

UNIVERSITA' DEGLI STUDI DI PADOVA

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CHARACTERIZATION OF BIO-BASED REINFORCED COMPOSITE AEROGELS

Relatore: *Prof. Alessandro Martucci* Correlatore estero: *Prof. Tobias Abt*

Francesca Del Pioluogo 2017287

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Abstract

Aerogels are highly porous materials that contain a large amount of air inside and have a very low density (approximately 0.1 g/cm³). Due to their properties of low density, large specific area and low thermal conductivity, they are used in many applications such as heat insulators, particle filters, packing and catalyst supports.

Inorganic aerogels tend to be brittle which has led to the generation of polymer-based aerogels with properties similar to polymeric foams. However, most of the raw materials of polymerbased aerogels are petrol-based which has stimulated a great research effort to find natural alternatives for these polymers. Polysaccharides and proteins are two families of biopolymers that have met with great success in research as natural precursors of aerogels for making viable alternatives to replace more pollutant petroleum-based materials such as expanded polystyrene or polyurethane foams, among others. Polysaccharides, such as cellulose, have been used in many applications requiring porous, non-toxic and biodegradable structures. Proteins can be either of animal origin, such as gelatine, or plant origin, such as egg white protein, soy protein or corn zein. The use of proteins as aerogel precursors is motivated by their biodegradability and biocompatibility characteristics.

The use of polymers as aerogel precursors produces an increase in the flammability of the material and this is a limitation for applications requiring fire resistance. To increase the fire resistance of polymer aerogels, it is necessary to add fillers and/or flame retardants.

In this project taking gelatine as bio-based polymer, different compositions will be made by mixing it with montmorillonite and tannic acid as crosslink agent with the final aim of finding a balance in properties that make them suitable for industrial applications. Therefore, the final composition must offer good mechanical, thermal and fire resistance properties at the same time.

The characterisation of the material is done with various instruments: Ubbelhode viscometer, FTIR, thermal conductivity, compressive strength, moisture absorption, thermogravimetric analysis and cone calorimetry.

The thermal conductivity of the aerogel containing tannic acid, clay and gelatine at the same time increased as compared to the pure gelatine aerogel, from 0.037 W/m·K to 0.046 W/m·K. Mechanical properties also increased, both in terms of Young's modulus and yield strength, as compared to basic gelatine aerogel when tannic acid is present. The presence of tannic acid and clay improved the thermal stability of the material and decreased the rate of thermal degradation of the aerogel. Finally, due to the intumescent characteristic of tannic acid, it was also possible

to decrease the peak heat released, the flammability of the material and increase the ignition time.

In conclusion, the addition of tannic acid as a crosslinker and clay as a filler made it possible to increase both thermal and mechanical properties and fire resistance simultaneously.

Riassunto

Gli aerogels sono materiali altamente porosi che contengono una grande quantità di aria al loro interno e hanno una densità molto bassa (circa 0.1 g/cm³). Grazie alle loro proprietà di bassa densità, grande area specifica e bassa conducibilità termica, sono utilizzati in molte applicazioni come isolanti termici, filtri per particelle, imballaggi e supporti per catalizzatori.

Gli aerogels inorganici tendono a essere fragili, il che ha portato alla generazione di aerogels a base di polimeri, che sono materiali in grado di esibire proprietà simili alle schiume polimeriche. Tuttavia, la maggior parte delle materie prime degli aerogels polimerici sono a base di petrolio, il che ha stimolato un grande sforzo di ricerca per trovare alternative naturali a questi polimeri. I polisaccaridi e le proteine sono due famiglie di biopolimeri che hanno riscosso un grande successo nella ricerca come precursori naturali di aerogels per la creazione di alternative valide per sostituire i materiali più inquinanti a base di petrolio, come ad esempio il polistirene espanso o le schiume di poliuretano. I polisaccaridi, come la cellulosa, sono stati utilizzati in molte applicazioni che richiedono strutture porose, non tossiche e biodegradabili. Le proteine possono essere di origine animale, come la gelatina, o vegetale, come le proteine dell'albume d'uovo, le proteine della soia e la zeina di mais. L'uso delle proteine come precursori di aerogels è motivato dalle loro caratteristiche di biodegradabilità e biocompatibilità.

L'uso di polimeri come precursori di aerogels produce un aumento dell'infiammabilità del materiale e questo rappresenta un limite per le applicazioni che richiedono resistenza al fuoco. Per aumentare la resistenza al fuoco degli aerogels polimerici, è necessario aggiungere cariche e/o ritardanti di fiamma.

In questo progetto, prendendo la gelatina come polimero a base biologica, verranno realizzate diverse composizioni mescolandola con montmorillonite e acido tannico come agente reticolante, con l'obiettivo finale di trovare un equilibrio nelle proprietà che li renda adatti alle applicazioni industriali. Pertanto, la composizione finale deve offrire allo stesso tempo buone proprietà meccaniche, termiche e di resistenza al fuoco.

La caratterizzazione del materiale viene effettuata con diversi strumenti: viscosimetro Ubbelhode, FTIR, conducibilità termica, resistenza alla compressione, assorbimento di umidità, analisi termogravimetrica e calorimetria a cono.

La conducibilità termica dell'aerogel contenente acido tannico, argilla e gelatina allo stesso tempo è aumentata rispetto all'aerogel di gelatina pura, passando da 0,037 W/m·K a 0,046 W/m·K. Anche le proprietà meccaniche aumentano, sia in termini di modulo di Young che di resistenza allo snervamento, rispetto all' aerogel di gelatina, in presenza di acido tannico. La presenza di acido tannico e argilla migliora la stabilità termica del materiale e ne diminuisce la

velocità di degradazione termica. Infine, grazie alla caratteristica di intumescenza dell'acido tannico, è stato possibile diminuire il picco di calore rilasciato, l'infiammabilità del materiale ed aumentare il tempo di ignizione.

In conclusione, l'aggiunta di acido tannico come reticolante e di argilla come riempitivo ha permesso di aumentare contemporaneamente le proprietà termiche e meccaniche e la resistenza al fuoco.

Table of contents

INT	INTRODUCTION			
СН	APTER 1 - STATE-OF-THE-ART	3		
1.1	AEROGEL	3		
	1.1.1 Definition	3		
	1.1.2 Origin			
	1.1.3 Structure and properties	4		
	1.1.4 Classification of aerogels	5		
1.2	SOL-GEL PROCESS	6		
1.3	DRYING METHODS	8		
1.4	POLYMER-BASED AEROGEL BY FREEZE DRYING	10		
	1.4.1 Fossil-based and biodegradable aerogels	11		
	1.4.2 Bio-based and biodegradable aerogels	12		
1.5	REINFORCING PROPERTIES OF AEROGELS	12		
	1.5.1 Aerogel composites	12		
	1.5.2 Bio-based/inorganic hybrid aerogel	13		
1.6	FACTOR INFLUENCING THE STRUCTURE AND PROPERTIES OF			
AE	ROGELS	14		
1.7	ECOFRIENDLY AEROGELS AS FLAME RETARDANCE SYSTEM	14		
СН	APTER 2 - MATERIALS AND METHOD	17		
2.1	POLYMERS	17		
	2.1.1 Gelatine	17		
2.2	ADDITIVES	20		
	2.2.1 Tannic Acid	20		
	2.2.2 Sodium Hydroxide	22		
2.3	FILLERS	23		
	2.3.1 Montmorillonite clay	23		
2.4	SOLVENTS	26		
	2.4.1 Deionised water	26		

2.5	AEROGEL PREPARATION	
	2.5.1 Equipment for aerogel preparation	
	2.5.2 Sol-gel preparation	27
	2.5.3 Freeze-drying (lyophilisation)	
	2.5.4 Sample nomenclature	
2.6	CHARACTERIZATION	
	2.6.1 Intrinsic viscosity	
	2.6.2 Fourier transform infrared spectroscopy	40
	2.6.3 Thermal conductivity	
	2.6.4 Stabilisation	43
	2.6.5 Density	
	2.6.6 Compressive strength	45
	2.6.7 Moisture absorption	
	2.6.8 Thermogravimetric analysis	
	2.6.9 Cone calorimetry	
CH	APTER 3 - RESULTS AND DISCUSSION	
3.1	INTRINSIC VISCOSITY	51
3.2	FOURIER TRANSFORM INFRARED SPECTROSCOPY	
3.3	THERMAL CONDUCTIVITY	55
3.4	STABILISATION	55
3.5	DENSITY	
3.6	COMPRESSIVE STRENGTH	57
3.7	MOISTURE CONTENT	59
3.8	THERMOGRAVIMETRIC ANALYSIS	60
3.9	CONE CALORIMETRY	
EN	VIRONMENTAL IMPACT ANALYSIS	67
BU	DGET AND/OR ECONOMIC ANALYSIS	69
CO	NCLUSIONS	71
GL	OSSARY	73
RE	FERENCES	75

