thermal conductivities through the solid phase are named \( \lambda_{f1}, \lambda_{f2}, \) and \( \lambda_{f3} \), respectively.

### 5.1.2. Thermal conductivity through gaseous phase

The thermal conductivity through the gaseous phase is calculated as follows [198]:

\[ \lambda_{g} = \frac{\varepsilon}{1 + 2\beta \delta_{Kn}} \cdot j'_{g} \]  

(34)

where \( j'_{g} \) is the thermal conductivity of the gas equipped the cells which is 0.026 W/m.K for air at ambient conditions. \( \beta \) is the efficiency of the energy transfer between gas molecules and cell walls and is equal to 2 for polymeric foams [193,198]. \( \delta_{Kn} \) is the Knudsen number and is expressed as follows:

\[ \delta_{Kn} = \frac{l_{mean}}{\varphi_c} \]  

(35)

where \( l_{mean} \) is the mean free path of gas molecules equipped the cells. Value of \( l_{mean} \) for air at ambient conditions is equal to \( 7 \times 10^{-8} \) m.

### 5.1.3. Thermal conductivity by radiation

A fundamental type of heat transfer is heat transfer by radiation taking place with and without any intervening medium. This type of heat transfer is dependent on the thermal emission wavelength. An ideal surface for radiation is called blackbody. All the incident radiation regardless of direction and wavelength is absorbed by a blackbody. A blackbody also emits the most energy compared to other surfaces at all temperatures and wavelengths [199]. According to this concept, the emissivity of any surface at a temperature is defined as the ratio of its emitted radiation to the emitted radiation by a blackbody at that temperature. Classical radiative transfer between two media accounts for scattering, absorption, and transmission. The radiative heat flux \( (q') \) between two plates at distance of \( d \) from each other is as follows [199]:

\[ q' = \frac{\sigma(T_1^4 - T_2^4)}{\frac{1}{4} + \frac{3}{4} - 1} \]  

(36)

where \( \sigma \) is the Stefan-Boltzmann constant and is equal to \( 5.67 \times 10^{-8} \) W m\(^{-2}\)K\(^{-4}\). \( T_1 \) and \( T_2 \) are the temperatures of the plates with the emissivities of \( \varepsilon_1 \) and \( \varepsilon_2 \), respectively. For two blackbodies, \( \varepsilon_1 = \varepsilon_2 = 1, q' = \sigma(T_1^4 - T_2^4) \). One of the fundamental assumptions of the Planck’s law is the larger distance between two bodies, \( d \), and their dimensions than the wavelength of the thermal radiation [200]. Therefore, this concept for blackbody radiation is only valid in heat transfer radiation of two medium with dimensions and localizing in a distance larger than the thermal radiation wavelength [199]. This concept is called far-field radiation. In the other hand, when the distance between two mediums or their dimensions is decreased and becomes comparable with or shorter than the thermal radiation wavelength, the near-field effect becomes vital [199,200].

Despite the good development of the near-field theory to describe the nanoscale radiation [199–204], this has not been effectively used for the...
nano cellular foams. A recent publication [205] is the first one attempted to introduce the near-field theory to the nano cellular foams with solid cell walls for the closed cell foams. The modeling was verified only for limited points of cell size and the foam density because of the difficulties unites in making the largely expanded low density nano-cellular foams.

It was proved that the radiation of blackbody is no longer valid for nanoscale radiation according to Rytov’s fluctuational electrodynamics incorporated with the theorem of the fluctuation dissipation [206]. Planck’s law, despite the well description of spectral energy distribution of the radiation of blackbody, is limited for cases where the distance between the mediums and their sizes are smaller than the wavelength of thermal radiation [207]. In this case, the contribution of the radiative energy transfer can increase considerably by evanescent waves tunneling and propagating waves interference between the gaps [203,208–210]. Since this near-field thermal radiation is significant in tunneling and propagating waves interference between the mediums and their sizes are smaller than the wavelength of the thermal radiation [207]. In this case, the contribution of the radiative energy transfer can increase considerably by evanescent waves tunneling and propagating waves interference between the gaps [207].

