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PhD in ENGINEERING, EARTH AND PLANETARY SCIENCES

INNOVATIVE MATERIALS FOR THERMAL INSULATION OF BUILDINGS

Based of polymer composites

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Abstract

The demand for sustainable and energy-efficient materials in the construction sector has driven rapid advancements in modern technology, paving the way for innovative solutions to meet environmental challenges. Renewable bio-based materials are emerging technologies within the construction industry, providing inventive solutions for reducing material waste and the carbon footprint of an inherently carbon-intensive sector. This thesis explores the potential of sustainable and environmentally friendly composites for thermal insulation, using poly(lactic acid) (PLA) or poly(urethane) foam (PUF) as matrices, and fillers like silica aerogel (SA), crushed eggshells (ES), and cork powder (CO). The composites were analyzed for their mechanical, thermal, and spectroscopic properties. The findings revealed that PUF was unsuitable due to fast hardening, excessive rigidity, and poor filler dispersion. In contrast, PLA showed promise as a matrix due to its ease of processing, enabling the creation of both extruded composites and spray-deposited slurries. Composites with SA provided the best thermal insulation, achieving thermal conductivities as low as 0.036 W/m.K. CO-based composites performed reasonably well, with thermal conductivities as low as 0.049 W/m.K, while ES-based composites showed lower performance in thermal insulation. Although the addition of fillers slightly reduced the mechanical robustness of the PLA matrix, the changes were not significant. The study suggests that PLA composites with SA or CO represent viable options for sustainable thermal insulation in applications such as building materials, given their biodegradability, recyclability, and cost-effectiveness.

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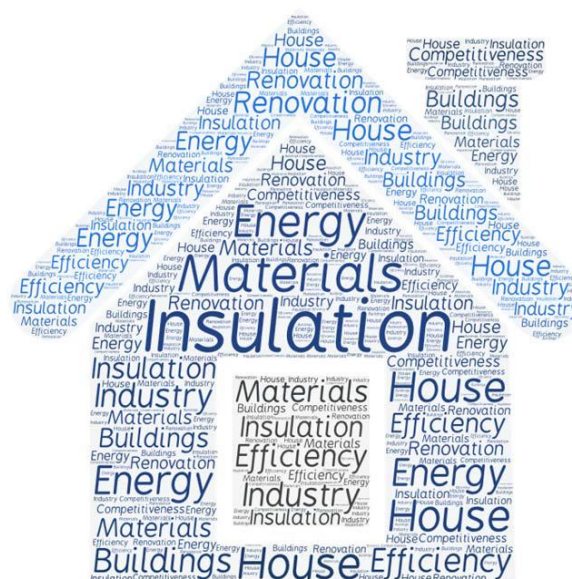
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Preface

Significant advancements in thermal insulation are emerging worldwide, driven by the growing demand for energy-efficient buildings. Among the myriad of materials explored, polymer-based solutions have emerged as a cornerstone in modern construction, offering versatility, adaptability, and enhanced performance.

This thesis is focused on exploring the potential of polymer-based innovative materials for thermal insulation used in buildings, particularly Polyurethane and Polylactic acid (PLA), which insulation properties can be improved using environmental-friendly fillers like SA, ES, and CO. In the initial phase, investigations and studies were conducted to identify composite insulation materials holding promises under the points of view of easy availability, economic viability and environmental sustainability. Then, after selecting the materials and creating appropriate samples for tests, the materials have been characterized with respect to their main mechanical, functional and thermal insulation properties. The obtained results have been analyzed and evaluated, to identify strengths and weaknesses of the proposed approaches in the fabrication and formulation of the composites, and conclusions have been drawn to provide general guidelines for the formulation of environmentally sustainable, thermally insulating composites. The project was carried out during my doctoral study, between January 2022 and December 2024.

Mohsen Afshani



1. INTRODUCTION

In recent decades, energy saving has become a strategic global goal aimed at protecting the environment and conserving natural resources. Heating and cooling buildings is one of the major sources of energy consumption in many countries. Consequently, reducing this class of energy consumption has become a pressing issue. In more detail, in developed countries the energy consumption in buildings has reached approximately the 40% of total end-use energy, where nearly half of it is used for heating and cooling [1]. The energy consumption in the European Union (EU) in 2014 reached the lowest value over the 27-year period from 1990 to 2016. 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) shown in **Fig.1**. Transportation segment with consumption of 33.15% 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.

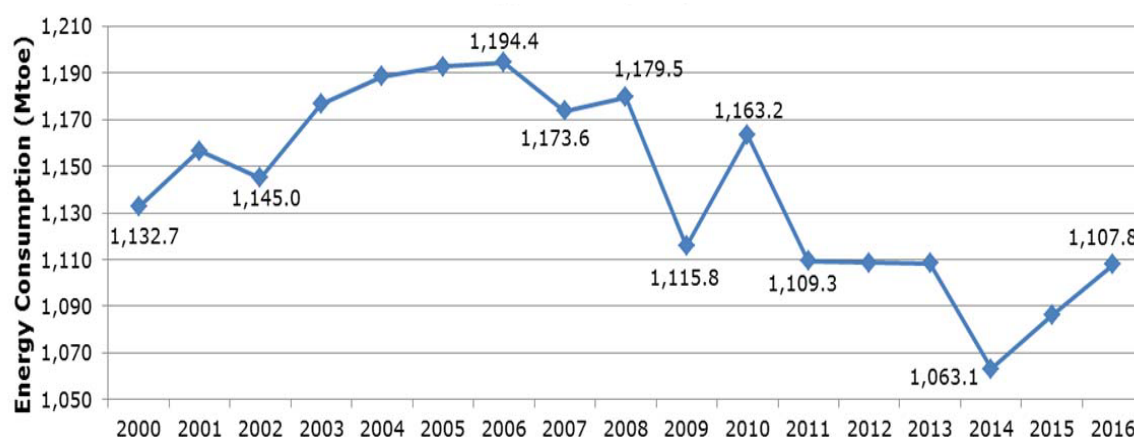


Figure 1. Final Energy Consumption in the EU-28 (2000-2016) [2]

According to the IEA report in 2022 [3], 34% of global energy consumption accounts for building operations [4], of which around 20% includes the energy consumption by electricity and heat and around 10% relates to direct energy consumption of the building [5].

Thermal insulation is undoubtedly one of the best ways to reduce the energy consumption due to both winter heating and summer cooling. Insulation materials play an important role in this scenario since the selection of the correct material, its thickness and its position, allow to obtain good indoor thermal comfort conditions and adequate energy savings. Specifically, combination of natural and architectural elements, such as insulation materials, shading

devices, optimal orientation, and the incorporation of thermal mass in the building structure, diminish the energy consumed for cooling and heating purposes in buildings [6, 7]. Thermal insulation consists of materials or combinations of materials that, when applied correctly, effectively impede heat flow through conduction, convection, and radiation. Selecting appropriate insulation materials and techniques is essential to ensure optimal performance, also in view of other functional requirements of buildings, like sound insulation, resistance to fire, water vapor permeability and impact on the environment and on human health.

On the other hand, improving the thermal insulation of the building envelope (floors, walls, roofs and so on) represents one of the most effective solutions for the reduction of the final energy consumption, for both new and already existing buildings. The insulation facilitates energy efficiency both in the civil sector and in the industrial one, as for example food cold storage, refrigeration, and petroleum and liquefied natural gas pipelines.

According to the Joint Research Centre (JRC) of the European Commission [8], the global thermal insulation market accounted for USD 22.73 billion in 2015 and is expected to rise to USD 38.69 billion by 2027. The European Union has the largest thermal insulation market, followed by North America, as mentioned in **Fig.2**.

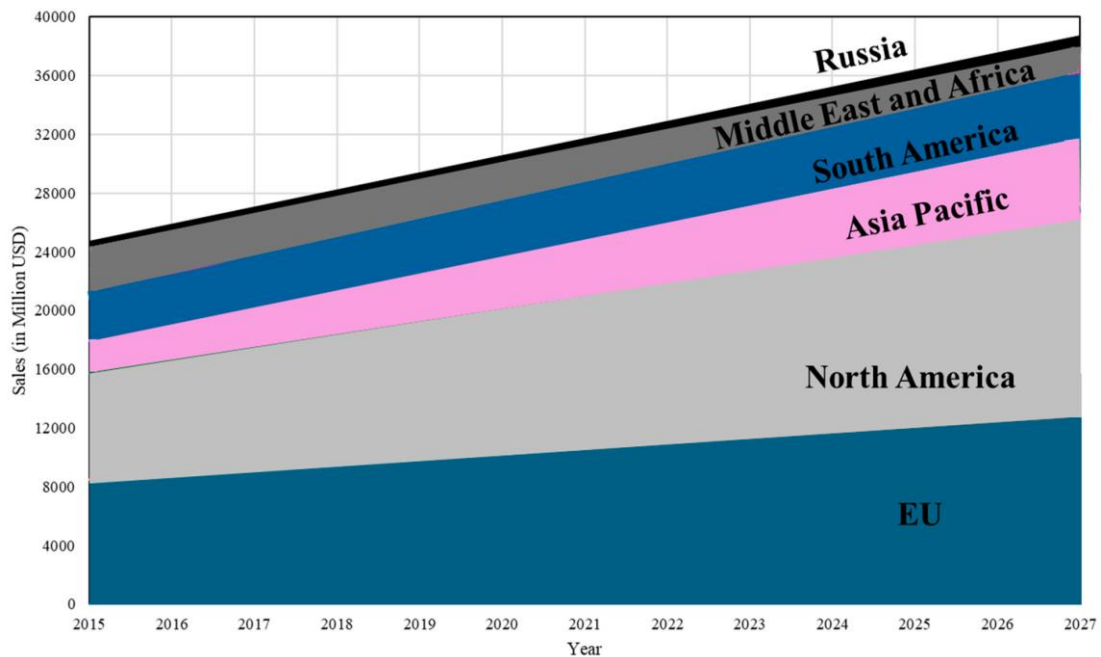


Figure 2. Global thermal insulation market forecast from 2015 to 2027 [8]

Building insulations can be made of a material or composite material with a high thermal resistance and can reduce the heat flow rate. Due to advancements in research, various materials, such as fiberglass, cellulose, mineral wool, aerogel, polystyrene, and foam, already

reached the implementation stage [9-11]. On the other hands, properly selecting insulation material depends on various aspects, including the surrounding environment, cost, availability, and insulation goals. For example, a newly developed insulation material such as aerogel has lower thermal conductivity of close to 0.02 W/m.K, is lightweight, fire resistant, and has sufficient strength. However, its high cost (~ 8 US $\$/\text{cm}^3$ [12]) may limit its uses for some regions where other suitable and low-cost alternatives can serve the purpose [13].

Under another point of view, waste products for building insulation play an important role in achieving sustainability in building materials [14]. Waste materials such as recycled textiles, paper, and glass wool can be repurposed to develop eco-friendly and cost-effective insulation materials with improved thermal performance, contributing to waste reduction and resource conservation [15, 16]. Furthermore, repurposing waste into insulation materials not only improves thermal properties but also promotes sustainability and reduces environmental impact.

Among various insulating materials, inorganic fibrous materials such as glass wool and stone wool accounted for 56% of the thermal insulation market in Europe in 2022, and foamy organic materials (expanded and extruded polystyrene and Polyurethane) for a further 34%, as shown in **Fig.3** [17]. The market share of renewable insulations, in Europe, is still small in comparison to conventional ones, reaching 2% in 2022.

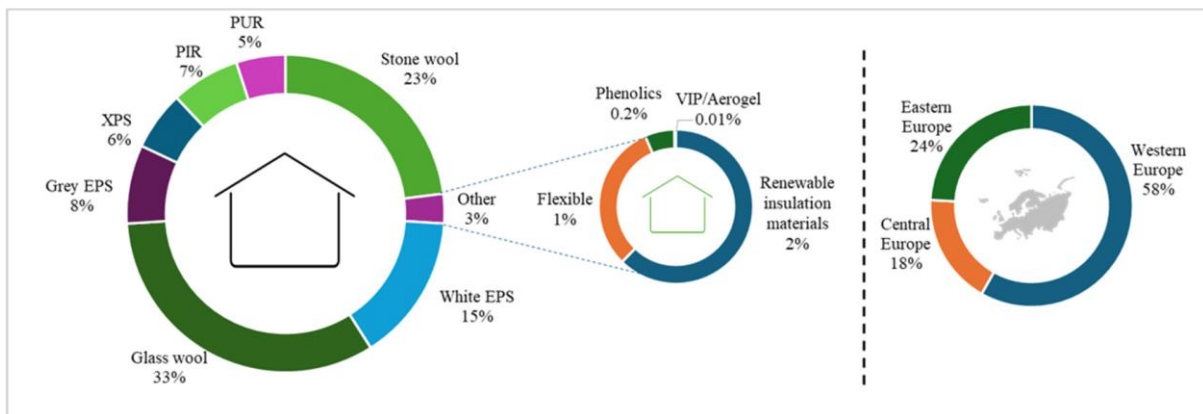


Figure 3: European thermal insulation market in 2022 (European thermal insulation market by product per m^3 , and by region-2022) [18]

1.1 Thermal Insulation Materials - Overview

The main characteristic of insulating materials is their thermal conductivity (k , measured in W/m.K), which is defined as “the rate of heat flow through a unit thickness of material over a unit area, with a unit difference in temperature” [19, 20]. This means that the lower the thermal conductivity, the better the thermal insulation of the material. Current insulation materials used in construction industry are generally polymer-based, such as polystyrene and polyurethane foam; they have a high performance in thermal insulation and a low heat flow (polystyrene-made box gave a heat flow rate of 4.46W), but the environmental impacts in their production processes are significant, because many of the most common building materials are not-renewable, and the related raw material supplies are finite and cannot be replenished. However, material producers and builders often use conventional or traditional, less energy-efficient techniques or old-fashioned, highly polluting equipment.

All insulation materials for building applications are classified into organic and inorganic categories, shown in **Fig.4**, each offering distinct thermal properties. Inorganic materials can be divided in traditional materials and new innovative materials. Organic materials are also separated into two groups, i.e. petrochemical and natural, renewable materials [21-23].

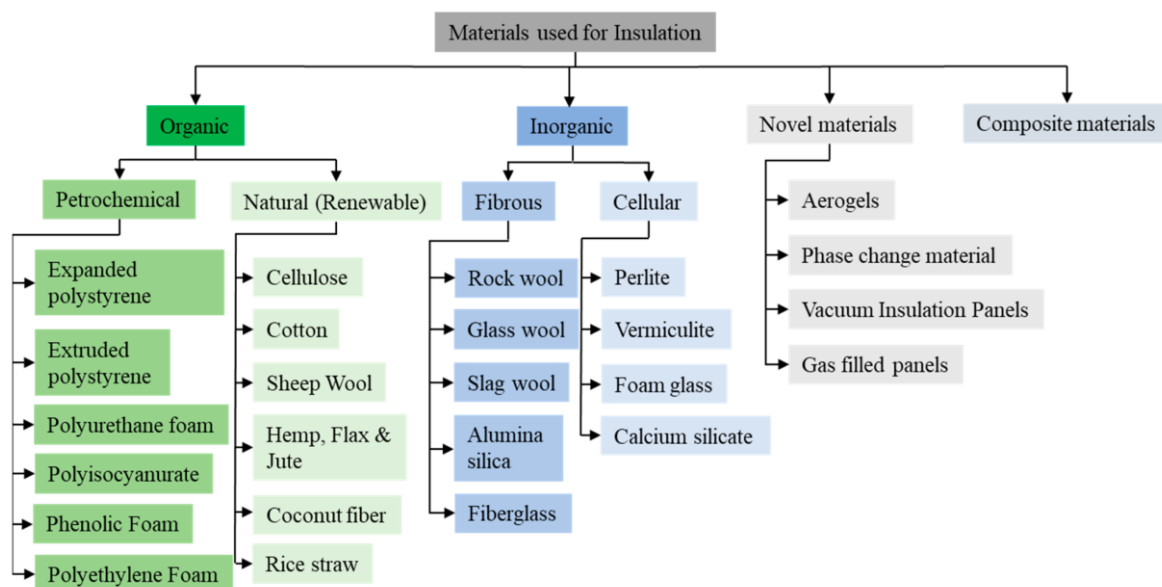


Figure 4. Classification of thermal insulation materials [21, 22, 24, 25]

Nevertheless, according to the literature [26, 27], around 60–65% of the insulation materials in the market worldwide are inorganic-based (mineral wool), around 21-27% are organic-based materials, and the remaining account for new and composite materials, as mentioned in **Fig.5**.

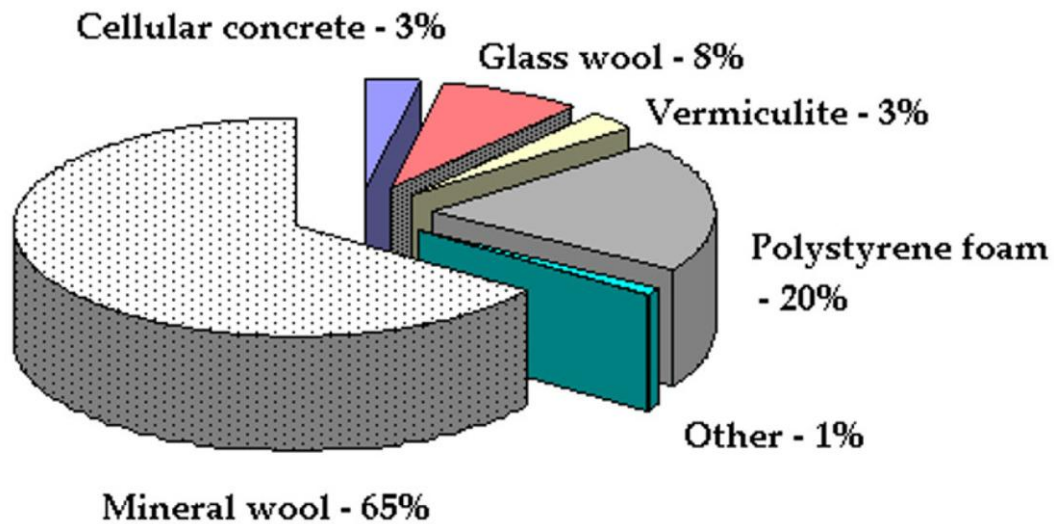


Figure 5. World market of insulation materials.

To study and investigate insulation materials, it is necessary to know some technical terms for thermal properties. Some of them are briefly explained here:

- *k value*: Thermal conductivity, also known as Lambda (denoted by the Greek symbol λ) or k , is the measure of how easily heat flows through a specific type of material, independent of the thickness of the material in question. The lower the thermal conductivity of a material, the better the thermal performance (i.e. the slower heat will move across a material). It is measured in Watts per Meter Kelvin (W/m.K).
- *R-Values*: The insulating material's resistance or R-value refers to the ability of insulation material to resist heat flow through a given thickness of material. It is calculated by dividing the thickness of the material in meters by its thermal conductivity in W/m.K, and it is measured in meters squared Kelvin per Watt ($\text{m}^2\text{K/W}$) [28]. Insulation with higher R-values is better for thermal performance. For example, 50 mm thick polystyrene and 80 mm thick glass wool both have similar R-values (approximately 1.5).
- *U-Values*: Thermal transmittance, also known as U-value, is the heat flow rate divided by the area and temperature difference in the surroundings of both sides of a system at a steady state, and is a concept utilized to define the insulation properties for building materials [29]. The lower the U-value, the better insulated the building element is. In its simplest form, the U-value of a single material is the inverse of the R-Value ($U=1/R$). It is measured in units of $\text{W/m}^2\text{K}$ (Watts per meter squared Kelvin).

The thermal conductivity k is an intrinsic property of materials, and it influenced by temperature, aging, and moisture accumulation. A general overview of the thermal insulation properties of selected building materials is given in Table 1. Among the thermal properties of insulation materials, k is considered the most critical, as it directly impacts the R-value and U-Value. Other thermal properties, such as specific heat capacity (c) and density (ρ), become significant under transient conditions.

Table 1. Properties of some common insulation materials [21]

Insulation Material	ρ [kg/m ³]	k [w/m.K]	C [J/kgk]	Approximate cost [€/m ³]
Inorganic				
Glass Wool	15–75	0.030–0.040	1000	77.5-147
Rock Wool	40–200	0.030–0.040	1000	102.08-179.5
Calcium Silicate	200–240	0.059–0.065	1000	95-285
Foam Glass	100–200	0.038–0.055	1000	357.38-445.5
Silica Aerogel	3-500	0.012 – 0.02	1800	8 US \$/cm ³
Perlite	80–150	0.040–0.060	800	207.89
Vermiculite	30–150	0.040–0.064	900	152.6
PETROCHEMICAL				
Expanded Polystyrene	10–35	0.032–0.045	1250	61.42-186.56
Extruded Polystyrene	32–40	0.025–0.040	1700	156-180
Phenol Formaldehyde	160–40	0.020–0.021	1190	302.63
Polyurethane	15–45	0.022–0.035	1400	303.78
Polyisocyanurate	30–45	0.020–0.035	1450	250.12-286.59
Urea Formaldehyde	15	0.045	1200	400
RENEWABLE				
Cellulose (Paper Wool)	30–80	0.038–0.040	1300	175.71
Coconut	70–120	0.040–0.045	1670	482
Flax (Flax Wool)	20–100	0.035–0.040	1600	116.77
HEMP (HEMP WOOL)	30–82	0.038–0.040	1700	108.07-138.93
RECYCLED COTTON	25–45	0.039–0.044	1600	138
Sheep wool	10–25	0.035–0.045	2100	200
Wood wool	55–140	0.038–0.058	2100	190-236.44
EXPANDED CORK	100–170	0.037–0.043	1700	155.98-319.14

However, when placed in the building envelope, thermal insulation materials can be exposed to significant ambient temperature and humidity variations depending on the prevailing climatic conditions. Ignoring the temperature dependency of these material properties can result in under and over estimations of buildings energy uses and of the corresponding equipment sizing. Table 2 summarizes the values of thermal conductivity of some insulation materials measured at different mean temperatures, apart from the room temperature (22 °C), the k -value was measured at elevated temperatures of 35, 50 and 65 °C.

Table 2. Thermal conductivity value of insulation materials measured at different temperatures [30]

Material	ρ [kg/m ³]	Temperature [°C]			
		k [W/m.K]			
		22	35	50	65
Molded Polystyrene	19	0.0355 ± 0.0003	0.0385 ± 0.0006	0.0402 ± 0.0002	0.0423 ± 0.0004
	38	0.0330 ± 0.0002	0.0343 ± 0.0002	0.0382 ± 0.0013	0.0404 ± 0.0006
Extruded Polystyrene	34	0.0312 ± 0.0006	0.0324 ± 0.0009	0.0340 ± 0.0002	0.0352 ± 0.0006
Injected Polystyrene	34	0.0332 ± 0.0002	0.0358 ± 0.0004	0.0380 ± 0.0002	0.0387 ± 0.0005
Polyurethane Board	28	0.0244 ± 0.0000	0.0286 ± 0.0002	0.0305 ± 0.0006	0.0320 ± 0.0002
	33	0.0220 ± 0.0004	0.0266 ± 0.0003	0.0291 ± 0.0001	0.0298 ± 0.0006

In order to improve conventional thermal insulation materials, innovative options such as agricultural and industrial wastes, as well as natural fibers, are increasingly studied as green insulation materials. These alternatives are eco-friendly and cost-effective compared to conventional oil-based materials, and their end-of-life cycle does not pose significant problems. Other benefits include relatively extended periods of indoor thermal comfort, a higher specific heat capacity, acoustic insulation capabilities, fire protection (when properly prepared), etc. These materials will lead to more energy-efficient systems compared to conventional materials [31].

A comprehensive review conducted by Hasanzadeh et al. [32] highlights that the low thermal conductivity, low density, low cost, high compressive strength, ease of handling and installation, and resistance to water absorption make polymeric foams a promising material for thermal insulation with a bright future. In this context, materials such as cork, cellulose, glass wool, rock wool, vacuum insulation panels (VIPs), aerogels, and polymeric foams have been investigated as potential candidates for thermal insulation applications. Based on the results of the Multi-Criteria Decision Making (MCDM) analysis, they found that; *I*) the polymeric foams were the most promising thermal insulating materials for different applications. *II*) Aerogel (0.013-0.02 W/m.K) is in the priority only for some special applications especially when the thermal conductivity is very important. In other cases, its low density and considerable high specific cost (almost 12 times larger than polymeric foams) impede its applications. *III*) Although mineral wools (0.03-0.05 W/m.K) are in the next ranks after the polymeric foams, but 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. *IV*) VIPs have the lowest values of the thermal conductivities among

the thermal insulating materials (0.004 W/m.K). However, their high specific cost, low density, low compressive strength, and low maximum service temperature significantly impede their applications and give the last ranks to VIP. V) Polymeric foams (0.03-0.04 W/m.K) are the most promising thermal insulating materials for different applications.

The limited availability of landfill space, limits for greenhouse gas emissions and waste-stream runoff have prompted the search for alternative solutions to conventional waste management methods, and this applies also for thermally insulating materials. In the review article by Abu-Jdayil et al. [33], was conducted an intensive literature survey, up to 2019, on different types of thermal insulation materials, methods of manufacturing, and characteristics. Their focus was on the need to create insulating materials that had excellent properties while being environmentally friendly and relatively cost-effective. The researchers have found that currently there exist no optimum thermal building insulation material which satisfies at the same time the needed requirements with respect to the most essential properties, like low thermal conductivity, mechanical resistance, environment and human health safety, and low cost. Therefore, due to the technological advancements in the field, more attention should be paid to develop suitable insulators to meet all requirements.

In this regard, considerable attention has been devoted to research on the development of thermal insulation and building materials using renewable resources and waste materials. Bayada et al [34] found that, potentially, plant-based by-product and/or industrial waste insulation is an affordable and sustainable alternative to conventional materials, with properties comparable to those of traditional materials, offering several advantages, amongst which:

- Natural materials, agricultural and/or industrial waste as insulating materials can be readily recycled at the end of the building's life cycle, which does not require much energy or labor, and the recycled material can be used in other applications, such as packaging, mixing it with cement to allow it to become lighter, etc. The most important consideration is that the environmental impact of discarded waste is less than that of other building materials.
- These materials are often biodegradable; in this case they can be used to produce bioenergy or as biofertilizer for plants to improve their growth and/or in agriculture, providing in this case advantages like improvement of the performance of cultivated soils, especially by amelioring air renewal and moisture control.

1.2 Inorganic-Based Insulation

Inorganic insulation materials are obtained from non-renewable sources, deriving from several different resources, categorized into cellular and fibrous materials. In this section, various commonly used inorganic-based materials will be discussed.

1.2.1 Fibrous Insulation Materials

Mineral wool is the most used inorganic type of material for buildings, made from rock, glass, and slag wool. These materials are sourced from cullet, quartz sand, diabase, and basalt [35-37]. They are available commercially in batt and board forms. The denser and more rigid mineral wool boards are typically used for floors, walls, and roofs, while the lighter, softer mineral wool batts are preferred for use in framed structures and various other applications [24]. The production of mineral wool insulators is energy-intensive, requiring temperatures of up to 1400 °C to transform borosilicate glass into glass fibers, and 1500 °C to melt rock for rock wool. **Fig.6** illustrates the production process and post-consumption recycling of mineral wool.

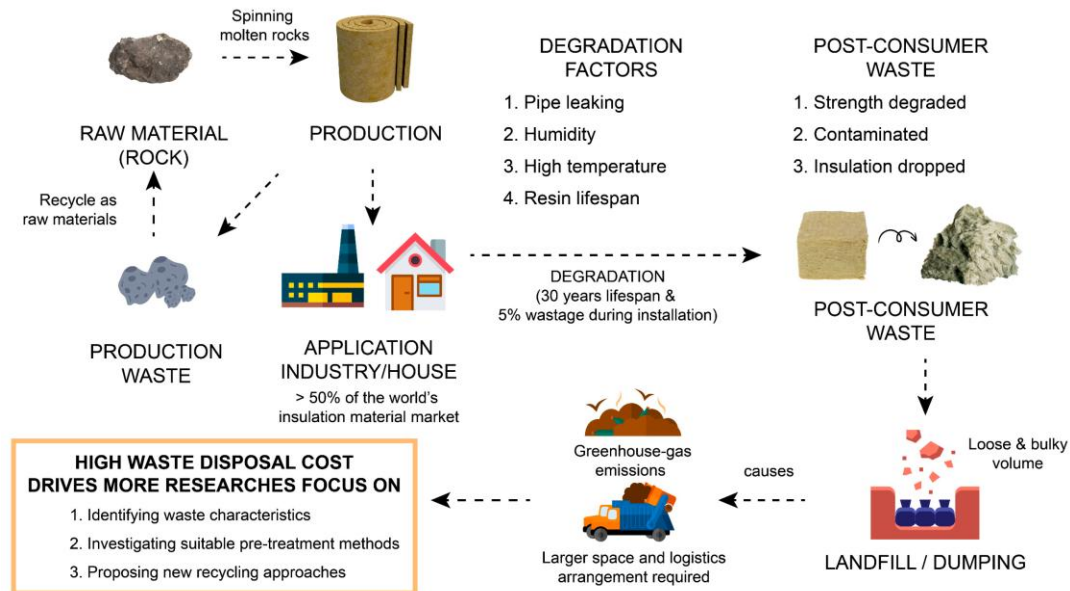


Figure 6. Production process of the mineral wool and its post-consumption recycling [38].

Mineral wool outperforms other insulation materials, such as fiberglass batts, boasting a notably higher R-value per inch, typically ranging from 22% to 37% greater efficiency. Moreover, it exhibits a stronger environmental profile with 70% recycled content, making it a

more sustainable choice than fiberglass, with 20% to 30% recycled material. Mineral wool also maintains its structural integrity better than fiberglass or cellulose, mitigating the risk of settling within wall cavities and the subsequent creation of cold spots along the top plate. Furthermore, its resistance to air infiltration ensures that moisture does not compromise its thermal efficacy, and its composition does not support the growth of microorganisms [3, 39]. Nagy et al. [40] measured the thermal conductivity of mineral wool in the range of 0.01–0.5 W/m.K using a guarded hot plate instrument. To enhance thermal performance and other characteristics, phenolic resins and dust abatement oils are used to bind the rock and glass fibers together [41].

Fiberglass, composed of ultrafine glass fibers with diameters ranging from 0.5 to 3 μm , is a versatile inorganic fibrous insulation material for both panels and building applications. Its good thermal insulation (about 0.030 – 0.043 W/m.K with a density value between 8.5 – 40 kg/m^3) attributes arise from the minimal diameters of the glass fibers [42]. Cozzarini et al. [43] utilized recycled fiberglass waste to fabricate novel composite insulation material with appealing thermal and acoustic properties. This novel material shows an open porous structure, with density between 170 and 320 kg/m^3 , thermal conductivities between 0.035 and 0.065 W/m.K, a noise-reducing factor of 0.25–0.45 and compressive strengths as high as 0.3 MPa, making it an interesting candidate for applications which require a good combination of low weight, thermal/acoustic insulation and a minimal amount of mechanical strength. The developed composite material was also found to be beneficial regarding sustainability and cost-effectiveness.

1.2.2 Inorganic Cellular Insulation Materials

Cellular inorganic materials like perlite, vermiculite, calcium silicate, and foam glass (shown in Fig.3) are less commonly used for building thermal insulation compared to mineral wool, due to their limited market availability. However, expanded perlite is occasionally employed as an insulation material in certain cases.[44, 45]. Inorganic cellular insulation materials (include perlite, vermiculite, calcium silicate, tuff, expanded clay and foam glass) are primarily composed of chalk, sand, cellulose fibers, cullet, dolomite, as well as oxides such as aluminum and silicon, and magnesium-aluminum silicate.

Perlite, an acidic extrusive rock, can be rapidly heated to temperatures ranging from 900 to 1200 °C, producing expanded perlite characterized by low density and thermal conductivity [44]. However, the fabrication process of expanded perlite entails substantial energy consumption [46], and its exploitation or smashing process gives rise to significant

environmental pollution and the generation of substantial amounts of perlite tailings. Vaou et al. [47] investigated a novel thermal insulation material derived from perlite tailings, demonstrating exceptional performance characterized by remarkably low thermal conductivity value of 0.03 W/m.K, and high compressive strength of 0.78 MPa. The development of this innovative thermal insulation material employed a pioneering technique similar to the geopolymer preparation process, involving the activation of perlite tailings through NaOH + H₂O₂. The proposed method holds significant promise, as it not only utilizes perlite tailings as raw material, mitigating environmental concerns associated with expanded perlite production, but also exhibits energy-saving attributes.

Foamed insulating materials possess low thermal conductivity owing to their high porosity. While this porosity enhances their thermal insulation capabilities, it also reduces their mechanical strength, and it increases their hygroscopic properties [33]. **Fig.7** shows that the thermal conductivities of these inorganic thermal insulation materials can vary in the range 0.12–0.0375 W/m.K.

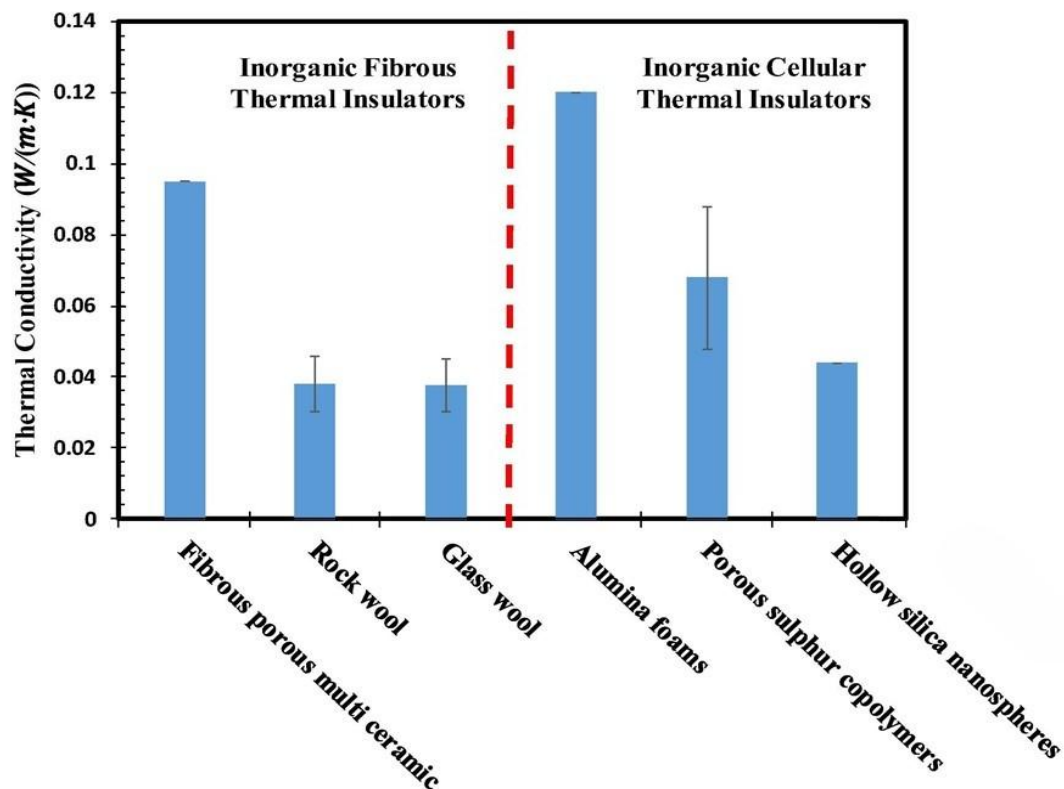


Figure 7. Thermal conductivity of common inorganic thermal insulators.[33]

Gao et al.[48] developed an innovative foamy insulation material using perlite tailings. This new insulation comprises perlite, sodium silicate, hydrogen peroxide (H₂O₂),

cetyltrimethylammonium bromide, and rock wool shown in **Fig.8**. The resulting foamy insulator is not only lighter than other inorganic materials but also exhibits low thermal conductivity and comparatively high mechanical strength. Specifically, in detail, the density of the produced sample ranged from 0.181 to 0.244 g/cm³, the thermal conductivity values varying between 0.051 and 0.056 W/m.K, the compressive strength of 0.39 MPa, and flexural strength ranged from 0.57 to 0.83 MPa.