List of Figures

Figure 1. Evolution of aerogels
Figure 2. 3-D network of silica aerogel with its detailed molecular structure [7]5
Figure 3. Schematic illustration of aerogel classification [10]
Figure 4. Methods for obtaining bio-based aerogels [13]7
Figure 5. Supercritical drying path in the Pressure-Temperature phase diagram
Figure 6. Phase diagram of ambient pressure drying
Figure 7. Phase diagram of freeze drying process
Figure 8. Example of types of bioplastics, both biodegradable and non-biodegradable.
*Naturally occurring polymers: their synthesis involves enzyme-catalysed, chain growth
polymerization reactions of activated monomers, which are typically formed within the
cells by a complex metabolic process. They include carbohydrates, proteins and oils and
fats (lipids) that are produced as macromolecules by biological systems such as
microorganisms, plants, and animals. ** Polymers that are synthesized chemically but
are derived from biological starting materials such as amino acids, sugars, natural fats, or
oils11
Figure 9. Classification of aerogels according to the nature of the material used [13]12
Figure 10. Upper left is interpenetrating of organic and inorganic molecules; upper right is
incorporation of organic molecules (enzymes, dyes, etc.); lower left is oxidation of
oxidic materials with organic substances; and finally lower right is a dual network [8]. 13
Figure 11. Combustion mechanism [26]
Figure 12. Collagen triple helix structure
Figure 13. Chemical structure of gelatine [35]18
Figure 14. Chemical structure of gelatine with evidence of amine groups [37]
Figure 15. Denaturation of collagen produce thermoreversible gelatine [40]19
Figure 16. (a) Tannic acid powder [43]; (b) Example of extraction source [44]20
Figure 17. Chemical structure of tannic acid [46]21
Figure 18. Chemical structure of sodium hydroxide [54]
Figure 19. 2:1 layered structure of Montmorillonite [57]
Figure 20. Powder of Montmorillonite
Figure 21. Equipment for aerogel preparation: (a) METTLER TOLEDO balance; (b)
AGIMATIC-E magnetic stirring; (c) Ultra-Turrax T25 [63]; (d) pH-meter series PH20
[64]27
Figure 22. Schematic illustration of the preparation of the precursor mixture
Figure 23. Schematic representation of the process in real conditions

Figure 24. (a) Ethanol and solid CO ₂ bath; (b) Freezing phenomenon inside the sample with
ice formation; (c) Frozen compression sample
Figure 25. Schematic representation of some protein-water interactions A) hydrogen bonds;
B) hydrophobic interactions [66]
Figure 26. Chemical reaction between tannic acid and NaOH [68]30
Figure 27. Different reaction mechanisms can occur when tannic acid is in an alkaline
environment: Schiff base formation, hydrogen bond and Michael addition [72]
Figure 28. Bidirectional freezing
Figure 29. Freeze-drying process of ceramic aerogels [76]
Figure 30. Samples after the freeze-drying process
Figure 31. Polishing of the sample
Figure 32. (a) Freeze-dryer laboratory, UPC Barcelona; (b) Freeze-dryer equipment: 1.
Condenser with 8 valves; 2. LCD display; 3. Pressing buttons panel; 4. Draining pipe; 5.
Electrical connection; 6. Main switch; 7. Vacuum pump [77]
Figure 33. (a) Ubbelhode 1B viscometer [80]; (b) Precision bath for the viscometer [81] 38
Figure 34. Indicator line in Ubbelhode 1B viscometer [83]
Figure 35. Nicolet 6700 spectrophotometer [86]
Figure 36. Thermal conductivity of a porous material through the different phases present
[28]
Figure 37. (a) C-Therm TCi for thermal conductivity analysis [89]; (b) Positioning of the
sample during the test
Figure 38. Sequence of the stabilisation process: the top picture shows the controlled
environment in which the specimens are maintained. In the bottom picture, the various
specimens are weighed to monitor the change in weight. The process is repeated until
stabilisation, that is until there is no further change in mass
Figure 39. Universal testing machine (ZwickRoell Z010, 10 kN RetroLine) for for the
compression test [94]
Figure 40. Positioning of the specimen
Figure 41. Moisture Analyzer HE53 with the specimen evenly distributed in the weighting
pan47
Figure 42. TGA/DSC 1 instrument (Mettler Toledo, Columbus, Ohio) [101]. The crucible,
containing the sample to be analysed, is placed on top of the balance
Figure 43. In the first image is the front view of the calorimetric cone, in the second image is
the side view of the calorimetric cone
Figure 44. Figure A. Shows the sample before being burnt. Figure B. shows the burning
process. Figure C. Shows the residue obtained at the end of the process
Figure 45. Reduced or inherent viscosity versus concentration
Figure 46. FTIR spectra for each compositions

Figure 47. Evolution of moisture absorption in function of the time	. 56
Figure 48. Compressive stress-strain curves of various compositions	. 57
Figure 49. Aerogel anisotropy due to different ice growth directions	. 58
Figure 50. Graph of mass loss as a function of temperature for each composition	. 61
Figure 51. Graph of decomposition rate as a function of temperature for each composition.	. 62
Figure 52. (a) Heat release rate vs. time; (b) Zoom of the initial part of the heat release rate	•
vs. time curve; (c) Broken G5T3C5B, left, and G5T4C5B, right, samples prior to testi	ng.
	. 64
Figure 53. Samples after the combustion process.	. 65

List of Tables

Introduction

The first aerogel was produced by Kistler [1] in 1931 and this term refers to foam-like materials, prepared by the sol-gel process, that possess low density, large specific area and low thermal conductivity. Due to these properties, aerogels are used in many applications such as heat insulators, particle filters, packing and catalyst supports. Aerogels can be made from various materials, including silica aerogels, which are the most studied and commercially used, nonsilica inorganic aerogels, i.e. those made from clay, metal, graphene and others, and finally polymer aerogels. The group of polymer aerogels also includes bio-based and biodegradable polymers, which have recently been experiencing enormous research development. The increased demand for sustainable and renewable products has led to the development of biobased materials. This increase in demand is based on several reasons including reducing the use of materials that degrade in the long term and would therefore lead to problems with climate change and the accumulation of waste in the seas. Biopolymers can come from various sources, but there are mainly two categories: polysaccharides and proteins. These natural polymers are used as environmentally sustainable precursors in the preparation of aerogels to replace petroleum-derived precursors. Unfortunately, most bio-based aerogels like traditional polymer foams exhibit low flame resistance. This makes it necessary to optimise their thermal and fire resistance properties in order to be competitive in the market.

In order to overcome this drawback, in this study, it was decided to use clay as a natural filler, thus creating a polymer/clay-based aerogel that allows the fire resistance properties of the material to be increased. In addition, tannic acid, which is a natural intumescent material that reduces free radicals during fire, was used for additional flame retardancy.

Aerogel polymer/clay possesses high brittleness due to the presence of clay, which limits its application. In order to increase the material's strength above the values obtained from pure gelatine aerogel, the cross-linking effect of the tannic acid with the gelatine is studied.

The objective of this thesis is the characterisation of a natural aerogel in order to find the best composition to achieve a good compromise of mechanical, thermal and fire resistance properties.

As a natural material, gelatine, which is a biodegradable material of animal origin, was used as a precursor to the aerogel. Clay, which is a constituent of the natural environment and is one of the most abundant materials in the earth's crust. Finally, tannic acid, which is extracted from many plants and is the second most abundant natural material after cellulose, hemicellulose and lignin.

Previous studies have already investigated the characterisation of a composite clay/polymer aerogel. This inorganic material increases the fire resistance of the polymer aerogel, but reduces the mechanical properties due to its brittleness. In this project, the focus is on the effect of variation of tannic acid concentration on aerogel properties. Due to the enormous amount of phenol groups in the chain, it allows the fire resistance to be further increased. Furthermore, due to its cross-linking effect with gelatine, it allows the compressive strength of the polymer aerogel, which has been reduced due to the presence of clay, to be recovered.

In order to be able to identify the optimal composition of these three materials so as to have a good balance of the properties indicated above, various methods are used for characterisation:

- Intrinsic viscosity calculation
- FTIR, to understand the chemical structure
- Thermal conductivity
- Compressive strength, to calculate mechanical properties
- TGA to analyse thermal degradation
- Calorimetric cone, for studying fire resistance

In chapter one, information are gathered on the state of the art of aerogels, with a focus on biodegradable and bio-based aerogels. Chapter two summarises the main characteristics of the materials used, the preparation of aerogels using the sol-gel method and the freeze-drying process is explained in detail and also characterisation methods are explained. Finally, in chapter three, the results obtained for the different compositions are analysed.

Chapter 1 State-of-the-art

1.1 Aerogel

1.1.1 Definition

In literature, can find many definitions of aerogels. IUPAC defines an aerogels as "Gel comprised of a microporous solid in which the dispersed phase is a gas" [2]. For the scientific community this definition is considered incorrect because it considers that aerogels are exclusively microporous materials, but for aerogels it is common to have multiple sizes and types of pores, such as mesopores. More appropriate definitions have recently been developed.

The first definition is based on the aerogel production process: "An aerogel is an open nonfluid colloidal network or polymer network that is expanded throughout its whole volume by a gas and is formed by the removal of all swelling agents from a gel without substantial volume reduction or network compaction" [3]. From this definition is understandable that aerogels are materials derived from gels, but there is not any specification about the extent of the changes in the gel structure during drying for it to be called an aerogel.

The second definition is based on the characteristics: "Aerogels are solids that feature very low density and high specific surface area and consist of a coherent open porous network of loosely packed, bonded particles or fibers" [4]. Coupling these two last definitions, we can achieve a more complete information about the process of fabrication and the material properties.

1.1.2 Origin

The first aerogel was prepared in 1931 by Steven S. Kistler [1]. Using the supercritical drying approach that remove the fluid from a wet silica gel, he obtained a solid material filled with air almost in the same volume as the original wet one. Kistler characterised not only silica aerogels but also aerogels from many other materials, including alumina, tungsten oxide, ferric oxide, tin oxide, nickel tartrate, cellulose, cellulose nitrate, gelatine, agar, egg albumen and rubber [5].

The aerogels became a quite forgotten material for about 30 years because of the complexity of the production process. The researchers returned to them only when the evolution of the sol-gel method was combined with the supercritical extraction technology.