The effective thermal conductivity by radiation for blackbody is calculated as follows [195,205]:

\[
\lambda_r = \frac{16\pi^2\sigma T^3}{3k_B} \tag{37}
\]

where \(n\) is the effective index of refraction and is close to 1 for polymeric foams and \(T_r\) is the mean temperature (300 K at ambient conditions). \(K_R\) is the Rosseland mean extinction coefficient of the polymeric foam and demonstrates the radiative energy attenuation. \(K_R\) is a harmonic mean of \(K_s\), the spectral extinction coefficient as follows [211]:

\[
\frac{1}{K_R} = \int_0^\infty \frac{\hat{\xi}_s(\lambda, T) d\lambda}{\hat{\xi}_s(\lambda, T) d\lambda} \tag{38}
\]

where \(\hat{\xi}_s(\lambda, T)\) is the spectral distribution of blackbody Planck’s law and is calculated as follows [119,211]:

\[
\hat{\xi}_s(\lambda, T) = \frac{\partial e_{\lambda,T}}{\partial T} = \frac{A_1}{2\lambda^2 \exp\left(\frac{\lambda}{\lambda_s} - 1\right)} \tag{39}
\]

where \(e_{\lambda,T}\) is the spectral intensity of blackbody at a wavelength of \(\lambda\). \(A_1\) and \(A_2\) are auxiliary constant and are calculated as follows [212,213]:

\[
A_1 = \frac{2\pi hc^2}{k_B} \tag{40}
\]

\[
A_2 = \frac{hc}{k_B} \tag{41}
\]

where \(c\) is the light speed, \(h\) is the Planck constant, and \(k_B\) is the Boltzmann constant. Their values are as follows [212,213]:

\[
h = 6.62607015 \times 10^{-34} \text{ J s}
\]

\[
c = 2.99792458 \times 10^8 \text{ m s}^{-1}
\]

\[
k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}
\]

The spectral extinction coefficient, \(K_s\), can be calculated using \(f_s\), the strut fraction of the polymeric foams, as a weighted factor as follows [197,214,215]:

\[
K_s = f_s K_{s,strut} + (1 - f_s) K_{s,wall} \tag{42}
\]

where \(K_{s,strut}\) and \(K_{s,wall}\) are, respectively, the spectral extinction coefficients related to struts and walls. The details of calculating \(K_{s,strut}\) and \(K_{s,wall}\) are available in [205] for microcellular and nanocellular polymeric foams based on the scattering and absorption by cell walls and struts.

Propagating and evanescent modes based on Rytov’s fluctuational electrodynamics should be considered in the radiative energy transport to enhance the reliability and the accuracy of the modeling.

The effective thermal conductivity by radiation of microcellular and nanocellular polymeric foams, \(\lambda^{eff}_r\), can be calculated by multiplying \(\lambda_r\) with \(\psi\), a correction factor, as follows [205]:

\[
\lambda^{eff}_r = \psi \lambda_r \tag{43}
\]

where \(\psi\) is the deviation of the energy transfer by radiative based on fluctuational electrodynamics from that based on blackbody radiation and can be obtained as follows [205]:

\[
\psi = \frac{G^{eff}_r}{G_r} = \frac{h^{eff}_r}{h_r} \tag{44}
\]

where \(G_r\) and \(h_r\) are the radiative heat conductance and the radiative thermal transfer coefficient based on blackbody radiation. \(G^{eff}_r\) and \(h^{eff}_r\) are the effective radiative heat conductance and the effective radiative thermal transfer coefficient based on fluctuational electrodynamics. The radiative heat conductance is determined as the ratio of the thermal conductivity by radiation to the length of heat transfer, \(d\), as follows [205]:

\[
G_r = \frac{\lambda_r}{d} \tag{45}
\]

\[
G^{eff}_r = \frac{\lambda^{eff}_r}{d} \tag{46}
\]