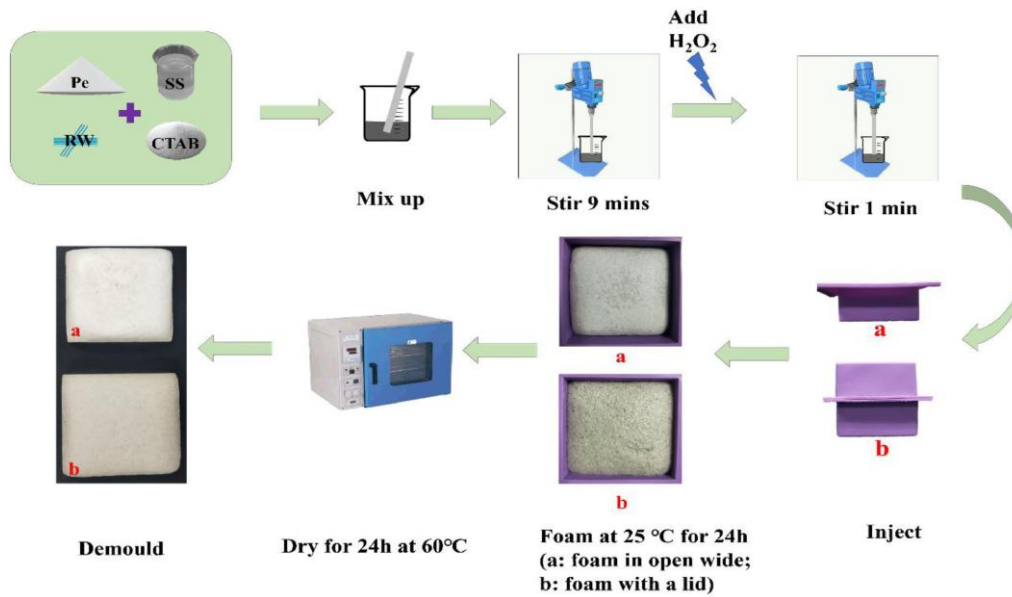


Figure 8. The preparation process steps of the foamy thermal insulation materials (a: foam in open wide environment; b: foam with a lid).

The detailed properties of inorganic-based insulation materials are presented in Table 3. Additionally, Table 4 highlights the advantages and disadvantages of utilizing inorganic-based thermal insulation materials.

Table 3. Important properties of various inorganic-based insulation materials.

Material Category	Material Type	k [W/m.K]	R -value [m ² K/W]	P [kg/m ³]	C [J/kg.K]	Fire Class	U -Value	Refs.
Fibrous	Rock Wool	0.029–0.042	17 – 19	40–200	0.8–1.0	A1–A2	1.0–1.3	[24, 49]
	Glass Wool	0.031–0.037	12 – 14	13–100	0.9–1.0	A1	1.0–1.1	[50]
	Slag Wool	0.04	23 – 24	50	0.7	A1	0.5	[24]
	Fiberglass	0.030–0.050	12 – 28	10–100	0.8–1.0	A1	1.0–1.3	[51]
Cellular	Perlite	0.04–0.06	15	32–176	0.2	A1	3.5	[24]
	Vermiculite	0.04–0.064	12 – 13	64–130	0.84–1.08	A1	3–5	[52]
	Foam Glass	0.038–0.045	17 – 24	100–120	0.21	A1	–	[53]
	Calcium Silicate	0.045–0.065	15	115–300	1.3	A1	6–20	[51]

Table 4. Advantages and disadvantages of inorganic based insulation materials.

Advantages	Disadvantages
– Abundant in supply – High durability – Moisture resistance – Resistance to decay – Good thermal resistance – Excellent thermal stability – Easy to install – Most are environmentally friendly and do not release harmful gases	– Comparatively heavier than organic insulators – Brittle in nature – Requires additional structural support – Higher production energy – Some inorganic materials can release harmful airborne particles irritating to skin (e.g., fiberglass) – Upon exposure to moisture, their thermal properties can vary

1.3 Organic-Based Insulation

The organic thermal insulation materials can be obtained from natural and renewable resources, and therefore, thermal insulation with such materials can be also an appealing option. Additionally, organic foams have been widely utilized as building external wall insulation material due to their lightweight and low thermal conductivity [54, 55]. Such materials include natural and renewable materials such as cellulose, sheep's wool, cotton, rice straw and foams based on polystyrene (Expanded polystyrene and Extruded polystyrene), polyurethane, phenolic resins and polyethylene. Among them, polyurethane foam (PUF) and extruded polystyrene (XPS) with thermal conductivity values of about 0.024 – 0.026 and 0.027 – 0.040 W/m.K at 300 K, respectively, are widely used [56-58]. In general, most organic insulation products have several appealing qualities, including renewability, recyclability, non-toxicity, environmental friendliness, and minimal resource production needs. A more detailed list of organic materials used for insulation and their important thermal properties are listed in Table 5. This part discusses various examples of each group with its application and limitations.

Table 5. Important properties of organic-based insulation materials.

<i>Material Category</i>	<i>Material Type</i>	<i>k [W/m.K]</i>	<i>R-value [m²K/W]</i>	<i>P [kg/m³]</i>	<i>C [kJ/kg.K]</i>	<i>Fire Class</i>	<i>u-Value</i>	<i>Refs.</i>
<i>Petro-chemical</i>	EPS	0.029–0.041	21 – 25	18–50	1.25	E	20–70	[59, 60]
	XPS	0.030–0.040	28	25–45	1.45–1.70	E	80–150	[33, 51, 58]
	PUR	0.022–0.046	20 – 38	30–100	1.30–1.45	D–F	50–100	[49, 61] [62]
	PIR	0.018–0.028	27 – 47	30–45	1.40–1.50	B	55–150	[60, 63, 64]
	Phenolic Foam	0.018–0.034	38 – 42	40–160	1.30–1.40	B–C	35	[51, 65, 66]
<i>Renewable</i>	Cotton	0.058–0.082	21	150–450	0.13	E	-	[24]
	Sheep Wool	0.038–0.054	20 – 22	10–20	1.3–1.7	E	4–5	[49]
	Hemp	0.038–0.123	20	25–100	1.7–1.8	E	1–10	[24]
	Flax	0.030–0.045	20	20–80	1.6	C	1–5.28	[51]
	Jute	0.038–0.055	22	35–100	2.4	-	0.2–0.56	[26]
	Rice Straw	0.039	7 – 9	80–100	0.6	E	3.2–5.47	[67, 68]
	Coconut Fiber	0.042–0.086	-	174–664	2.6	E	1–10	[24]
	Paper waste	0.04–0.093	18 – 21	200–348	0.37–1.4	-	2.3–3.9	[69, 70]
	Cork	0.036–0.065	20 – 23	65–240	1.5–1.7	E	5–54.61	[71]

1.3.1 Expanded Polystyrene (EPS)

Currently, there are many different types of polystyrene foam in use, along with a wide variety of methods for producing them, the most popular being expanded polystyrene (EPS). EPS is a well-established insulation material widely used for various applications due to its lightweight and rigid foam structure, excellent thermal insulation properties, and high impact resistance (**Fig.9-a**) [33].

The thermal conductivity of EPS usually varies between 0.029 and 0.041 W/m.K depending on the moisture content and density, because changes in temperature, moisture content, and mass density have a direct effect on thermal conductivity value [59]. EPS foam is commonly incorporated into concrete floors as a resilient material to reduce noise transmission and preserve heat, resulting in energy savings. It is a rigid foam material made from closed-cell beads of polystyrene (with gaps between them that give it some characteristics resembling open-cell behavior), and it offers benefits such as cost-effectiveness, energy efficiency, cushioning for shock-sensitive goods, and moderate resistance to water absorption [59, 72, 73]. EPS foam is also utilized in geotechnical applications as geofoam in road and airfield pavements, railway track systems, beneath refrigerated storage buildings, sports arenas, and storage tanks to prevent ground freezing and heaving, as well as in below-ground building segments to reduce seasonal heating and cooling requirements. Overall, EPS foam is a versatile and effective insulation material with many applications in the construction and packaging industries [59, 74]. Importantly, it is also inexpensive.

1.3.2 Extruded Polystyrene (XPS)

On the other hand, extruded polystyrene (XPS) is a thermoplastic polymer derived from melted polystyrene sourced from crude oil (**Fig.9-b**). To create XPS, an expansion gas (also termed as *blowing agent*) such as hydrofluorocarbons (HFC), carbon dioxide (CO₂), or hexane (C₆H₁₆) is added to a PS molten mass, causing it to expand when extruded through a nozzle with pressure release. The resulting insulation material is produced in continuous lengths and then cut after cooling [33]. XPS possesses a fully closed-cell structure, rendering it stronger and with higher mechanical performance than EPS, however, it is typically more expensive than EPS (XPS: 66.89 \$/m³ and EPS: 43.51 \$/m³) [75]. It has attracted much attention because of its outstanding performance, due to low thermal conductivity (0.030–0.040 W/m.K) and its lightweight nature with a density range of approximately 25 – 45 kg/m³ [26]. Thermal conductivity of XPS, like EPS, can be affected by factors such as temperature, humidity and

density, and also XPS insulation is easily affected by high temperature and intense sunlight, which damages XPS characteristics. In addition, XPS is highly flammable, hence most building fires can be attributed to XPS, such as the one occurred to the Grenfell Tower [76].

1.3.3 Polyurethane

Polyurethane foam (PUF) is another widely used organic material for thermal insulation purposes. When a di- or poly-isocyanate and a polyol (alcohol containing multiple hydroxyl groups) react, a closed-cell thermoset polymer called polyurethane (PU) is created. If a foaming agent is included in the reaction mixture, the system evolves as a foam, generating a polyurethane foam (PUF), which may be flexible (PUFF or FPUF) or rigid (PUR or R-PUF), depending on the starting chemical structures of the two co-monomers [77, 78]. It is offered in closed-cell and open-cell formulations, acting as insulation for various uses, including pipes, industrial systems, floors, roofs, and cavity walls shown in **Fig.9-c** [79]. Typical thermal conductivity values for PUs are between 0.020 and 0.046 W/m.K, i.e., considerably lower than mineral wool and of many other organic insulators. The thermal conductivity of PUFs varies with temperature, moisture content and mass density (i.e., the amount of gas trapped in the PU matrix). As an example, the thermal conductivity of PUF may increase from 0.025 to 0.046 W/m.K with increasing moisture content from 0 to 10% vol., respectively [33]. Also, a smaller cell size of the foam also results in a lower heat conductivity for PUFs, due to the higher number of discontinuities present in the material, which increases the barriers for the phonon motion throughout the material [78].

1.3.4 Polyisocyanurate (PIR)

Polyisocyanurate (PIR), shown in **Fig.9-d**, is also a foam-based organic material renowned for its superior R-value (between 27 – 47 m²K/W) leading to enhanced energy efficiency compared to other foam-based insulation materials. PIR molecular structure consists of highly crosslinked isocyanurate rings, which enhance thermal stability, flame-retardance, and mechanical behavior [80]. PIR achieves thermal resistance from blowing agents, typically a pentane gas mixture trapped in the foam cells [63]. However, PIR's thermal conductivity (like PUF and EPS products) can vary due to gas exchange with environmental gases during operation and in low-temperature environments with blowing gas condensation [64]. Over time, environmental factors lead to aging in closed-cell PIR foam as air diffuses into the foam cells, and the blowing agent gas diffuses out, altering the cell gas composition and thermal

conductivity. These aging factors are influenced by environmental air, radiation temperature, humidity, chemical agents, and microorganisms [81].

1.3.5 Phenolic Foam

A phenolic foam (PF) is a rigid, thermosetting organic polymer that is low in cost (\$5.5 m²), dimensionally stable, and has excellent flame resistance (**Fig.9-e**). It is produced using components such as resin, surfactant, blowing agent, and curing agent. Specifically, PF is made from liquid phenol-formaldehyde resin, to which a foaming agent is added. According to Arthur H. Landrock in the Handbook of Plastic Foams, PF production can be achieved by mechanical, physical, or chemical methods [82]. PFs possess a combination of properties that make them attractive for various engineering applications, including insulation, energy absorption, and fire protection. Additionally, PFs are free from chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs), water-resistant, and chemically inert [51, 83]. Nevertheless, PFs are notable for their low thermal conductivity (0.018–0.034 W/m.K), density (40–160 kg/m³), and also exhibit, when treated with proper additives, excellent fire-retardant behavior (Class O according to the appropriate UK regulations (highest fire rating)/ Dutch NEN 6065/6066 Class 1/ Belgian A1/ French M1/ German class B1-DIN 4102) [84, 85], but have insufficient mechanical properties (e.g. low resistance to fatigue, poor flexural properties and friability) for different applications in comparison to other foam materials. To resolve this problem, Chen et al. [86] have discovered a relationship between density and the improvement of the mechanical properties of PF products. They prepared the PF samples with density of 40 (PF1), 50 (PF2) and 60 (PF3) kg/m³ by adjusting the amount of blowing agent. Results of this study can clarify that changing the density of PF with amount of foaming agent will not affect its chemical properties, but the ratio has impact on its physical properties. The FT-IR spectra and distributions, also, demonstrated that the chemical structure of the samples was not affected by the ratio of blowing agent. Therefore, as the density rises, the average compressive strength of PF1, PF2 and PF3 was 0.100 MPa, 0.150 MPa and 0.264 MPa, respectively. Additionally, thermal properties of three samples were measured in air atmosphere, but the variation of density had little effect on it. However, at the same temperature, PF3 with the density of 60 kg/m³ showed the highest thermal conductivity (0.13-0.18 W/m.K), which the thermal stability was positively correlated with the sample density, so that compared with the density of 40 kg/m³, the residual rate of 60 kg/m³ and 50 kg/m³ increased by 15.5% and 17.5% respectively. Finally, they found that, the production method of adjusting PF density by changing blowing

agent ratio will not affect the chemical properties, but has obvious impact on their physical properties.

1.3.6 Polyethylene Foam

Unlike PF, Polyethylene foam (PEF), shown in **Fig.9-f**, is known for its elasticity and high porosity. It also exhibits good thermal insulation properties, with thermal conductivity value of 0.030–0.034 W/m.K and density range of 31–173 kg/m³. It possesses notable tensile strength, water resistance, and low vapor permeability. The PEF can be hot air welded, but its combustibility limits its applications [3]. As per report by Wu et al. [87] PEF has poor heat resistance, and its structure is destroyed at 160 °C. Additionally, the technology of welding products based on PEF enables the formation of seamless insulating shells, which can be placed on smooth walls, roofs, and any structures in contact with the ground. Moreover, practically zero water absorption makes this material stable in different humidity environments [88]. According to the Plastics Europe Report, PE is the most widely used polymer for packaging in Europe. In this context, PEF is widely used in facades and roofs for heat, soundproofing, and waterproofing purposes, as well as in hangar insulation systems. Various companies, such as Foam Factory (Canada), UFP Technologies (USA), and The Rubber Company (UK), have contributed to its development [3, 89]. Although organic-based insulation materials offer several advantages, they also have drawbacks that can occasionally limit their commercial application, e.g. the maximum utilization temperature of EPS and XPS insulation materials is 75 °C. Due to this limitation, these materials are used with certain restrictions in places with a high risk of fire, in buildings that are adjacent to each other, and in multi-story structures. In contrast, rock wool (as inorganic-based insulator) is classified as an A-class material (according to the DIN 4102 standard) and offers exceptional fire resistance, with a maximum utilization temperature of 750 °C [90]. Table 6 highlights the benefits and limitations of using organic-based insulation materials.

Table 6. Advantages and disadvantages of using organic-based insulation materials.

Advantages	Disadvantages
– Low-density and lightweight – High thermal resistance – Sustainable and renewable – No health problems – Moisture resistance – Environmentally friendly – Easy to install in batts	– Higher upfront cost – Vulnerable to fire – Larger space requirement for installation – Higher production energy and need chemical treatments – Can emit toxic gases upon catching fire



Figure 9. Organic insulation material (Petrochemical-based) a) Expandable polystyrene (EPS), b) Extruded polystyrene (XPS), c) Polyurethane (PU), d) Polyisocyanurate (PIR), e) Phenolic Foam (PF) and f) Polyethylene Foam (PEF)

1.4 Synthetic, Sustainable Natural and Recycled Materials

According to the report by Arif et al.[91], for the period 2020–2023 the production growth of natural and synthetic plastics should be around 13% per annum. Thus, synthetic polymers pose a risk to the environment due to their exceptionally stable nature, which causes the accumulation of waste. In this regard, as the idea of “sustainability” spread throughout the construction industry, various researchers recently prioritized insulation solutions made of natural and recycled materials [92].

In a recent research, Cai et al.[93] have found that the amount of studies on synthetic polymers for thermal insulation has exponentially increased (**Fig.10**). Especially since 2002, the number of articles on this research field has nearly doubled every five years. The article number on this topic has already reached 142,152 in 2022. On the other side, there is still an ongoing lack of research on sustainable insulation materials, hence their ability to enhance the thermal performance of buildings is rarely known, which is, at least in part, an explanation for why these materials are not commonly used for insulation globally.

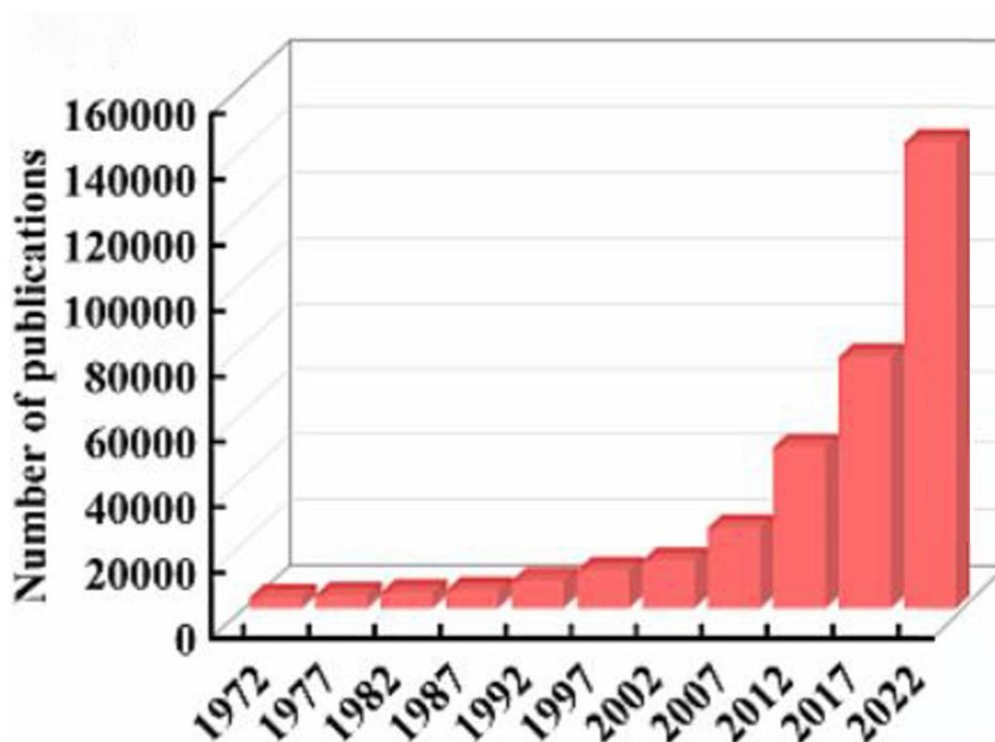


Figure 10. Growing importance of synthetic polymer-based thermal insulation materials is reflected in the increasing number of publications [93].

Nevertheless, the global market for building insulation estimated the use of synthetic plastic-based thermal insulation materials in buildings was at almost 30 billion USD in 2021. Since synthetic plastics are hardly biodegradable and are not very easy to recycle, these numbers suggest that various harmful environmental impacts, especially at the end of the life cycle of these manufacts, can be foreseen in the next years [94]. To address this issue, the Sustainable Development Goals, established by the United Nations in 2015, are pivotal objectives for society [95], and recycling technologies have significant potential to address some of these challenges. For instance, recycling technologies enable the reuse of waste materials, ultimately reducing overall waste, promoting a cleaner environment, and contributing to an improved quality of life for all species. These benefits ultimately help to achieve some of the Sustainable Development Goals like; Goal 6: Clean water and sanitation, Goal 13: Climate action, and Goal 15: Life on land, as depicted in **Fig.11**.



Figure 11. The schematic diagram shows the Sustainable Development Goals which can be achieved through recycling and resuming of polymer composites [96].

Various available natural insulation materials are listed in **Fig.12**. The utilization of such natural and sustainable materials could be particularly significant and helpful in developing countries that lack clear recycling rules and that have disposal problems, thanks to the abundance of agricultural and industrial byproducts. Utilizing such insulation materials will not only lower the environmental effects of the building industry, but also focus on improving the energy efficiency of buildings [97].

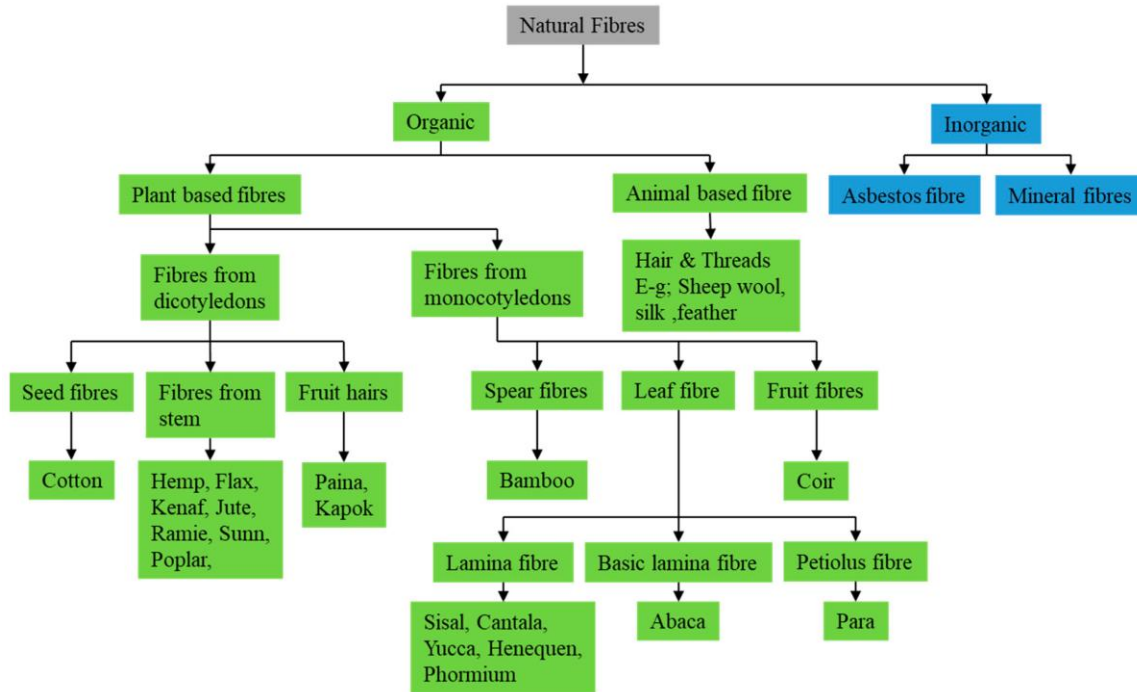


Figure 12. Classification of some commonly used naturally available insulation materials.

Regarding environmental impacts, Cosentino et al.[98], in a recent review article, acknowledged that insulation materials are one of the largest contributors to emissions and, therefore, to the environmental impacts of the construction materials. Research on 503 buildings found that 26.1% of total carbon emissions came from insulation material production, the largest after concrete production that represents 33% [99]. In another work, Magwood et al.[100] studied the material carbon emission (MCE) of 20 different insulation materials for a specific area and thermal resistance value. From the graphs, in the **Fig.13**, it was observed that the natural insulation material had minimum carbon emission compared to other insulation materials. It is also worth mentioning that inorganic-based insulation materials such as XPS, EPS, aerogels, and spray foam have the highest carbon emissions.

Insulation Emissions Comparison for 100 m² @ R5

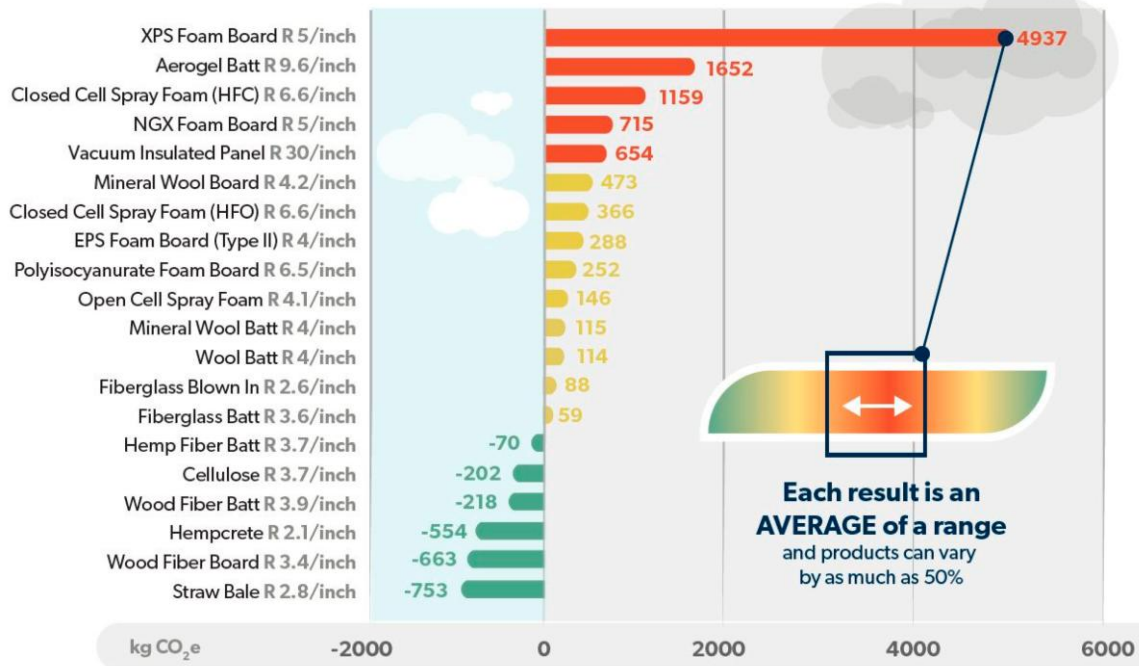


Figure 13. Material carbon emission for various commonly used insulation materials [100].

Therefore, the need for developing sustainable and renewable synthetic thermally insulating materials is highly evident. In the following, various natural and renewable organic-based materials potentially useful for thermal insulation, such as cotton, rice straw, hemp, flax, reed grass, linen, hay, lichens, and other organic fibers, are overviewed.

1.4.1 Cellulose

Cellulose, a natural renewable insulation material made from recycled paper fibers, is a viable option for panel and building insulation [101]. This eco-friendly material is widely available as a filler, suitable for various applications including cavity walls and as board or batt insulation in envelopes (**Fig.14-a**) [102]. Cellulose fiberboard is the other common form used in building insulation. Typical thermal conductivity values for cellulose insulation are between 0.040 and 0.050 W/m.K. The thermal conductivity of cellulose insulation varies with temperature, moisture content and mass density. As an example, the thermal conductivity of cellulose insulation may increase from 0.040 to 0.066 W/m.K with increasing moisture content from 0 to 5 vol%, respectively [33]. However, cellulose has up to now a limited use compared to traditional insulation materials. This can be attributed to a number of reasons, among which

the lack of expertise in its application and properties, possible hazards linked to the high flammability of cellulose (which is however prevented by adding appropriate flame retardants), a high increase of thermal conductivity upon humidity intake (which is very easy for these materials) and the presence on the market of competing materials, which often has similar or slightly higher prices, but with better insulation properties.

Further research and promotion of cellulose insulation could help increase its adoption in the construction industry [98]. For example, Marín-Calvo et al.[103] manufactured an insulating material by reusing materials such as recycled paper and rice husks. The fabricated material was evaluated using three different compositions, with tests including tensile strength, compressive strength, and thermal conductivity. The experimental results indicated improvements in tensile strength and compressive strength of samples including rice husks, even though this addition led to a decrease in thermal conductivity, which ranged from 0.0409 to 0.04607 W/m.K for rice husk percentages of 9% and 19.5 wt.%, respectively.

1.4.2 Cotton

Cotton, derived from textile waste, is an eco-friendly insulation material for panels and building insulation (**Fig.14-b**). Indeed, the cotton used for insulation is composed by 85% of recycled cotton and 15% plastic fibers (wt.%), in order to provide the resulting material with sufficient mechanical properties. Cotton insulation offers an R-value of about 17 to 22 m²K/W making an effective thermal insulator when dry, with thermal conductivities around 0.05 and 0.08 W/m.K [24]. However, its susceptibility to moisture and fire (which can be reduced, however, using appropriate flame retardants) is a notable disadvantage that must be considered when selecting insulation materials for specific applications. For these reasons cotton is often considered as a filler in composites, for example using cement as a binder, even though in these cases the overall thermal conductivity is markedly influenced by the thermal properties of the binder matrix, which usually is a worse insulator than cotton. Moreover, Binici et al. [104] used waste cotton with fly ash to fabricate composite blocks, and they observed that the thermal conductivity coefficient of the composite blocks (~ 0.26 - 0.30 W/m.K) was 29 % less than that of the concrete ones (~ 0.38 W/m.K).

1.4.3 Sheep Wool

Sheep wool is one of the essential natural materials considered in sustainable building requirements, with a density ranging from 9.9 to 25.9 kg/m³ and a thermal conductivity value

of 0.034–0.067 W/m.K [105]. Sheep wool is the textile fiber obtained from sheep (**Fig.14-c**), and categorized as a bio-product derived from sustainable biological resources, emerges as a promising alternative insulating material for buildings due to its ability to trap air within its fibers [106]. Generally, sheep wool consists of an average of 60% animal protein fibers, 15% moisture, 10% fat, 10% sheep sweat and 5% impurities and its usually used as a batt for thermal insulation [33]. Zach et al.[107] reported that the thermal insulation from sheep wool has excellent acoustic and thermal insulating properties and comparable characteristics with mineral/rock wool, and even performs better in some applications. Additionally, in comparison to mineral wool, sheep wool is more ecological and has fewer damaging health aspects. Furthermore, Dénes et al.[108] found that the effects of increasing density on thermal conductivity vary between binders of sheep wool-based composites, with binders based on latex demonstrating two minimum conductivity points at 62.03 and 116.27 kg/m³ and binders based on synthetic resin (acrylic-polyurethane resin) showing only one minimum conductivity point at 98.27 kg/m³. The lowest thermal conductivity values of 0.0331 and 0.0324 W/m.K were achieved with high-density and low-binder latex samples.

1.4.4 Cork

Cork is a lightweight, reusable, and biodegradable material obtained from the bark of the cork oak tree (*Quercus Suber*), harvested every 9–12 years. It possesses a homogeneous cell structure with thin and regularly arranged cell walls, lacking intercellular spaces. Countries such as Portugal, Spain, Italy, and North Africa are primary sources of cork oak. Cork insulators are commercially available as both filler material and insulation boards (**Fig.14-d**). Furthermore, Cork-based materials exhibit favorable acoustic properties, making them suitable for impact insulation, airborne insulation, and sound absorption [109, 110].

The thermal conductivity of cork insulators varies depending on the material's state (granular or compact) and density, however, the thermal conductivity of insulation cork boards ranges from 0.036 to 0.065 W/m.K, with densities varying between 65 and 240 kg/m³, and specific heat falling within 1.5 to 1.7 kJ/kgK [71, 111]. Additionally, due to the inner structure of cork, cork-based materials demonstrate useful properties for moisture insulation [112, 113].

Due to their vegetal nature, cork is very versatile, and can be used also as multilayered panels. For example, Lakreb et al.[114] presented an experimental study on the physical and thermal conductivity properties of six innovative types of cork and Aleppo pine-based multilayer sandwich panels, specifically designed for building insulation purposes, finding that

all the produced sandwich panels proved to be effective thermal insulators, with thermal conductivity values ranging from 0.041 to 0.067 W/m.K.



Figure 14. Natural and renewable organic-based materials a) Cellulose, b) Cotton, c) Sheep wool and d) Cork

There are other naturally available organic-based materials used for thermal insulation in buildings, such as reed panels, which are considered a classical insulation material. Reed panels typically have a density range of 130–190 kg/m³ and a thermal conductivity of 0.045 – 0.056 W/m.K. Despite being abundant, their usage remains limited [115].

Other natural materials researched for thermal insulation applications include Bagasse (a byproduct of sugar production consisting of the dry pulpy fibrous material that remains after crushing sugarcane or sorghum stalks to extract their juice and usually disposed of as waste fibre), which has been investigated to fabricate thermal insulation boards presenting thermal conductivity of 0.046 W/m.K with density in the range of 70 to 120 kg/m³ [116].

Cattail plant fibers or *Typha angustifolia* L., commonly known as the Narrow-leaved Cattail, is a perennial aquatic plant belonging to the family Typhaceae. It grows up to 2 meters

tall, with linear, erect leaves and distinctive brown, rod-shaped inflorescences. This species is widely distributed across temperate and tropical regions and is typically found in wetlands, marshes, lakes, ponds, and along the edges of slow-moving water bodies. Cattail can provide thermal insulation panels with thermal conductivity and density values ranging from 0.0438 to 0.0606 W/m.K and 200 to 400 kg/m³ [117].

Several other natural materials, like date palm waste [118], durian peel [118], oil palm fibers [119], pineapple leaves [120], rice hulls [121], polyester-reinforced Sansevieria fibers [122], sunflower composites [15], wheat straw bales [123] and many other ones [124, 125] can be used as sustainable thermally insulating materials. **Fig.15** illustrates various types of bio-sustainable materials that can be used for thermal insulation and Table 7 outlines the advantages and disadvantages of utilizing natural materials for thermal insulation.



Figure 15. Various bio-mass-based sustainable materials for thermal insulation; (A) wood hardboards; (B) medium density wooden fiberboard; (C) Hemp panel; (D) Cellulose panels in compacted form; (E) recycled textile fibers; (F) mixture of cotton, flax and hemp fibers; (G) hemp fibers; (H) cellulose fiber in loose fill; (I) wheat husk; (J) millet husk; (K) flax panel; and (L)wheat straw bales [126].

Table 7. Advantages and disadvantages of using natural materials for thermal insulation.

Advantages	Disadvantages
– Low to zero toxin, significant health benefits – Low-carbon footprint – Sustainable and renewable – Biodegradable – Locally available – Good hygroscopic behavior and moisture-regulating ability – Easy to install in batts – Higher thermal and acoustic performance	– Higher upfront cost – Lower mechanical strength – Vulnerable to fire – Larger space requirement for installation – Non-biodegradable binders added in some cases – Can emit harmful gases in some cases – Low market worldwide

Recycled materials or industrial by-products have also been widely investigated for insulation purposes, providing interesting opportunities for new, sustainable and environmentally friendly applications of these materials in the construction industry. For instance, Majumder et al.[124] presented innovative materials, made from locally sourced natural and recycled products, which demonstrated good thermal performance with reduced environmental impact. The samples were prepared using wool fibers (from mattress stuffing, couches, and chair padding), hemp shives (directly from the hemp stalks), jute fiber (from recycled jute bags), opus signinum (from crushed tiles) and clay (from local extraction in central Sardinia). Based on the result, by using of recycled materials, they obtained plasters with a conductivity about 32% lower than traditional plasters using gypsum and/or lime. Additionally, the use of natural fibers (sheep wool and thistle fibers) inside lime putty allowed for a decrease in thermal conductivity of up to 62% (between 0.146–0.272 W/m.K). They also found that the use of jute inside building elements to realize insulating panels, shows promising results, with conductivity values always lower than 0.162 W/m.K. Furthermore, Valverde et al.[125] utilized polyester and polyurethane as waste materials in the textile industry to fabricate heat insulation panels. The panels were experimentally tested for their thermal performance. Depending upon the density, thermal conductivity was found to be in the range of 0.053 and 0.041 W/m.K, indicating the panels' higher thermal resistance.