In 1968 Teichner, followed by Russo in 1986, created an aerogel using an organic precursor, namely the alkoxylans of tetramethyl orthosilicate (TMOS) and tetraeltil orthosilicate (TEOS)

respectively, an organic solvent and thanks also to the development of carbon dioxide supercritical fluid drying they succeed to facilitate the production of aerogels.

The research of aerogels was limited to silica and various inorganic compositions until 1980 when Pekala developed organic and carbon aerogels using an organic polymer, namely resorcinol-formaldehyde (RF). This marked the beginning of organic and polymer aerogels. At the beginning of the twenty-first century, research was expanding with new types of aerogels such as non-silica, chalcogenide aerogel, gradient aerogel and other types of aerogels. Aerogels based on carbon nanotubes (CNTs), graphene, silicon and carbide or carbonitride have recently been developed [6]. Figure 1 shows the historical evolution of aerogels.

_		Evolution of aerogel			
	1930's	1970's	1989's	2010's	
	Kistler invented the first aerogel	SiO₂ aerogel by Teichner	RF aerogel by Pelka	CNTs and graphene based aerogel	\checkmark

Figure 1. Evolution of aerogels.

1.1.3 Structure and properties

Aerogels are materials with a low content of solid material and a high content of air inside them, which corresponds to around 99%. From a structural point of view, it is composed by particles fused together with a lot of air in between. The Figure 2 shows the 3-D structure network of the silica aerogel where the SiO_2 particles are separated by large empty spaces, which are filled with air. From the micrograph the continuous structure and large pores of the aerogel are noted. These two characteristics gives aerogels the properties of lightweight and compact structure.



Figure 2. 3-D network of silica aerogel with its detailed molecular structure [7].

The main characteristics of aerogels are [7]:

- Low density and high porosity. Due to the high porosity they have an extremely low density which ranges from 0.0011 to 0.5 g/cm³. Aerogels have an open pore structure with air inside the pores. The pore's dimensions range from <1 to 100 nm. They have a wide internal surface of 10-2000 m²/g, which leads to a low average path for gas diffusion.
- Acoustic properties. Aerogels have large sound absorption characteristics.
- Low thermal conductivity. Aerogels are materials that exhibit excellent isolation properties due to the air inside them that inhibits both convection and gas-phase conduction.
- Colour. Aerogels can be coloured, transparent and opaque.
- Functionalization. The aerogel's surface can be functionalized with functional groups by chemical reaction and physical deposition techniques.

All these characteristics have made aerogels a useful material for multiple application such as thermal insulators, biomedical implants and devices, particle filters, particle trappers and catalyst supports [8].

1.1.4 Classification of aerogels

There exist different types of classifications for aerogels [9]:

- Based on the appearance we can distinguish monolith, powder and film aerogels.
- Based on the production we have aerogels, xerogels or hydrogels.

- Based on the microstructure is graded as microporous aerogel (< 2 nm), mesoporous aerogel (2-50 nm), macroporous (> 50 nm) and mixed porous aerogel.
- Based on the chemical composition three groups are formed: inorganic, organic and composite aerogels depending on whether the precursor is organic, inorganic or a mixing of both, respectively.

A scheme of the different possibilities for classifying aerogels according to appearance, microstructure or composition is shown in Figure 3.



Figure 3. Schematic illustration of aerogel classification [10].

1.2 Sol-gel process

The sol-gel method is a process in which solid nanoparticles dispersed in a liquid (sol) agglomerate together forming a 3-dimensional network that extends over the entire liquid (gel). Before describing the process, the following terms are defined [11]:

- Colloids: mixture of two different phases intimately mixed together. A colloid typically consists of a continuous phase within which a different dispersed phase is found. Phase means the solid, liquid or gaseous form of some substances.
- Sol: in sol the continuous phase is liquid and the dispersed phase is solid. The sol differs from a noncolloidal liquid solution because solid nanoparticles are dispersed throughout the liquid.
- Gel: the continuous phase is a solid network and the dispersed phase is a liquid. Gel is a wet solid-like material in which nanoparticles are interconnected and form a solid network covering the volume of a liquid medium. The composition of a gel tends to be mostly liquid, but the cohesion is similar to that of a solid.

The advantage of using the sol-gel method for the preparation of aerogels lies in the simplicity of controlling the nanoarchitecture during the synthesis process [12]. The sol-gel method offers the ability to tailor the material properties for a specific application. Depending on the reaction

conditions, such as pH, solvent, temperature, time, catalysts and agitation, the aerogel's properties can be adjusted and optimised for a specific application.

Four main steps can be identified in sol gel processing [12]: preparation, gelation, ageing and drying.

The preparation stage includes the formation of a colloidal suspension as a result of the dispersion of solid nanoparticles, derived from a precursor material, in a solvent.

After that starts the transition of sol to gel (gelation). Sol can become a gel when the dispersed solid particles join together to form a network in the liquid. Some particles have reactive groups on the surface that condense together to form bonds, for other nanoparticles, however, bonding is difficult and requires some additives, or the removal of some functional groups from the surface of the particles to bond them together. The network particles extend over the entire volume of liquid, and at the same time the viscosity increases until the immobilization of the liquid.

After the gel formation the aging in mother solution takes place in order to increase the backbone and mechanical strength of the gel.

Finally, the solvent is removed from the pores by a drying process, avoiding the gel fracture and/or the reduction of the volume or compaction of the network. The drying involves evaporation of the solvent, extraction of the solvent or sublimation during xerogel, aerogel and cryogel synthesis, respectively.



The different phases for the preparation of bio-based aerogels can be seen in Figure 4:

Figure 4. Methods for obtaining bio-based aerogels [13].

1.3 Drying methods

To obtain the aerogel the fundamental step is drying as it affects the morphology, porosity and integrity of the final structure [6]. As mentioned above, the highly porous structure needs to be preserved and this is not possible with conventional methods due to the capillary pressure that is generated at the vapour/liquid interface that could induce collapse and cracking of the gel pores. Other methods are possible such as supercritical drying (using alcohol, acetone or carbon dioxide), ambient pressure drying, freeze drying, microwave drying and vacuum drying [6].

• Supercritical drying. This method consists in heating the wet gel in conditions where the temperature and pressure exceed the critical values Tc and Pc of the solvent that is inside the pores of the gel (Figure 5). The solvent becomes a supercritical fluid, where the vapour and liquid phase are indistinguishable and therefore capillary forces do not occur. Due to the fact that there is no liquid/gas interface, this method prevents the formation of a liquid-vapour meniscus that shrinks during the emptying of the pores. Once the fluid is released and the cooling process is finished, the aerogel can be removed. The critical conditions vary depending on the fluid that is inside the pores, the most common one is CO₂. This method turns out to be the most effective to prevent the collapse of the pores. The main disadvantage is the time-consuming procedure. Moreover, significant quantities of solvents and relatively expensive supercritical gas processing are required, this means that cost and environmental impact are high.



Figure 5. Supercritical drying path in the Pressure-Temperature phase diagram.

 Ambient pressure drying. It consists in the passivation of the inner surface of the pores in such a way that, during the compression due to the drying efforts, no new chemical bonds are formed. Once the solvent has evaporated (Figure 6), the aerogel is no longer subject to capillary forces and therefore resumes its wet dimension due to spring back. Ambient pressure drying is a simple and energy-saving process that can be applied on a large scale for industrial purposes. The disadvantage of this method is the high withdrawals that hydrogel undergoes, which can also lead to the formation of solids without porosity.



Figure 6. Phase diagram of ambient pressure drying.

• Freeze drying (also called "lyophilisation"). Two phases can be distinguished in this process: freezing and sublimation (Figure 7). During the first phase, the liquid is frozen inside the gel, with the formation of large ice crystals. In the second phase these are eliminated by sublimation at low pressures, leading to the proliferation of macropores and the shrinking of volume. The resultant porous material is called "cryogel" that unlike an aerogel has a higher density, the porosity reaches 80%, and a lower surface, about half of what is obtained in an aerogel. They also show less shrinkage and a narrower distribution of pore size. This process is simple, economical, and environmentally friendly and also can be used for bio-based polymers, such as casein, pectin, alginate, gelatine, hyaluronic acid, and cellulose. As disadvantages there are the time-consuming procedure, the volume expansion that causes the solidification of the water, which could then lead to the cracking of the aerogel, and finally a high energy consumption.



Figure 7. Phase diagram of freeze drying process.

• Other methods. Microwave drying is used to obtain aerogel with high surface area and suitable porosity. The porosities obtained are smaller than those obtained with freeze drying. Another method is via jet cutting for the production of spherical biopolymer particles, after that the particles were subject to solvent exchange in ethanol and then to supercritical drying. As a result, the particles have a large surface area with good absorption stability capacity.

1.4 Polymer-based aerogel by freeze drying

Silica aerogel, like most inorganic aerogels, is obtained by the sol-gel method by which silica particles are connected to each other forming a 3-dimensional network. This structure turns out to be very fragile due to the weak bonds that are formed, causing difficult processing, manipulation and low resistance to tensile stress. Another disadvantage is that production costs are about 8-20 times higher than those for polyurethane foams [14]. For these reasons, many organic materials such as graphene, carbon nanotubes and metal oxides have been developed. In addition, many recent studies have shown that the mechanical properties of silica aerogel improved by incorporating organic materials as reinforcements [15].

Recently there have been developed polymer-based aerogels, a new material that possesses a low thermal conductivity and density, good characteristics of flexibility and elasticity are also easily available and multifunctional.