The radiative thermal transfer coefficient is defined as the ratio of the total heat flux to the infinitesimal temperature differential as follows [205]:

\[
h_r = \lim_{\Delta T \to 0} \frac{q_r}{\Delta T} \tag{47}
\]

\[
h^{eff}_r = \lim_{\Delta T \to 0} \frac{q^{eff}_r}{\Delta T} \tag{48}
\]

where \(q_r\) and \(q^{eff}_r\) are, respectively, the total heat flux based on blackbody radiation and the effective total heat flux based on fluctuational electrodynamics.

\[
q_r = \sigma T^4 \tag{49}
\]

\[
h_r = 4\sigma T^3 \tag{50}
\]

All of the dimensions involved in thermal radiation including the dimensions of the mediums and their distance are assumed to be much longer than the temperature-dependent thermal wavelength in Planck’s law. The temperature-dependent thermal wavelength, \(\lambda_T\), is determined as follows [203,209]:

\[
\lambda_T = \frac{hc}{k_B T} \tag{49}
\]

By replacing the values of \(h\), \(c\), and \(k_B\) and at the temperature of 300 K, \(\lambda_T\) is obtained about 8 µm. Therefore, the model based on the Planck’s law unable to delineate the heat transfer by radiation when the separation gap is smaller than the wavelength of thermal radiation, i.e. for nanocellular polymeric foams. The details about the evanescent and propagating modes are available in [205].

However, producing largely-expanded nanocellular foams is not available with the current state of foam processing technology. Therefore, the range of the cell size was considered larger than 20 µm in the present study and the assumptions of the Planck’s law are valid. As a consequence, \(K_R\), the Rosseland mean extinction coefficient, can be calculated as follows [217]:

\[
K_R = K_{s,strut} + K_{s,wall} \tag{50}
\]

where \(K_{s,strut}\) and \(K_{s,wall}\) are the extinction coefficients due to the struts and walls, respectively. \(K_{s,wall}\) is the extinction coefficient of the solid poly-
mer. 

\[ K_{\text{mean}} = 4.10 \frac{\sqrt{\frac{L}{d}}}{\rho_\text{c}} \]  

(51)

\[ K_{\text{wall}} = (1 - f_r) \frac{\rho_F}{\rho_P} \]  

(52)

5.2. Model validation

The overall thermal conductivity is obtained through three roots including the Placido model’s root, the first Kaemmerlen model’s root, and the second Kaemmerlen model’s root. These three overall thermal conductivities are named \( \lambda_{1,PF} \), \( \lambda_{1,K1} \), and \( \lambda_{1,K2} \), respectively.

In this section, comparison between the theoretical and experimental results of the thermal conductivity is performed to validate the theoretical model. The reported experimental results collected in Table 6 are used to verify the presented model of section 5. It should be noted that to ensure the validation procedure, one foam from ref. [197], three foams from ref. [217], six foams from ref. [218], ten foams from ref. [219], and one foam from ref. [220] are selected.

Fig. 6 shows the experimental and theoretical results. \( \lambda_{1,K1} \) presents the best prediction in comparison to the other roots almost in all cases, as the results indicated.

The prediction errors of the all roots are tabulated in Table S.1 (available in Supplementary Information).

The results demonstrate that the mean prediction errors of \( \lambda_{1,PF} \), \( \lambda_{1,K1} \), and \( \lambda_{1,K2} \) are 14.32%, 4.65%, and 19.52%, respectively. This result illustrates that \( \lambda_{1,K1} \) can estimate the overall thermal conductivity of polymeric foams with an error smaller than 5% which is significantly a minor error.