1.5 Novel Insulation Materials

Strategies for reducing environmental impacts have been studied and identified by Wiprächtiger and colleagues [127]. They include, among other actions, increasing the recycling rate, which offers the most significant improvement in the life cycle of materials. The biogenic insulation materials (thermal insulation materials derived from plant and animal biomass) play a key role in this strategy, often being utilized in a cascading approach with energy recovery after their use as insulation. A comparison of material flows between the "increased recycling rate" scenario and the baseline scenario for 2055 is illustrated in **Fig.16**. (The baseline scenario represents the continuation of current trends, relying on conventional materials.).

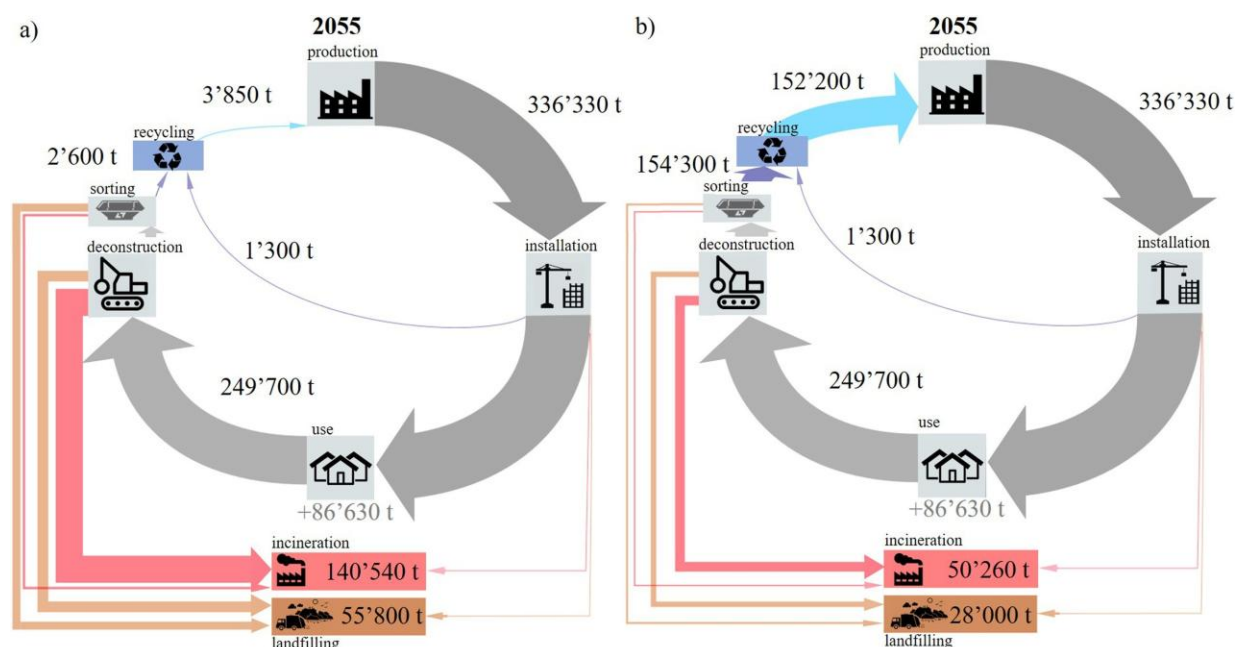


Figure 16. Insulation material flows in 2055 a) for the baseline scenario and b) for the increased recycling scenario.

Also appropriate construction practices, such as screwing instead of gluing, or using single material troughs to collect the materials deriving from building deconstruction, facilitate increased recycling. With these attentions, the authors claim that compared to the baseline scenario, greenhouse gas (GHG) emissions can be reduced by 30% with respect to standard deconstruction practices. While concepts like “smart building deconstruction” are a desirable best practice, it is unlikely that they will be widely implemented in the near term. Therefore, the construction industry is increasingly exploring eco-friendly insulation materials to enhance

energy efficiency, minimize harm to human health, and reduce environmental damage, or novel concepts that use old materials for achieving the same goal.

In recent years, extensive research has been carried out on new thermal insulation materials [128-130]. Table 8 show the general properties of some of these novel thermal insulation materials. They are also sometimes referred to as “super insulation” materials.

Table 8. Properties of various novel and super insulation materials.

<i>Material</i>	<i>k [W/m.K]</i>	<i>R-value [m²K/W]</i>	<i>P [kg/m³]</i>	<i>C [kJ/kg.K]</i>	<i>Fire Class</i>	<i>Ref.</i>
<i>Aerogel</i>	0.01–0.02	58	70–150	1.05	A1–A2	[131]
<i>PCM</i>	0.1–0.54	-	530–830	1.9–2.22	A, B, E	[132-134]
<i>VIP</i>	0.002–0.008	142	150–300	0.8	A1	[135]
<i>GFP</i>	0.010–0.035	31 – 62	32–38	-	A	[136, 137]

1.5.1 Silica Aerogel

Aerogels are low-density nano-porous solids, among the lightest known solid materials of Earth, with a fine, open-pore structure resulting in exceptionally low densities (0.003–0.5 g/m³), high porosity (80–98%) and large surface areas (500–1500 m²/g). Aerogels are also referred to as “frozen smoke” due to the foam like structure [138]. This combination of properties makes them unique in many senses, opening a possibility to a huge number of applications as thermal insulation, some of which have been commercialized already. IUPAC defines the aerogel as “gels comprised of a microporous solid in which the dispersed phase is a gas” [139]. This definition is however considered incorrect by the scientific community as it states that aerogels are exclusively microporous materials [140]. In fact, most aerogels typically contain pores of various types and sizes, particularly mesoporous ones [141-144]. In another better definition according to Smirnova and Gurikov [145] an aerogel is an open colloidal or polymeric network consisting of loosely packed, bonded particles or fibers that is expanded throughout its volume by a gas and therefore exhibits very low density and high specific surface area. Aerogel production process is traditionally divided in 3 steps: *I*) gel formation (chemical reaction, crosslinking, and sol-gel transformation), *II*) solvent exchange (if required by the following drying) and *III*) drying. Sometimes, some post-processing (hydrophobization, coating etc.) is needed [146]. The shape of the final aerogel (monolith, granules, powder) is mainly obtained during the gel formation (for example by molding), which are usually formed by removing all swelling agents from an initial gel without substantial volume reduction or

network compaction or degradation. Initial gel can consist of virtually any material or combination of different ones as hybrid aerogels. Table 9 illustrates some types of aerogels and their properties.

Table 9. Some types of aerogels with their typical selected properties.

<i>Sample</i>	<i>Bulk density (g/cm³)</i>	<i>Specific surface area (m²/g)</i>	<i>Pore size (nm)</i>	<i>Porosity (%)</i>	<i>Ref.</i>
<i>Silica Aerogels</i>	0.003–0.35	600–1000	5–100	>90	[142, 147]
<i>Zirconia Aerogels</i>	–	55–112	7–15	–	[143, 147]
<i>Alumina Aerogels</i>	0.18–0.31	~290–700	20–36	~90	[148, 149]
<i>Titania Aerogels</i>	0.37	~80 - ~600	15–58	–	[150]
<i>Vanadium Oxide Aerogels</i>	–	280	–	98.0	[151–153]
<i>Manganese Oxide Aerogels</i>	–	250	32	–	[154]
<i>Ceria Aerogels</i>	–	225 – 34	14 - 24	–	[155–157]
<i>Cellulose Aerogels</i>	0.02–0.2	100–400	1–100	–	[158]
<i>Polyamide Aerogels</i>	0.06 – 0.29	215–470	3–60	81–94	[159, 160]
<i>Polyimide Aerogels</i>	~0.21	429	19.2	85.6	[144]
<i>Polyurea Aerogels</i>	0.02–0.54	4–321	6.6–54	53–99	[161, 162]
<i>Polyurethane Aerogels</i>	0.09–0.87	0.5–239	8.3–66.5 15–210	28–92	[163, 164]
<i>Carbon Aerogels</i>	0.05–1.0	400–1100 up to ~3000	0.5–50	80–98	[165–167]

Regarding the porosity of aerogels, Lui et al.[168] reported that k_g value (gas conductivity) decreases with increasing aerogel density. The reason is that the Knudsen effect [169] is enhanced as the pore size becomes smaller. Since the heat conduction is energy transport by atoms, k_g is related to the mobility of gas molecules. The higher mobility means that the energy carried by gas molecules can be transported further per unit time, which promotes thermal conduction. (Knudsen effect implies that when cell size is comparable or smaller than the mean free path of the liquid or gas, the molecules of the latter collide more often with the molecules forming the surrounding solid part than among them. Therefore, the energy transfer through the gas molecules is reduced.).

The special nanoscale porous network structure, shown in **Fig.17**, generates the several unusual properties in aerogel materials, all linked to its exceptionally high surface area and to its lightness, which allow its application in fields as different as thermal insulation and energy efficiency, catalysis for the chemical industry, aerospace thermal insulation applications, and so on [170, 171].

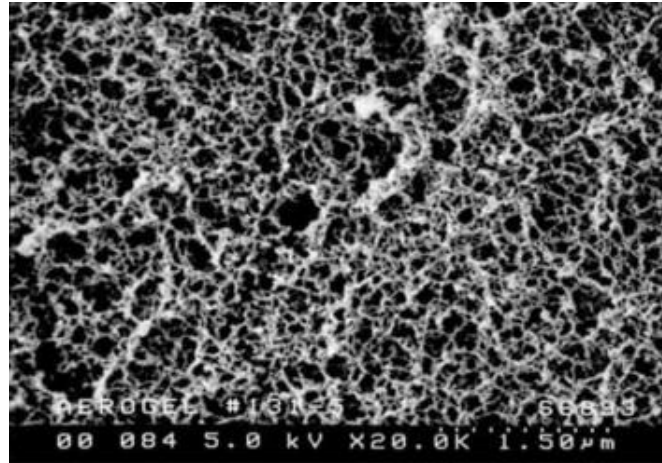


Figure 17. Scanning electron micrograph of silica aerogel network

Hrubesh [171] had summarized the currently explored or actively used applications of aerogel materials, as resumed in see Table 10.

Table 10. Identification of aerogel properties and features, and of their applications.

<i>Properties</i>	<i>Features</i>	<i>Applications</i>
<i>Thermal</i>	– Best insulation solid – Transparent – High temperature – Lightweight	Building insulation materials, Space vehicles and detection, casting molds
<i>Density/porosity</i>	– Lightest synthetic solid – Homogeneous – High specific surf. area – Multiple compositions	Catalysts, sorbers, sensors, fuel storage, ion exchange
<i>Optical</i>	– Low refractive index solid – Transparent – Multiple compositions	Cherenkov detectors, lightweight optics, special effect optics
<i>Acoustic</i>	– Lowest sound speed	Sound absorption materials, impedance matchers for transducers, range finders, speakers
<i>Mechanical</i>	– Elastic, lightweight	Energy absorber, hypervelocity particle trap
<i>Electrical</i>	– Lowest dielectric constant – High dielectric strength – High surface area	Dielectrics for ICs, spacers for vacuum electrodes, vacuum display spacers, capacitors

One such effort was fabricating clay-based aerogel composite, which is fabricated using the “lyophilization process”, where the product is dehydrated, then frozen and sublimated under vacuum, which allows the ice stage to change directly to the gaseous state without going through the liquid state. Using this process it is possible to create aerogels that are similar in nature to silica aerogels. Due to their layered structure, smectite clays are usually used for such aerogels [172, 173].

Among the novel thermal insulation materials, silica aerogel (SA) is one of the most promising ones. SAs are materials with unusual properties such as high specific surface area (500–1200 m²/g), high porosity (80–99.8%), low density (~0.003 g/cm³) (the silica skeleton density of ~ 2200 kg/m³, but since it incorporates such high amounts of gas – usually air – its actual density can be as low as 3 kg/m³), high thermal insulation value (0.005 W/m.K), ultra-low dielectric constant (~ 1.0–2.0) and low index of refraction (~1.05), and were first produced in the 1930s [142, 174-176].

Drying of the gel is the most critical step in the synthesis of aerogels, as it can affect the pore structure (porosity and surface area) of the product due to the shrinkage induced by capillary pressure. To dry a gel, different methods, such as supercritical drying (using CO₂, methanol, ethanol, acetone, 2-propanol and water)[177], ambient pressure drying [178], freeze-drying [179, 180], microwave drying and vacuum drying [181] can be applied (Fig.18).

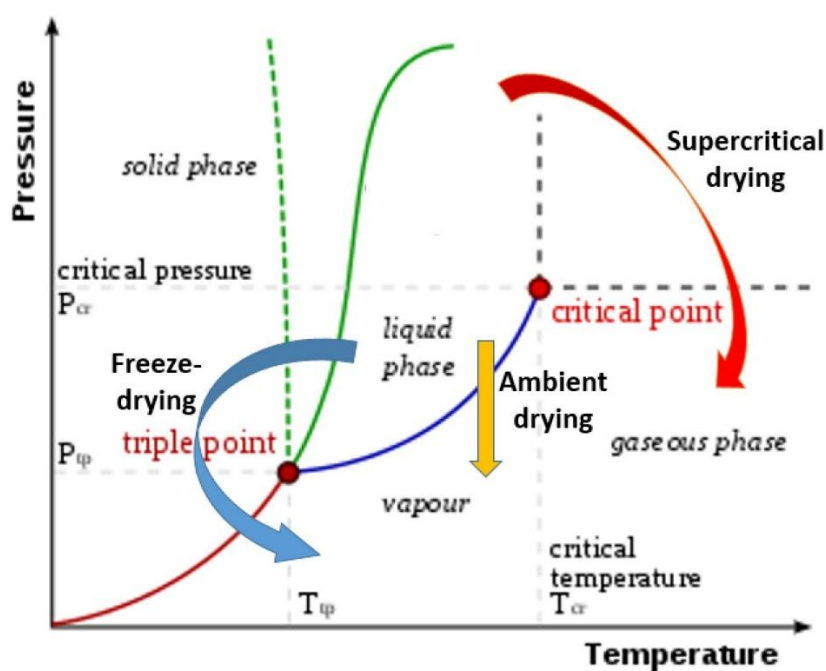


Figure 18. Phase diagram of a pure compound and overview of the different pathways that follow each of the available aerogel drying techniques. Red arrow: Supercritical drying, Blue: Freeze-drying and Yellow: Ambient drying.

However, SA are synthesized through a two-step process, initially involving traditional low-temperature sol-gel chemistry. Unlike Xerogels, where wet gels are typically dried via evaporation, aerogels are primarily dried through a process known as “Supercritical Drying”, which refers to draw off the liquid without collapse of the solid matrix in the gel, i.e. the liquid within the pores is removed above its critical pressure (P_{cr}) and critical temperature (T_{cr}) (Fig.18). At this point there is no capillary pressure, as there is no liquid–vapour interface [182]. This method enables the preservation of the intricate three-dimensional pore structure, contributing to the unique material. Depending upon the fabrication method and purity, the pores of the aerogel account for 85 to 99.8% of the total volume of aerogel [131, 183]. SAs consist of SiO_2 -chains in cross-linked system with such high porosity with huge quantity of tiny air filled pores. The pore size ranges from 10 to 100 nm [137, 184]. Silica aerogels can be obtained as granules, powder, and monoliths of various shapes. **Fig.19-a** shows a typical silica aerogel “brick”, highlighting its high fire resistance and insulation capabilities, while **Fig.19-b**, illustrates a range of aerogel applications in buildings and industry.

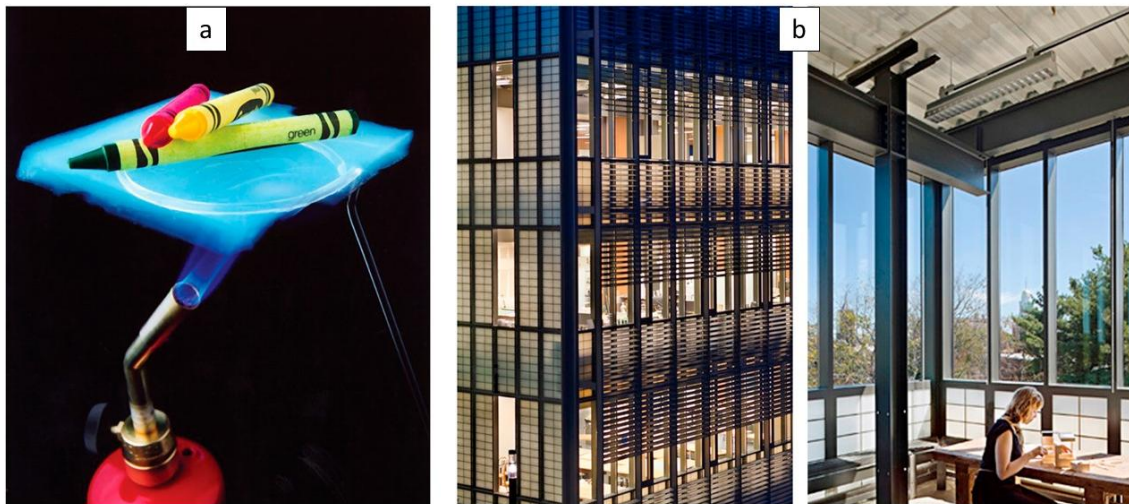


Figure 19. a) A silica-based aerogel brick submitted to direct flame can effectively shield objects from both fire and heat; b) application of silica aerogel in the building sector, as translucent insulation used in a curtain wall at the Sculpture building and gallery of Yale University (New Haven, Connecticut – USA) [131].

SA is widely recognized as a remarkable super-insulation material, exhibiting a thermal conductivity lower than that of air under normal conditions, typically 0.015 W/m.K . However, mechanical strength of aerogels is definitely low, due to the concurrent rigidity of the silica

frame and the high porosity of the material, with a Young's module value of 0.93 – 2.46 MPa for density between 0.1423 – 0.1758 g/m³ [185] and a shore hardness of 70 [186, 187]. Other still open problems for a wide application of this material include high manufacturing and application costs and complex preparation processes [13]. Due to its fragility, SA is mostly used as a filler in composites, for which matrices provide mechanical properties matching the technological needs. For instance, several examples of SA-based blankets/panels, using polymeric materials as matrices, are described in literature [13, 188-190].

In addition, SAs are used as components of insulation and building materials in various forms such as blankets, aerogel powder and granules. Concrete has a typical range of thermal conductivity between 0.2 and 1.9 W/m.K (for lightweight concrete), and between 0.6 and 3.3 W/m.K (for conventional concrete), values that strongly suggest to use insulation layers for ensuring decent energy efficiency performance in buildings [191]. Hence, several researchers explored mixtures of concrete with aerogel powder or granules, looking for good thermal insulation and adequate compressive strength. For instance, Buratti et al. [192] introduces an innovative granular aerogel-based plaster that is both breathable and insulating, utilizing natural lime and silica aerogel. The thermal conductivity values obtained were 0.013–0.018 W/m.K for granular silica aerogel, 0.004 W/m.K for evacuated monolithic silica aerogel, 0.014–0.016 W/m.K for aerogel-based plaster (96%-99% aerogel), and 0.050 W/m.K for a commercial solution with 80% aerogel, compared to 0.50 W/m.K for traditional natural plaster. The aerogel-based plaster achieved a 97% reduction in thermal conductivity compared to conventional solutions, and its application decreased the thermal transmittance (U-value) of walls by 6%–20%, depending on wall stratigraphy. Table 11 shows the k values for different types of commercial plasters as compared with the innovative aerogel based plasters.

Table 11. Comparison with traditional solutions: Thermal conductivity values [193].

<i>Plasters</i>	<i>ρ (kg/m³)</i>	<i>k (W/m K)</i>
Coating/mortar with different sizes of aggregate	600	0.29
Coating/mortar with different sizes of aggregate	1000	0.47
Coating/mortar with different sizes of aggregate	1200	0.58
Lime based plaster	1400	0.70
Gypsum based plaster	1200	0.35
T0–Natural plasters without aerogel	2200	0.50
T1–Natural plasters with aerogel (80%–90%)	275–300	0.045–0.050
T2–Natural plasters with aerogel (91%–95%)	126–136	0.019–0.021
T3–Natural plasters with aerogel (96%–99%)	115–125	0.014–0.016

However, due to the increasing demand for aerogel insulation in the global market, as reported by Precedence Research Company, the market share is expected to be worth about \$6761.49 million by 2034, which is almost 7 times the current market (**Fig.20**) [194], research is likely to focus on improving the manufacturing processes of aerogels to make them more cost-effective and scalable, while simultaneously enhancing their mechanical properties.

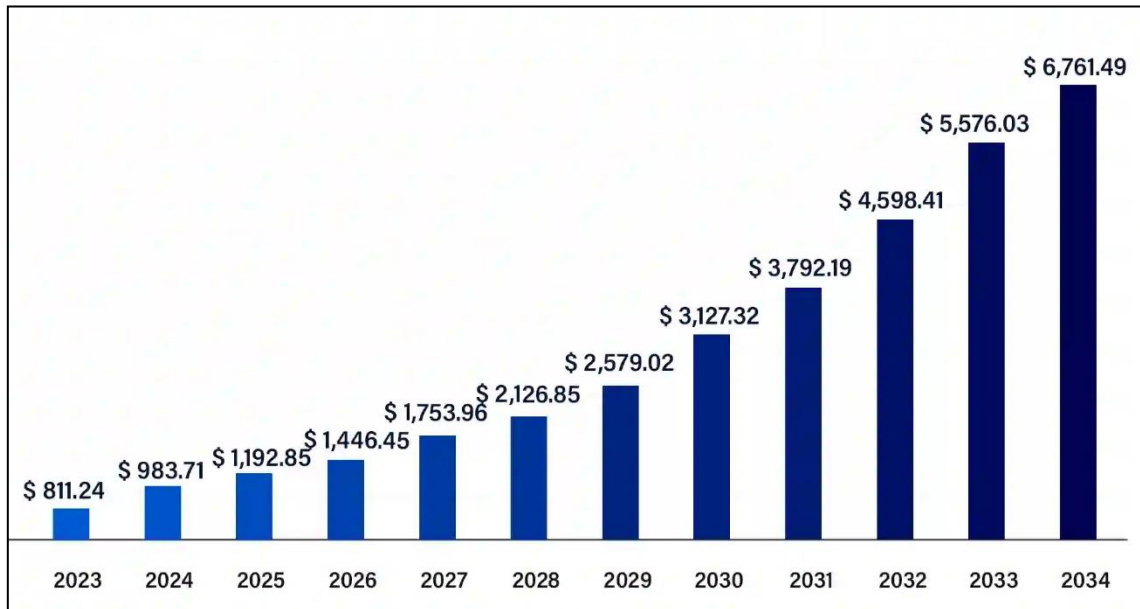


Figure 20. Aerogel Insulation Market Size 2024 to 2034 (USD Million)

1.5.2 Phase Change Material

Phase Change Materials (PCMs) are compounds or groups of compounds that are capable of accumulating, absorbing, and losing energy in the phase transition temperature range [195]. These materials, though not being strictly “thermal insulators” are usually considered as such because they can provide a great help in improving energy efficiency in buildings.

Typically, a phase transition useful for energy efficiency purposes occurs between the first two fundamental states of matter: solid and liquid. However, phase transitions can also occur between non-classical states of matter, such as different crystalline structures, where the material shifts from one crystalline form to another, which may be in a higher or lower energy state [196]. PCM-containing materials are widely applied in the construction industry as thermal insulation for both the interior and exterior of buildings. Due to their favourable thermal conductivity parameters and high heat storage capacity, these materials enhance

thermal comfort more effectively than traditional insulation solutions, such as mineral wool, PIR, or EPS [195, 197, 198]. **Fig.21-left** illustrates the mechanism of PCMs and their role in thermal energy storage. In this Figure can be seen how PCMs absorb and release latent heat during the phase change process, effectively regulating the heat flow without significant changes in their own temperature. This mechanism is very important for the use of these materials as thermal insulation and their application in energy efficiency. **Fig21-right** also, indicates the application of PCM for buildings [197]. While they are often associated with heat absorption and release for hot weather insulation, their unique properties make them equally suitable for cold climates.

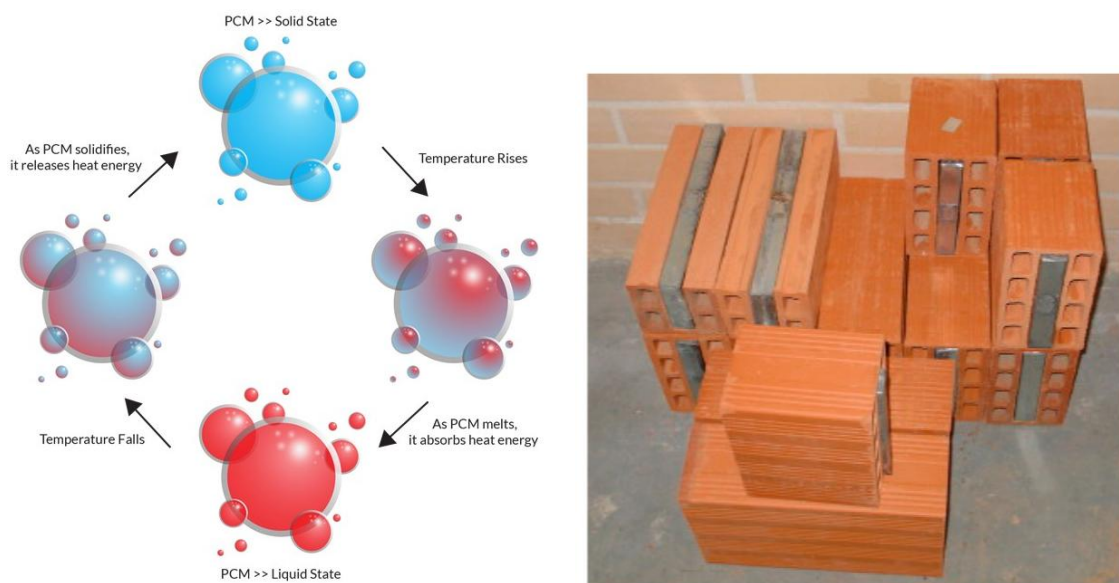


Figure 21. Mechanism of Phase Change Materials (PCMs) (left) and application of PCM in buildings (right).

Fig.22 indicates the classification of PCMs based on their chemical properties. This classification includes categories such as organic PCMs, inorganic PCMs, and eutectics, which are a combination of organic and inorganic PCMs. Each category has distinct characteristics and applications, making them suitable for various thermal energy storage.

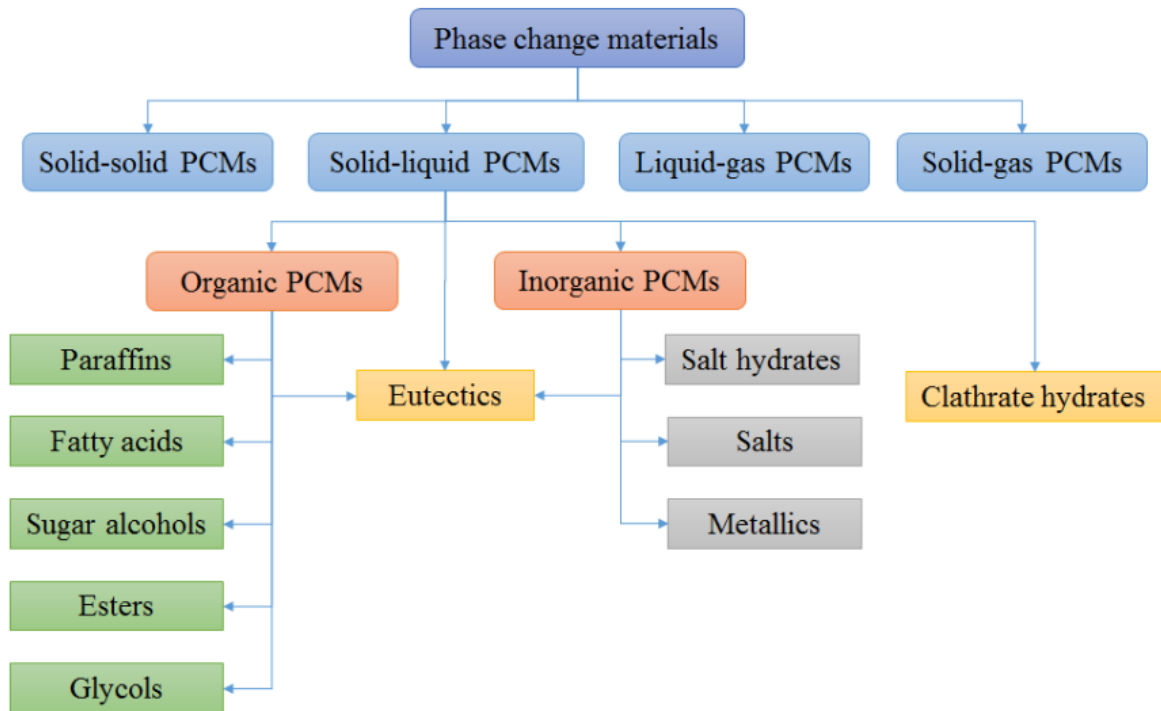


Figure 22. Phase change materials (PCMs) classifications.

For thermal insulation to be optimal, the specific heat should be as high as possible. The specific heat capacity tells how much heat energy is absorbed or released depending on the temperature difference and mass [199]. A good insulator has a higher specific heat capacity because it takes time to absorb more heat before it actually heats up (temperature rising) to transfer the heat. High specific heat capacity is a feature of materials providing thermal mass or thermal buffering (decrement delay) [200]. Furthermore, the most popular paraffin-based PCM materials, known for their high thermal conductivity (~ 0.36 W/m.K [201]), may initially seem unsuitable as an additive to insulation materials because they can compromise the insulation properties.

However, it is possible to achieve satisfactory performance of overall energy efficiency when PCMs are used, along with an increase in total heat capacity of the building. In view of this, as shown in Fig.21-right, PCMs are mainly added to solid building materials such as bricks, concrete and plaster (exterior and finishing layers) to increase their thermal capacity. For example, the use of foamed geopolymers doped with PCM materials can increase the specific heat of the composite by up to 180% without significantly compromising its insulation properties [195]. This is a very attractive solution from an application point of view, because

the use of non-combustible insulations that are able to accumulate heat can bring great benefits in case of mass-scale implementation.

In cold weather, PCMs can operate by releasing stored heat into the surroundings as they freeze (phase change from liquid to solid) and absorbing heat when they melt (phase change from solid to liquid). This property helps maintain a more stable indoor temperature and reduces the need for active heating systems. In extremely cold environments where temperatures can drop below freezing, solid state PCMs can assist in preventing heat loss through walls and roofs, thereby enhancing building energy efficiency and reducing heating costs [3]. In an experimental study by Lee et al.[202], the enhancement of the thermal performance of walls with PCM (mixed directly with cellulose insulation) was investigated using two test houses (one with PCM and one without) constructed with typical residential frame wall designs under real weather conditions (**Fig.23**). The experimental results showed an average 1.5-hour delay in peak heat flux, with reductions varying across walls: 26.0% (north), 38.5% (east), 16.1% (south), and 20.8% (west). The daily average reduction for individual walls was 25.4%, while the overall reduction for all walls combined was 26.6%, attributed to the staggered timing of peak fluxes. Therefore, by reducing heat flux through the use of PCM-enhanced insulation, energy efficiency was improved, and consequently, heating costs were reduced.

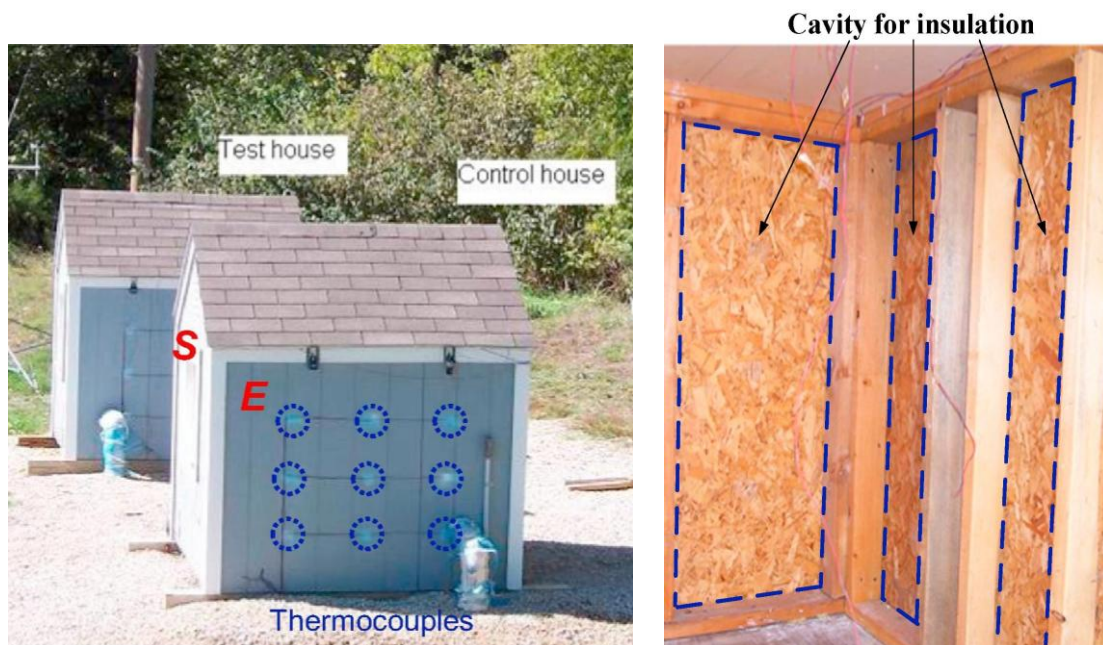


Figure 23. Test houses (E: east-facing wall; S: south-facing wall)-(left) and Internal structure of test house walls (right)

1.5.3 Vacuum Insulation Panels (VIP's)

Vacuum insulation panels (VIP) are high performance thermal insulation solutions and fall within the category of the so-called “super insulation materials”. A VIP consists of a porous core enveloped by an air and vapour tight barrier (within a metallic foil), which is heat sealed. The core is of an open pore structure to allow all the air to evacuate, and create a vacuum. The envelope needs to be air and vapour tight for the panel to uphold its thermally insulating properties over time. **Fig.24** shows a normal schematic of a VIP.

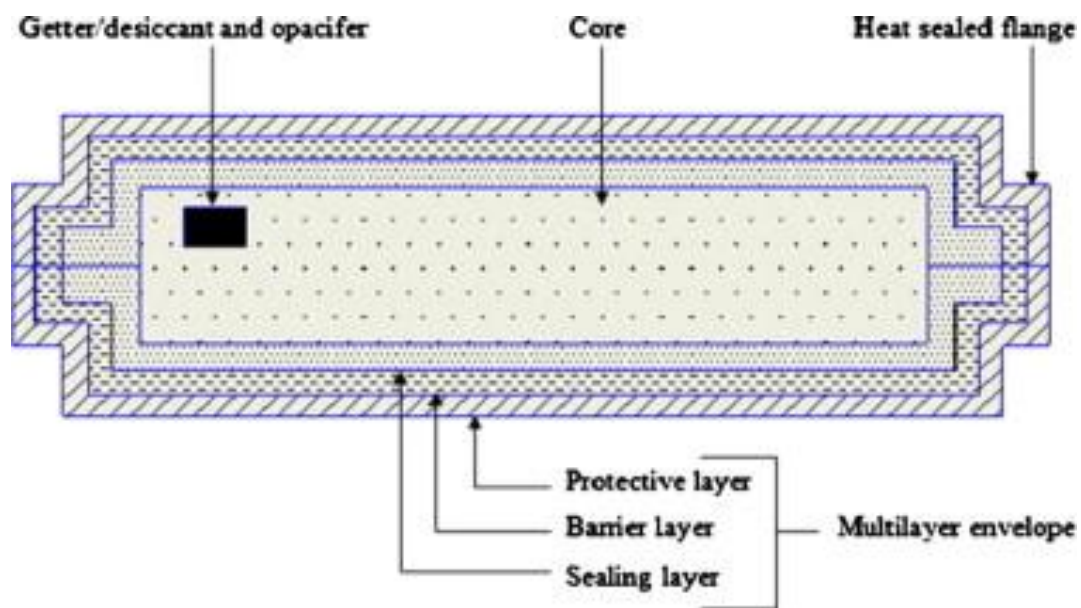


Figure 24. Schematic of a Vacuum insulation panels (VIP) [203].