Most synthetic polymers (Polyurethane (PU), polyurethane-acrylate (PUA), polyimide (PI)) and natural polymers (cellulose, starch, and alginate) can be employed for aerogels manufactured through sol-gel technology. The preparation of aerogels of polymeric nature by supercritical drying method allows to obtain a structure with high porosity and large surface area and therefore the material has a great thermal insulation property. The disadvantage of this technique is the large amount of organic solvent that is removed and also the use of carbon dioxide.

Although the freeze-drying process produces materials with a lower surface area and does not form microporosities, it has the advantage of being simple, economical, environmental-friendly and uses water as a solvent. In addition, this method can be used for a wide range of polymers, both synthetic and bio-based such as casein, pectin, alginate, gelatine, hyaluronic acid and cellulose [16].

The most recent studies are based on the production of bio-based polymers as the use of these compounds is an excellent alternative to reduce environmental impacts. Figure 8 shows the

classification of "bio-based" polymers, which are derived from biomass, and "fossil-based" polymers, that is polymers derived from petrochemical feedstocks.



Figure 8. Example of types of bioplastics, both biodegradable and non-biodegradable. *Naturally occurring polymers: their synthesis involves enzyme-catalysed, chain growth polymerization reactions of activated monomers, which are typically formed within the cells by a complex metabolic process. They include carbohydrates, proteins and oils and fats (lipids) that are produced as macromolecules by biological systems such as microorganisms, plants, and animals. ** Polymers that are synthesized chemically but are derived from biological starting materials such as amino acids, sugars, natural fats, or oils.

The ASTM_D5526 ("American society for testing and materials") standard defines the characteristics that a biodegradable polymer must have [17]. A material to be defined as biodegradable must be characterized by a degradation mechanism caused by a natural action of microorganisms that break the old bonds and/or form new bonds in the polymer chain. This causes macroscopic changes in the material such as the decrease in mechanical properties.

1.4.1 Fossil-based and biodegradable aerogels

As can be seen from Figure 8 not only bio-based polymers are biodegradable, but also those from fossil sources can reduce the impact of polymers on the environment, such as polyvinyl alcohol [18]. It can therefore be concluded that the biodegradation capacity of a polymer does not depend on its source, renewable or fossil, but on its chemical characteristics.

1.4.2 Bio-based and biodegradable aerogels

Research on bio-based and biodegradable polymers is increasing, because the use of these materials is an excellent alternative for reducing environmental impact [19]. Usually renewable sources to produce aerogels are divided into two categories, as also shown in Figure 9: polysaccharides (starch, cellulose, chitosan, alginate, etc.) and proteins (both of animal and vegetable origin). Aerogels that use biopolymer precursors (such as chitosan, alginate, pectin, lignin, cellulose, protein) have had enormous success in the biomedical field with regard to tissue engineering, regenerative medicine, and drug delivery systems [20].



Figure 9. Classification of aerogels according to the nature of the material used [13].

1.5 Reinforcing properties of aerogels

1.5.1 Aerogel composites

A composite consists of one or more materials that have different properties, where in an appropriate combination they can enhance the properties of the single component. In fact, the advantage of using a composite aerogel is to achieve a synergy effect, meaning to increase certain properties to achieve better performance. From an environmental sustainability point of view, an attempt is made to utilise the properties of both inorganic and organic natural materials in order to obtain hybrid composites with intermediate properties of the individual constituents [21].

1.5.2 Bio-based/inorganic hybrid aerogel

Inorganic aerogels resist high temperatures very well, but are very brittle; instead, polymer aerogels possess good mechanical properties, but low resistance to high temperatures [22].

The porous structure of polymer aerogels can be reinforced by making a composite material from inorganic materials. The resulting composite material has better mechanical and thermal properties than single polymer aerogels.

In this research, a composite material based on bio-based gelatine and clay is made, as the introduction of clay allows increased stiffness and flame retardancy, and as a synergistic effect, less brittleness occurs due to the good mechanical properties of the polymer [6].

To modify an inorganic aerogel with an organic material the most used method is sol-gel, there are several ways to do this as can be seen from Figure 10.



Figure 10. Upper left is interpenetrating of organic and inorganic molecules; upper right is incorporation of organic molecules (enzymes, dyes, etc.); lower left is oxidation of oxidic materials with organic substances; and finally lower right is a dual network [8].

Most biopolymers have hydrophilic groups in the chain, which makes some of them watersoluble. To achieve a good dispersion of clay, the best solvent is water, since clay is hydrophilic. These two characteristics make it possible to fulfil the requirements necessary to create an aerogel based on the biopolymer-clay system, namely:

- Formation of suspension or a polymer-clay colloid where no phase separation occurs
- During the freezing process, the solvent used must crystallise

At the moment, this type of composite finds application in packaging and insulation.

1.6 Factor influencing the structure and properties of aerogels

The properties and structure of composite aerogels based on the polymer-clay system can be modified by chemical or physical means:

- Chemical: by performing a chemical crosslink [23]
- Physical: by using fillers and nanoparticles as reinforcing adhesives [24].

1.7 Ecofriendly aerogels as flame retardance system

When we talk about flammability, we mean the ease with which a material can be ignited, its ability to spread fire, the intensity with which it burns and releases heat to the outside world and also the speed at which it creates smoke and combustion products [25].

For combustion to occur, three basic components are required as schematised in Figure 11: fuel, oxygen and heat. In a combustion reaction, fuel is heated and reacts with oxygen.



Figure 11. Combustion mechanism [26].

It is possible to divide the combustion process of organic materials into six main steps [27]:

- 1. An ignition source heats the matrix material.
- 2. Degradation of the heated material begins.
- 3. Polymer chains are broken and a decrease in the mechanical properties of the polymer occurs.
- 4. In the presence of excess oxygen, combustion begins because ignition of steam or combustible gas occurs.
- 5. This ignited steam/gas causes combustion on the surface of the material.
- 6. Subsequently, flame formation occurs with the emission of smoke and gases from the surface.

To increase the fire resistance of a polymer, flame retardant additives are used. Flame retardants interfere with the combustion process and are divided into two categories according to the type of interaction, which can be physical or chemical. With regard to physical interaction, the processes that can be found are cooling, dilution or the formation of a protective layer. While chemical interactions can take place in two different states: solid or gaseous. In the gaseous state, reactions occur between the additives and reactive species present. In the solid phase, two distinct mechanisms can occur: char formation, that is, the formation of an insulating barrier between flame and polymer, or intumescence, that consists of the swelling of the blowing agents forming a barrier. In this work, tannic acid was used as a flame retardant material, which is a natural material and not based on halogens that can cause environmental problems due to their non-degradability in the environment.

There are several techniques to characterise the fire resistance properties of materials: Limited Oxygen Index (LOI), the Standard for Safety of Flammability of Plastic Materials for Parts in devices and Appliances testing (UL94) and the calorimetric cone. For the characterisation of bio-based aerogel in this research, the calorimetric cone is used and the principle of operation will be described in Chapter §2.6.9.

The use of aerogels derived from sustainable sources is an excellent solution for providing the flame resistance property, compared to petroleum-based aerogels that are non-biodegradable. Sustainable materials include two broad categories: polysaccharides and proteins. Polysaccharides are generally highly flammable due to their long organic carbohydrate chains. For this reason, it is necessary to improve the fire resistance of this material by adding flame retardant materials. Proteins have sulphide, nitrogen and phosphate in their chains and therefore act naturally as flame retardants [28].

Examples of bio-based aerogels and additives used as flame retardant systems are shown in the following Table 1:

Bio-based material	Additives	Properties	Reference
Cellulose	Graphene oxide, sepiolite	Resistance to fire	[29]
Alginate fiber	MMT clay	Low flammability aerogel	[30]
Casein		Fire resistance foam	[31]
PVA	NaOH, TA	Low flammability	[32]
Gelatine	Attapulgite	Fire resistance	[33]

Table 1. Examples of flame retardant system

Chapter 2 Materials and method

2.1 Polymers

2.1.1 Gelatine

Gelatine is defined as a product of the partial hydrolysis of collagen that is extracted from the bones, skin and connective tissue of animals [34].

Since gelatine is derived from collagen, it is necessary to understand the structure of this macromolecule in order to understand the structure and composition of gelatine.

Collagen is the most abundant component of the extracellular matrix (ECM) in animals. Fibrillar-type collagen is what is used to produce gelatine. As can be seen in Figure 12, collagen consists of three polypeptide chains that twist onto each other and are linked by intermolecular crosslinks to form a triple helix structure. The single fibrillar form is composed of a uniform triplet of cyclic amino acids of -Gly-X-Y- where the X position is usually occupied by proline and the Y by hydroxyproline.



Figure 12. Collagen triple helix structure.

The thermal denaturation of collagen produces gelatine, which is a high molecular weight protein containing amino acids that are bound to each other by peptide bonds. The amino acid sequence is the same as that found in collagen, which is -GLY-X-Y-, where X and Y correspond to proline and hydroxyproline respectively, as can be seen in Figure 13.



Figure 13. Chemical structure of gelatine [35].

Gelatine is rich in functional groups such as hydroxyl, carboxyl and amino groups. Due to the abundance of hydroxyl and amino groups (Figure 14), gelatine dissolves easily in water. In addition, the presence of the high nitrogen content increases its ability to be a low-flammability material [36].



Figure 14. Chemical structure of gelatine with evidence of amine groups [37].