In order to quantitatively comparison between the performances of the model’s roots, the root mean square (RMS) parameter is used as Eq. (40).

\[
\text{RMS} = \sqrt{\frac{\sum (\text{Experiment}_i - \text{Model}_i)^2}{M}}  
\]

(40)

where \( M \) is the number of the nodes. The smaller the RMS is, the better the performance is.

The results of RMS parameter are presented in Table 7. \( \lambda_{1,K1} \) with the smallest RMS of 2.142 is the best model to predict the overall thermal conductivity. Therefore, this model is used in the following to obtain the desired results.

6. Experimental achievements

Table 8 summarizes some of the most recent experimental achievements in the field of thermal insulation performance of polymeric foams. Arduini-Schuster et al. [220] examined the thermal conductivity of the XPS foams produced by the extrusion foaming technology with a high expansion ratio about 36 and a cell size of 200 \( \mu \text{m} \). They showed that these foams had a considerably low thermal conductivity as 33.1 mW.m\(^{-1}\).K\(^{-1}\). They also indicated that the PUR foams produced by reactive foaming process with the expansion ratio of about 33 and the cell size of 200 \( \mu \text{m} \) had a thermal conductivity as low as 26.7 mW.m\(^{-1}\).K\(^{-1}\).

Ameli et al. [221] showed that the thermal conductivity of the solid PLA samples (250 mW.m\(^{-1}\).K\(^{-1}\)) was reduced to 150 mW.m\(^{-1}\).K\(^{-1}\) by regular foam injection molding in expansion ratios of about 1.43. They achieved the thermal conductivity of 90 mW.m\(^{-1}\).K\(^{-1}\) by further enhancement of the expansion ratio to 2.86 using the foam injection molding process equipped by mold-opening technology. Gong et al. [198] produced the PS foams using the batch foaming process with and without MWCNTs as the additives. They concluded that the foaming process could reduce the thermal conductivity of pristine PS from 185 mW.m\(^{-1}\).K\(^{-1}\) to 38.6 mW.m\(^{-1}\).K\(^{-1}\) in a cell size of 5 \( \mu \text{m} \) and an expansion ratio of 17. As a very valuable result, they showed that the radiations with the wavelengths smaller than the cell size (i.e. 5 \( \mu \text{m} \)) were completely blocked by the cellular morphology but the radiations with larger wavelengths were transmitted through the foams. Accordingly, they added MWCNTs as a very effective black body to absorb the thermal radiation. As a consequence, they achieved the thermal conductivities as low as 32.8 mW.m\(^{-1}\).K\(^{-1}\) in PS foams with a large expansion ratio (18-fold), a microcellular cell size (5 \( \mu \text{m} \)) and 1 wt% of MWCNTs.

Notario et al. [222] performed an experimental investigation to validate the Knudsen effect in nanocellular PMMA foams. They produced the PMMA foams with a wide cellular range using the batch foaming process. They showed that the thermal conductivity of neat PMMA was reduced from 215 mW.m\(^{-1}\).K\(^{-1}\) to 107.2 mW.m\(^{-1}\).K\(^{-1}\) using foaming process with a cell size of 820 nm and an expansion ratio of 2.08. They indicated that the addition of 5 wt% of block copolymer poly (methyl methacrylate)-co-poly(butyl acrylate)-co-poly(methyl metha- crylate) (MAM) decreased the cell size from 820 nm to 235 nm and
increased the expansion ratio from 2.08 to 2.33. As a consequence, the thermal conductivity was reduced from 107.2 mW.m$^{-1}$K$^{-1}$ to 92.5 mW.m$^{-1}$K$^{-1}$. They revealed that the thermal conductivity of nanocellular polymeric foams was smaller than that of the microcellular polymeric foams at the same expansion ratio.

Wang et al. [223] produced the PMMA foams with the batch foaming process with a relatively high expansion ratios and small cell sizes. They showed that producing the PMMA foams with a cell size of 445.9 µm and an expansion ratio of 21 reduced the thermal conductivity of PMMA foams at a same expansion ratio.