Depending on the core material used (illustrated in **Fig.25**), the thermal conductivity of VIPs at the centre of the panel can be below 0.0045 W/m.K in pristine conditions, making VIPs the most effective thermal insulation material on the market in terms of minimal thermal conductivity, which allows to realize insulating panels with low thicknesses [204].

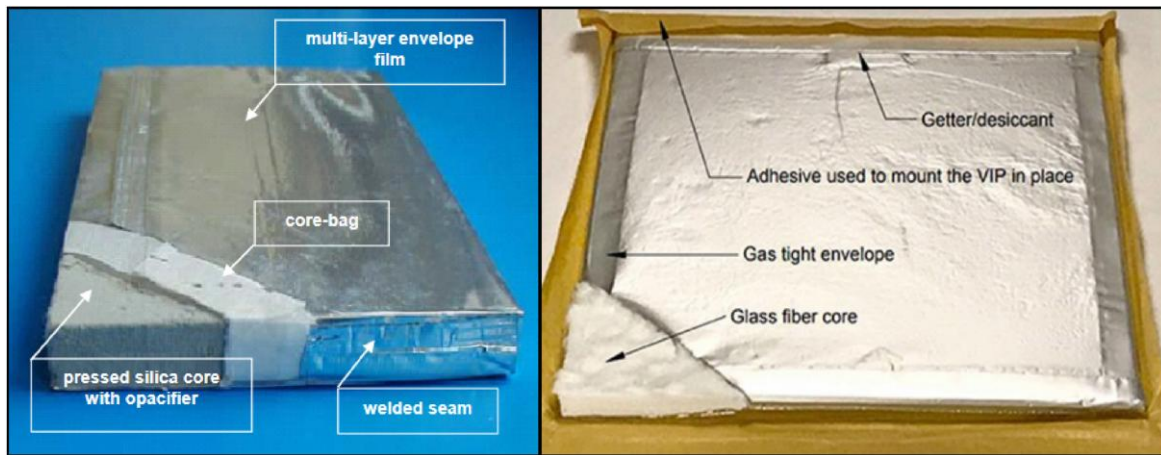


Figure 25. Left panel: Components of a fumed silica core: Fumed silica is obtained from silica heated to high temperature and condensed from the vapour state in a powdery form, and the effective thermal conductivity for fumed silica VIPs with a service life of 25 years ranges from 0.007 to 0.009 W/m.K-(left) [204]. Right panel: glass fibre core VIP: One corner of the gas-tight envelope has been removed to show the evacuated open-pore core. The getter/desiccant is in a sachet in the raised area at the top-centre. The brown wax paper backing covers the adhesive that is used to mount the VIP in place- (right) [205].

Therefore, VIPs are primarily used in applications where their superior insulation performance and low thickness can be an advantage, including cold chain applications (e.g., refrigerators, transportation boxes) [206], heat storage devices [207] and buildings [208]. This exceptional structural configuration confer a remarkable thermal resistance per unit thickness, thus rendering VIPs conducive to curbing building space conditioning energy demand. Yuk et al.[209] conducted a study evaluating the effectiveness of VIP technology in preserving building envelopes, particularly roofs, while improving energy efficiency. Based on the result, simulations demonstrated that applying VIPs to the roof reduced annual electricity consumption by 2526.95 kWh and improved cooling energy efficiency by 55% due to lowered thermal transmittance. The study underscored the importance of materials that satisfy energy-saving standards, (particularly in Korea, where U-value criteria are region-specific). Moreover, although historic buildings cannot fully meet net-zero design standards, advanced insulation materials as VIP insulations can provide decisive improvements in energy efficiency.

1.5.4 Gas Filled Panel (GFP)

The technology of Gas-Filled Panels (GFP) is similar to that of VIPs. GFPs are the new advanced applications of ambient-temperature thermal insulation, and consist of a barrier envelope and a low conductivity gas between reflective layers (a baffle). A low-emissivity barrier envelope is used to enclose the gas and to decrease the heat transfer due to radiation, while a low-emissivity baffle structure is included to decrease inner gas convection and radiation. As a result, both flexible and stiff GFPs are possible [136]. **Fig.26** shows an inside view of GFP on the barrier foil with baffle structure.



Figure 26. An inside view of GFP on the barrier foil with baffle structure (up) [136] and Honeycomb structure of the GFP by cutting one panel.

The thermal conduction through the gas is the most important heat transfer mechanism in a GFP. High performance GFPs use gases with a low thermal conductivity; since the panel structure makes it composed mostly by gases, the overall thermal conductivity will be very

low. As a gas, air itself or gases with lower thermal conductivity than air, such as argon (Ar), krypton (Kr), and xenon (Xe), indicated in Table 12, are typically used instead of a vacuum (as is the case in VIPs) [136, 210].

Table 12. Ideal still-gas thermal conductivity at 25 °C of gases, i.e. their potential thermal conductivity applied in GFPs and cost estimates of the gases [211].

<i>Gas type</i>	<i>Air</i>	<i>Ar</i>	<i>CO₂</i>	<i>N₂O</i>	<i>CF₄</i>	<i>SF₆</i>	<i>CFC-12</i>	<i>HFC-134a</i>	<i>HCFC-22</i>	<i>Kr</i>	<i>Xe</i>
<i>k (mW/m.K)</i>	26.2	17.8	16.6	16.2	16.0	14.0	9.4	14.0	11.0	9.4	5.6
<i>Approximated gas cost, \$/m³</i>	0	1.27	4.24	10.6	170	63.5	42.4	170	16.9	508	9500

The choice of the filling gas (some examples reported in Table 13) of GFPs is usually based on three general rules; *I)* gases with higher molecular weight typically exhibit lower thermal conductivity, *II)* monoatomic gases, such as noble gases, have lower thermal conductivity compared to polyatomic gases of the same molecular weight due to the additional energy transfer mechanisms in polyatomic gases, such as molecular rotation and vibration. *III)* Finally, the selected gases should not be greenhouse gases like CO₂, CH₄, N₂O, or O₃; they should be stable and their production should be environmentally friendly [136].

Table 13. Optimum number of cavities with their effective thermal conductivity, based on the lowest marginal cost of the fabrication of the gas-filled panels [212].

<i>Thickness</i>	<i>Gas Filled</i>	<i>Air</i>	<i>Argon</i>	<i>Krypton</i>	
	<i>Gas cost.</i>	0.00 \$/l	0.002 \$/l	0.30 \$/l	0.50 \$/l
25 mm GFP	<i>Optimum cavities</i>	4	6	12	13
	<i>k_g (W/m.K)</i>	0.0350	0.0213	0.0106	0.0103
	<i>Cost (\$/m²)</i>	2.26	5.30	12.22	21.54
50 mm GFP	<i>Optimum cavities</i>	6	9	20	24
	<i>k_g (W/m.K)</i>	0.0380	0.0226	0.0106	0.0104
	<i>Cost (\$/m²)</i>	3.02	6.70	26.81	39.46

Gas-filled panels used in thermal insulation are made of two types of polymer films: *I)* metallized ones, that are used in a tied assembly called “the baffle”, aimed at producing a cellular structure in the panel for effectively suppressing convection and radiation, and *II)* a low-diffusive gas-barrier foil, used for creating a hermetic envelope aimed at keeping the inner gas-filling sealed within the system (see Fig.25). Depending on the type of foils used for the structure, these panels can be made either stiff or flexible [136]. Shrestha et al.[213] presented

an experience study conducted at Oak Ridge National Laboratory tested the thermal performance of wall assemblies with two layers of GFPs insulation, one layer of GFP, and no GFP using the Rotatable Guarded Hot Box (RGHB) for ASTM C 1363 standards. Generally, referring to Table 14, the use of GFP significantly improved thermal insulation, with R-values increasing approximately fourfold for Two Layers of GFP and threefold for One Layer of GFP. However, results in function of temperature showed that the R-value of walls with two layers of GFP decreased significantly as GFP temperature increased, while walls with one GFP layer maintained a stable R-value (Table 14). They also mentioned that several factors (such as cost of materials, transportation, energy, and weather conditions, application) would need to be considered to determine whether it is cost effective to use one layer or two layers of GFP in construction sectors.

Table 14. The calculated surface-to-surface R-values

<i>Wall Configuration</i>	<i>Two Layers GFP</i>			<i>One Layer GFP (on Climate Side)</i>			<i>No GFP</i>		
<i>Temperature [°F]</i>	<i>80/40</i>	<i>100/60</i>	<i>120/80</i>	<i>80/40</i>	<i>100/60</i>	<i>120/80</i>	<i>80/40</i>	<i>100/60</i>	<i>120/80</i>
<i>M-FAN-PWR</i>	3.9	3.9	3.9	3.8	3.8	3.8	3.9	3.8	3.8
<i>M-HTR-PWR</i>	271.4	287.5	305.3	329.8	331.9	332.7	1132.6	1013.2	1052.3
<i>M-VEL-PWR</i>	20.2	20.0	19.7	20.0	19.6	19.3	19.7	9.9	9.9
<i>Q_{mb}</i>	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1
<i>TMP-DC</i>	295.4	311.3	328.7	353.6	355.3	355.8	1156.0	1026.9	1065.9
<i>T-DIFF</i>	40.0	40.1	39.9	40.0	39.9	40.0	40.1	40.1	39.9
<i>R-value</i>	8.662	8.232	7.762	7.241	7.192	7.183	2.218	2.500	2.396

([M-FAN-PWR = Meter fan power, Btu/h][M-HTR-PWR = Meter heater power, Btu/h][M-VEL-PWR = Meter velocity probe power, Btu/h][Q_{mb} = heat flow rate through metering box walls, Btu/h][TMP-DC = Total heat flow rate into meter box, Btu/h][T-DIFF = Average temperature difference across wall surfaces, °F][R-value = Surface to surface R-value of the wall, h.ft².°F/Btu])

Nevertheless, like other thermal insulation materials, the novel insulation materials also have some drawbacks and strong points, which are described in Table 15.

Table 15. Advantages and disadvantages of using super insulation materials.

<i>Advantages</i>	<i>Disadvantages</i>
– Higher thermal performance – Requires less thickness – Lightweight in nature – Usually hydrophobic in nature – High fire resistance capacity – Moisture and pest resistance	– Extremely higher cost – Difficult to manufacture – Difficult installation – Requires higher production energy – Not commonly used for housing insulation – Usually, the material is not environmentally friendly, and a sustainable option

1.5.5 Composite Insulation

While there are higher-performing insulation materials, such as aerogels, their use is limited due to relatively high costs. Compared to traditional inorganic insulators, composite insulators offer advantages including lightweight properties, ease of transport and installation, lower cost, and enhanced ability to prevent pollution flashover [214]. For example, a thick layer of aerogel may be required to achieve a specific thermal resistance value for any particular region, which results in high costs. Reducing aerogel's required thickness and achieving the desired thermal resistance can be possible by mixing it with another low-cost material or even with another layer of insulation material. This other layer could be a waste product such as wastepaper pulp from the paper industry, polyester, and polyurethane obtained as waste material from the textile industry, or any sustainable material discussed above [3].

Sezgin et al.[89] reported an experiment study which focuses on developing composite insulation board from 100% recycled materials, as alternative insulation solutions. They used waste cotton fibers and polypropylene/polyethylene fibers obtained from waste bottles and containers, which the PP/PE fibers were used as reinforcement material. The Insulation board fabricated by pressing layers of each material with a heated plate, indicated in **Fig.27-a**. The results offered thermal and acoustic insulation comparable to commercial insulators, with an observed improvement in R-value up to $0.11 \text{ m}^2\text{C/W}$.

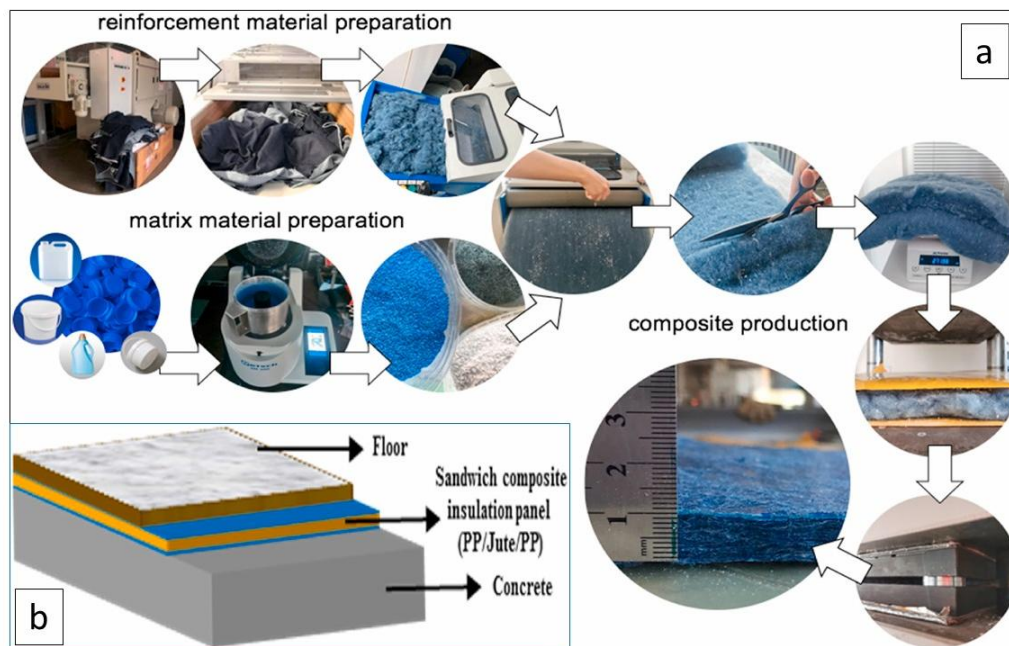


Figure 27. a) Fabrication of a composite insulation material using waste cotton and PP/PE fibers [89] and b) a schematic diagram for the application of the sandwich composite panel (PJ) inside the floor's system.

In another work, Aly et al.[215] investigated the acoustic and thermal insulation performance of sustainable thermoplastic sandwich composite panels for building floor systems, using recycled nonwoven jute, polyester (PET), and hybrid jute-polyester fabrics (80:20%) as reinforcements with polypropylene (PP) as the matrix (**Fig.27-b**). The thermal composite panels were produced via compression molding with varying reinforcement and matrix ratios. Based on the result, the panels reinforced with 1-layer of fabric (PJ sample (PP/Jute/PP) and PT sample (PP/PET/PP)) exhibited the lowest thermal conductivity of 0.03549 and 0.03795 W/m.K and highest resistivity of 28.1793 and 26.3494 mk/W compared to all samples, with jute composites storing more heat than polyester. Similarly, Zhao et al.[216] developed also composite vacuum insulation panels utilizing glass fiber and wood pulp as core material. Based on the result, with 50% glass fiber content, the thermal conductivity decreased to 0.0469 W/m.K, comparable to commercial products (0.0648 W/m.K), and showed good aging performance, remaining at 0.0742 W/m.K after 365 days under conventional conditions of 30 °C and 60% relative humidity, and even in the accelerated aging condition after 28 days, the increase in the thermal conductivity was less than 0.05 W/m.K (from 0.0469 to 0.0881 W/m.K). This composite core insulator, like as previous examples, demonstrated hence promise for vacuum insulation panels.

In light of the challenges and advancements discussed so far, this thesis focuses on the development of innovative composite insulation materials for the construction industry. Specifically, it explores the potential of polymer-based composites, with an emphasis on Polyurethane (PU) and Polylactic acid (PLA), as a sustainable and high-performance solution. Drawing on three years of dedicated PhD research, this work provides a comprehensive investigation into the methods for realizing polymer-based insulation composites, incorporating advanced fillers such as aerogel, cork, and eggshell. Furthermore, the study highlights the practical applications and benefits of these materials, addressing key considerations such as environmental impact, cost-effectiveness, rapid deposition on large surfaces and performance optimization. By advancing the understanding and application of green composites, this thesis aims to contribute to the development of composite insulation materials tailored to the evolving needs of modern and eco-environmentally construction.

2. AIM OF THE THESIS

In light of the challenges and advancements discussed so far, this thesis focuses on the development of innovative composite insulation materials for the construction industry. Specifically, it explores the potential of sustainable polymer-based composites, with an emphasis on Polyurethane (PU) and Polylactic acid (PLA), as a high-performance solution to the looming problem of recycling/disposal of the huge amount of currently used polymeric insulation materials, like EPS. Drawing on three years of dedicated PhD research, this work provides a comprehensive investigation into the methods for realizing polymer-based insulation composites, incorporating advanced and equally sustainable fillers such as silica aerogel, cork and eggshell.

Furthermore, the study highlights the practical applications and benefits of these materials, addressing key considerations such as environmental impact, cost-effectiveness, rapid deposition on large surfaces and performance optimization. By advancing the understanding and application of these composites, this thesis aims to contribute to the development of composite insulation materials tailored to the evolving needs of modern and eco-environmentally construction.

3. EXPERIMENTAL SECTION

3.1 Road Map

Before starting the work, a general road map for the flow of activities was prepared, as detailed in **Fig.28**.

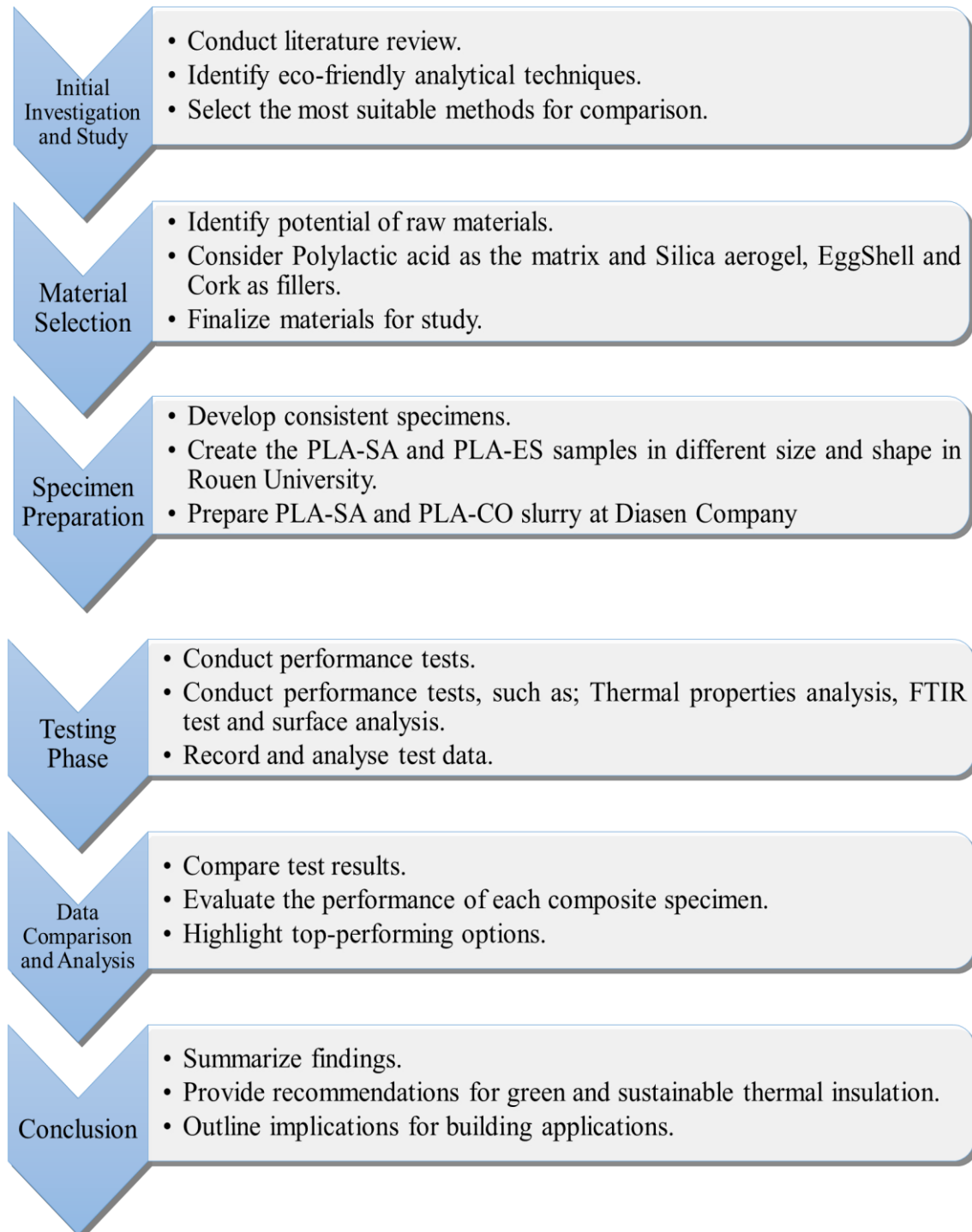


Figure 28. Work scheme; the overall procedure for producing composite samples and the necessary analyses.

3.2 Materials and Methods

3.2.1 Materials

- Amorphous PLA material in the form of granules has been purchased from Nature Works LLC (Ingeo Biopolymer 4043D). The polymer has a density of 1.24 g/cm^3 , a peak melting temperature of $145\text{-}160^\circ\text{C}$, and a glass transition temperature (T_g) of $55\text{-}60^\circ\text{C}$. Its melt flow index is 6 g/10 min , measured at 210°C with a load of 2.16 kg .
- The used PU (polyurethane) foam is a commercial one (AXTON, “Schiuma PU multiuso Isola e riempie”), and it has been purchased from a Pescara local store.
- SA (silica aerogel) has been purchased from Cabot (Silica Aerogel P100). The used SA has a particle density of $120\text{-}140 \text{ g/cm}^3$, a bulk density of $80\text{-}100 \text{ Kg/m}^3$, an average pore diameter of 20 nm , a surface area of $600\text{-}800 \text{ m}^2/\text{g}$ and a declared thermal conductivity of about 0.023 W/m.K .
- ES (eggshell) have been collected from local restaurants, and have been crushed using a ball milling machine and sieved through a 500 BSS mesh (British Standard Sieve) for obtaining particles of size less than $25 \mu\text{m}$. The so-obtained particles have been furnace heat-treated for 3 hours at 110°C for removal of the soft inner layer of the ES and of the moisture[217].
- CO (powdered cork, brand Grancork) were prepared from Diasen Company with a grain size of 3 mm , an average density of 150 kg/cm^3 , specific heat of 1670 J/kgK and a thermal conductivity value of $0.040 - 0.045 \text{ W/m.K}$.
- Tetrahydrofuran (THF) has been purchased from Avantor (VWR Chemicals BDH, THF $>99\%$, stabilized ACS) and used without further purification.
- 1,4-Dioxan ($>99\%$) has been obtained from CARLO ERBA Reagents S.r.l. and used without further purification.

3.2.2 Instruments and Equipment

The instruments and equipment used during the experimental phase are described below:

- The ARE 5 Hotplate Stirrer for preparing the slurry composite.
- The extrusion machine Magnetic - MM112 M-J (IQAP Lap) model-single screw extruder with 4 temperature control zones to produce, to produce of filaments samples.
- Hydraulic Presses model of Specac Atlas Manual 15T for produce the film sample.
- Airbrush Gun-Nozzle 1.5 Aluminium (tank 600 ml-4 bar) for spray-coating.
- Injection molding machine Babyplast 6/6 model, plunger-type injection for creating the dumbbell-shaped sample.
- The Hot Disk Thermal Analyzer-TPS 2500S employing the Guarded Hot Plate (GHP) method to measuring the thermal conductivity value.
- An Evolution R30 with an output of 30 V/5 A as first stabilized power supplies (alimentations)
- A Delta Elektronika E030-1 with an output of 30 V/1 A as second stabilized power supplies (alimentations)
- The heat flow meter HFM 446 Lambda Eco-Line instrument to measuring the thermal conductivity value of the dried slurry composite applied on surface of concrete samples.
- The Thermo Scientific Nicolet iS10 FTIR Spectrometer to determine the FTIR spectra of samples with utilize of award-winning Thermo Scientific OMNIC software.
- The Optical microscopy - Zeiss AXIO to surface analysis of samples.
- The universal testing Machines AllroundLine zwick roell Z030, using a 100 N cell to tensile test for dumbbell-shaped sample through test Xpert III Testing Software.

3.2.3 Methods and Preparation Protocols

In the following some general description of the main methods used to realize the investigated composites is given. The detailed methods used for preparing the composites are given in the Results and Discussion section, since in many cases the methods are directly linked to the final properties shown by the resulting material.

3.2.3.1 Composites Based on Polyurethane (PU)

As a first approach, different formulations of PU composites with different content of SA have been prepared. Despite, in other work related to PU, for creating composites based on PU, fillers were always added during the production process of PU, as shown in **Fig.29**, but in this work for creating composites based on PU, fillers were added to the precast PU foam (PUF).

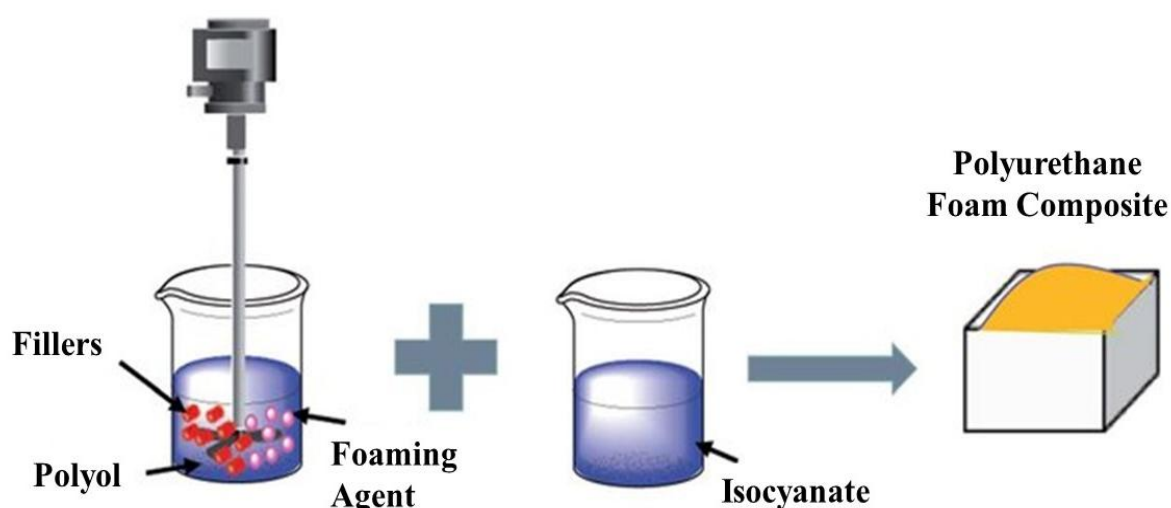


Figure 29. Schematic of the synthesis of rigid polyurethane foam (PUF).

In more detail, first attempts to produce the composites have been carried out by direct mixing SA with commercially available PU foam dispensers (**Fig.30-left**). The used PUF was designed to produce a rigid foam after the product exited the container, with only a few minutes passing from the moment in which the foam was expelled by the container and the moment of stiffening of the expelled foam.

Several attempts to mix the SA to the just expelled foam provided limited success in preparing homogeneous composites, since already the still un-cured PUF was very viscous and relatively stiff. Moreover, the curing phenomenon was so fast that it was not possible to allow

for a good homogenization of the SA/PUF composite, obtaining rather large SA aggregates segregated in the rigidified PUF matrix (**Fig.30-right**).



Figure 30. Purchased PUF from the local store (left) and mix of PUF and SA (right)

Several unsuccessful attempts have been made in order to try to overcome these problems, including adding the PUF to a solvent prior to rigidification (in order to dilute the foam, hence to slowing down the curing process).

However, after much time spent on trying to circumvent the problem, it has been decided to change the whole composite system, moving from a matrix based on PUF to a matrix based on PLA (poly lactic acid), as described in the following paragraph.

3.2.3.2 Composites Based on Poly-Lactic Acid (PLA)

The use of PLA has been decided on the basis of its optimal environmental compatibility and degradability. Moreover, PLA has good mechanical properties (Young's modulus of 3.6 Mpa, Tensile strength at break of 53 Mpa) and this makes it a good candidate to work as a robust matrix for thermoinsulating composites.

In order to prepare a composite suitable for industrial application, two main routes have been explored:

- 1) Slurries composites; so to be able to spray them onto substrates as a convenient, fast and effective method of creating thermo-insulating layers onto various, different surfaces.
- 2) Solid-state composites; obtained via extrusion mixing, injection molding and hydraulic presses of PLA and the selected filler, with no liquid solvent.

- Under the approach No.1), ternary systems have been developed using PLA, Tetrahydrofuran (THF) (or a mixture of THF and around 1% 1,4-Dioxan) as the solvent, and SA and CO as fillers, to fabricate different slurry composite materials. The choice of the solvent was critical for achieving a uniform dispersion of fillers within the PLA matrix. After extensive investigation and practical testing of numerous solvents compatible with PLA, and in line with the use of eco-friendly materials, THF was selected as the most promising solvent.

- Under the approach No.2), solid pellets of PLA have been mixed with the SA and ES as fillers using an Extrusion machine, Injection molding machine and Hydraulic press machine, obtaining solid composites ready for testing.

In both the mentioned approaches the composites have been realized at different percentages of fillers, so to have the possibility to evaluate the effect of systematically varying these parameters on the thermal insulation and mechanical properties of the resulting composites.

3.3 Results and Discussion

The initial attempts of using PUFs as matrices did not provide meaningful results. Therefore, in the following only the outcomes of using PLA as the composite matrix are described.

3.3.1 Composites via Slurries

3.3.1.1 General Slurry Preparation Procedure

The slurries based on PLA have been prepared by testing different solvents. Among them, THF was found to be one of the most effective and suitable for the needs of creating stable and sprayable slurries.

THF is a chemical solvent used in the manufacture of polymers as well as agricultural, pharmaceutical, and commodity chemicals, also it is directly used for synthetic fibers, synthetic resins, synthetic rubber, as well as a solvent for many polymeric materials [218]. According to Michigan State University on the topic of "Chemical Reactivity", THF with a dielectric constant of 7.6, is an aprotic solvent and, also a moderately polar solvent. This property allows it to dissolve a wide range of both nonpolar and polar chemical compounds [219]. THF is also nontoxic, except for extremely high doses.

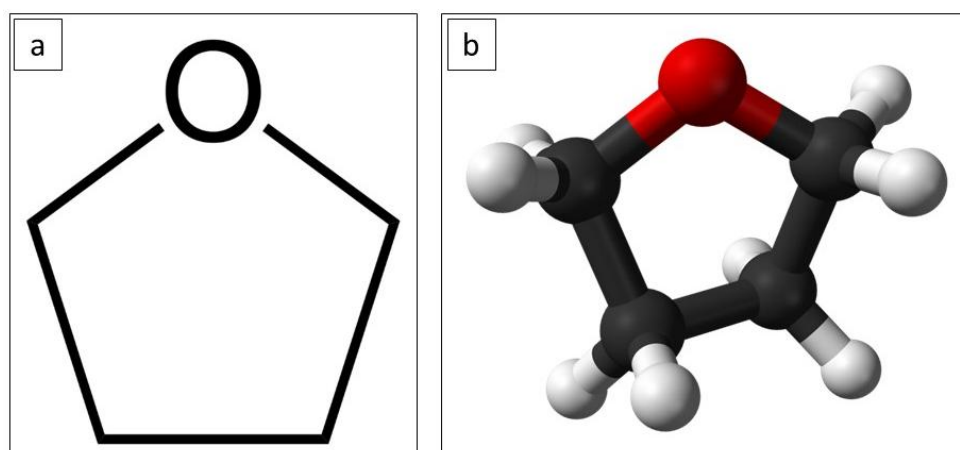


Figure 31. a) Skeletal formula of THF. b) Ball-and-stick model of the THF molecule

Based on the overall investigations, the interactions between PLA, THF, and SA were expected to yield a lightweight, environmentally friendly, and highly effective solution for thermal insulation, making it suitable for use in green and energy-efficient construction system.

However, THF has two main drawbacks: *I)* a very strong and penetrant odor, which can make it unpleasant for people, and *II)* a limited ability to dissolve PLA (i.e., PLA has a poor

solubility in THF, ranging around 8-10% w/v)[220, 221]. While the first problem can be readily solved by operating under a fume hood for laboratory tests and by wearing a convenient face mask for outdoor applications, the second issue makes it difficult to obtain solutions with a high load of PLA, which in turns is translated into a high weight amount of solvent in the solution. This composite solutions that have a marked tendency to present marked shrinking and to develop cracks in the remaining solid PLA when the solvent is evaporated from the solution. In any case, after a complete dissolution of the PLA in THF, the considered filler (i.e., SA, ES or CO) has been added to the system, obtaining a slurry that has been deposited on a carefully chosen substrate.

The preparation of the ternary slurry, particularly the dissolution of PLA in THF, was accomplished using several different methods. These included stirring at ambient temperature, heating the mixture close to the evaporation point of THF (61°C), and continuous magnetic stirring at elevated temperatures (**Fig.32**) to ensure complete dissolution. The resulting solution should be homogeneous and free of any undissolved particles. Once the PLA was fully dissolved in THF, the filler was gradually added to the solution, in the appropriate weight percentages. Because the goal was to create a uniform ternary slurry, the addition of filler should have been done slowly and with constant stirring to ensure even distribution of the filler particles throughout the slurry. The stirring of the slurry was continued for a specified period (in general around 30 min) to achieve a uniform dispersion of the filler within the PLA/THF solution. Finally, the obtained homogeneous slurry was used to produce the different types of composite samples, as will be explained below.



Figure 32. The slurry production process under the magnetic stirring at elevated temperatures

3.3.1.2 Preparation of Solid Samples from Slurries via Deposition in Mold

The prepared ternary slurry in the previous section, was poured into a mold, which consisted of a glass container covered with aluminum foil. Since the ratio between THF and filler was relatively high (maximum solubility of PLA in THF of 8-10% w/), the progressive evaporation of the solvent left the composite with marked volume loss, leading to remarkable shrinking of the prepared samples, and often of large cracks (**Fig.33-b** and **c**). In order to limit this problem, the THF evaporation step was conducted placing an aluminum foil as a lid on the vessel used for the deposition of the slurry. Several holes have been pierced through the aluminum foil, as shown in **Fig.33-a**, to allow moderated solvent evaporation, slowing down the solidification process.

The drying process have been carefully monitored to minimize shrinkage and deformation. While this can be done using various techniques, such as solvent evaporation (Atmospheric drying), Hot-air drying, compressed-air drying, Vacuum drying, Sorption drying, depending on the desired properties of the final composite [222], for the experiments here described the vacuum drying, using a normal double membrane pump, has been used.

In order to improve the quality of the resulting samples and prevent defects, after conducting extensive experimental work, approximately a 1% (V/V with respect to THF) of 1,4-Dioxan was added to the slurry during the stirring process before pouring. This addition was made because 1,4-Dioxan is a reasonable solvent for PLA (being able to dissolve it up to about 17 wt.% [223], hence it prevents rapid solidification of PLA caused by the fast evaporation of THF, thereby reducing cracks and deformation during the solvent evaporation and solidification stages.

To ensure complete evaporation of the solvent from the composite material during solidification, an atmospheric drying method was employed under ambient laboratory conditions. This process took 3 to 5 days, and finally, high-quality, homogeneous composite samples have been obtained (**Fig.33-d**); however, due to the lack of a suitable mold, the resulting products were geometrically deformed. In order to regain their planarity, the so-obtained samples have been hence subjected to the application of a heavy load, leading to the complete recovery of a substantial planarity (image not shown).