The denaturation of collagen is carried out by hydrolysis under acidic, alkaline or enzymatic conditions and this chemical treatment allows the bonds between the filaments to be broken. Following this procedure, through an extraction process in hot water at a temperature of around 40°C, collagen dissolves, taking on a disordered spiral structure as the breaking of the hydrogen and hydrophobic bonds that are necessary for the stabilisation of collagen has occurred. Subsequently, there is the breaking of the intramolecular bonds between the triple helix chains [38]. The just-formed gelatine attempts to recreate the structure of the collagen as the temperature decreases below the melting point, so as to rebuild stability by reforming the cross-links between the chains [39]. By increasing the temperature, the disordered aqueous phase structure of the gelatine can be re-obtained (Figure 15).



Figure 15. Denaturation of collagen produce thermoreversible gelatine [40].

Gelatine is extracted from the raw material by an acidic or alkaline process using an acidic or alkaline medium, respectively. Using the first extraction method results in an A-type gelatine with an isoelectric point between pH 6 and 9 that carries a net positive charge [38]. On the other hand, performing the extraction with an alkaline treatment results in a B-type gelatine that will have an isoelectric point between 4 and 5, which generates a net negative charge.

The properties of gelatine vary depending on temperature, pH, concentration, ash content, thermal history and method of preparation. Some of the properties of gelatine are listed below [41].

- Amphoteric properties: Gelatine in solution is amphoteric, so it can behave either as a base or as an acid depending on the pH of the solution in which it is found. Under alkaline conditions it is negatively charged and migrates as an anion. Under acidic conditions it is positively charged and migrates as a cation. The midpoint is the pH value of the solution where it has no net charge and this is referred to as the isoelectric point.
- Gel strength: When gelatine is in solution form at a concentration of approximately 0.5%, the viscosity increases during cooling below 35°C until a gel forms. This is because the gelatine tries to form the ordered structure of collagen. The strength of this gel depends on a number of parameters such as temperature, pH and additives present.
- Viscosity: The effect of viscosity is strongly dependent on molecular weight. As the concentration increases and the temperature decreases, the viscosity increases.
- Colour: Gelatine in solution can appear colourless to a faint yellow. As the concentration increases, the colouring becomes orange-brown.

For this study, gelatine supplied by Drogueria Boter (S. L. C/Vlar, 7108911 Badalona, Barcelona, Spain) is used. As it is a food-grade powdered gelatine, no specifications are given on the extraction method, so we cannot know a priori whether it is a type A or B gelatine. A pH analysis of the pure gelatine was carried out (5g/100ml H₂O) and a value of 4.76 was obtained, i.e. type A and therefore positively charged. Assuming the isoelectric point to be around pH 5, having obtained a pH value below the isoelectric point, protonation of the amine groups occurs, thus creating a positively charged gelatine.

2.2 Additives

2.2.1 Tannic Acid

Tannic acid (TA) is the most abundant natural material after cellulose, hemicellulose and lignin, which is found in numerous plants such as the bark of pine, oak, chestnut and mangrove [21, 42].



Figure 16. (a) Tannic acid powder [43]; (b) Example of extraction source [44].

Tannic acid is formed by the condensation of one molecule of glucose and five molecules of digallic acid, which in turn are formed by the esterification of two molecules of gallic acid [45].

The structure of this natural material contains 2-12 galloyl units per molecule, and is shown in Figure 17.



Figure 17. Chemical structure of tannic acid [46].

Its unique properties derive from complex polyphenol compounds containing aromatic catechol and pyrogallol ring structures. The main properties that this structure confers are listed below [21]:

- Solubility: The solubility of TA is 300 g/L in water, and the water solution of TA is stable in air, which allows it to be stored for long periods.
- Biocompatibility. Generally, it is biocompatible, hydrolysable, and biodegradable under certain hydrolytic conditions where foreign bond breaking between two pyrogallol groups occurs.
- Adhesiveness. Its surface affinity and adhesiveness under water conditions result from reactions between TA and various nucleophiles on a protein-rich surface.
- Meta-chelating. Due to functional metal chelation, tannic acid can participate in biological processes allowing the construction of new structures and sensors. Thanks to the aromatic rings in the chain, it enables the reduction of noble metals to the corresponding metal nanoparticles, providing them with stabilisation through steric hindrance and electron donor and acceptor interactions between the various adjacent phenolic groups.
- Bonding with polymers. Ability to bond with various natural polymers through a supermolecular interaction.

Tannic acid is the main crosslinker of gelatine [47, 48, 49, 50]. The main applications are against plant fungi and insects due to its antibacterial and antioxidant properties [51, 52]. It is also used as a flame retardant because the tannins form graphite during the combustion process, forming graphite-carbon layers that are bad conductors of heat, reducing tree fires. Focusing on this last characteristic, it has been shown that tannic acid is a natural intumescent material as it reduces radicals and oxidants during a fire [42].

For this study, tannic acid (M_w = 1701.2 g/mol) supplied by Merck (Mollet del Vallés, Barcelona, Spain) is used.

2.2.2 Sodium Hydroxide

Sodium hydroxide (NaOH), also called 'caustic soda' due to its high corrosive action, is an inorganic compound with the brute formula NaOH. It is a strong base that easily reacts with carbon dioxide to become NaHCO₃ and Na₂CO₃ by means of this reaction:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$
 (2.1)

When dissolved in water a strongly exothermic process occurs, the reaction that takes place is as follows:

$$NaOH_{(s)} \rightarrow Na^+_{(l)} + OH^-_{(l)}$$
 (2.2)

The result of this solution is colourless and odourless.

Figure 18 shows its structure composed of the equivalent ions Na⁺ and OH⁻ linked together by an ionic bond, while in the hydroxyl group there is a covalent bond between the oxygen and hydrogen [53].



Figure 18. Chemical structure of sodium hydroxide [54].

One method of preparing sodium hydroxide is by slaked lime treatment:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$$
 (2.3)

This reaction is also referred to as 'carbonate caustification' and allows high yields when the concentration of sodium carbonate is low. The reaction takes place by placing a solution of sodium carbonate and calcium oxide in series boilers heated by steam. The first exothermic reaction that occurs is that between calcium oxide and water:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
 (2.4)

It is then decanted and filtered to separate the insoluble calcium carbonate. The concentration of this solution is 10% and to increase it, evaporators are used to remove some of the water, increasing the concentration to 50%. To increase it further, this final solution is placed in special
cast-iron boilers at 300°C where the complete elimination of water occurs and is then poured into moulds. To obtain purity of this final product, it is necessary to dissolve the caustic soda in ethyl alcohol where the impurities are typically insoluble. Finally, the alcohol is evaporated and the residue is re-melted and poured to obtain pure caustic soda.

Another method of preparing caustic soda is by electrolysis of aqueous solutions of sodium chloride. In this electrolytic process, an electric current passes through a sodium chloride solution, the decomposition of the chloride to form NaOH takes place, with the development of H_2 at the cathode and Cl_2 at the graphite anode, according to this reaction:

$$2NaCl + 2 H_2O \rightarrow H_2 + Cl_2 + 2 NaOH$$
(2.5)

At the cathode occurs:

$$2H_2O \rightarrow 2OH^- + H_2 \tag{2.6}$$

As the concentration of OH⁻ ions increases, they migrate towards the anode reacting with Cl₂ and generating hypochlorite:

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$$
(2.7)

Resulting in a loss of chlorine and caustic soda. To prevent the diffusion of substances, it is necessary to use porous concrete diaphragms or bells where the separation of the two liquids takes place by means of the difference in density between the denser cathode solution, NaOH, and the less dense anode solution, NaCl [53].

Sodium hydroxide was purchased in granule form from Riser S.A. (Les Franqueses del Valles, Barcelona, Spain).

2.3 Fillers

2.3.1 Montmorillonite clay

Montmorillonite (MMT) is a mineral from the family of smectite clays. Its 2:1 layered structure is composed of two tetrahedral O-Si-O sheets that 'sandwich' between an octahedral O-Al-O sheet as can be seen in Figure 19. The layers are held together by electrostatic and van der Waals forces [55].

The chemical structure is: $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ where M corresponds to a monovalent cation that can undergo isomorphic substitutions such as Si⁴⁺ with Al³⁺ in the tetrahedral layer and Al³⁺ with Mg²⁺ in the octahedral layer. Due to these substitutions, the MMT possesses a residual negative charge that is compensated for by the cations in the intermediate space [56].



Figure 19. 2:1 layered structure of Montmorillonite [57].

Clay is an abundant natural material in the earth's crust with many interesting properties and at the end of its life cycle it returns to the earth. The largest reserves of montmorillonite are found in the Himalayas (China), Urals (Pakistan), Caucasians (Georgia, Russia), Andes (Peru, Ecuador), and Wasatch (UT, USA) [58].



Figure 20. Powder of Montmorillonite.

The physical properties of the MMT are listed in Table 2 [58]:

Property	Description
Density	$2-3 \text{ g/cm}^3$
Hardness	1-2 on Mohs scale, soft, possess fine-grained occurrence
Crystal system	Monoclinic
Cleavage	Perfect
Luster	Earthy, dull
Fracture	Irregular
Transparency	Translucent
Colour	White, buff, yellow, green, rarely pale pink to red (presence of high valance
	Mn produces pink to red coloration)

Table 2. Properties of the Montmorillonite.

It is a material that has low cytotoxicity and is therefore used in the biomedical field, such as for drug delivery [59, 60, 61].

Montmorillonite is the raw material for the production of nanoclays. It has recently attracted attention as a filler for polymeric materials to improve the properties of these nanocomposites, due to its low cost, high cation exchange capacity, swelling and expansion, degree of intercalation/exfoliation and also because MMT is a hydrophilic material and therefore has compatibility with most organic polymers [56].

In order to be homogeneously dispersed in polymers, its surface must be modified so that it becomes organophilic.