Table 8
Experimental achievements in the field of thermal-insulation polymeric foams in recent years.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Processing method</th>
<th>Polymeric matrix</th>
<th>Additive</th>
<th>Cell size (µm)</th>
<th>Expansion ratio</th>
<th>Thermal conductivity (mW.m$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ameli et al. [221]</td>
<td>Foam injection molding</td>
<td>PLA</td>
<td>–</td>
<td>–</td>
<td>1.43</td>
<td>150</td>
</tr>
<tr>
<td>Ameli et al. [221]</td>
<td>Foam injection molding equipped by mold-opening</td>
<td>PLA</td>
<td>–</td>
<td>–</td>
<td>2.86</td>
<td>90</td>
</tr>
<tr>
<td>Arduini-Schuster et al. [220]</td>
<td>Extrusion foaming process</td>
<td>XPS</td>
<td>–</td>
<td>200</td>
<td>35.94</td>
<td>33.1</td>
</tr>
<tr>
<td>Arduini-Schuster et al. [220]</td>
<td>Reactive foaming process</td>
<td>PUR</td>
<td>–</td>
<td>200</td>
<td>32.89</td>
<td>26.7</td>
</tr>
<tr>
<td>Lorusso et al. [225]</td>
<td>Batch foaming process</td>
<td>PS</td>
<td>–</td>
<td>5</td>
<td>17</td>
<td>38.6</td>
</tr>
<tr>
<td>Wang et al. [224]</td>
<td>Batch foaming process</td>
<td>PS</td>
<td>1 wt% MWCNT</td>
<td>5</td>
<td>18</td>
<td>32.8</td>
</tr>
<tr>
<td>Notario et al. [222]</td>
<td>Batch foaming process</td>
<td>PMMA</td>
<td>5 wt% MAM</td>
<td>0.235</td>
<td>2.33</td>
<td>92.5</td>
</tr>
<tr>
<td>Wang et al. [223]</td>
<td>Batch foaming process</td>
<td>PMMA</td>
<td>–</td>
<td>445.9</td>
<td>21</td>
<td>37.32</td>
</tr>
<tr>
<td>Wang et al. [223]</td>
<td>Batch foaming process</td>
<td>PMMA</td>
<td>–</td>
<td>5.4</td>
<td>21</td>
<td>35.86</td>
</tr>
<tr>
<td>Wang et al. [224]</td>
<td>Batch foaming process</td>
<td>PMMA</td>
<td>1 wt% TPU</td>
<td>0.205</td>
<td>8</td>
<td>24.8</td>
</tr>
<tr>
<td>Lorusso et al. [225]</td>
<td>Reactive foaming process</td>
<td>PUR</td>
<td>–</td>
<td>400</td>
<td>–</td>
<td>25.4</td>
</tr>
<tr>
<td>Lorusso et al. [225]</td>
<td>Reactive foaming process</td>
<td>PUR</td>
<td>4 wt% TiO2 nanoparticles</td>
<td>375</td>
<td>–</td>
<td>24.4</td>
</tr>
<tr>
<td>Lorusso et al. [225]</td>
<td>Reactive foaming process</td>
<td>PUR</td>
<td>8 wt% halloysite clay nanotubes</td>
<td>285</td>
<td>–</td>
<td>23.8</td>
</tr>
<tr>
<td>Gong et al. [193]</td>
<td>Batch foaming process</td>
<td>PS</td>
<td>1 wt% MWCNT</td>
<td>5.8</td>
<td>28</td>
<td>30.2</td>
</tr>
<tr>
<td>Zhao et al. [226]</td>
<td>Foam injection molding equipped by mold-opening</td>
<td>LPP</td>
<td>–</td>
<td>–</td>
<td>7</td>
<td>73</td>
</tr>
<tr>
<td>Zhao et al. [226]</td>
<td>Foam injection molding equipped by mold-opening</td>
<td>LPP</td>
<td>–</td>
<td>–</td>
<td>10</td>
<td>60</td>
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<tr>
<td>Zhao et al. [226]</td>
<td>Foam injection molding equipped by mold-opening</td>
<td>LPP</td>
<td>5 wt% nano PTFE</td>
<td>–</td>
<td>7</td>
<td>54.5</td>
</tr>
<tr>
<td>Zhao et al. [178]</td>
<td>Foam injection molding equipped by mold-opening</td>
<td>LPP</td>
<td>5 wt% nano PTFE</td>
<td>–</td>
<td>18</td>
<td>36.5</td>
</tr>
<tr>
<td>Zhao et al. [178]</td>
<td>Foam injection molding equipped by mold-opening</td>
<td>BPP</td>
<td>–</td>
<td>–</td>
<td>8</td>
<td>62</td>
</tr>
<tr>
<td>Zhao et al. [178]</td>
<td>Foam injection molding equipped by mold-opening</td>
<td>BPP</td>
<td>1 wt% nano PTFE</td>
<td>–</td>
<td>25</td>
<td>32.4</td>
</tr>
<tr>
<td>Wang et al. [227]</td>
<td>Foam injection molding equipped by mold-opening</td>
<td>PEBA</td>
<td>–</td>
<td>–</td>
<td>11</td>
<td>38</td>
</tr>
<tr>
<td>Wang et al. [228]</td>
<td>Foam injection molding equipped by mold-opening</td>
<td>HIPS</td>
<td>–</td>
<td>–</td>
<td>3.5</td>
<td>60.4</td>
</tr>
<tr>
<td>Hou et al. [229]</td>
<td>Batch foaming process</td>
<td>LPP</td>
<td>–</td>
<td>–</td>
<td>45</td>
<td>37.2</td>
</tr>
</tbody>
</table>