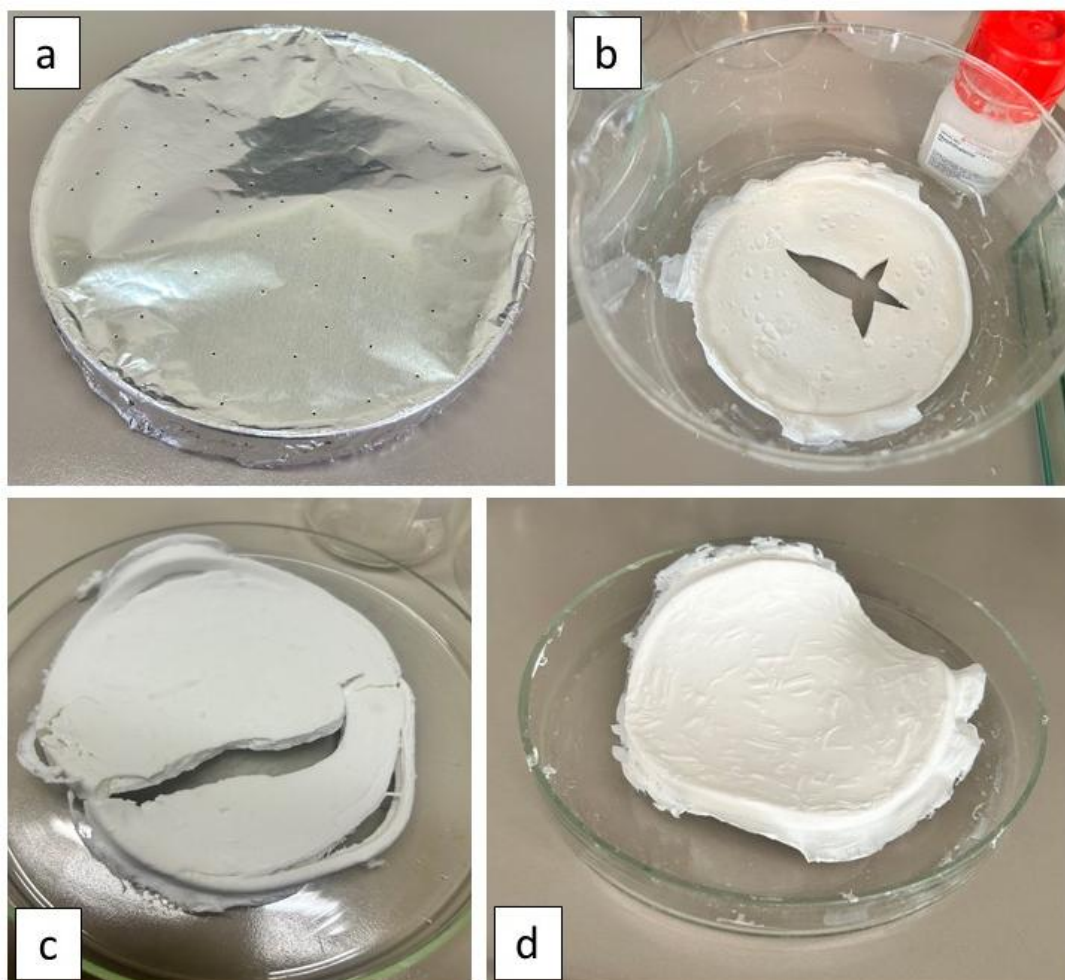


Figure 33. The resulted composite in different conditions: a) Needle-punched foil to control air flow, b) The crack occurred in the PLA-sample made without airflow control, c) The crack occurred in the PLA-sample made without addition 1% 1,4-Dioxan and d) The final product made by 1% 1,4-Dioxan in the airflow controlled but deformed due to lack of suitable mold.

3.3.1.3 Preparation of Solid Samples from Slurries via Spray Deposition onto Substrates

Before delving into the practical aspects of this part, I would like to provide an introduction to spray coating. The process employs a nozzle to atomize the coating material into fine droplets, which are then sprayed onto a target surface. This method is valued for its precision, scalability, and ability to handle diverse materials, including polymers, composites, and functional additives. The basic principle of the spray process to produce overlay coatings consists of three primary steps: *I*) creating a coating material of appropriate composition in powder, wire, or rod form, *II*) imparting sufficient kinetic and thermal energy to create a

confined high-energy particle stream, and *III*) propelling the energetic particles toward the substrate using high-pressure carrier gas [224]. Generally, there are two main categories for this method:

- 1) If all the energy is kinetic in nature with absence of any significant thermal contribution, the process falls within “cold spray” technology.
- 2) If a combination of kinetic and thermal energy is involved, the process is in the category of “thermal spray” technology.

The relative contribution of kinetic and thermal energy in various spray processes is shown in the temperature-velocity diagram of **Fig.34** by Papyrin [225].

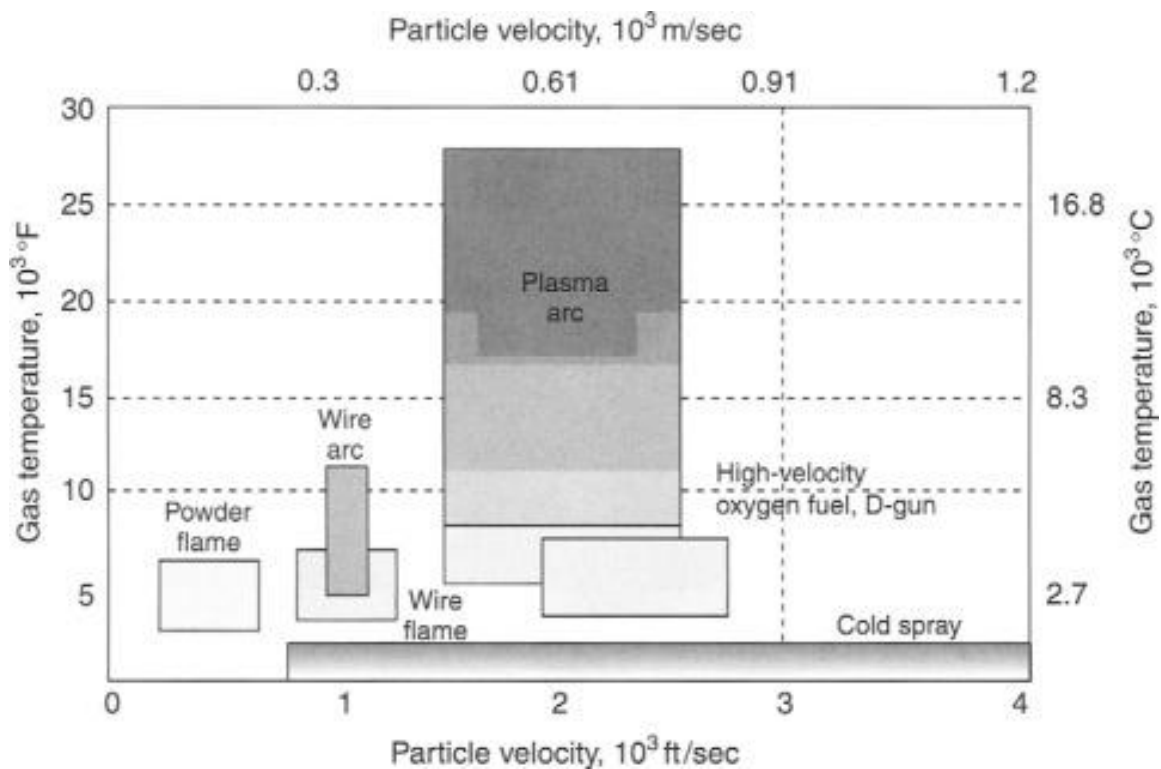


Figure 34. Gas temperature-particle velocity regimes for various thermal spray processes and the cold spray process.

On the other hand, a wide range of coating methods and materials is available for various applications, all sharing the common goal of protecting parts or structures from mechanical or chemical damage [226]. Most scientific literature describes various reliable spray coating methods, demonstrated in **Fig.35**.

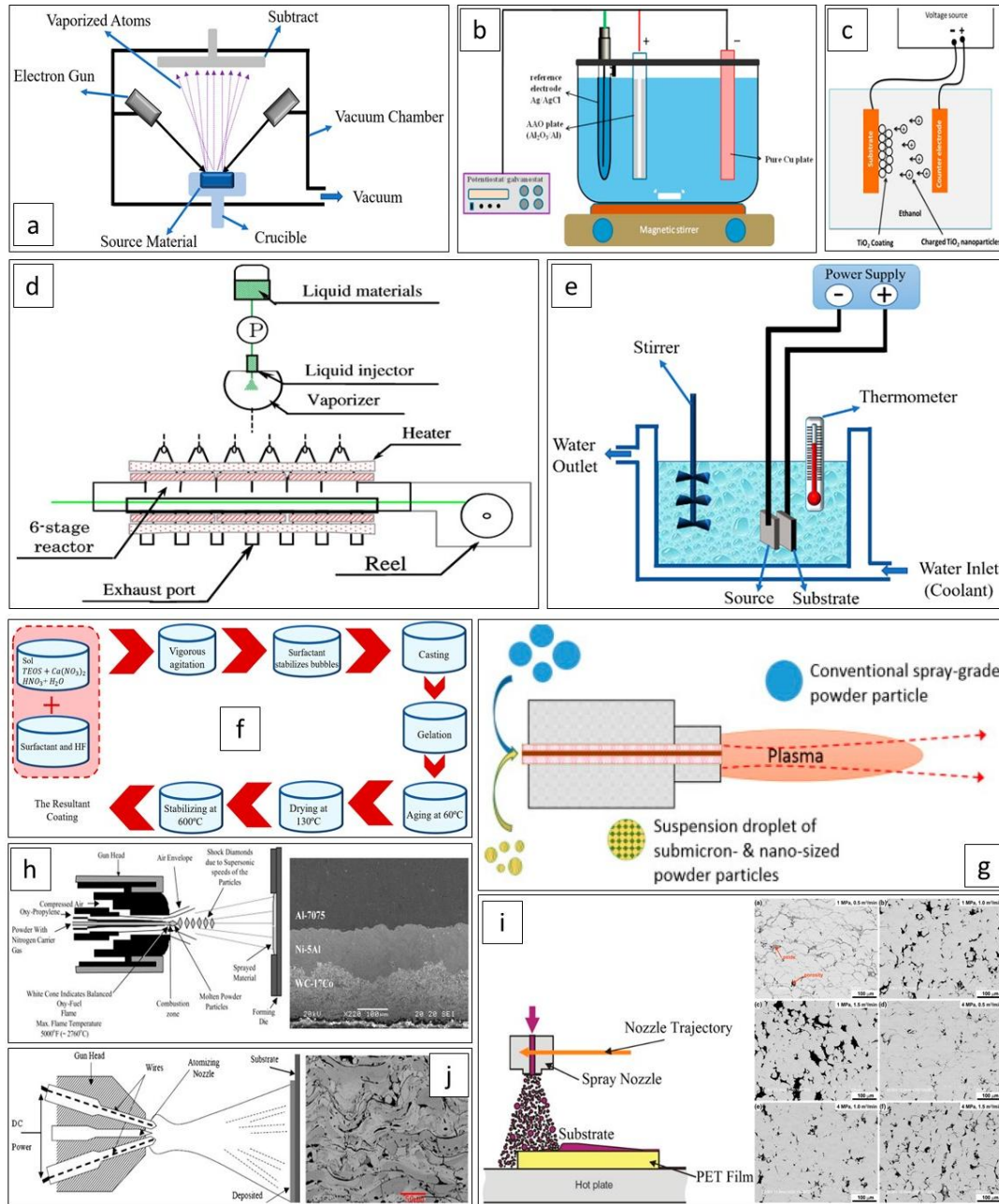


Figure 35. **a)** Schematic view of a Physical Vapor Deposition (PVD) machine using electron beam as the heat source [227]. **b)** Schematic setup for electrodeposition (ELD) of copper metal particles over aluminum oxide [228]. **c)** Sketch of the electrophoretic deposition process (EPD) [229]. **d)** Schematic chemical vapor deposition (CVD) setup, mechanical parts, and operation mechanism [230]. **e)** Schematic view of micro-arc oxidation (MAO) process [231]. **f)** Schematic sol-gel coating process from solution preparation to the final solid structure formation [232]. **g)** Schematic plasma spray coating setup and its parts (Thermal Spray Coating) [233]. **h)** Schematic setup of a high-velocity oxy-fuel (HVOF) coating system (Thermal Spray Coating) [234]. **i)** A schematic of warm spray coating technique and its setup (left) [235]. Cross-section BSE micrographs of warm spray-deposited Ti-6Al-4V on low-carbon steel substrate processes spray pressure and nitrogen flow rates of (a) 1 MPa and 0.5 m³/min, (b) 1 MPa and 1 m³/min, (c) 1 MPa and 1.5 m³/min, (d) 4 MPa and 0.5 m³/min, (e) 4 MPa and 1 m³/min, and (f) 4 MPa and 1.5 m³/min, respectively (right) [236]. **j)** Schematic arc wire spray coating setup and mechanism of operation (left) [237]. SEM micrograph of arc wire spray-coated surface by Tafa's steel (95MXC) cored wire feedstock. The substrate material is not mentioned in Reference (right) [238].

In this work the cold spray coating has been used to prepare a layer of composite over available substrates prepared in the frame of a collaboration of my Department with an Italian company "Diasen srl", which is active in the field of natural thermal insulation.

Cold spray coating is a technique that relies on impact of particles on substrates to perform coating, without using a heat source. The general working mechanism of cold spray coating depends on particle size, the temperature of the target, material properties of coating particles, and a critical velocity [239]. Powder materials are fed to a stream of high-velocity mediums to achieve the desired kinetic energy. After particle-substrate impacts take place, this energy deforms the particles and bond them to the substrate. In some cases the particles can penetrate inside the substrate. Using a high flow rate of accelerated particles, the surface is coated with desired materials [240]. **Fig.36** shows SEM micrographs of cold spray-treated surfaces and a schematic view of cold spray coating process.

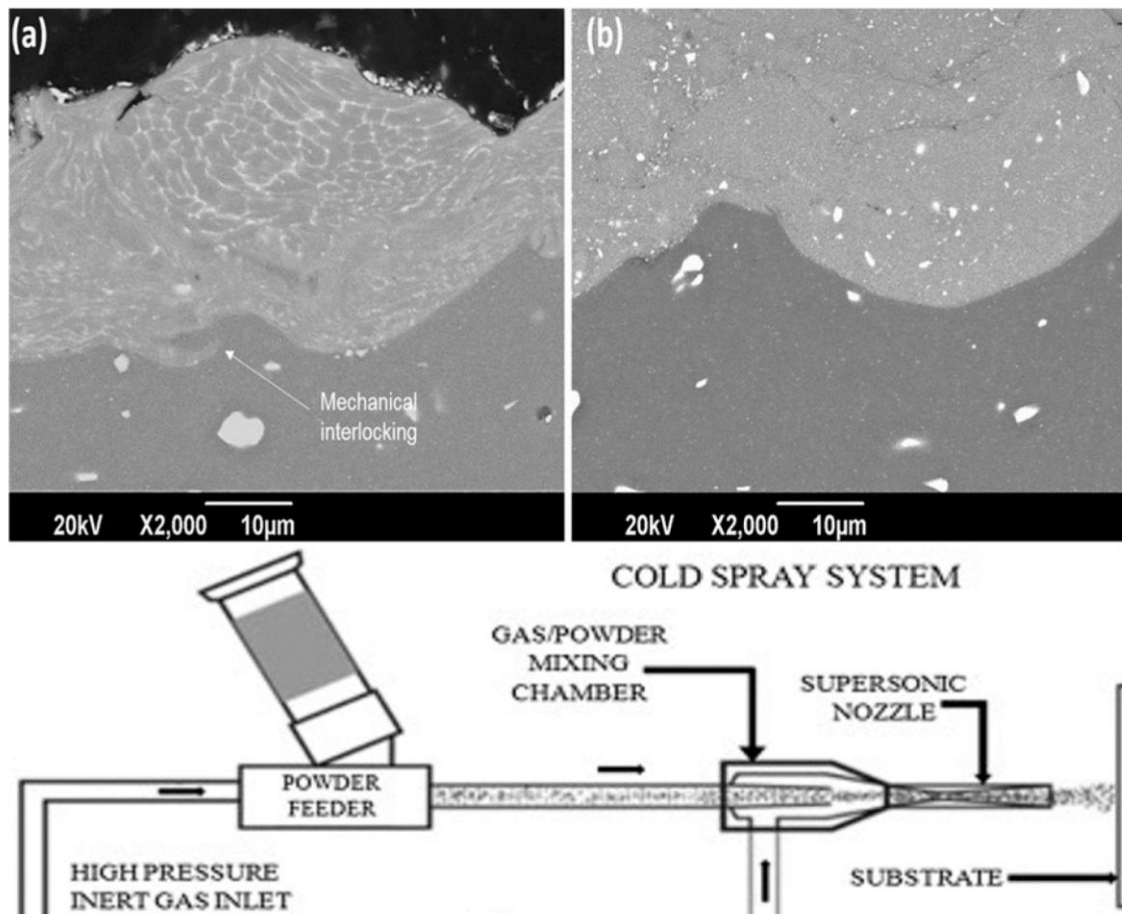


Figure 36. SEM micrographs of cold spray-coated AA6061 substrate by (a) as-received and (b) heat-treated AA7075 particles with a mechanical interlocking between the coating and the substrate (Top) [241]. A schematic view of cold spray coating process (Bottom) [242].

For the here presented work, the base materials used to create the specimens were specifically manufactured by Diasen under the name "Calce Storica," which translates to "Classic Concrete." This material is a premixed, single-component mortar (Calce Storica type) based on natural hydraulic lime (NHL-5), that is completely concrete-free and is characterized by satisfactory mechanical resistance and high adhesion to substrates. The specific data sheet for this material is outlined in Table 16.

Table 16. Physical and Technical Data sheet of Calce Storica made in Diasen Company

<i>Characteristic Data</i>	<i>Value</i>	<i>unit</i>
Concrete yield	17±10% kg/m ² per cm of thickness	kg/m ²
Appearance	Powder	-
Colour	Light Grey	-
Blending Water %	18-23 % 4.50-5.75 L for each bag (25 kg)	L/kg
Maximum Grain Size	1.0	mm
Max Application Thickness per Layer	2.5	cm
Anhydrous Mass Weight (Powder Material) (UNI EN 998-2)	1240 ± 20	kg/m ³
Application Temperature	+5 /+35	°C
Drying Time (T=+23°C; R.H.50%)	8	hour
Conservation	12	month
Packaging	A bag of 25 kg	kg

To prepare the Calce Storica samples, approximately 23% water was added to the mortar. After mixing and pouring the mixture into specific molds (**Fig.37-a**), the samples were allowed to cure at ambient temperature for two days (**Fig.37-b**), then they have been removed from the molds (**Fig.37-c**). Following the curing period, the specimens were placed in an oven to remove all moisture. The samples were oven-dried (**Fig.37-d**), with their weight measured daily until stabilization was achieved, indicating that the tile-shaped specimens were ready for further processing.

The so-obtained tiles have been characterized in terms of thermal conductivity (k). This step allowed to obtain a reference value of k_s for the tile-shaped substrate, thanks to which the k_c of the composite has been determined, as described in the following.

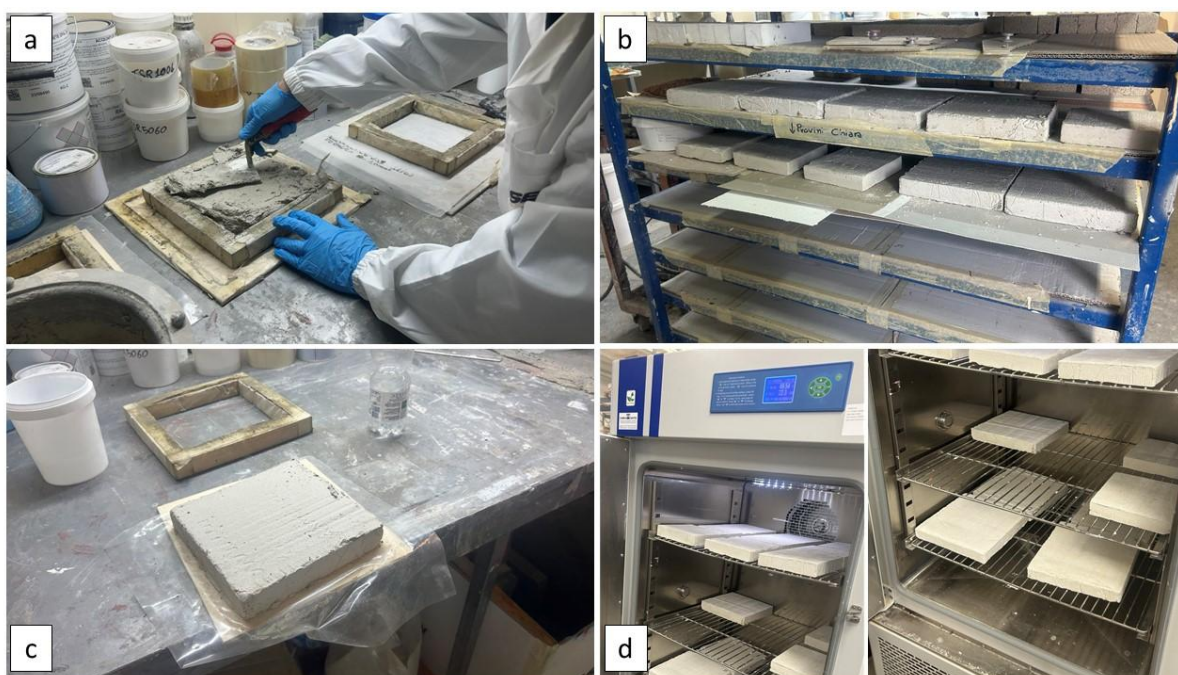


Figure 37. Concrete sample being manufactured and manufactured at Diasen Company; a) Pouring the prepared concrete and water mixture into molds, b) Allowing the samples to dry at ambient temperature for two days, c) Removing the samples from the molds, d) Oven-drying concrete samples

The so-prepared substrates have been treated with cold sprays of composite slurries. In more detail, the slurry composites (with different percentages of fillers) have been prepared with the compositions specified in Table 17. In order to ensure an overall homogeneous slurry, at first the pure PLA was weighed and then dissolved in THF while being placed on a magnetic stirrer at a temperature of $\sim 45^{\circ}\text{C}$ (**Fig.38**) for at least 5 hours in a closed vessel (taking care to avoid excessive pressure build up).

Table 17. Percentage of composite solutions

No.	Composite ID	Total Weight (g)	PLA (wt.%)	SA (wt.%)	CO (wt.%)	THF (ml)	Preparation Time
1	Neat PLA	100	100	-	-	500	5h
2	P-S1	100	99	1	-	500	5h
3	P-S2	100	98	2	-	500	5h
4	P-S5	100	95	5	-	500	5h
5	P-C2	100	98	-	2	500	5h
6	P-C5	100	95	-	5	500	5h
7	P-C10	100	90	-	10	500	5h
8	P-C15	100	85	-	15	500	5h

* For more information; P-S1 means PLA + 1% of SA (wt.%)

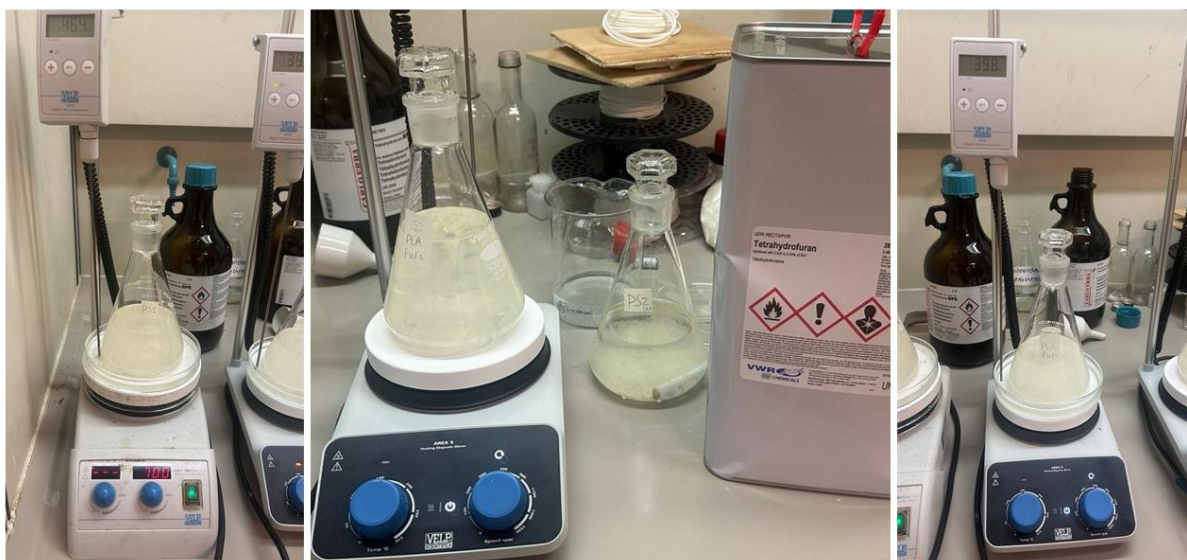


Figure 38. The solution Composite (Slurry composite) in preparation phase

Once prepared, the composite mixtures have been transported to the Diasen Company. Here they have been deposited onto the surfaces of the Calce Storica specimens using a cold spray coating application process. This process ensured a uniform coating, facilitating the compatibility (i.e., avoiding possible delamination of the dry composite) with the underlying substrate. The coated specimens were subsequently left to cure under ambient conditions for at least 24 hours to allow for the complete evaporation of the solvent (THF) and to ensure the stability and performance of the applied composite layers.

Fig.39 illustrates the specimens before applying the composite solution, during application and after the drying process, clearly demonstrating the transformation as the solution solidified into a uniform coating. Once prepared and dried the samples have been characterized in terms of thermal conductivity. Since the used thermal conductivity determination system was unable to separate the contribution of the composite from that of the underlying Calce Storica substrate, the thermal conductivity of the deposited and dried composite layer was determined by comparing the previously determined k_s of the Calce Storica substrates (with their geometrical parameters, including the tile thicknesses), with the k value defined for the composite/tile ensemble, as will be better described in the following paragraphs.



Figure 39. Spray coating process at Diasen Company. a) Pouring the slurry composite into the coating spray tank, b) applying of the slurry composite (using the air pressure), c) concrete specimen with measured baseline thermal conductivity, ready for coating, and d) freshly coated specimens, still wet.

3.3.2 Solid Composite Based On Poly-Lactic Acid (PLA)

In addition to slurry-derived composite layers, also all-solid composites obtained via mechanical approaches (such as; extrusion, injection molding and hydraulic press) have been prepared, taking care of varying the material composition in the most systematic way possible, so to investigate the effect of changing percentages of fillers over the properties of the resulting composites. The reason for investigating also this composite realization approach lies in the extreme practicality of the mechanical techniques, which allows to obtain already solid materials having a reasonable homogeneity, hence reproducible materials that could be easily incorporated into other matrices (like plastics, lime, concrete, etc.). Moreover, being a much diffused preparation technique, extrusion mixing would ensure a subsequent rapid industrializability should the explored composite formulations present points of interest in performance and/or rapid applicability. The following paragraphs describe hence the mechanical methods used to prepare, PLA-based composites.

3.3.2.1 Sample Preparation Process

In this method, a polymer must be completely dry (i.e., it must not contain appreciable levels of water or humidity). This property is required for two main reasons: *I*) any included water would generate vapor bubbles during the extrusion process (which takes place thanks to the complete melting of plastics), and these bubbles could be included within the extruded material, generating a porous material, rather than a compact one; *II*) the presence of water, especially if high temperatures are reached (as is the case for extrusion), can cause hydrolysis of the processed polymer, degrading it. This latter phenomenon is particularly critical for PLA, which is prone to fast and easy hydrolysis, hence a proper drying step is necessary prior to its extrusion mixing. Drying of PLA takes usually place in the range of 80–100 °C [243], but also other temperatures can be used, as shown in Table 18.

Table 18. Drying half times for PLA pellets (Amorphous and crystalline) under different temperatures [244].

<i>Drying temperature (°C)</i>	<i>Drying half time (h)</i>
Amorphous pellets	
40	4.0
Crystalline pellets	
40	4.3
50	3.9
60	3.3
70	2.1
80	1.3
100	0.6

Commercial grade PLA pellets are usually crystallized, which allows drying at higher temperatures to reduce the required drying time. The crystallization process is useful also because amorphous pellets must be dried below the glass transition temperature (T_g) (~60 °C) to prevent the resin pellets from sticking together, which can bridge and plug the dryer [243]. Therefore, in accordance with these discussions, PLA granules have been dried in a vacuum oven at 60°C for 4 hour to eliminate any residual moisture.

To achieve the composite samples, three different shapes of specimens have been prepared: 1) Pellet samples, 2) Film samples, and 3) Dumbbell-shaped samples. These different shapes have been selected in order to better carry out the subsequent characterization steps (for example, the mechanical behavior is better elucidated using a dumbbell-shaped sample, while the thermal conductivity is better measured from a film-shaped sample).

Therefore, in this part, four types of PLA-based composites have been prepared:

- 1) Pellet PLA in the form of granules having a diameter of 6-8 mm, with SA-5 wt.%, using the extrusion machine to produce *Filament Samples* (**Fig.40**). (identified as P-S5)

* Due to the size of the extrusion machine available, a large volume of material was required for each sample production run. For this reason, this method was used exclusively for manufacturing this sample, while more cost-effective methods were employed for the production of other samples.*

- 2) PLA in the form of powdered granules (~ 2mm), with SA powdered by a diameter of about 0.3 mm, using the hydraulic hot press to produce *Film samples* (**Fig.42**) and using the injection molding machine to produce *Dumbbell-shaped Sample* (**Fig.43**) (identified in the following as P-P-S#, where # stands for the percentage of powdered SA used in the composite formulation, Illustrated in Table 21);

In this step, due to the inhomogeneity and non-uniform distribution of unpowdered SA, which was initially used, a powdering step was added to ensure better dispersion of the filler within the PLA matrix. This modified formulation is identified as P-P-S#, where # represents the percentage of powdered SA used in the composite formulation, and -P- denotes crushed SA.

- 3) PLA with powdered ES (identified in the following as P-ES#, where # stands for the percentage of ES used in the composite formulation, Illustrated in Table 22);

* *Film samples* and *Dumbbell-shaped Sample* were produced from this mixture.*

- 4) PLA with a combination of both SA and ES (identified in the following as P-S#-ES#, where # stands for the percentage of the corresponding filler used in the composite formulation, Illustrated in Table 23). The combinations of the two fillers have been investigated in order to verify any possible synergy among them in terms of thermal conductivity decrease.

* *Film samples* were produced from this mixture.*

The extrusion machine conditions for making PLA/SA composite filaments are shown in Table 19. Therefore, PLA granules and the SA have been at first dried and then manually premixed with each other, before feeding them to the extrusion machine .Upon extrusion, filaments of composite have been obtained. For example, **Fig.40-b** shows these types of filament for P-S5 composites. The obtained filaments have been put in a separated granulation instrument (which was made by a lab technician) to create a composite pellet (**Fig.40-c**), later used for further processing aimed at the realization of samples for mechanical resistance tests.

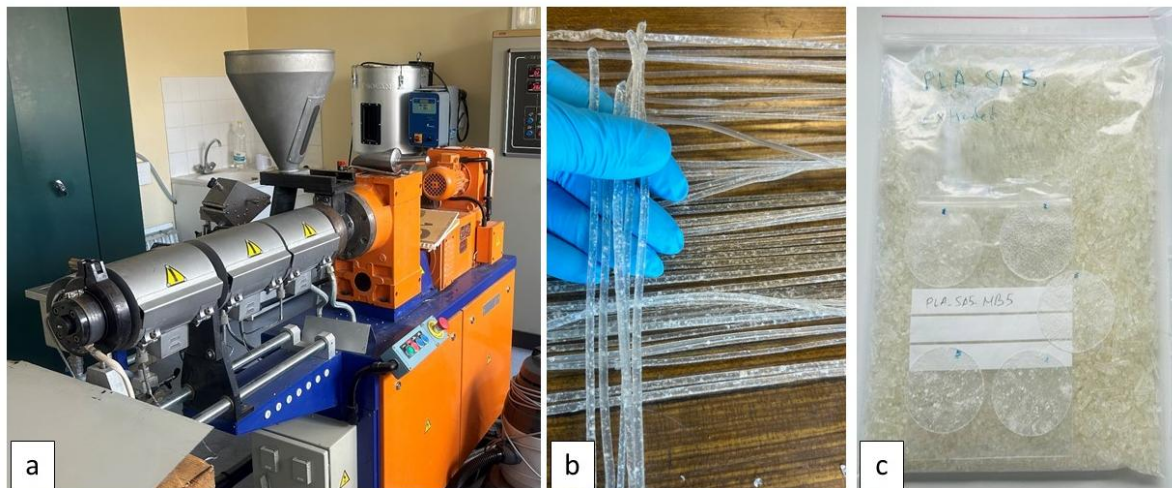


Figure 40. a) The extrusion machine to create the filaments of PLA/SA composite. b) The filaments of PLA/SA composite reinforced by SA-5 wt.%, c) the pellets of PLA/SA (5 wt.%)

Table 19. Extrusion machine conditions to produce composite filaments (P-S5 samples).

<i>Temperature of the first section of the screw, after the hopper (TZ1)</i>	170°C
<i>Temperature of the second section of the screw (TZ2)</i>	180°C
<i>Temperature of the last section of screw (TZ3)</i>	190°C
<i>Temperature of the die head (TZ4)</i>	200°C
<i>Screw rotating speed</i>	7 rpm
<i>Pressure in the extrusion chamber</i>	13 bar

For specific measurements of the composite properties, a precise sample geometry was necessary. For example, the thermal conductivity measurement equipment required to have film-shaped samples; therefore, a number of film-shaped samples have been also produced.

To achieve this geometry, a fine PLA powder was necessary, rather than the starting pellets. Therefore, the grinding machine shown in **Fig.41-a**, has been used under four different experimental conditions detailed in Table 20, followed by a crushing process. The first three conditions have been found to be unsuitable for the crushing process, due to problems of

polymer degradation and unwanted thermal joints between PLA pellets/powders. The most effective processing conditions for obtaining a PLA powder suitable for the desired needs was found to be the No.4, i.e. via a previous freezing of the PLA under nitrogen gas (N₂) treatment, and the resulting powder have been hence used for the preparation of the composite films.

Table 20. The crushing process and conditions of PLA in details; from pellet to powder

1	Drying at 80°C for 4 hours	In this condition, was dried the PLA powder at 80°C for 2 hours before crushing it. The heat likely removed any moisture, making the powder more brittle and easier to crush.
2	In the fridge at 6°C for 6 hours	Here, was cold the PLA pellet in the fridge at 6°C for 4 hours before crushing it. Theoretically, the cold temperature might have affected its properties, potentially making it more rigid or less prone to sticking together during crushing.
3	In the freezer at -20°C for 12 hours	Freezing the PLA pellet at -20°C for 12 hours, probably had a similar effect as refrigeration, but at a lower temperature. The extended freezing time might have further altered its behavior.
4	Using liquid nitrogen (LN ₂) during crushing	Liquid nitrogen is extremely cold (around -196°C), so using it during crushing would have flash-frozen the PLA pellet. This could lead to a very brittle state, making it easier to crush.

To create the samples of composite films, the crushed PLA was hence sieved to obtain particles smaller than 2 mm, and then mixed with different fillers, as described above. In the following Tables 21, 22 and 23 the exact compositions of these samples is provided.

In more detail, Table 21 reports about the composition of pure SA-loaded PLA, differentiating two composites characterized by incorporating SA particles at different granulometries, the “-P-” are referred to powdered or crushed SA ($\sim 300\mu\text{m}$), and the other ones are referred to SA granules of about ($\sim 1500\mu\text{m}$) diameter.