The functional properties of montmorillonite are [58]:

- Cation exchange: Defined as the amount of positively charged cations that are retained by the negatively charged surface. The absorbed cations increase the electrical conductivity in the clay. The smaller the particle size, the greater the surface area per unit mass and therefore the greater the amount of cations that are absorbed.
- Electrical conductivity: Clays are porous materials and the electrical conductivity of a porous material is given by both the matrix and the fluid contained within the pores. When the fluid contained in the pores has a low conductivity, the conductivity of the material is attributed to the contribution of the matrix. If the fluid inside the pores has a high conductivity then the total conductivity of the clay improves.
- Heat resistance: It is an excellent thermal insulator and for this reason it is often used as a filler in composite materials to produce a thermal barrier effect.
- Water absorption: water tends to absorb into the spaces between silicate layers. When MMT interacts with water, a swelling effect occurs.

For this study sodium montmorillonite (Na-Mt) PWG from Nanocor Inc is used, which has a cation exchange capacity of 145 meq/100 g (approx. 10%) and aspect ratio of 200-400.

2.4 Solvents

2.4.1 Deionised water

Demineralised water, also called deionised water, is without mineral salts and instead contains dissolved gases. Demineralised water is not microbiologically pure and can therefore contain microorganisms and bacteria in it.

This type of water is obtained by the demineralisation process using ion exchange resins that are able to replace the cations and anions in the water with $H3O^+$ and OH^- ions respectively. These two ions react with each other to form water following this reaction:

 $H_{3}O^{+}+OH^{-} \rightarrow 2 H_{2}O \tag{2.8}$

It is used in various technological sectors where low salinity water is required, in chemical laboratories, in car batteries among others [62].

2.5 Aerogel preparation

2.5.1 Equipment for aerogel preparation

A number of equipment was used to prepare the sol precursor of the aerogel, which are explained below.

- A METTLER TOLEDO balance (made in Switzerland, PB303DR) with a sensitivity of ± 0.01 g was used to weigh the amount of material required for each composition. Figure 21a shows the balance used.
- A magnetic stirring was used to dissolve the powder in the solvent using the AGIMATIC-E instrument, JP SELECTA S.A. (Figure 21b). Magnets are fixed in the motor of the instrument, which allows the rotation of another magnet located inside the solution. The movement of the magnet within the liquid creates a vortex that keeps the solution stirring. To facilitate and accelerate the reactions, a heating plate is used, which is equipped with an electrical resistance that allows the solution to be heated. This device allows the rotation speed to be adjusted within a range of 60-1600 rpm, and the temperature of the heating plate to be set between 50 °C and 350 °C, with an accuracy of ± 2 °C.
- The Ultra-Turrax T25 digital, by IKA (Figure 21c), is used to homogenise some solutions. This is a mixer that possesses a high shear power due to the high rotation speed achieved by the motor, which allows the fluid to be pumped into the dispersion tool and then pushed radially through slots. In these slots, turbulence is generated, which allows excellent mixing. It is possible to vary the rotation speed in a range between 3000 and 25000 rpm.

• A pH-meter series PH20, by VWR (Figure 21d) is used to check for basic conditions. The instrument has an electrode connected to an electrical device which collects the signal from the sensor and calculates the corresponding pH.



Figure 21. Equipment for aerogel preparation: (a) METTLER TOLEDO balance; (b) AGIMATIC-E magnetic stirring; (c) Ultra-Turrax T25 [63]; (d) pH-meter series PH20 [64].

2.5.2 Sol-gel preparation

The first step in the preparation of aerogels is the creation of the aerogel precursor sol using the sol-gel process explained in Chapter §1.2. Figure 22 shows a scheme of the preparation of the precursor mixture, which is explained in detail below.



Figure 22. Schematic illustration of the preparation of the precursor mixture.

The gelatine powder is dissolved in the solvent, in this case deionised water, at a temperature of 60°C [65] to achieve complete dissolution by magnetic stirring (J.P. SELECTA, S.A.) until a completely homogeneous mixture is obtained. The pH of the gelatine is corrected to a value above 8 using a solution of NaOH (46%) [50]. Simultaneously, the tannic acid is dissolved in

a beaker containing deionised water, again by magnetic stirring. Once complete dissolution is achieved, the pH is corrected to basic (pH= 12) with NaOH (46%) and the change from an orange to a dark brown colour is noted. Then, once these two homogeneous mixtures have been obtained, the TA solution is slowly added to the gelatine solution at 60°C. At the same time, the MMT is dispersed in deionised water to form a suspension. The homogeneous dispersion is done using an Ultra-turrax instrument at a maximum speed of 9000 rpm. Finally, the clay mixture is placed in the previously prepared solution and dispersed using Ultra-turrax at a temperature of 60°C. After approximately 20 minutes, a homogenous suspension of clay particles in the gelatine-TA mixture is obtained. This mixture is quickly poured into cylindrical moulds (diameter approx. 32 mm and height approx. 25 mm) and square moulds (100 mm x 10 mm) for the compression test and the calorimetric cone test, respectively.

This process, represented in Figure 23 under real conditions, is repeated equally only by varying the amount of tannic acid by 0, 1, 2, 3, 4 grams respectively. Mixtures of basic gelatine and acid gelatine are also made to be used as a reference.



Figure 23. Schematic representation of the process in real conditions.

The second step is the ageing of the gel. In this step, the gel is aged in the mother solution in order to increase the mechanical strength of the gel and to increase the backbone. Therefore, the solutions are left to stand for a long period (about 3-4 hours) before being frozen.

The third step is freezing at -80°C in a bath of ethanol and dry ice (solid CO₂) for approximately 30 minutes. In this way, the gel takes the shape of the mould when gelation takes place. Figure 24 shows the three freezing steps, i.e. Figure 24a shows the specimen in the ethanol-CO₂ bath, Figure 24b the subsequent formation of ice inside the specimen and finally, Figure 24c the final result obtained of a compression sample after freezing.



Figure 24. (*a*) *Ethanol and solid* CO₂ *bath;* (*b*) *Freezing phenomenon inside the sample with ice formation;* (*c*) *Frozen compression sample.*

The last step in the production of aerogel is drying. Before analysing freeze-drying (lyophilisation), a topic that will be discussed in the next section §2.5.3, the chemical reactions occurring between the various materials are analysed.

Gelatine in water

Gelatine in cold water is insoluble and swells, on the contrary in hot water it hydrates easily and is therefore soluble. There are several groups in the polypeptide chain that are involved in the reaction with water molecules, including ionic groups that create an ion-dipole interaction, polar groups through a dipole-dipole interaction and finally groups that create a hydrogen bond. These reactions are also shown in Figure 25. It is also necessary to analyse how the water molecules group with the hydrophobic groups in the protein chain. Several scenarios can occur [66]:

- Constitutional water that fits inside the chain.
- Interfacial water that is found on the surface and in the cavities.
- Peripheral water whose mobility is limited due to the macromolecule.



Figure 25. Schematic representation of some protein-water interactions A) hydrogen bonds; B) hydrophobic interactions [66].

Tannic acid and NaOH

In the first preparations of aerogels precursors, an immediate reaction between gelatine and tannic acid was observed, due to the high reaction kinetics, leading to the formation of a compact, non-homogeneous gelatinous compound. The addition of NaOH avoids coagulation of the tannic acid by means of deprotonation.

The chemical reaction is:

$$C_{76}H_{52}O_{46} + 2NaOH \rightarrow 2H_2O + Na_2C_{76}H_{50}O_{46}$$
 (2.9)

The reaction product can be observed in Figure 26.

When tannic acid is in an alkaline environment, its ionised form is generated through the dissociation process [67].



Figure 26. Chemical reaction between tannic acid and NaOH [68].

Gelatine and tannic acid

Several postulates have been developed to describe the different chemical reaction pathways that can occur between gelatine and tannic acid:

- 1. The functional group of amino acid units reacts with the phenolic reactive site of TA when given alkaline conditions to form the C-N covalent bond and this generates a cross-link network [50]. This type of covalent bond between the phenolic group and the protein allows for greater rigidity and thermal stability than other interactions. This pathway requires an initial oxidation of the phenolic structure so that when it is in alkaline conditions, it can form an intermediate quinone that reacts very quickly with the nucleophiles of the reactive amino groups in the protein chain. These reactions are complicated and it is difficult to understand the mechanism of cross-link formation, especially with regard to the chemical structure of the intermediates and the chemistry of the cross-link covalent bond [69].
- 2. A second type of reaction that can occur is between the hydroxyl group in the serine unit of the gelatine, which makes a reaction similar to the one described in the previous point [50].
- 3. A hydrogen bond can be formed between the carboxyl and hydroxyl group of the tannic acid and the gelatine chains. This type of bond can form between gelatine and polyphenols under acidic or neutral conditions [70].

Finally, Quixia Zhao et al. [71] sustains that hydrophobic aggregation occurs when gelatine dissolves in water with the formation of 'hydrophobic pockets'. The tannic acid once added to the reaction moves within the 'hydrophobic pockets' and hydrogen bond formation occurs between the polar groups of the gelatine and the hydroxyl phenolic groups of the tannic acid. This reaction generates a precipitation of the TA-gelatine mixture due to the strong hydrophobic interactions and hydrogen bonds occurring in several places. Precipitation is inhibited by working under alkaline conditions with the probable formation of a single binding point between gelatine and tannic acid.

In summary, three different reaction mechanisms can occur when tannic acid is under alkaline conditions, as illustrated in Figure 27 where the tannic acid reacts with cyclohexane-1,4-diamine, which has the same amine functional group as gelatine.