using batch foaming process for thermal-insulation applications. They produced PS foams containing 1 wt% MWCNT with an expansion ratio of 28 and a bimodal cellular structure having secondary cells with a size of 5.8 µm. These foams showed a considerably low thermal conductivity as low as 30.2 mW.m$^{-1}$K$^{-1}$.

Zhao et al. [226] produced the LPP foams using the foam injection molding equipped by mold-opening with and without nano PTFE. They used different mold-opening distances to achieve various expansion ratios. The thermal conductivity of the solid LPP was 231 mW.m$^{-1}$K$^{-1}$. This value was reduced to 73 mW.m$^{-1}$K$^{-1}$ in the LPP foams with the expansion ratio of 7. Since the foaming ability of the LPP is low, the highest achievable expansion ratio in the neat LPP was 10. The thermal conductivity in this case was 60 mW.m$^{-1}$K$^{-1}$. The thermal conductivity of the LPP foams containing the nano PTFE with the expansion ratio of 7 was reduced to 54.5 mW.m$^{-1}$K$^{-1}$. As can be seen, the thermal conductivity was decreased by the addition of the nano PTFE even in the same expansion ratio. This reduction was due to the decrement of the cell size in the presence of the nano PTFE. The foaming ability of the LPP was enhanced by adding the nano PTFE and therefore, the most obtainable expansion ratio was improved to 18. In this case, the thermal conductivity was reduced to 36.5 mW.m$^{-1}$K$^{-1}$.  

Zhao et al. [178] studied the thermal insulation performance of BPP foams fabricated by foam injection molding equipped by mold-opening. They produced the BPP foams with an expansion ratio of 8 and observed that the thermal conductivity was reduced from 229 mW.m$^{-1}$K$^{-1}$ (in the case of solid BPP) to 62 mW.m$^{-1}$K$^{-1}$ (in the case of the BPP foam). They showed that the thermal conductivity was reduced to 32.4 mW.m$^{-1}$K$^{-1}$ by addition of 1 wt% nano PTFE and increment of the expansion ratio to 25. They observed that the thermal conductivity of the BPP/
PTFE foam was smaller than that of the BPP foams even at a same expansion ratio due to the better cellular structure. Wang et al. [227] indicated that the thermal conductivity of the PBEA was reduced from 185 mW.m\(^{-1}\).K\(^{-1}\) to 38 mW.m\(^{-1}\).K\(^{-1}\) using the foam injection molding process equipped by mold-opening and production of the PBEA foams with an expansion ratio of 11.