Table 21. PLA and SA specimen preparation formula

<i>Sample ID</i>	<i>PLA (wt.%)</i>	<i>SA (wt.%)</i>	<i>PLA (mg)</i>	<i>SA (mg)</i>
PLA	100.00%	0.00%	2000	0
P-S1	99.00%	1.00%	1980	20
P-S2	98.00%	2.00%	1960	40
P-S5	95.00%	5.00%	1900	100
P-S10	90.00%	10.00%	1800	200
P-S15	85.00%	15.00%	1700	300
P-P-S2	98.00%	2.00%	1960	40
P-P-S5	95.00%	5.00%	1900	100
P-P-S10	90.00%	10.00%	1800	200
P-P-S15	85.00%	15.00%	1700	300

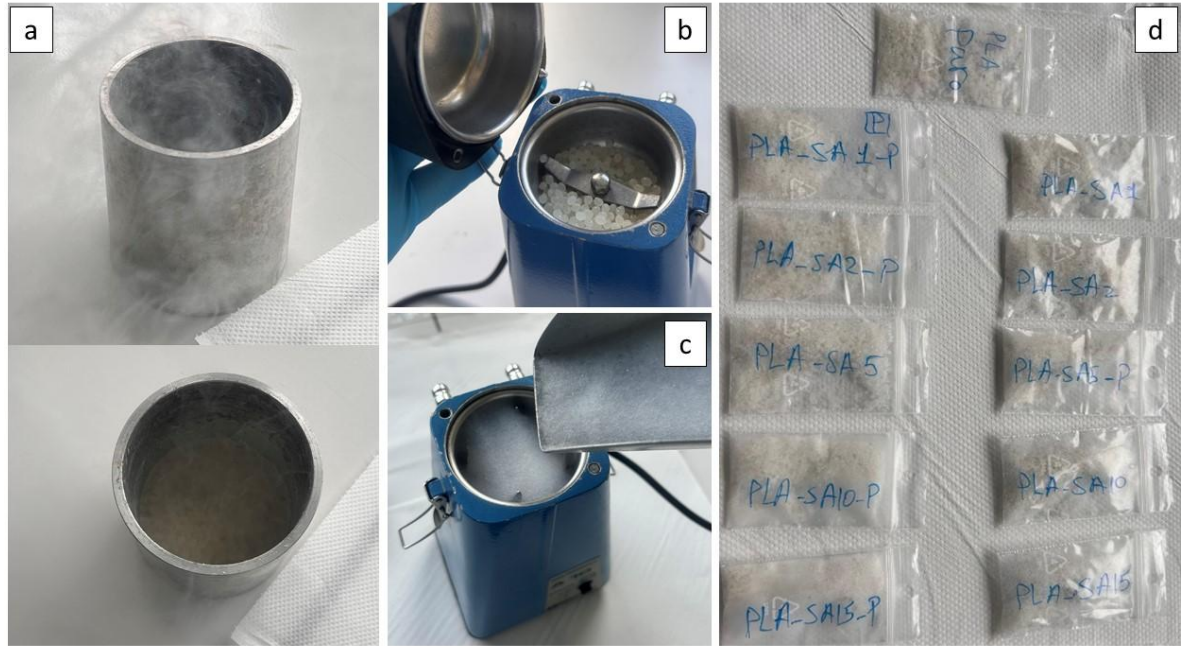


Figure 41. a) PLA pellet mixed with liquid nitrogen before crushing process b) the mill mashie for crushing the PLA pellets and c) SA granules, d) The mix package of PLA powder with SA granules or non-crushed (right) and SA Powder (left).

For preparing the ES-filled composites a ball milling machine was used to pulverize the ESs. The so-obtained powder was then sieved with a 500 BSS mesh to obtain particles smaller than 25 microns. The so-obtained ES powder was hence added to the pulverized PLA, in various weight fractions (2, 5, 10, and 15 wt.%), to obtain the PLA/ES film specimens shown in Fig.42 and with the compositions shown in Table 22.

Table 22. PLA/ES specimen preparation formula

<i>Sample ID</i>	<i>PLA (wt.%)</i>	<i>ES (wt.%)</i>	<i>PLA (mg)</i>	<i>ES (mg)</i>
PLA	100.00%	0.00%	2000	0
P-ES2	98.00%	2.00%	1960	40
P-ES5	95.00%	5.00%	1900	100
P-ES10	90.00%	10.00%	1800	200
P-ES15	85.00%	15.00%	1700	300

PLA powder, SA powder and ES have also been mixed together to generate a ternary composite, with the aim of joining the thermal insulation ability of SA and the mechanical robustness of ES. These fillers were mixed with PLA powder in various weight percentages, ranging from 0.5 to 6 wt.%, according to the compositions described in Table 23.

Table 23. PLA/SA/ES specimen preparation formula

<i>Sample ID</i>	<i>PLA (wt.%)</i>	<i>SA (wt.%)</i>	<i>ES (wt.%)</i>	<i>PLA (mg)</i>	<i>SA (mg)</i>	<i>ES (mg)</i>
PLA	100.00%	0%	0.00%	2000	0	0
P-S0.5-ES0.5	99.00%	0.5%	0.5%	1980	10	10
P-S1-ES1	98.00%	1%	1%	1960	20	20
P-S2-ES3	95.00%	2%	3%	1900	40	60
P-S4-ES6	90.00%	4%	6%	1700	80	120

The fabrication of the composite film samples, some of which can be seen in **Fig.42-b**, involved the use of a hydraulic hot press, shown in **Fig.42-a**. After numerous tests under different conditions, the optimal condition for creating the film samples suitable for the subsequent measurements was determined to be 4 minutes under 5 tons of pressure.



Figure 42. a) The Specac Atlas™ Manual 15T Hydraulic hot presses used to produce film specimen, and b) The film samples made by the Hydraulic hot presses

The dumbbell-shaped samples have been prepared using an injection molding machine, using the following procedure. At first, the raw materials (PLA mixed with either SA or ES) have been prepared in the required composition (see Table 24) and thoroughly mixed to ensure homogeneity.

Table 24. Dumbbell-shaped specimen preparation formula

<i>Sample ID</i>	<i>PLA (wt.%)</i>	<i>ES (wt.%)</i>
PLA	100.00%	0.00%
P-S15	85.00%	15.00%
P-P-S2	98.00%	2.00%
P-P-S5	95.00%	5.00%
P-ES2	98.00%	2.00%
P-ES5	95.00%	5.00%
P-ES10	90.00%	10.00%
P-ES15	85.00%	15.00%

The so-prepared materials were fed into the injection molding machine, shown in **Fig.43-a**, and have been heated until the PLA matrix was molten. The composite material was hence injected into a mold cavity shaped like a dumbbell. This was done under high pressure (about 100 bar) to ensure that the mold was completely filled. Once the mold was filled, the material was allowed to cool and solidify within the mold. Cooling channels and water flow within the mold helped to speed up the cooling process. After the material has solidified, the mold was opened, and ejector pins pushed the finished dumbbell-shaped sample out of the mold (**Fig.43-b**). The Table 25 shows the specific conditions used to produce the dumbbell-shaped samples (common for both the PLA/SA and PLA/ES composites). Subsequently, the dumbbell-shaped samples have been used for mechanical testing (such as tensile strength tests).

Table 25. Parameters used in the Injection Molding Machine for producing the dumbbell-shaped samples.

<i>Screw Temperature (TZ1)</i>	180°C
<i>Chamber Temperature (TZ2)</i>	190°C
<i>Nozzle Temperature (TZ3)</i>	200°C
<i>Injection pressure</i>	100 bar
<i>Maintenance pressure</i>	120 bar
<i>Holding time</i>	4s
<i>Cooling time</i>	4s

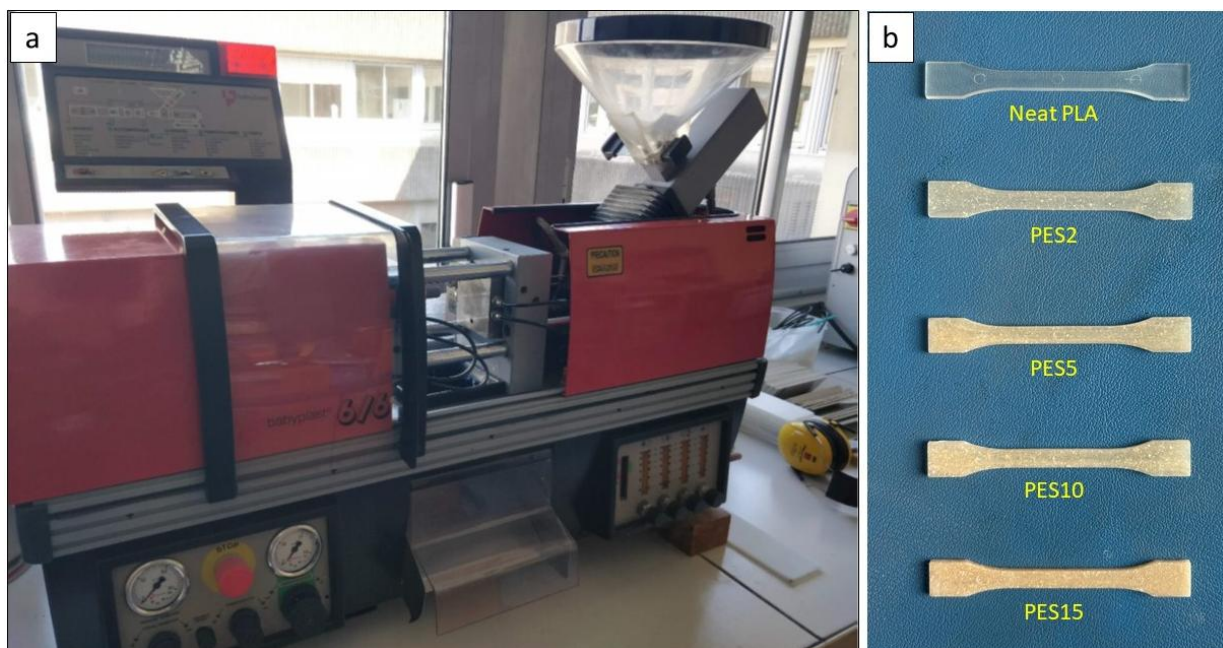


Figure 43. a) The injection molding machine used to produce dumbbell-shaped samples and
b) some dumbbell-shaped samples made by injection molding machine

3.4 TESTING AND ANALYSIS

3.4.1 *Thermal Conductivity Measurements*

The thermal properties of the composite specimens were thoroughly evaluated through an extensive series of tests and analyses to ensure their suitability for practical applications. These evaluations included the measurement of thermal conductivity, which determines the material's ability to conduct heat. All tests were performed under carefully controlled laboratory conditions designed to replicate real-world operating environments, ensuring the reliability of the findings. The data obtained from these tests have been meticulously analyzed to determine the composite material's efficiency in terms of thermal insulation and of its ability to maintain thermal stability under varying environmental and temperature conditions.

Thermal conductivity measurements were performed in two stages to investigate the actual performance of the composite in real-life conditions, in addition to laboratory conditions. This approach was designed to provide a comprehensive evaluation by simulating different practical scenarios. The first stage focused on testing the composite material under standard laboratory conditions (in the laboratory of Rouen University), while the second stage replicated more dynamic, variable environmental factors that could be encountered in real-life applications (jointly in the Chieti University's Lab. and Diasen Company).

In the following some details of the findings from both tests, providing a full description of the performance and reliability of the composite materials under various conditions, are provided.

3.4.1.1 **Test 1. Rouen University Laboratories**

A first determination of the k values for the tested composites was carried out at the University of Rouen (France, in the laboratories “Groupe de physique des matériaux – GPM UMR 6634”, in which I spent the PhD period abroad).

The thermal conductivity measurements were carried out using the instrument shown in **Fig.45**, using the Guarded Hot Plate (GHP) method. The GHP is an absolute measurement technique based on steady-state unidirectional heat flow. It creates a temperature gradient across a specimen by sandwiching it between a heater plate and an isothermal cold plate. The GHP setup exists in two configurations: double-specimen (**Fig.44-left**) and single-specimen (**Fig.44-right**), which in this work double specimen configuration have been used.

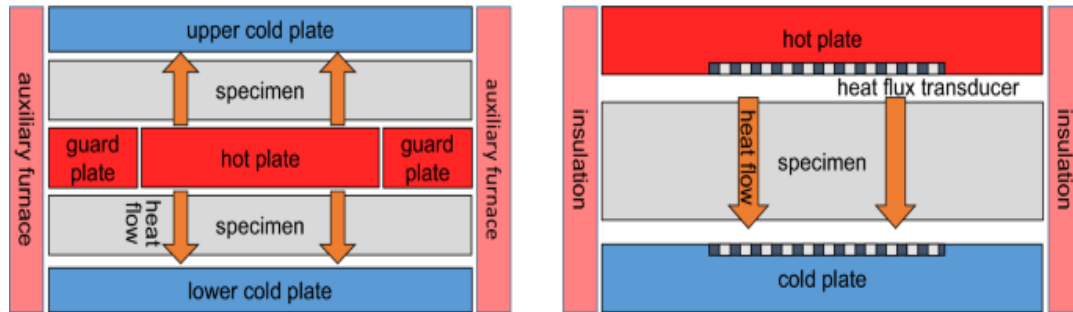


Figure 44. The apparatus of guarded hot plate method for thermal conductivity measurement: left) two specimens with/without auxiliary heaters and secondary guards, and right) single-specimen.

There is a specimen on either side of the heater plate and then cold plates on either side of the two specimens. In the single specimen configuration, there is a specimen and cold plate on one side of the heater plate and on the other side are insulation, an auxiliary heater plate matched to the temperature of the primary heater plate, another layer of insulation, and another cold plate. This stack of specimens and plates is mounted horizontally, so that heat flows vertically from the heater plate, through the specimen(s) to the cold plate(s). The temperatures on either side of the specimen are measured, and the heat flux is determined by them amount of electrical power supplied to the heater. The electrical power is maintained at a fixed value to obtain an appropriate steady-state temperature gradient through the specimens. Then knowing the specimen thickness and the area through which the heat passes, the apparent thermal conductivity of the specimen can be calculated. This simple calculation, based on Fourier’s law, assumes that all of the power supplied to the heater goes through the specimen to the isothermal cold plate, and that none of the heat is lost to the environment at the edges of

the heater plate and/or specimens. Thermal conductivity measurements of insulating materials used in building applications, performed using the GHP method in accordance with the standards EN 12667 [245] or ISO 8302 [20], are usually limited to the temperature range from -20 to 80°C. This well-known steady-state technique gives the lowest uncertainty (better than 1 %) for thermal conductivity measurements on low conducting materials [246, 247].

The GHP method ensures accurate and reliable measurements by minimizing heat loss and maintaining a steady-state heat flow through the specimen. The equipment was calibrated prior to use, and each specimen was subjected to separate measurements at room temperature (indeed varying between 20 and 27 °C).

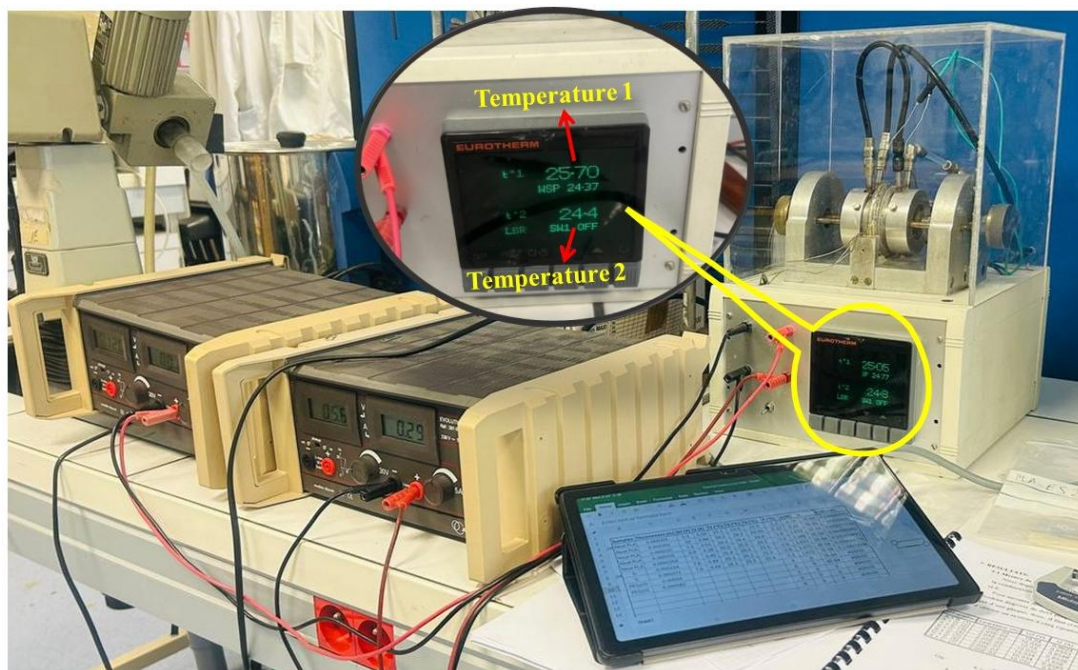


Figure 45. Hot disk thermal analyzer - instrument presented in Rouen University materials laboratory, to measurement thermal conductivity by GHP method.

After preparing the specimens with different compositions, as explained in chapter 3.3.2.1, using hydraulic hot presses, and the following procedure was used for testing;

To conduct the test, it was necessary to select two specimens with the same composition and dimensions (as much as possible), since the thermal conductivity testing machine is equipped with one hot plate (center) and two cold plates on both sides, as illustrated in **Fig.46-a**. The two identical specimens were placed symmetrically between the hot plate and the cold plates, with one specimen on the right side and the other on the left side.

Cold Plate | Specimen 1 | Hot Plate (Guarded) | Specimen 2 | Cold Plate

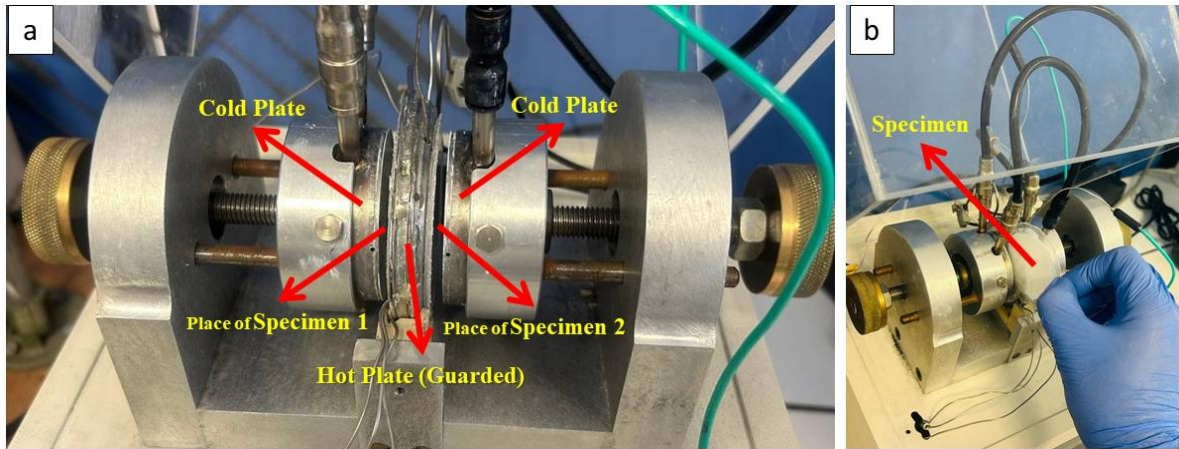


Figure 46. a) Specimen Placement on the thermal conductivity analyzer. b) Placing a specimen whose surface was covered with special cream (layer of paste)

Before placing the samples, a uniform layer of special paste was applied to both the surfaces of the samples to improve the thermal contact and increase adhesion between the specimen and the plates (**Fig.46-b**). This step ensured better thermal conductivity and more accurate measurements. Then, the screws were carefully tightened to secure the samples in place during the test. The hot plate was electrically heated to increase its temperature. To achieve this, two stabilized power supplies (alimentations) were used (**Fig.47**):

These power supplies provided a stable and controlled heat source, ensuring consistent and reliable temperature increases for the hot plate. This setup allowed for precise temperature control, which is crucial for accurate thermal conductivity measurements.



Figure 47. The power alimentations used for hot disk thermal analyzer

Before starting the device, the wirings have been thoroughly checked to verify the absence of short circuits or cable breakages. Also the water tap was then opened to allow water to flow during the process and its sealing was inspected to prevent any leakage. Subsequently, the power supply No.2 was switched on, and the desired voltage was selected. According to the machine's manual, a 10V potential is suitable to produce a temperature between 30°C and 37°C, depending on the water flow. However, this test began at 5.5V to approximate the ambient temperature more closely. Before starting the heating, the system temperature was continuously monitored using the instrument No.2. Once the temperature was stabilized, the power supply No.1 was turned on, and the test was started.

The test time was set to be at least 4 hours (according to its manual), and sometimes it could be as long as 8 hours. After a suitable time, when the temperature readings of regulator No.1 and regulator No.2 were equal $T_1 = T_2$, which ensures that a steady-state thermal equilibrium has been achieved within the system. Thus, it confirms that there is no temperature gradient within the guard zone, meaning no lateral heat flow occurs. This ensures that all the heat generated by the heater plate flows unidirectionally through the specimen, as required by the GHP method for accurate thermal conductivity measurements. In addition careful attention was given to the values of voltage (U) and current (I). At this point, thermocouple T_1 was removed and inserted into the designated hole located on the cold plates to register the temperature of the cold source. The temperature of the cold source was then recorded as T_1 on the regulator. During these measurements, it was crucial to switch off power supply No.1 to avoid interference. After the measurement was completed, thermocouple T_1 was returned to the guard zone to prepare for the next test.

Using the GHP method, the heat transfer rate through a samples can be determined using the below reported Eq.1:

$$Q = V \cdot I \quad \text{Equation 1}$$

Where Q is the heat transfer rate in watts (W), V is the potential difference across the heating plate in volts (V), I is the current passing through the heating plate in amperes (A).

The obtained results have been recorded, and the k value of each specimen was calculated using the below reported Eq.2;

$$Q = kA \frac{\Delta T}{\Delta x} \rightarrow k = \frac{Q \Delta x}{A \Delta T} \quad \text{Equation 2}$$

Where ΔT is the temperature gradient, expressed in K. The temperature gradient is indeed the temperature difference across the thickness Δx of the tested sample (The sum of the thicknesses of the two samples used for testing), expressed in m. A is the cross-sectional area, or surface area, of the tested sample, expressed in m² [248]. The so-obtained results have been subsequently collected and organized in Table 26.

Table 26. Measurement k value through Guarded Hot Plate method.

No.	Sample ID	Thicknesses (mm) (R&L)	T (°C)	k (W/m.K)	t (h)
1	PLA-Neat	0.31 + 0.235	20.1	0.075	4
2	P-P-S1	0.355 + 0.322	21	0.058	8
3	P-P-S2	0.405 + 0.34	20.8	0.077	5
4	P-P-S5	0.445 + 0.545	21.1	0.069	5
5	P-P-S10	0.61 + 0.645	21.5	0.090	5
6	P-ES2	0.255 + 0.245	24.8	0.060	4
7	P-ES5	0.385 + 0.395	24.9	0.103	5
8	P-ES10	0.435 + 0.39	25.6	0.100	5
9	P-ES15	0.41 + 0.395	27.8	0.088	5
10	P-S0.5-ES0.5	0.37 + 0.395	27	0.092	4
11	P-S1-ES1	0.42 + 0.385	26.3	0.086	5
12	P-S2-ES3	-	-	-	-
13	P-S4-ES6	-	-	-	-

Before analyzing the results, it must be noted that due to the limitations of the GHP method and the lack of proper equipment to produce suitable samples, the actual k values may not be accurately determined.

As seen in the results, the k values of each specimen vary based on their composition, as the addition of fillers or reinforcements, in some cases significantly influences the thermal properties of the PLA matrix. In this test, the thermal conductivity of various composite samples was measured, and the results from four distinct specimens, PLA neat, P-P-S, P-ES, and P-S-ES, were analyzed. Meanwhile, missing data for P-S2-ES3 and P-S4-ES6 shown in

Table 26, due to measurement device failure, prevents full comparison between sample types. Let's explore and predict the possible outcomes;

- PLA Neat

PLA neat, without any additives or reinforcements, typically exhibits a relatively low k value between of 0.0320 - 0.170 W/m.K [249], because it is inherently a poor conductor of heat. In this test, PLA neat (Sample 1) has a relatively low k value of 0.075 W/m.K, the result falls within the specified range at a temperature of 20°C.

- P-P-S Composite

In this test, P-P-S samples made by PLA powders and crushed SA were used. k values are generally low, ranging from 0.058 to 0.090 W/m.K. SA such as one of the lightest and most thermally insulating materials known, when incorporated into the PLA matrix in varying percentages, Theoretically it should reduce overall thermal conductivity due to its high porosity and extremely low density [250]. However, it has been observed that with increasing SA content, instead of a decrease, the k value increased. This outcome can be influenced by various parameters, such as, temperature, thickness, density, and etc [26].

- P-ES Composite

ES, composed primarily of calcium carbonate (CaCO_3), are a bio-derived filler that, contrary to our expectations, can increase the thermal conductivity of PLA [251]. However, k values for P-ES series samples range from 0.060 W/m.K (P-ES2) to 0.103 W/m.K (P-ES5). The k values increase as expected between samples 6 (P-ES2) and 7 (P-ES5), while a decrease is observed in samples 8 (P-ES10) and 9 (P-ES15). However, the k value depends also, on the ES size, distribution, and concentration within the composite.

- P-S-ES Composite

This composite combines the effects of both SA and ES within the PLA matrix. While SA reduces the k due to its insulating properties, the ES contribute to locally increase it. The balance between these two opposing effects determines the overall thermal behavior of this composite, making it a versatile material for applications requiring moderate k and a completely bio-based and green material. Therefore, k values for P-S0.5-ES0.5 (0.092 W/m.K) and P-S1-ES1 (0.086 W/m.K) are moderately high compared to other samples. The thicknesses

of P-S0.5-ES0.5 and P-S1-ES1 range from 0.755 to 0.805 mm, and these samples were tested at relatively high temperatures (26–27 °C), which could potentially impact the k values.

- Summary:

Thermal conductivity measurement for all samples have been performed in Rouen University's lab. The k values of the samples varied depending on their composition, with fillers or reinforcements significantly affecting the thermal properties of the PLA matrix. PLA neat, without additives, exhibited low k value, measuring 0.075 W/m.K, within the expected range at ~ 20°C. PS samples, contrary to expectations, showed an increase in k value as SA content rose, possibly due to thicker samples conducting heat more effectively. P-ES samples, generally showed increasing k values from 0.060 W/m.K to 0.103 W/m.K as sample thickness and density changed, although temperature also played a role in slightly lowering the k values in some cases. In P-S-ES samples, combining the effects of SA and ES, the k was moderately high (0.086 to 0.092 W/m.K), as the balance between the insulating effect of SA and the heat-conducting effect of ES determined the overall behavior. However, missing data for P-S2-ES3 and P-S4-ES6, due to measurement device failure, prevented a full comparison across all sample types.

3.4.1.2 **Test 2.** Composite Layers Spray-Deposited onto Concrete Plates, Conducted at the Diasen Company

Another set of thermal conductivity measurements have been carried out on spray-deposited composite layers, rather than on all-solid samples. In more detail, during the part of the PhD work carried out at the private company Diasen srl, in which I carried out a six-month external research period, the thermal conductivity properties of the prepared composites have been tested.

As described in section 3.3.1.1, the composites have been prepared as slurries to be deposited using a spray coating system onto concrete tiles. After the concrete tiles preparation, the dried specimens were placed into a heat flow meter instrument (HFM), as shown in **Fig.48**, which analyzes the heat flow rate through the specimens and accurately measures their k_{concr} value in accordance with ASTM C518 and ISO 8301 standards [19, 252]. In this instrument the sample is positioned between a heated and a cooled plate, creating a setup that resembles a single-specimen guarded hot plate system. A temperature gradient is applied to the sample, and the heat flow through the specimen is measured. The heat flow rate (Q) per unit time and area is determined using a calibrated heat flux transducer, and the test is conducted after the system reaches thermal equilibrium. The instrument was located in the R&D lab of the Diasen Company, allowing the specimens to be taken directly from the oven and tested immediately. Each test was conducted for approximately 1.5 to 2 hours per sample under controlled conditions to ensure reliable and precise results. In order to ensure a significant set of results, each sample has been prepared in triplicate or quadruplicate.

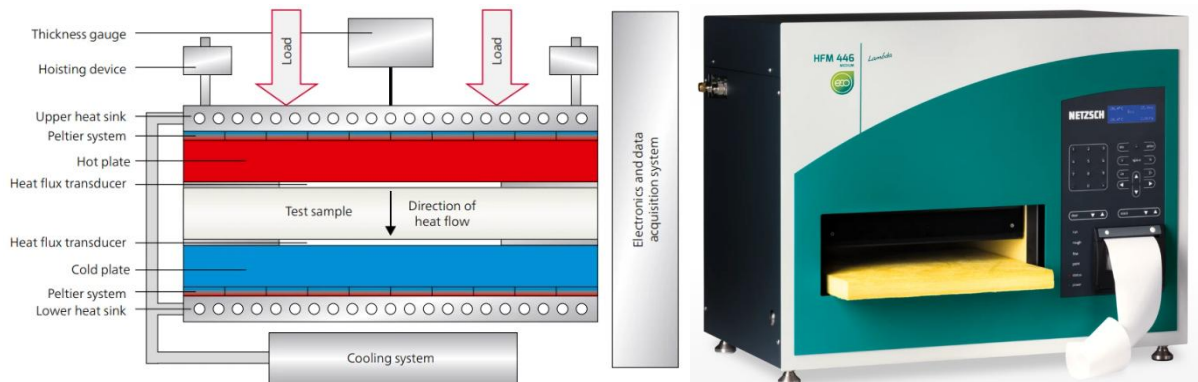


Figure 48. Heat Flow Meter instrument - HFM 446 Lambda Medium Eco-Line, used to measure thermal conductivity

The tiles had a size of about 20×20×3 cm or 15×15×3 cm (depending on the available mold). To determine the thermal conductivity of the composite-coated samples, it was necessary to establish a baseline value for the uncoated concrete. Therefore, as mentioned in the section 3.3.1.2, the concrete specimens were dried in an oven (shown in Fig.37). The drying process took approximately one week for each sample to ensure the complete removal of moisture. In the following the procedure used to determine the thermal conductivities of the sprayed layers is described, together with the obtained results.

3.4.1.2.1 Determination of k Value for Sprayed, Composite Layers

In order to determine the k for the sprayed composite layers the following procedure was carried out:

- At first the k_{concr} of the bare concrete tile has been measured for each concrete tile;
- The concrete tiles has been spray-coated with the chosen insulating material (pristine PLA as a control layer, and the different composites);
- the k_{sample} of the insulating material-coated concrete tile (i.e., of the ensemble concrete tile/insulating layer) has been measured;
- the k_{comp} of the insulating composite layer has been determined, using the thermal resistance relations between k and thickness of the tested samples, as described in the following,

The Fourier's law provides a basis for rationalizing the heat transfer between two surfaces of a body, with the constraint of having the heat flow strictly perpendicular to the surfaces, and with no lateral heat flow (**Fig.49**).

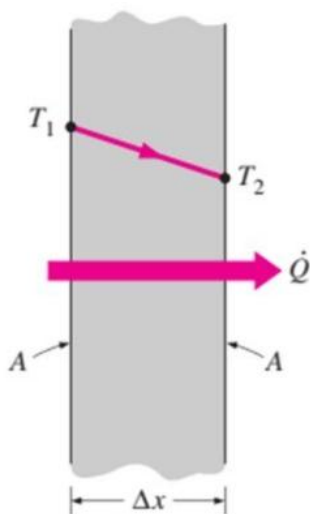


Figure 49. Scheme of the heat flow through a thickness Δx of a body at which two surfaces of area A are placed at two different temperatures T_1 and T_2 .

In these conditions the heat flow can be calculated according to Eq.3, hereby recalled for convenience:

$$Q = k \cdot A \cdot \left(\frac{\Delta T}{\Delta x}\right) \quad \text{Equation 3}$$

Where:

- Q = heat flow [W]
- A = surface area crossed by the heat flow [m²]
- $\Delta T = T_1 - T_2$ = temperature difference between the two sides of the probed sample [K]
- Δx = distance traveled by the heat flow, which in systems to which the Fourier's law is applicable corresponds to the thickness of the probed sample.

In the here analyzed case $A = 10.2 \times 10.2 = 104.04 \text{ cm}^2$, and $\Delta T = 10 \text{ K}$. To obtain the heat flow through the insulating composite layer, it has been considered that the total thermal resistance of the sample (concrete + insulating layers) is:

$$R_{sample} = R_{concr} + R_{comp} \quad \text{Equation 4}$$

Where:

- R_{sample} = heat flow through the concrete tile coated with the insulating layer
- R_{concr} = heat flow through the concrete tile
- R_{comp} = heat flow through the insulating composite layer

The thermal resistance R_{concr} has been at first determined for the bare concrete tile, obtaining also the k_{concr} of the concrete, via the following Eq.5.

$$R_{concr} = \frac{\Delta x_{concr}}{(k_{concr} \times A)} \quad \text{Equation 5}$$

After that the thermal resistance for the coated sample (consisting in the concrete tile coated with the insulating layer), R_{sample} , was similarly determined, as well as the k_{sample} . According to Eq.4;

$$R_{comp} = R_{sample} - R_{concr} \quad \text{Equation 6}$$

Therefore;

$$\frac{\Delta x_{comp}}{(k_{comp} \times A)} = \left(\frac{\Delta x_{sample}}{(k_{sample} \times A)} \right) - \left(\frac{\Delta x_{concr}}{(k_{concr} \times A)} \right) \quad \text{Equation 7}$$

The final k_{comp} has been hence calculated by means of Eq.7, as follows:

$$k_{comp} = \left(\frac{\Delta x_{comp}}{\left(\frac{\Delta x_{sample}}{k_{sample}} - \frac{\Delta x_{concr}}{k_{concr}} \right)} \right) \quad \text{Equation 8}$$

The so-calculated k_{comp} of the measured samples (including those coated with pristine PLA) are reported in Table 27.

Table 27 – Measured and calculated data for the spray-deposited layer samples.