Figure 27. Different reaction mechanisms can occur when tannic acid is in an alkaline environment: Schiff base formation, hydrogen bond and Michael addition [72].

When the process conditions are basic, a reaction between phenols and amines can occur with a Michael addition or a Schiff base formation although there is no certainty as to which mechanism prevails over the other in any given case. These reactions occur from the reaction between a quinone of tannic acid and the amino group of gelatine.

Gelatine-tannic acid and montmorillonite

According to Talibudeel and Panzavolta et al. [73] an ionic interaction occurs due to an interchange between the Na^+ of the bentonite and the NH_3^+ present in the protein chain. Similarly, an ionic interchange can be assumed to take place between the Na^+ of the sodium-montmorillonite and the NH_3^+ of the gelatine.

The presence of tannic acid allows it to interact with the montmorillonite and thus increases the strength of the gel.

Finally, an important consideration concerns the size of the clay particles: as the size decreases, the specific surface area increases and thus the surface area available to react is larger [73].

2.5.3 Freeze-drying (lyophilisation)

Freeze drying (FD) is a special technique that allows the creation of a controlled porous structure in different types of materials, such as ceramics, metals, polymers or biopolymers [74]. Generally speaking, this type of process consists of an initial controlled solidification of a solution, suspension, sol or gel, and thus begins a phase separation with the formation of the solid solvent (using water results in ice). Subsequently, sublimation of the solid solvent occurs under low pressure, thus creating a porous structure. The final porous structure is greatly

influenced by the type of solvent used. There are different types of solvents, the one used for this research is water with which a lamellar crystal structure is obtained. Furthermore, the morphology of the pores is influenced by the type of solidification that is carried out, in this case using dry ice (solid CO₂) and ethanol (Chapter §2.5.2) at a temperature between -60°C and -80°C. By using a glass mould (for the compression specimens) and a plastic mould (for the cone specimens), and immersing them in the cooling bath, what is obtained is a bidirectional freezing with ice growth in the radial direction along the x-direction and longitudinal growth along the z-direction (Figure 28).



Figure 28. Bidirectional freezing.

Depending on how freezing parameters vary, such as speed, direction, temperature and the application of external forces, the size and thickness of the walls can change. For example, at low freezing temperatures, thin walls and narrow pores are formed; this morphology allows for a reduction in local stresses. Conversely, larger crystals are obtained if cooling is slow [74].

Following the freezing phase, solvent sublimation occurs by freeze drying (lyophilisation). During sublimation, the transition from solid to gas takes place, then using water as the solvent, the transition from ice to steam occurs. For this to be possible, two basic parameters must be considered: pressure and temperature. During freezing, there is a decrease in temperature at room pressure with the transition from liquid to solid. Subsequently, in order to obtain the vapour phase without passing through the liquid phase, it is necessary to decrease the pressure below 0.06 atm (referring to the state diagram of water) and simultaneously increase the temperature above 0°C. Operating in this way, the liquid phase cannot exist stably.

Sublimation does not significantly affect the final microstructure of the material. Two distinct phases can be distinguished in this process [75]:

1. Primary drying phase: by lowering the pressure to a few millibars and raising the temperature, sublimation of 95% of the water contained within the material occurs. The temperature must not be too high so as not to alter the structure of the material, which is why this phase takes so long. Heat is supplied by conduction or radiation. Pressure is controlled using vacuum, which also accelerates sublimation.

2. Secondary drying phase: the objective of this phase is the removal of residual unfrozen water. It is necessary to break the bonds formed between the water molecules and the ice and this is done by raising the temperature above 0°C. To promote desorption, the pressure is also usually lowered. Once the process is complete, it is necessary to bring the material back to atmospheric pressure by breaking the vacuum.

The final product obtained involves a low water content typically between 1% and 4% and a high porosity [75].

In Figure 29 there is a schematic illustration of freeze-drying process of ceramic aerogels.



Figure 29. Freeze-drying process of ceramic aerogels [76].



The pictures below (Figure 30) show the samples obtained after the freeze-drying process.

Figure 30. Samples after the freeze-drying process.

The last process is the post-treatment of the material. In this step, the cylindrical specimens are prepared for the subsequent mechanical characterisation. Due to the growth of ice in the z-direction, it is necessary to make the two cylindrical faces smooth and parallel. In addition, it is necessary to respect the conditions on specimen dimensions imposed by ISO 604 for the compression test:

$$\varepsilon_c^* \le 0.4 \cdot \frac{x^2}{l^2} \tag{2.10}$$

Where ε_c^* is the maximum nominal compressive strain, l is the length of the test specimen and x is the diameter of the cylinder, so setting $\varepsilon_c^* = 0.5$, the height of the test specimen must be adjusted to meet the norm.

A DAP-7 cleaner, Struers at 125 rpm is used for this operation. The polishing of the sample is shown in the Figure 31.



Figure 31. Polishing of the sample.

After cleaning, the weight, diameter and height are recorded for each sample.

Figure 32 shows the instrument used for this study, the CRYODOS freeze-dryer, Telstar.



Figure 32. (a) Freeze-dryer laboratory, UPC Barcelona; (b) Freeze-dryer equipment: 1. Condenser with 8 valves; 2. LCD display; 3. Pressing buttons panel; 4. Draining pipe; 5. Electrical connection; 6. Main switch; 7. Vacuum pump [77].

The operating conditions used with this machine are a temperature of -80°C and a pressure of 0.01 mbar. The duration of the process is variable. The freeze-dryer consists of: the vacuum pump and, a cooling coil connected to the refrigerator compressor. The unformed specimens are placed inside hermetically sealed chambers and connected to the condenser valves.

2.5.4 Sample nomenclature

Table 3 presents the nomenclature used to identify the samples. The letter G corresponds to gelatine, T to tannic acid and C to clay. Each number corresponds to the amount in grams of each element in 100 ml of deionised water. The letter A corresponds to acid pH and the letter B to basic pH (corrected with NaOH).

Sample	Gelatine (g)	Tannic acid (g)	Clay (g)
G5A	5	0	0
G5B	5	0	0
G5C5B	5	0	5
G5T1C5B	5	1	5
G5T2C5B	5	2	5
G5T3C5B	5	3	5
G5T4C5B	5	4	5

 Table 3. Sample nomenclature.

2.6 Characterization

2.6.1 Intrinsic viscosity

Intrinsic viscosity $[\eta]$ and molecular weight are very important properties to evaluate as they provide information on the industrial application of a material.

Size exclusion chromatography (SEC), size exclusion chromatography-multi-angle light scattering (SEC-MALLS) and sedimentation equilibrium can be used to determine the molecular weight of a polymer. In addition, the molecular weight can be determined from the intrinsic viscosity; this is an alternative method that does not require a great deal of experience and is also very low-cost. For the determination of intrinsic viscosity, the instrument used was an Ubbelohde 1B capillary viscometer, as it is a method from which useful results can be obtained for water-soluble macromolecules [78]. Using this viscometer, it is possible to assess the kinematic viscosity of fluids, meaning the flow time of a fluid within a capillary that has a known length and diameter. The intrinsic viscosity is directly proportional to the flow time. The type of viscometer used is 1B which means that the viscosity range is between 10-50 cst.

The equipment used with this technique consists of:

- Ubbelhode 1B viscometer, shown in Figure 33a.
- Precision bath for the VB-1423 SELECTA viscometer (Figure 33b): this allows the temperature to be adjusted between 5°C and 100°C and has a temperature stability of ± 0.05 °C [79].
- Thermometer.
- Caps: required to close the holes of the viscometer during fluid lift through the capillary.



Figure 33. (a) Ubbelhode 1B viscometer [80]; (b) Precision bath for the viscometer [81].

Viscosity is measured with deionised water, as a good solvent should not have a flow time of more than 100 seconds [82].

The first step is the preparation of the gelatine sample. Three different gelatine compositions, 0.1, 0.458, and 0.7 g·dL⁻¹, are prepared by dissolving it by stirring at a speed of 600 rpm in deionised water at a temperature of 37.5°C for 15 minutes. When the gelatine is completely dissolved, the values of relative viscosity $[\eta_{rel}]$ and specific viscosity $[\eta_{sp}]$ were calculated using the efflux times of the different gelatine concentrations (t) and the solvent efflux time (t₀) at a temperature of 37.5°C.

The relative viscosity is defined as:

$$\eta_r = \frac{t}{t_0} \tag{2.11}$$

Then from this it is possible to derive the specific viscosity value:

$$\eta_s = \eta_r - 1 \tag{2.12}$$

The following procedure was performed to measure the efflux times: the first step is to measure the efflux time of the solvent, which is deionised water. Approximately 10 mL of the solution is placed inside the viscometer and left for about ten minutes in the water bath at a temperature of 37.5°C to achieve thermal equilibrium. Then the solvent is pumped up above the indicator line, the caps are removed and the liquid flows down through the capillary due to gravitational force. Times are measured when the bottom of the bubble of solvent touches the first indicator line (line A in the Figure 34) until it touches the next line (line B in the Figure 34).



Figure 34. Indicator line in Ubbelhode 1B viscometer [83].

Two test times are measured and then further measurements are taken until a standard deviation of 0.02 is obtained from at least four successive times. The same procedure is repeated for the different sample concentrations.

Once the values of η_r and η_{sp} have been obtained, it is possible to derive the reduced viscosity $[\eta_{red}]$ from this equation:

$$\eta_{red} = \frac{\eta_{sp}}{c} = \frac{\eta_r - 1}{c} \tag{2.13}$$

In addition, the inherent viscosity $[\eta_{inh}]$:

$$\eta_{inh} = \frac{\ln \eta_r}{c} \tag{2.14}$$

Where c corresponds to the concentration in grams of polymer in 100 cm³ or grams per millilitre of solution.