Wang et al. [228] showed that the thermal conductivity of the HIPS was reduced from 172 mW.m\(^{-1}\).K\(^{-1}\) to 60.4 mW.m\(^{-1}\).K\(^{-1}\) using the foam injection molding process equipped by mold-opening and obtaining the foams with an expansion ratio of 3.5. Hou et al. [229] investigated the thermal insulation performance of the LPP foams fabricated by the batch foaming process. The thermal conductivity of the solid LPP was 256.8 mW.m\(^{-1}\).K\(^{-1}\). They produced the LPP foams with a high expansion ratio of 45. The thermal conductivity of these LPP foams was as low as 37.2 mW.m\(^{-1}\).K\(^{-1}\).

7. Conclusions, summary, and future perspectives

It is necessary to enhance the thermal insulation performance of buildings because of the need for reducing the greenhouse gas emission and potential effect of improving energy efficiency. Cork, cellulose, glass wool, rock wool, vacuum insulation panels (VIPs), aerogels and polymeric foams are some of the potential candidates for thermal insulation materials. Low thermal conductivity, low density, low cost, high compressive strength, easy handling and installation and no water absorption make the polymeric foams a promising thermal insulation material with a bright outlook. In this manuscript, a comprehensive review was conducted on the thermal insulation performance of the polymeric foams.

Multi-criteria decision making (MCDM) analysis showed that the polymeric foams were the most promising thermal insulation materials for different applications. Aerogel is in the priority only for some special applications especially when the thermal conductivity is very important. In other cases, its high density and considerable high specific cost (almost 12 times larger than polymeric foams) impede its applications. Although mineral wools are in the next ranks after the polymeric foams, their higher specific cost and larger required thickness in comparison with the polymeric foams prevent their widespread application range. Also, they have relatively high density and low compressive strength. VIPs have the lowest values of the thermal conductivities among the thermal insulation materials. However, their high specific cost, high density, low compressive strength, and low maximum service temperature significantly impede their applications and give the last ranks to VIP. Therefore, polymeric foams are the most promising thermal insulating materials for different applications.

The overall thermal conductivity of polymeric foams is decreased by reducing the cell size due to the reduction of the thermal conductivity through the gaseous phase (\(\lambda_g\)) and the thermal conductivity by radiation (\(\lambda_r\)). There is an optimum foam density to achieve the lowest thermal conductivity at all cell sizes. The overall thermal conductivity is affected by \(\lambda_g\) at high foam densities and is reduced by decreasing the foam density because the reduction of \(\lambda_g\). On the other hand, \(\lambda_g\) and \(\lambda_r\) are dominant heat transfer mechanisms at low foam densities. In this case, the overall thermal conductivity is increased because the increment \(\lambda_g\) and \(\lambda_r\).

Polymeric foams are promising candidates for thermal insulation applications with a bright outlook due to their unique properties. However, reducing the flammability of polymeric foams is an essential criterion for construction industry applications. The addition of the flame retardants is necessary for petroleum-based polymeric foams. However, the flame retardants commonly used for polymeric foams have undesirable environmental and health effects. Recent studies have shown that the nano-sized materials such as clays and graphenoids improve the fire retardancy performance of polymeric foams. Polymeric nanocomposite foams are promising class of thermal-insulation materials with excellent thermal insulation performance, desirable fire retardant, and good mechanical properties for future applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijepes.2023.101808.

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