Material type	Sample ID	Δx_{concr} [cm]	k_{concr} [W/mK]	R_{concr} [K/W]	Δx_{sample} [cm]	k_{sample} [W/mK]	R_{sample} [K/W]	Δx_{comp} [cm]	k_{comp} [W/mK]	Sample average	Ave k of insulating layer	Std Dev
Pristine PLA	PLA-1	2,97	0,26540	0,11654	3,27	0,24018	0,14147	0,29	0,122			
	PLA-2	3,16	0,34495	0,09529	3,44	0,28017	0,12768	0,28	0,090			
	PLA-3	3,37	0,31574	0,11110	3,51	0,29058	0,12578	0,14	0,100			
										PLA AVE	0,104	0,0167
P-S-1	P-S-1/1	3,05	0,36971	0,08586	3,65	0,27196	0,13971	0,60	0,116			
	P-S-1/2	2,84	0,35030	0,08435	3,61	0,24091	0,15607	0,77	0,112			
	P-S-1/3	3,34	0,31430	0,11061	3,45	0,27861	0,12890	0,11	0,063			
	P-S-1/4	3,18	0,34733	0,09532	3,44	0,28731	0,12468	0,26	0,092			
										P-S-1 AVE	0,0959	0,0244
P-S-2	P-S-2/1	3,84	0,30997	0,12896	3,93	0,32635	0,12529	0,088	0,040			
	P-S-2/2	3,21	0,33813	0,09879	3,31	0,31233	0,11017	0,10	0,088			
	P-S-2/3	3,06	0,40378	0,07878	3,35	0,29644	0,11749	0,29	0,078			
	P-S-2/4	3,27	0,29286	0,11630	3,37	0,25422	0,13790	0,10	0,046			
										P-S-2 AVE	0,0631	0,0236
P-S-5	P-S-5/1	3,39	0,34951	0,10104	3,52	0,29160	0,12553	0,12	0,053			
	P-S-5/2	3,57	0,32134	0,11557	3,62	0,29187	0,12889	0,046	0,036			
	P-S-5/3	3,25	0,29649	0,11387	3,34	0,26003	0,13359	0,094	0,049			
	P-S-5/4	3,23	0,28279	0,11890	3,67	0,19726	0,19348	0,44	0,061			
										P-S-5 AVE	0,0498	0,0103
P-C-2	P-C-2/1	3,63	0,34371	0,10991	3,86	0,30100	0,13353	0,23	0,102			
	P-C-2/2	3,59	0,35247	0,10598	3,71	0,33599	0,11493	0,121	0,141			
	P-C-2/3	3,47	0,33070	0,10904	3,71	0,27429	0,14065	0,2	0,080			
	P-C-2/4	3,19	0,29969	0,11072	3,53	0,25346	0,14480	0,34	0,103			
										P-C-2 AVE	0,106	0,0253
P-C-5	P-C-5/1	3,43	0,39514	0,09043	3,55	0,34495	0,10715	0,12	0,073			
	P-C-5/2	3,22	0,38242	0,08749	3,32	0,34456	0,10029	0,11	0,086			
	P-C-5/3	3,06	0,28897	0,11032	3,65	0,19763	0,19223	0,59	0,075			
	P-C-5/4	2,61	0,31596	0,08608	3,50	0,18908	0,19239	0,88	0,086			
										P-C-5 AVE	0,0800	0,0070
P-C-10	P-C-10/1	3,00	0,41429	0,07545	3,34	0,31402	0,11056	0,33	0,099			
	P-C-10/2	3,19	0,33969	0,09775	3,38	0,28152	0,12496	0,19	0,073			
	P-C-10/3	3,32	0,34267	0,10066	3,38	0,31895	0,11025	0,065	0,070			
	P-C-10/4	3,35	0,35364	0,09855	3,44	0,30594	0,11709	0,093	0,052			
										P-C-10 AVE	0,0734	0,0191
P-C-15	P-C-15/1	3,17	0,41391	0,07964	3,31	0,34977	0,09847	0,14	0,079			
	P-C-15/2	3,21	0,37829	0,08826	3,28	0,33025	0,10334	0,071	0,049			
	P-C-15/3	3,32	0,31508	0,10956	3,39	0,28720	0,12265	0,068	0,054			
	P-C-15/4	3,20	0,31283	0,10637	3,42	0,26359	0,13513	0,23	0,081			
										P-C-15 AVE	0,0657	0,0167

The obtained results have been at first analyzed in terms of homogeneous composites, i.e. comparing the effects of adding progressively more filler to the base PLA. For SA-filled composites the results of this analysis is reported in **Fig.50**.

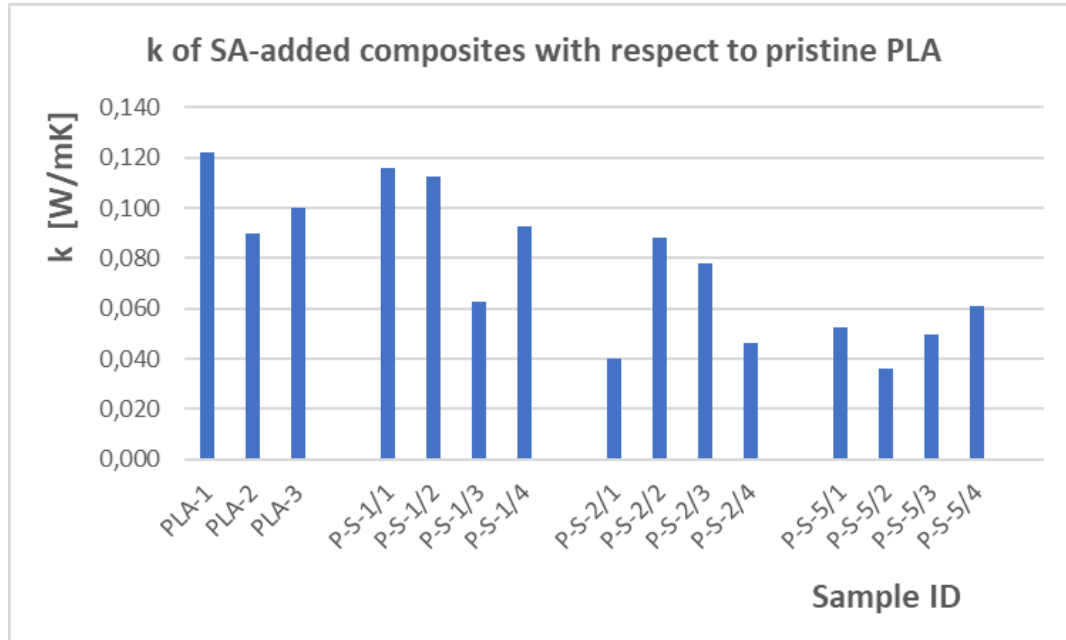


Figure 50– Comparison of k value for SA-filled composites with respect to pristine PLA.

As it can be seen, the general results are pretty dispersed. This can be ascribed to the fact that the manually conducted spray deposition process, together with some shrinking of the deposited layer after the solvent evaporation, led in some cases to relatively inhomogeneous thicknesses of the deposited materials. Moreover, the starting concrete tiles had also not perfectly uniform thicknesses. Finally, in general the obtained thicknesses of the insulating layer have been not very high, ranging around 1-2 mm, and this could have amplified possible inhomogeneities in the deposited layer.

In any case, averaging the obtained k values per type of samples, the overall results appear consistent with some literature data. For example, PLA-related k values range between 0.14 and 0.07 W/m.K [253, 254], depending on the type of considered PLA (molecular weight, possible previous thermal treatments), in line with the obtained average of about 0.08 W/m.K (**Fig.51**). The relatively low value of k obtained for the sprayed layer is attributed to the deposition procedure, in which the slow evaporation of the solvent mixture likely allowed a substantial polymer chains organization[253], leading to the observed low k value.

To confirm that the addition of SA to the PLA is effective in promoting a better thermal insulation, the general k values of the SA-added composites tend to decrease with the increase

of the SA percentage (Fig.51, where the standard deviation on the average values of the samples are shown as error bars). For the 1 wt.% SA-added composite (sample P-S1) the average k value is very close to that of the pristine PLA layer, but this could be due to the aforementioned morphological parameter of the spray-deposited layers, and to the fact the just a 1 wt.% of SA could have been poorly effective in limiting the heat flow in the examined samples. The higher SA-loaded samples, on the other hand, showed a rather impressive relative decrease of k even at very modest filler percentages, with the 5% loaded layer exhibiting an average k of 0.0498 W/m.K with respect to the 0.1 W/m.K of the PLA layer, i.e. a full halving of the thermal conductivity achieved upon an addition of just a 5% in weight of SA.

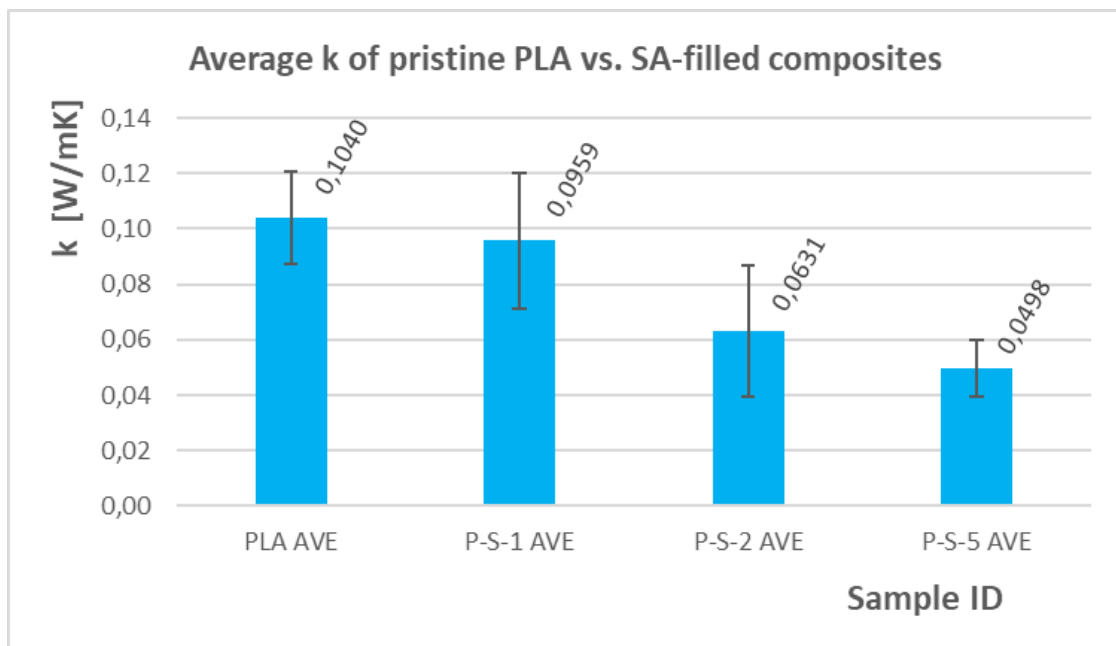


Figure 51 – Comparison of average k value for SA-filled composites with respect to pristine PLA.

With respect to CO-added composites, a comparison between the pristine PLA and the composites loaded with different amounts of CO provides large evidence that this material can be effective in enhancing the thermal insulation capability of the layers embedding it only if it is added to the composite in substantial amounts (apparently, from 5 wt.% onwards).

In more detail, as shown in **Fig.52**, samples with low loading levels of CO (P-C2, containing 2 wt.% of CO powder) do not evidence particularly marked improvements in terms of lowered thermal conductivity with respect to pristine PLA.

However, moving to higher CO loading percentages, from 5 wt.% up, the overall thermal conductivities of the samples gets progressively lower than that of the pristine PLA.

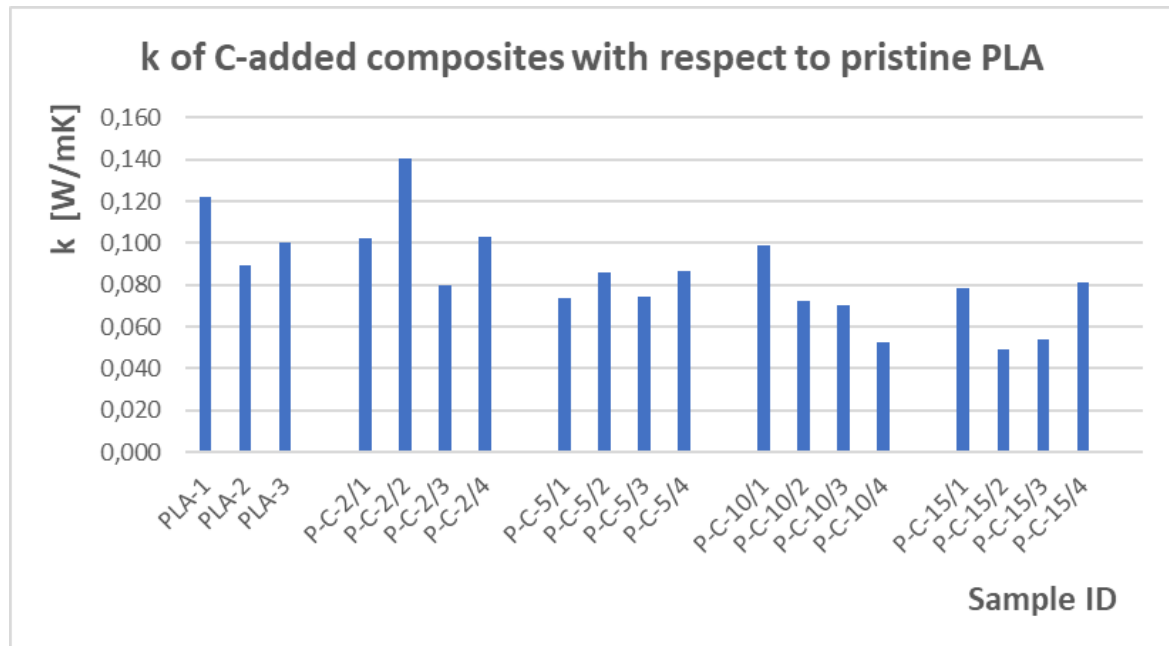


Figure 52 – Comparison of k value for C-filled composites with respect to pristine PLA.

This trend is more evident if the average between the considered samples is analyzed (**Fig.53**): composites loaded at 2 and 5% of CO powder present an actual k higher than that of pristine PLA, while for higher filler loading the k becomes lower than that of the pristine polymer, arriving to about a 30% less for the higher CO loading samples (P-C15 AVE.).

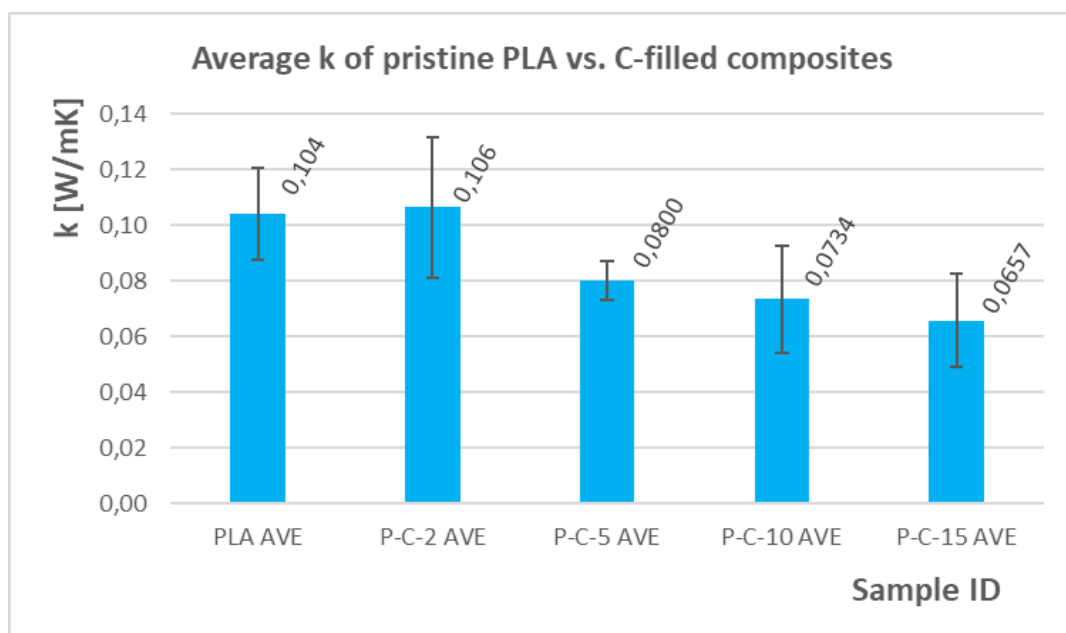


Figure 53 – Comparison of average k for SA-filled composites with respect to pristine PLA.

The higher k values for the lower loaded samples can be explained considering that the powdered CO particles are relatively large (average diameter around 0.3 mm), hence in the dispersion within the PLA matrix low amounts of particles are unable to provide a continuous network of low thermal conductivity material (the k of the used CO is in the range of 0.040 – 0.045 W/m.K, as assessed by the material provider, a datum in line with publicly available technical datasets [255]). Going from lower to higher C loadings, the overall average k of the resulting composites tend clearly to the CO thermal conductivity value, around 0,045 W/m.K (Fig.53). This situation is of course different from that of SA-loaded samples, where a visible decrease of k for the SA-PLA composites was detectable already at a mere 2 wt.% filler fraction, due to the smaller size of the SA powder used in those composites (from 0.1 to 0.05 mm as powder, to be compared with the 0.3 mm of the CO powder; the smaller powder size of the SA favors a more homogeneous dispersion within the PLA matrix, hence a better insulating effect at lower weight percentages of the filler).

The difference between SA- and CO-loaded composites is evident also with respect to the k values obtained at comparable wt.% loadings. Indeed, at a 2% loading, SA- and C-loaded samples obtain (on average) a k of 0.063 and 0.11 W/m.K, respectively, while at 5% loading the values of 0,05 and 0,08 W/m.K, respectively, are obtained. This sharp difference is attributable to the lower k of SA with respect to that of CO (around 0.02 W/m.K with respect to around 0.04, respectively).

All in all, the reported tests show that despite the different characteristics of the considered fillers, using low- k materials as fillers for creating PLA-based composites is a good strategy to decrease the thermal conductivity of the resulting composite, with improvements from 30 to 50% lower k , depending on the used filler and on the considered percentages of filler loading.

3.4.2 Structure Analysis - Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful analytical technique used to obtain the infrared spectrum of absorption or emission from a solid, liquid, or gas. The technique works by irradiating the sample with infrared radiation. Some of the radiation is absorbed, while the rest is reflected or transmitted. The part of the irradiated beam that passed through the sample holds information on the molecules of the sample that absorbed the light, providing a “molecular fingerprint” of the sample and offering detailed insights into its molecular composition and structure. Spectral data obtained from FTIR can be utilized to verify material purity, monitor chemical reactions, and compare experimental results with theoretical models or reference databases, enabling accurate and reliable interpretation [256].

ATR-FTIR spectroscopy is an effective tool for analysing the chemical composition of material. Attenuated Total Reflectance (ATR) allows for the direct analysis of solid or liquid samples with minimal preparation, making it especially useful for examining materials that are strong absorbers or difficult to prepare for traditional transmission spectroscopy. ATR operates on the principle of total internal reflection. In this technique, an infrared beam is directed onto an optically dense crystal with a high refractive index at a specific angle. When the IR light encounters the interface between the crystal and the sample, it undergoes total internal reflection, creating an evanescent wave that extends a few micrometers beyond the crystal surface into the sample. This evanescent wave interacts with the sample, and the absorption characteristics of the sample attenuate the reflected IR beam. The attenuated beam is then detected and analyzed to produce an IR spectrum representative of the sample's molecular composition [257, 258]. Infrared spectrometry of composite samples has been carried out during my period at the University of Rouen.

In more detail, for each realized specimen (see section 3.3.2.1), FTIR spectra have been collected mainly in Attenuated Total Reflection (ATR) mode using the ATR-imaging accessory with a germanium crystal, and in some cases (when specified) in transmission mode as an average of 16 scans in the range $4000\text{--}600\text{ cm}^{-1}$, in both cases with a 4 cm^{-1} resolution.

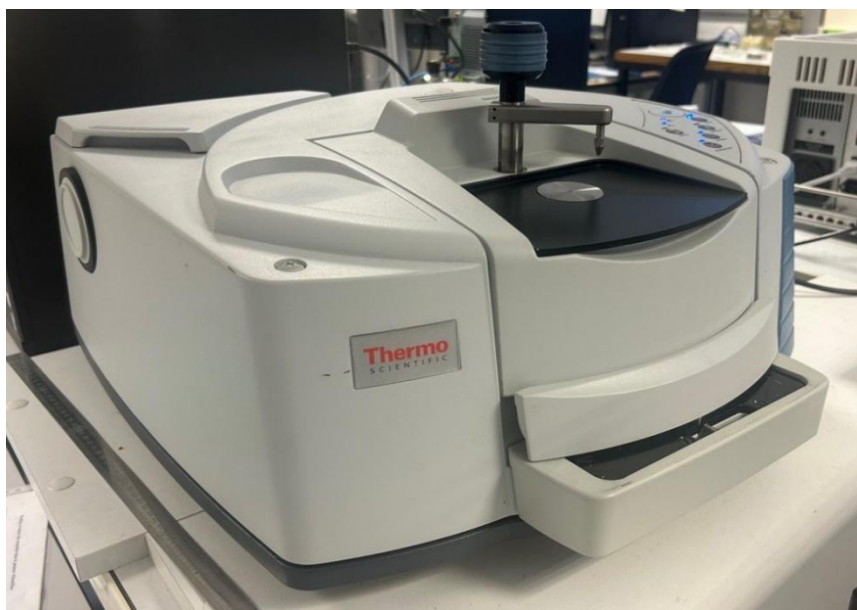


Figure 54. FTIR Spectrometer placed at Rouen University materials lab.

The PLA spectra obtained for the analyzed pristine PLA samples are similar to those reported in literature (see for example Grosvenor et al. [259]), confirming that the used PLA is of good quality for the here presented studies (**Fig.55**).

In the following some considerations linking the outcome of the ATR-FTIR spectra to the actual composition of the analyzed samples will be made, trying to correlate the spectroscopic data with the composition of the samples and with possible hints of intermolecular interactions occurring in the composites between the fillers and the PLA matrix.

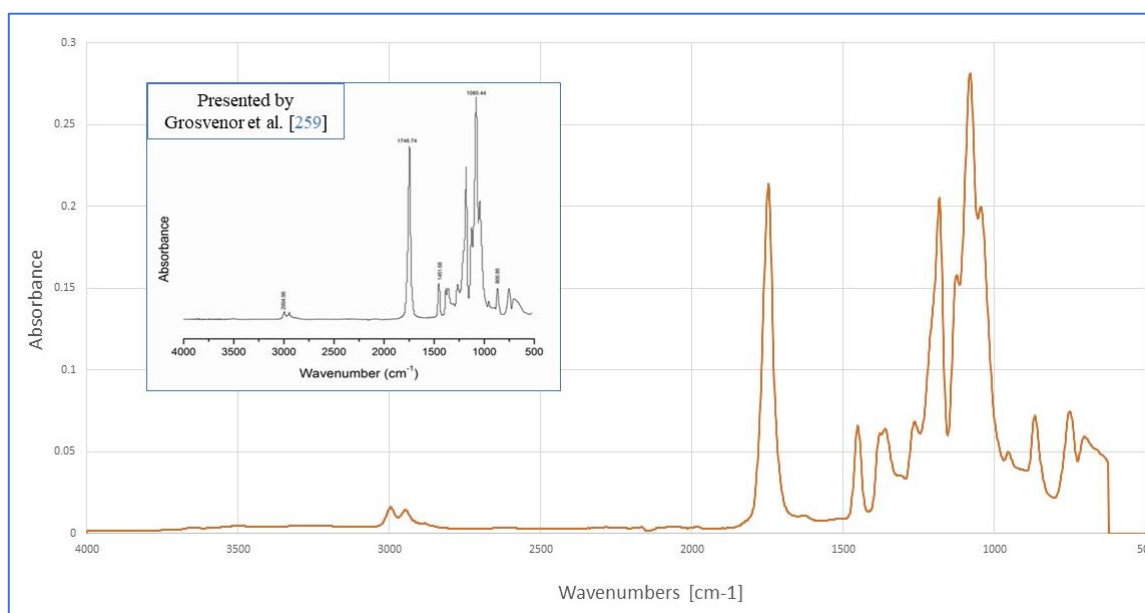


Figure 55. FTIR spectra of the used PLA and a PLA sample described in the available literature.

The acquired ATR spectra revealed distinct absorption signals corresponding to the characteristic functional groups and molecular vibrations of the analyzed material, as summarized in the Table 28, also illustrated in **Fig.56**. These signals provide valuable insights into the chemical composition and structural features of the sample. For example, absorption peaks in the region of 2800–3000 cm^{-1} are typically associated with C–H stretching vibrations from the aliphatic hydrocarbons of PLA (Fig.56, here reported for convenience), indicating the presence of saturated carbon chains. Similarly, the strong absorption band observed around 1700–1750 cm^{-1} corresponds to C=O stretching, a hallmark of carbonyl groups. The position of the band towards the higher frequency is in line with the presence of ester groups. Peaks in the fingerprint region (1200–1000 cm^{-1}) are linked to C–O stretching and C–H bending, which further validate the polymeric backbone structure. The low strength of the -CH stretching bands in the 3000 cm^{-1} region is in agreement with the relatively low number of -CH₂ groups in the PLA chain. The below reported table 34 provides a detailed breakdown of these assignments, correlating specific wavenumber ranges to their respective molecular vibrations and functional groups.

Table 28. Functional groups and mode of vibration from FTIR spectra of PLA [260].

Wavenumber [cm^{-1}]	Assignment
3010	=C–H Stretching
2996	-CH- Stretching
1747	-C=O Carbonyl Stretching
1452	-CH ₃ Bending
1362	-CH- Deformation
1260	-C=O Bending
1044	-C-O Stretching
956	-C-C Stretching
866	-C=O Bending (inorganic carbonate)

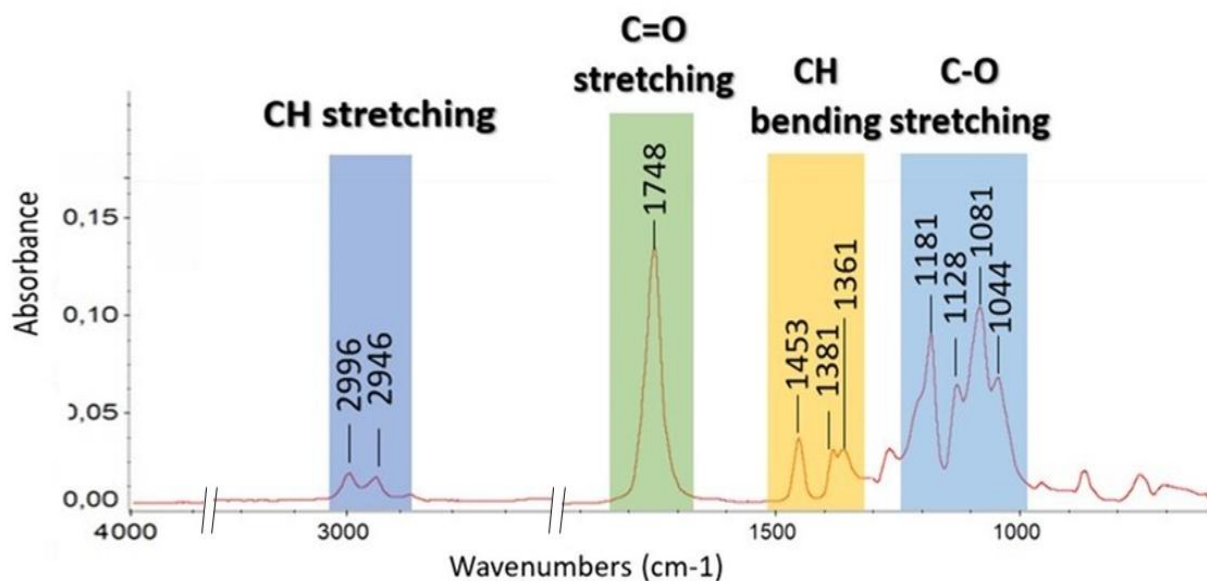


Figure 56. FTIR spectra of PLA

- P-SA Composites

FTIR spectra of P-SA sample are given in **Fig.57**. FTIR has been used in order to collect and compare information on the chemical structure of the specimens. The difference in peak intensity across the spectra somewhat highlight variations in chemical structure or the influence of SA as fillers in the PLA matrix. PLA Spectrum, exhibits clear, sharp peaks, especially at 1747 cm⁻¹ and 1183 cm⁻¹, typical of pure PLA [261]. Two peaks which do not belong specifically to PLA emerge clearly with the increase of percentage of the SA filler, around 1050 cm⁻¹ and 850 cm⁻¹ (see Fig.57, light orange and light blue boxes, respectively).

These peaks are attributable to the Si-O-C antisymmetric stretching (1050-1090 cm⁻¹) and symmetric stretching (800-870 cm⁻¹) [262, 263]. In the same spectral zone also some -C-O stretching can occur, but since the used SA is a hydrophobic one (hydrophobicity is obtained functionalizing the silica hydroxide particles with methyltrimethoxysilane [264], the presence of signals in these two bands can safely be ascribed to the mentioned functional groups. Moreover, examining the trend of the spectra in that zone with the increasing content of the SA filler, it becomes evident that the higher the SA loading, the higher the importance of these two signals. This trend can be considered a good confirmation of the proposed assignment for the two signals.

Interestingly, analyzing the -C=O stretching peak around 1750 cm⁻¹ it is evident that the SA filler do not interact appreciably with the carbonyl group, even at high SA loadings, since

no appreciable peak shift is observable. This finding is well in line with the aforementioned hydrophobicity of the SA, which having possibly no free -OH group (absence of any meaningful signal around 3500 cm^{-1}) due to the methylation carried out for water-proofing the material, cannot establish detectable interactions with the -C=O group. Moreover, since from the FTIR spectrum of PLA (Fig.55) it is possible to verify that the terminal -OH groups of the polymer are present in negligible amounts (almost no signal around 3500 cm^{-1}), the few existing free -OH groups as terminal groups of the PLA chains cannot establish detectable interactions with the -Si-O-Si- parts of the SA 3D network.

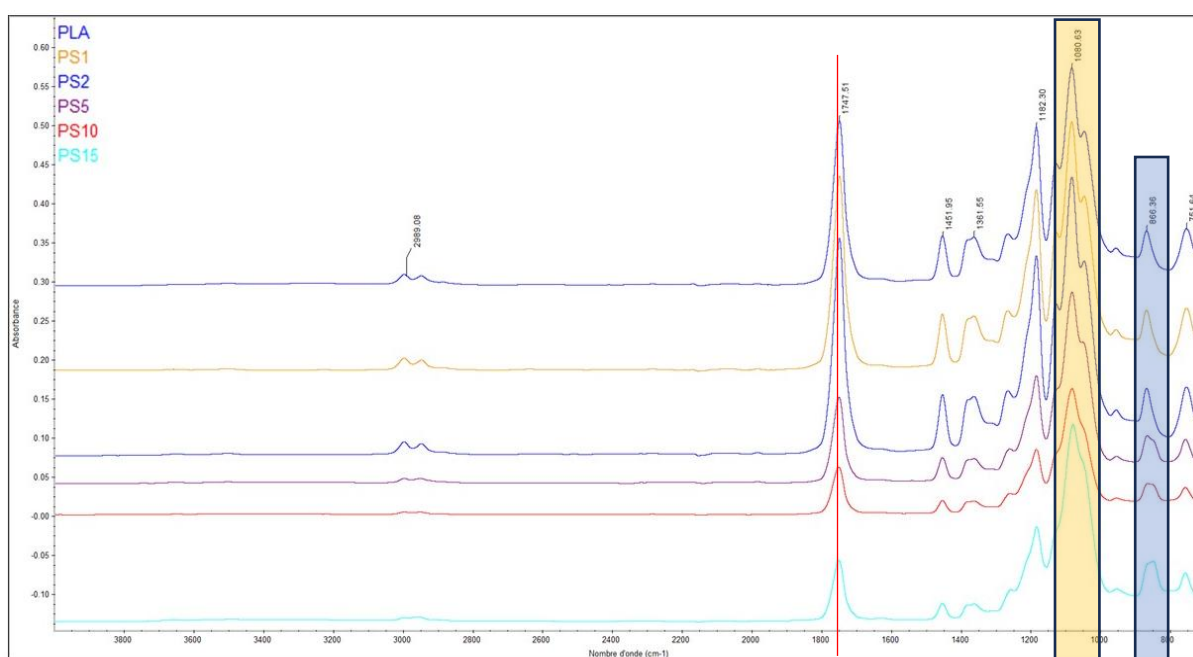


Figure 57. The FTIR result of the PLA reinforced by SA

- P-ES Composite

ESs are composed mainly (more than 95%) by calcium carbonate, in the form of aragonite crystals, to which must be added small amounts of phosphates, magnesium and organic materials, mostly proteins [265].

The commonly termed “eggshells” are actually composed by the properly intended “eggshell”, i.e. the mostly mineral, hard outer envelopment of the egg, and by the egg membranes (an inner and an outer one), which are less rigid and much richer in proteins (mainly collagen and glycoproteins, with the outer membrane including mineralization products at a minor extent), as is visible in **Fig.58**.

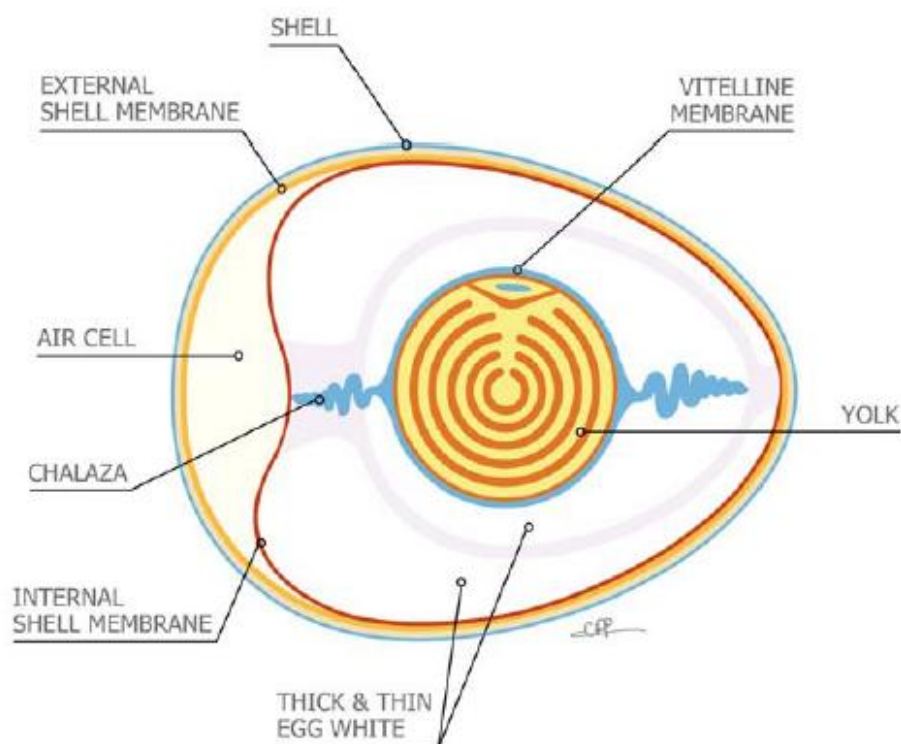


Figure 58 – Schematic structure of a hen egg.

It is interesting to notice that the rigid eggshell and the membranes have rather different FTIR spectra, as is logical considering that their composition is very different. In **Fig.59** the FTIR spectra of the outer, rigid shell and of the external membrane (the FTIR spectrum of the internal one is not very different from that of the external one).

In this study the eggshell filler was obtained by powdering of the ensemble of the eggshell plus the two membranes. Therefore, the overall FTIR spectra will contain information coming from both the parts of the egg. As is visible in **Fig.60**, the general features of PLA (for example with the -C=O stretching at 1748 cm^{-1} or the -C-O stretching at 1044 cm^{-1}) are kept unchanged even after the addition of amounts of ES up to a 15 wt.% loading, strongly suggesting that the nature of the filler/matrix interaction is merely of a dispersion nature. This behavior is in line with the chemical nature of the PLA matrix, which is poorly polar, and of the eggshell filler, which is mainly polar due to its inorganic component (CaCO_3). On the other hand, the effect of the presence of the ES filler is visible in the $750\text{-}1750\text{ cm}^{-1}$ range. In more detail, in the $1450\text{-}1600\text{ cm}^{-1}$ range (light violet box in Fig.60) a large shoulder arises with the increase in filler content. At the same time, around 1380 cm^{-1} it is possible to observe the increase of a secondary peak with the increase of the ES percentage. The $1450\text{-}1600\text{ cm}^{-1}$ shoulder is attributable to carbonates [266], while the 1380 cm^{-1} peak is ascribable to amines and amides found in the egg's membrane [267].

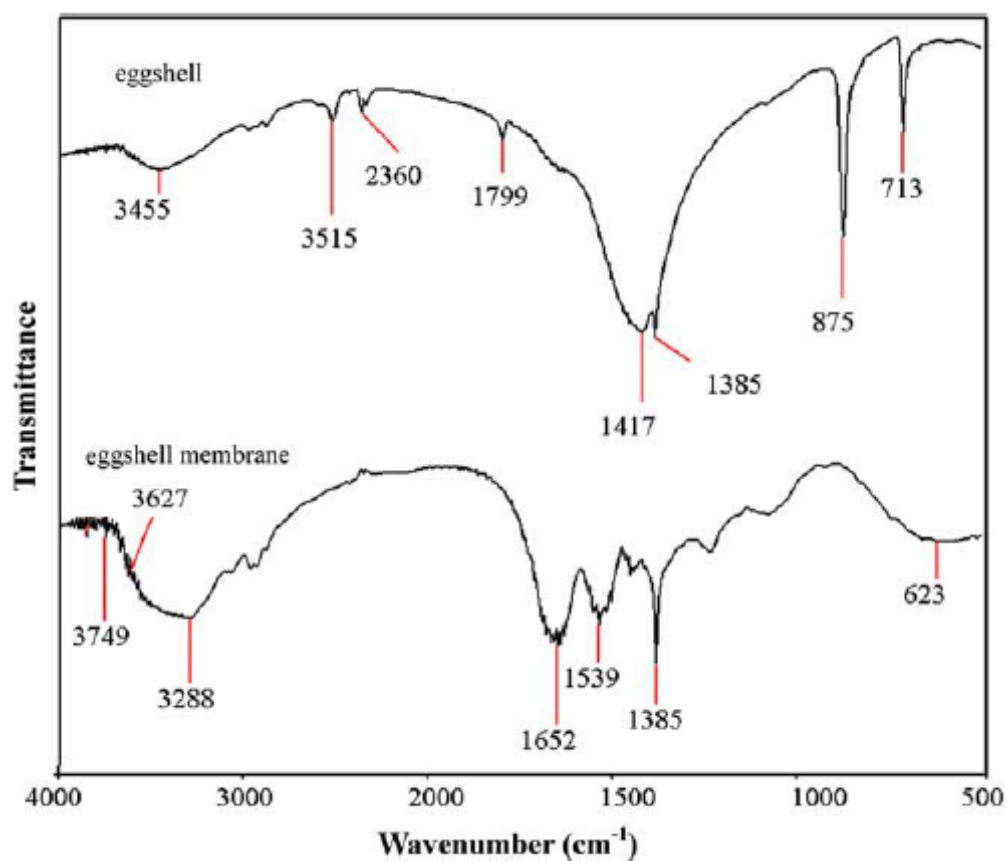


Figure 59 – FTIR spectra of rigid eggshell (upper panel) and outer eggshell membrane (lower panel) for a hen egg (from [267]).

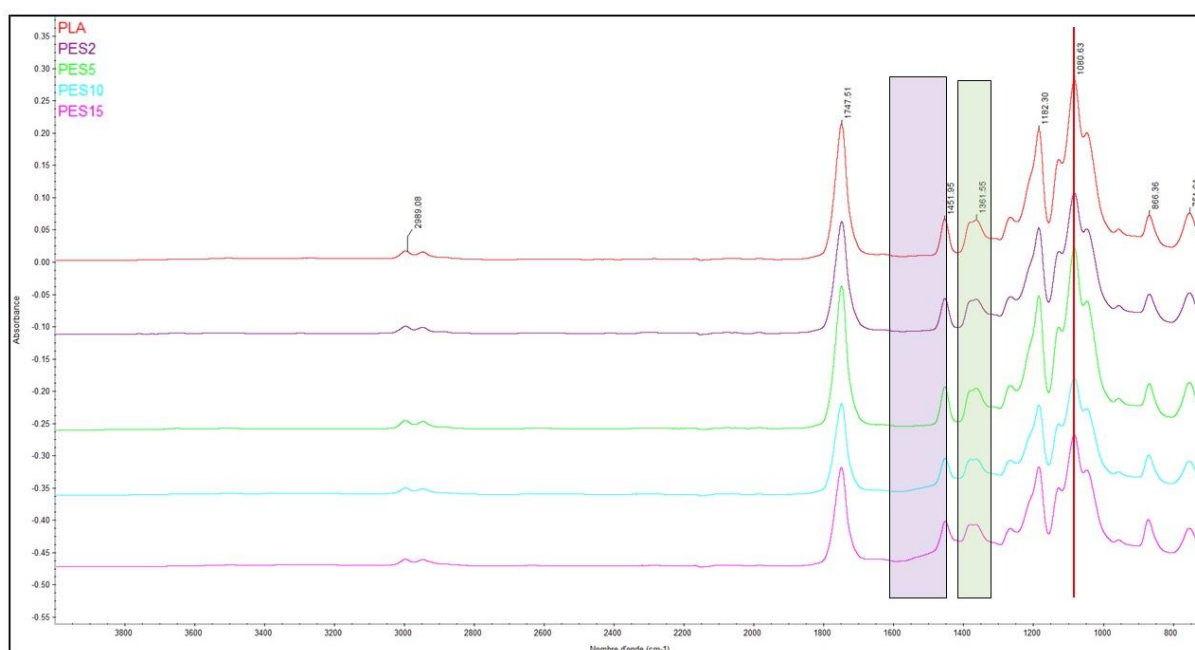


Figure 60. The FTIR result of the PLA reinforced by ES powders

3.4.3 Morphological Properties - Optical Microscopy Analysis of Prepared Composites

The prepared composites have been imaged using optical microscopy to get some information over the homogeneity of the achieved dispersion of the fillers in the PLA matrix. The image samples were obtained using the film samples prepared by the hydraulic hot press, without any changes on the surface of the samples. The surface of the film samples have been observed under different magnifications (2.5x, 5x, 10x and 20x) and for different filler types and concentrations.

Fig.61 and **Fig.62** demonstrates the surface finish of composite by different filler content (wt.%), as prepared in this study (section 3.3.2.1) shown in Fig.42. Surface analysis of samples is a critical step in understanding their morphology, interfacial interactions, and potential applications. Generally, the dark, irregularly shaped particles are the SA dispersed within the PLA matrix. The variation in particle size and shape is typical for different samples, indicating a non-uniform distribution. Some particles are nearly spherical, fragmented, or clustered, which surrounded by air bubbles. These irregularities could affect the composite's mechanical, thermal, and thermomechanical properties.

In Fig.61, two types of SA were examined: *I*) particle SA (granulate) (a) and *II*) crushed (powder) SA (b). In the right column (a) it is possible to clearly see the bulk SA irregularly dispersed in the matrix, which can result in zones with different mechanical and thermal characteristics. On the other hand, the samples with crushed SA (column b) appear to have a better dispersion within the PLA matrix. Therefore, decreasing the particle size of SA can enhance the uniformity of the dispersion, which is beneficial for the composite's performance, improving in turn the material's overall functional properties, such as strength, durability, and thermal insulation.

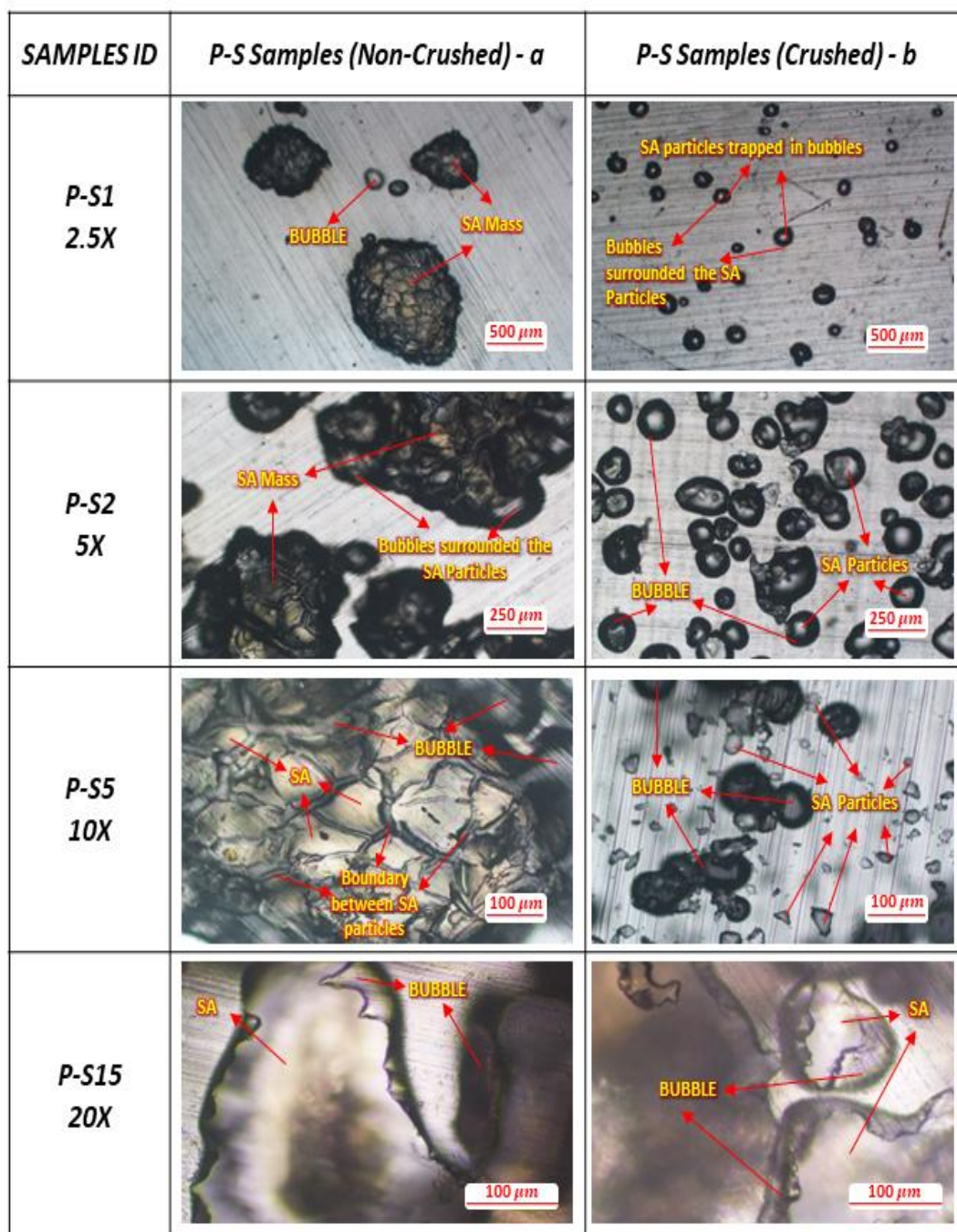


Figure 61. Optical microscopy images of specimen with varying SA content (1, 2, 5, 10 and 15 wt.%) at different magnifications (2.5x, 5x, 10x, and 20x). a) particle SA (granulate) b) crushed (powder) SA

In the first row, the SA particles appear as large, irregularly shaped structures, unevenly dispersed within the PLA matrix. The boundaries of the SA particles are distinguishable, with some clusters evident. However, in the crushed SA, the particles are more uniformly distributed. The size of the filler is reduced, leading to smaller, more uniform particles compared to the bulk particles.

In the second row, the surface features of the particles are more visible. The filler seems to form agglomerates, with varying sizes and irregular shapes. There is less interaction or blending with the PLA matrix. The crushed filler, similar to the previous image, exhibits finer dispersion. Individual particles are well-defined, with reduced agglomeration compared to bulk particles.

In the next row (P-S5-10X), the detailed internal texture of the SA particles is visible, with a porous appearance. The surface roughness of the particles (apparently) highlights the intrinsic porosity of SA. The crushed SA shows smaller, more fragmented particles. Improved dispersion is evident, but small agglomerates persist in some regions. At a higher optical magnification (20X, in this case shown on a P-S15 sample) the porous nature of SA particles start to be clearly visible. The edges of the particles are uneven for both large granule (first column) and pulverized samples (second column); while in the first case the irregularity is due to the SA producer's fabrication processes, in the second case the particles irregularity is linked to the mechanical fragmentation procedure used to crush the starting particles.

The optical appearance of ES filler in the PLA matrix (Fig.62) has been analyzed at low magnifications (2.5x and 5x). The ES particles appear to irregularly shaped (again, as a consequence of the mechanical crushing procedure) and exhibit rough, uneven surfaces. At lower filler contents (P-ES2), the ES particles are more uniformly dispersed, exhibiting only moderate agglomeration, while at higher filler content (P-ES5) clear indications of particle aggregation are already visible. However, some particles form small clusters, which could potentially affect the mechanical properties of the composite.

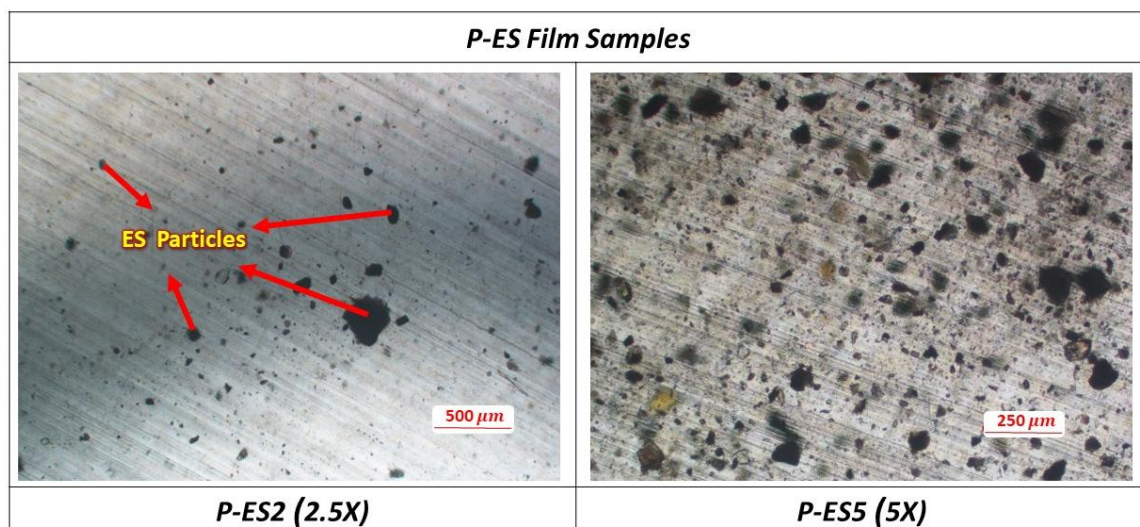


Figure 62. Optical microscopy images of specimen with varying ES content (2, 5, 10 and 15 wt.%) at different magnifications (2.5x, 5x, 10x, and 20x).

3.4.4 Mechanical Properties - Tensile Tests

The mechanical behavior of the different samples was assessed at room temperature with a 10 mm min^{-1} clamp separation rate. In this test, dumbbell-shaped specimens have been prepared according to technical standard ISO527 (type 1BA). The parameters of Young modulus (E_t), Yield stress (σ_Y), Elongation at break (ε_B), tensile strength (σ_M), Strain at maximum stress (ε_M) and Stress at break (σ_B) have been calculated from the obtained stress–strain curves as the average of at least two measurements for neat PLA, P-P-S (with pulverized SA) and P-ES samples.

A comparison between the tensile tests of pristine PLA and SA-filled composites, at 1 and 2% loading, was carried out. The 5% loaded percentage with pulverized SA was not tested due to excessive fragility of the so-realized dumbbell samples, and two 5% standard SA-loaded (i.e., with non-pulverized SA) samples were prepared and tested instead.

As is visible in **Fig.63**, the pristine PLA samples evidence a relatively good degree of plasticity, with an overall elongation at break around 4.5%, a datum not very far from that provided by the PLA manufacturer, which states a 6% of elongation at break (**Fig.64**).

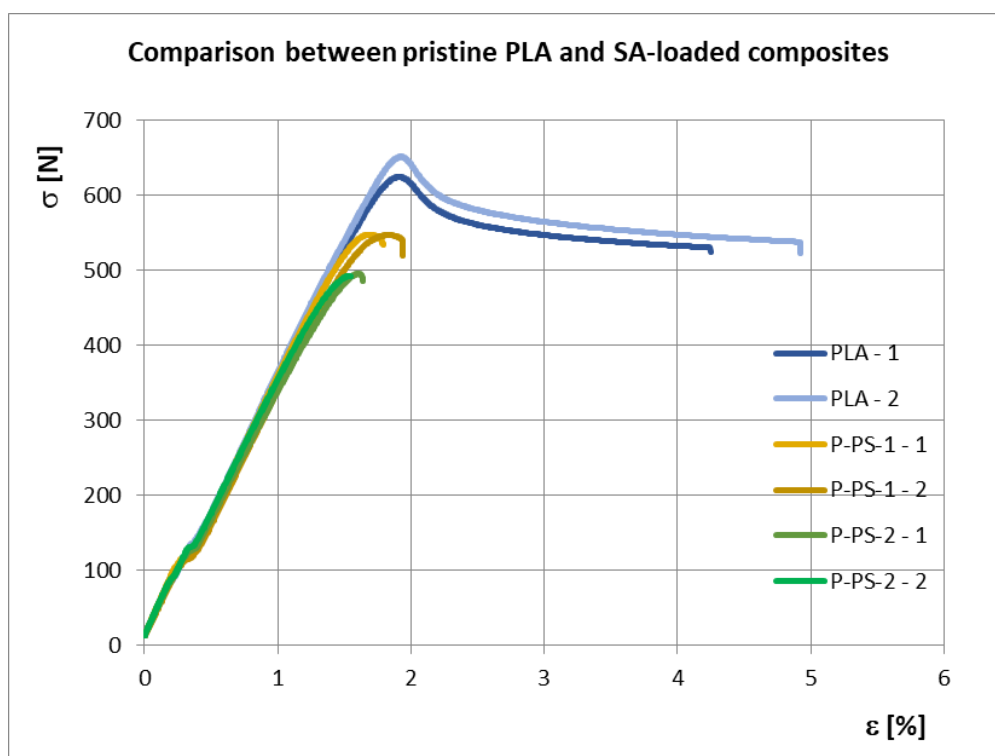


Figure 63. Comparison between PLA and SA-loaded samples of the results of the tensile tests.

Typical Material Properties ⁽¹⁾		
Physical Properties	Ingeo Resin	ASTM Method
Specific Gravity, g/cc	1.24	D792
MFR, g/10 min ⁽²⁾	6	D1238
Relative Viscosity ⁽³⁾	4.0	D5225
Clarity	Transparent	-
Peak Melt Temperature, °C	145-160	D3418
Glass Transition Temperature, °C	55-60	D3418
Mechanical Property		
Tensile Yield Strength, psi (MPa)	8700 (60)	D882
Tensile Strength at Break, psi (MPa)	7700 (53)	D882
Tensile Modulus, psi (MPa)	524,000 (3.6)	D882
Tensile Elongation, %	6	D882
Notched Izod Impact, ft-lb/in (J/m)	0.3 (16)	D256
Flexural Strength, psi (MPa)	12,000 (83)	D790
Flexural Modulus, psi (MPa)	555,000 (3.8)	D790
Heat Distortion Temperature, °C 66 psi (0.45 MPa)	55	E2092

(1) Typical properties for injection molded amorphous bars; not to be construed as specifications.

(2) 210 °C/2.16 kg

(3) RV measured at 1.0 g/dL in chloroform at 30°C

Figure 64. Mechanical parameters for pristine PLA as provided by the manufacturer.

The addition of the pulverized SA filler drastically reduce the plastic deformation of the samples, limiting the elongation at break below 2% even for the smaller SA loading (1 wt.%), and of course even less for the 2% loaded samples.

In **Fig.65** it is possible to appreciate that the 5% loaded sample, in which the SA particles were not crushed (hence they had a larger diameter, see Fig.61), also presented a much smaller plastic deformation zone with respect to the pristine PLA. The two tested samples had a relatively large variability, likely due to the problems of aggregation of the filler evidenced by optical microscopy analysis in the previous paragraph, which likely caused local inhomogeneities affecting the reproducibility of the tensile test; nonetheless, it is clear that the larger size of the SA particles for the 5 wt.%-loaded sample shown in Fig.65 had a sizeable effect on the plasticity of the samples, which resulted to be higher than that of the pulverized SA samples at just 1% of loading, and comparable to, or higher than, that of the 2%-loaded pulverized SA samples.

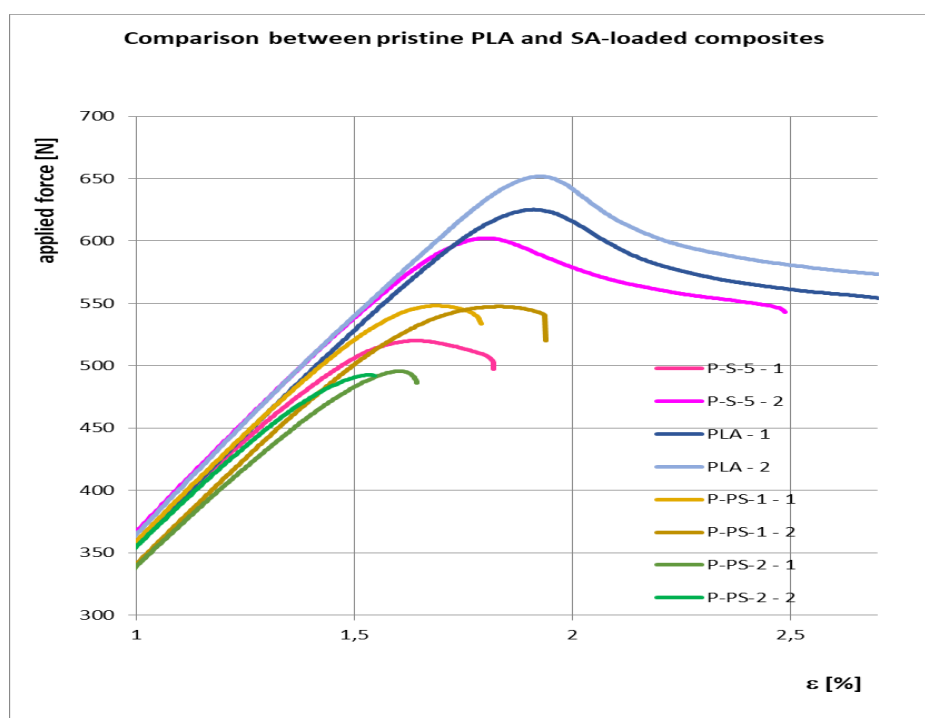


Figure 65. Magnification of the final part of the tensile test charts for the realized composites, including the samples loaded at 5 wt.% with large SA particles.

This effect is in line with the known trends of filler/matrix interactions [268], and with specific SA-filled polymeric matrices [269], where larger particle sizes, leading to lower surface area of the particles and hence to weaker matrix/filler interactions, result in decreased mechanical rigidity of the composite, hence in a higher plasticity (even for filler loadings 5-fold those of the pulverized samples). The general set of mechanical parameters of the prepared composites is visible in Table 29.

Table 29. Main mechanical parameters extracted from the tensile tests carried out on PLA and SA-loaded composites.

Sample ID	Young modulus	Yield stress	Tensile strength	Strain at max stress	Stress at break	Elongation at break
	E_t [MPa]	σ_Y [MPa]	σ_M [MPa]	ε_M [%]	σ_B [MPa]	ε_B [%]
PLA - 1	3066.24	59.36	60.35	1.93	48.46	4.92
PLA - 2	3376.60	57.44	57.89	1.91	48.58	4.25
P-P-S1 - 1	3628.48	49.95	50.75	1.68	49.42	1.79
P-P-S1 - 2	3368.59	48.56	50.69	1.83	48.18	1.94
P-P-S2 - 1	3255.29	45.60	45.89	1.60	45.02	1.64
P-P-S2 - 2	3171.74	45.62	45.62	1.54	45.55	1.55
P-S-5 - 1	3503.45	54.68	55.76	1.80	50.29	2.49
P-S-5 - 2	3435.85	47.23	48.15	1.64	46.07	1.82

As it can be seen, the overall stiffness of the SA-embedding composites is generally higher than that of the pristine PLA, which is in line with existing literature dealing with PLA and SA [270, 271]. However, for samples containing pulverized SA the increase of filler loading does not seem to result in Young's modulus increases, possibly due to the alkylated nature of the used SA, which is hydrophobic in nature, which allows it to act as an inherent plasticizer, even though as a structurally rigid one. Its rigidity is provided by its pearl-necklace-like three-dimensional network structure. This network structure is connected by rigid, Si-O-Si-linked inter-particle necks, which have sizes in the range of a few nm, making the inter-particle connection relatively rigid but very fragile [272]. It is interesting to notice that the 5% SA-loaded composite, although showing a relatively high Young's modulus, does not present radically different mechanical parameters with respect to the pulverized SA-loaded samples, even though the latter have a definitely lower filler content. This may be due to either the larger size of the SA particles or to the hydrophobic nature of the used SA, or to a mixture of both the factors, and more investigations on this topic will be needed in the future to clarify this point.

In general, from the here discussed tests, it is possibly to safely assume that the addition of SA to a PLA matrix delivers composites with mechanical robustness little lower than that of the starting PLA, showing higher rigidity (higher Young's modulus), relatively constant Stress at break and lesser Yield stress, Tensile strength and Strain at max stress. In **Fig.66** the obtained results of the mechanical properties for all tested P-ES samples are illustrated, together with those of pristine PLA for a proper comparison.

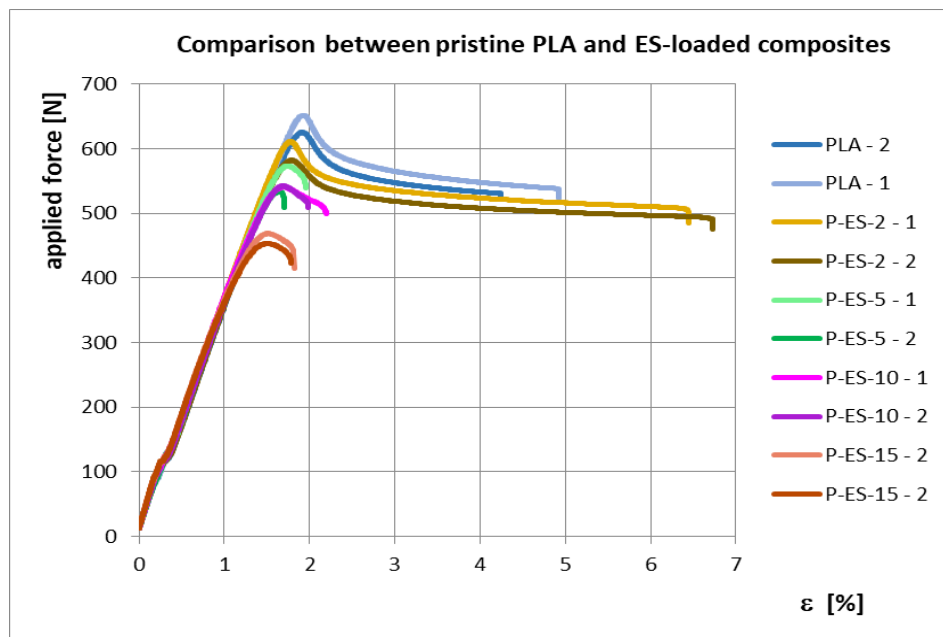


Figure 66. Comparison between PLA and SA-loaded samples of the results of the tensile tests

The conducted test show that for the lower percentage of ES filler the composite results to be more plastic than the pristine PLA, while as the ES filler content is increased this trend is reversed and moves to higher rigidity. Such an apparently erratic behavior has been previously reported in literature [273]. The observed augmented plasticity for lower percentages of ES in the composite could be attributed to a pseudo-plasticizer effect due to the well dispersed (at low filler loadings) small ES particles, which do not have particular reinforcing ability with respect to the inherent mechanical properties of PLA. On the other hand, the increased amount of ES particles in the polymer results in evident particles aggregation phenomena, which can cause internal rigidity of the composite due to sterical hindrance between neighboring particles/particle aggregates.

Looking at the ensemble of the mechanical properties of the PLA/ES composites (Table 30), it is possible to observe a general trend to increase the mechanical rigidity upon increase of the ES content, in all the considered parameters but the elongation at break. This general behavior can be ascribed to the general effects of the stiff ES particles, which transfer this property to the composite in which they are embedded into. Also this behavior is documented in previous literature [274-276].

In general, the composites with the higher amount of ES content showed an increased stiffness (higher Young's modulus), but an evident decrease in other mechanical parameters like Yield stress, Tensile strength, Strain at maximum stress, Stress at break, indicating that excessive amounts of ES filler degrade the mechanical resistance of the matrix PLA. However, these decreases are not dramatic, being limited to a 10-30% of the value of the pristine PLA.

Table 30. Main mechanical parameters extracted from the tensile tests carried out on PLA and ES-loaded composites.

Sample ID	Young's modulus	Yield stress	Tensile strength	Strain at max stress	Stress at break	Elongation at break
	E_t [MPa]	σ_Y [MPa]	σ_M [MPa]	ε_M [%]	σ_B [MPa]	ε_B [%]
PLA - 1	3066.24	59.36	60.35	1.93	48.46	4.92
PLA - 2	3376.60	57.44	57.89	1.91	48.58	4.25
P-ES2 - 1	3445.26	55.89	56.60	1.77	44.86	6.45
P-ES2 - 2	3420.29	52.89	53.89	1.80	44.00	6.73
P-ES5 - 1	3302.02	52.61	53.09	1.74	50.01	1.95
P-ES5 - 2	3188.44	49.29	49.42	1.65	47.15	1.70
P-ES10 - 1	3387.56	49.06	50.08	1.69	46.23	2.19
P-ES10 - 2	3559.81	49.35	50.20	1.68	47.21	1.99
P-ES15 - 1	3618.27	41.56	43.39	1.50	38.45	1.82
P-ES15 - 2	3707.32	40.67	41.95	1.49	39.11	1.79

4. CONCLUSIONS

In this work the potential of truly sustainable and environmentally compatible composites for thermal insulation made by poly(urethane) foam (PUF) or poly(lactic acid) (PLA) as the matrices and Silica Aerogel (SA), crushed eggshells (ES) or cork powder (CO) as fillers was investigated.

In more detail, different composites including one or more of the aforementioned materials have been prepared and characterized under the mechanical, spectroscopic and thermal points of view. The main results of these investigations are that:

- PUFs have been deemed not suitable for providing viable matrices for sustainable and environmentally friendly composites for thermal insulation, due to problems of excessively fast hardening, excessive rigidity once hardened and difficulties of homogeneously dispersing the fillers within the PUF matrix;
- PLA appears to be a promising matrix for composites, as it can be either melt or dissolved in appropriate solvents, hence it is easily processable. Thanks to this feature, two main types of composites have been realized for evaluation, i.e.:
 - Extruded composites including SA or ES as filler (with various loading percentages)
 - Spray deposited slurries, including SA or CO as filler (also here, with various loadings of the filler).
- The realized composites have been characterized under the points of view of their mechanical and thermal properties, showing satisfactory mechanical robustness, even though it was not possible to find compositions leading to a higher mechanical robustness than the parent pristine PLA; in particular, the addition of SA to a PLA matrix delivers composites with mechanical robustness little lower than that of the starting PLA, showing higher rigidity (higher Young's modulus), relatively constant Stress at break and lesser Yield stress, Tensile strength and Strain at max stress, while composites including ES showed that increasing the ES content the composite's stiffness (Young's modulus) gets higher, but on the other hand other mechanical parameters like Yield stress, Tensile strength, Strain at maximum stress, Stress at break decrease, indicating that excessive amounts of ES filler degrade the mechanical

resistance of the resulting composite. However, these decreases are not dramatic, being limited to a 10-30% of the value of the pristine PLA.

- In general, the most performing composites in terms of thermal insulation performance are the ones embedding SA as fillers, which delivered thermal conductivities as low as 0.036 W/m.K (for a SA content 5 wt.%). CO-containing composites delivered reasonably low thermal conductivities (down to 0.049 W/m.K for a 15 wt.% composite). ES embedding composites did not demonstrate particularly high performance as thermal insulators, reaching a minimum value of 0.088 W/m.K for a sample embedding 15 wt.% of ES filler.

The here resumed work have been conducted at the University of Chieti-Pescara, at the University of Rouen (France) and at the private company Diasen srl (sassoferato, Regione Marche, Italy), and have been aided by several other instrumental investigations, among which it is worth to cite:

- Optical microscopy for investigating size and possible aggregation phenomena occurring within the composites upon different filler loading percentages; this type of analysis showed that in the here considered composites filler particles aggregation actually occur at higher filler loadings.

- FT-IR spectroscopy to verify the type and intensity of interactions between the matrix and the filler; these analyses showed that no meaningful chemical interaction develops between the PLA matrix and the fillers.

Upon the discussed evidences it can be said that composites using PLA as the matrix and SA or CO as the filler can represent interesting opportunities for exploring truly sustainable thermal insulating materials. In fact, the inherent biodegradability of PLA and the recyclability and biocompatibility of both SA and CO represent an ideal basis for thermally insulating materials usable in extremely diffused applications, such as for example linings for the building industry. From an economical point of view, PLA and CO are pretty economic materials; and even though SA is rather expensive, the here presented data show that even very small amounts of it can decrease substantially the thermal conductivity of a composite. Moreover, the here presented spray deposition method for realizing composite layers directly onto concrete tiles exemplifies how fast and easy the large deployment of these materials can be.

As an outlook, the here presented research is considered to be a good starting point for exploring the potential of biodegradable, biocompatible and recyclable thermal insulators designed for mass production; nonetheless, much more research must be carried out on this subject, in particular regarding optimization of the spray deposition procedures, of the composites formulation for avoiding particle aggregation and of cost reduction via accurate selection of filler materials.

5. HIGHLIGHT WORK

1) Title: Sustainable Micro- and Nanocomposites for Thermal Insulation in Buildings Stage: Published Topics: Information on micro-and nanocomposites for thermal insulation with enhanced sustainability – Applicable of polyurethane (PU) in buildings – Addresses bio-based with a focus on silica aerogel (SA)-based materials - Sustainable composites for thermal insulation Publisher: Advanced Engineering Materials – Wiley
2) Title: Novel silica aerogel-polyurethane composites for thermal insulation – Conference Stage: Published Topics: Realize a composite with solid PU as the matrix – Silica aerogel (SA) as solid filler – Realize homogeneous composites by reducing 13% of thermal conductivity Publisher: Atti del Convegno" XVII Convegno nazionale AIMAT-AIMAT 2023 (https://ricerca.unich.it/handle/11564/820762)
3) Title: Novel Green Poly (Lactic Acid) – Silica Aerogel Composites for Thermal Insulation – Conference Stage: Published Topics: Realize a ternary solution (PLA + liquid solvent + Silica aerogel) – Thermal insulation slurry for use on construction materials. Publisher: IRIS – Book of abstracts del congresso (https://ricerca.unich.it/handle/11564/820678)
4) Title: Sustainable PCM for thermal enhancement in buildings Stage: In progress ...!! Topics: Main approaches of stored the thermal energy (SHS – LHS and TCS) – Focused on the Phase Change Materials (PCMs) as latent heat storage
5) Title: Novel thermal insulation made by elastomeric polyurethane/silica aerogel composite Stage: In progress ...!! Topics: polyurethane/silica aerogel composites of low thermal conductivity – Drawbacks of traditional thermal insulation
6) Title: PLA-based scaffolds structured at both the micro- and nanoscales for tissue engineering Stage: Submitted Topics: Generate micro-structured scaffolds by conventional FDM 3D-printing - Formation of nanostructures by self-assembly-based wet processing method (ASB-SANS) Publisher: Biofabrication – International Society for Biofabrication (ISBF)
7) Title: Investigating the thermal and mechanical effect of Silica Aerogel as filler in PLA matrix as thermal insulation in buildings Stage: In progress ... Topics: Realize the PLA composites filled with Silica Aerogel powder in different content as green thermal insulation – Improve the overall energy efficiency of buildings with environmental composites
8) Title: Eggshell-Reinforced PLA Composites as thermal insulation in buildings: A Green and Sustainable Approach Stage: In progress ... Topics: investigation of municipal solid waste (MSW) and energy recovery by waste-to-energy (WTE) – Various applications for waste Eggshell – Thermal insulation of PLA composites filled with ESs as a green and sustainable approach
9) Title: PLA/Cork Composites in Building Thermal Insulation: A Green and Sustainable Approach Stage: In progress Topics: An innovative, green approach to building insulation that aligns with sustainable development goals. Eco-friendly alternatives in the construction industry by PLA/cork composites.



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