According to Huggins [84] the intrinsic viscosity $[\eta]$ can be extrapolated from the graph of the reduced viscosity and the inherent viscosity versus concentration of an infinitely dilute solution:

$$[\eta] = \lim_{c \to 0} (\eta_{red}) = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c}\right) = \lim_{c \to 0} \left(\frac{\ln \eta_r}{c}\right) = \lim_{c \to 0} (\eta_{inh})$$
(2.15)

Graphically this means that plotting the reduced viscosity or inherent viscosity versus concentration gives a straight line whose intercept is the intrinsic viscosity.

Once $[\eta]$ has been derived, the Mark-Houwink equation can be used to calculate the average molecular weight M_w (g·mol⁻¹):

$$[\eta] = k \cdot [M_w^a] \tag{2.16}$$

Where k and a are empirical parameters that are a function of the material and operating conditions of the test.

The norm used is ASTM D2857.

2.6.2 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is an analysis method used to understand the structure of individual molecules and the composition of molecular mixtures. This technique uses infrared light, which is absorbed by the sample at specific frequencies that correspond to vibrational levels of bonds between atoms in the molecule. Each type of bond has a vibration at different energy levels, which allows different wavelengths of infrared radiation to be absorbed. A spectrum is obtained where the frequency and intensity of each individual absorption band can be analysed and thus the characteristic of the molecule can be traced [85].

For this analysis, the instrument used was a Nicolet 6700 spectrophotometer, WI, USA with Attenuated total reflectance (ATR) mode (Figure 35). Each sample obtained a result based on 30 scans with a resolution of 1 cm^{-1} and a wavenumber interval between 4000 - 400 cm⁻¹.



Figure 35. Nicolet 6700 spectrophotometer [86].

2.6.3 Thermal conductivity

The thermal conductivity (λ) of a material is defined as its ability to transfer heat by conduction, convection and radiation.

The open porous structure of aerogels gives them the characteristic of being the best known solid thermal insulating material [87]. The ability to have low thermal conductivity is mainly conferred by the small pore size. The air contained within the pores has a thermal conductivity value that is lower than that of the solid, resulting in a lower thermal conductivity (λ) than the solid monolith. Conduction in the gas phase depends mainly on the size of the pores [88].

From the definition of thermal diffusivity, the value of thermal conductivity can be derived if the density (ρ) and heat capacity (c_p) values of the material are known:

$$D = \frac{\lambda}{\rho \cdot c_p} \tag{2.17}$$

Therefore:

$$\lambda = D \cdot \rho \cdot c_p \tag{2.18}$$

In a porous material, thermal conductivity is given by the sum of 4 components: conductivity through the solid phase (λ_s), heat conductivity in the gas phase (λ_g), convection in the gas phase (λ_c) and radiation in the foam cells (λ_r) [28]:

$$\lambda = \lambda_s + \lambda_g + \lambda_c + \lambda_r \tag{2.19}$$

The largest contribution is made by the solid phase, which means that to decrease the thermal conductivity of a material, it is necessary to have a high porosity with a small fraction of solid. The thermal conductivity of aerogels is low because the conductivity of the gas phase is minimised due to the fact that the cell size is of the order of nanometres, which allows the Knudsen effect to be exploited. Knudsen diffusion occurs when the average pore size is smaller than or similar to the average free gas path. This increases the collisions between the gas molecules and the solid phase walls rather than between two gas molecules and therefore the energy transfer through the gas phase is minimised [28].

Figure 36 shows the different contributions of thermal conductivity through a porous material.



Figure 36. Thermal conductivity of a porous material through the different phases present [28].

The machine used for the thermal conductivity analysis is C-Therm TCi, which employs the Modified Transient Plane Source (MTPS) and is illustrated in Figure 37.



Figure 37. (a) C-Therm TCi for thermal conductivity analysis [89]; (b) Positioning of the sample during the test.

The operation of the instrument is based on conductors arranged in series with respect to the direction of heat flow. The temperature drop across the conductors is equal to the thermal resistance. This instrument works by comparison: by measuring the temperature drop in a material with known thermal resistance and the temperature drop of an unknown specimen arranged in series, the thermal resistance of the specimen can be assessed [90].

The working parameters are listed below:

- Radius of sensor: 3.189 nm
- Power level: 60 mW
- Test time: 2.7 s
- Cooling time: 90 s
- Sample's dimensions: Cylindrical samples (D= 30 mm, h = 25 mm)
- Flattening the surface using polishing machine (Madrid, Spain)

2.6.4 Stabilisation

Due to the hygroscopicity of aerogels, they tend to absorb moisture present in the atmosphere and this affects the material's performance [91].

The amount of moisture in a porous material is evaluated in terms of volumetric moisture content, which is defined as the ratio of the volume of water (V_w) to the volume of the material containing the water $(V_{material})$, and is usually expressed as a percentage [92]:

$$\theta = \frac{V_w}{V_{material}} \cdot 100 \tag{2.20}$$

Moisture content can also be expressed in terms of mass:

$$\theta_{mass} = \frac{m_w}{m_{material}} \cdot 100 = \frac{m_i - m_{material}}{m_{material}} \cdot 100$$
(2.21)

Where m_w represents the mass of water, $m_{material}$ represents the mass of dry material and m_i the current mass material. The moisture calculation follows ASTM D 5229/D 5229M.

Due to the fact that the mechanical properties of an aerogel are influenced by moisture, an attempt is made to work under controlled environmental conditions so that all samples are at equal working conditions.

To achieve this, a stabilisation of the samples was carried out. The procedure involved drying the samples over-night in a vacuum oven (VACIOTEM-TV 4001490) operating at 60°C at a pressure of approximately 70 mbar. They are then removed from the oven, weighed using a balance (model: SHIMADZU AUM120D, sensitivity ± 0.01 mg) and placed in a hermetically sealed environment containing 37 ml sulfuric acid and 100 ml water. The exposure environment of the aerogel samples has a temperature of approximately 21°C and a humidity of 50-55%. On the first day, the weight of each sample is measured every hour for a total of 6 hours, because the absorption of moisture at the beginning is very rapid until stabilisation is achieved. For this reason, subsequent measurements will be taken at approximately 24-hour intervals. Figure 38 show the sequence of the stabilisation process.



Figure 38. Sequence of the stabilisation process: the top picture shows the controlled environment in which the specimens are maintained. In the bottom picture, the various specimens are weighed to monitor the change in weight. The process is repeated until stabilisation, that is until there is no further change in mass.

2.6.5 Density

When discussing porous materials, two types of density must be defined: bulk density and true density. Bulk density (ρ_a), also called apparent density, is defined as the ratio of the mass of the material to the entire volume of the material including open or closed pores [93].

The true density of the material (ρ_t) is defined as the ratio of the mass to the true volume of the material, that is, only the volume of the solid without considering pores.

In this study, only the bulk density is considered. For the calculation of bulk density, four specimens of each composition were analysed. A SHIMADZU AUM120D balance with a sensitivity of ± 0.01 mg was used to measure the mass of the specimens. The volume measurement was carried out using a digital caliper.

2.6.6 Compressive strength

The mechanical properties of the test specimens are characterised by compression testing using a Universal testing machine (ZwickRoell Z010, 10 kN RetroLine) according to ISO 604. The crosshead rate was set at 1 mm/min with a maximum deformation of 50%. Figure 39 shows the machine used for this test.



Figure 39. Universal testing machine (ZwickRoell Z010, 10 kN RetroLine) for for the compression test [94].

The cylindrical specimen must comply with the dimensions imposed by the standard, specifically equation (2.10).

The specimen must be placed under and in the centre of the load cell orientated in the direction of ice accretion as it has anisotropic properties, as shown in Figure 40. The material is subjected to a uniaxial compressive force uniformly distributed over the entire cross-section.



Figure 40. Positioning of the specimen.

The force is normalised to the cross section of the sample. A stress-strain curve of the material is obtained from which some important parameters such as the yield stress and Young's modulus can be derived. What can be observed from the curves obtained for aerogels is very similar to the elasto-plastic behaviour obtained with polymer foams, i.e. for low deformations (approximately less than 5%) a linear elastic trend is observed; in this region, the material is able to recover the deformation suffered once the load is removed. Then for intermediate deformations there is a plateau and finally a rise in the curve for high deformations due to densification of the material [95].

The stress-strain curve highlights three different stages of the compression process. In the first stage the pores within the material begin to deform under the action of the load. In the second stage there is most densification mainly due to pore deformation and finally in the third stage there is complete collapse of the pores.

From the first part of the curve, i.e. the elastic region, one can calculate the elastic modulus of the material (E), which corresponds to the slope of the curve. The second part of the curve, which corresponds to the plastic behaviour, yield strength can be derived by making the intersection of the tangent of the curve of the elastic region and the tangent of the plateau of the plastic region.

2.6.7 Moisture absorption

Due to the high porosity and hygroscopicity of aerogels, they are susceptible to moisture absorption from the surrounding environment [96].

Gelatine has a hygroscopic nature and this causes a limitation in its industrial applications as an increase in water content within the material worsens the mechanical properties. In addition, the moisture content also affects the thermal conduction properties by increasing its value [97].

The Moisture Analyzer HE53, by Mettler Toledo Greifensee, Switzerland, was used to check the moisture content absorbed by different aerogel specimens. The operating conditions used are temperature of 160°C for a time of 30 minutes. The instrument is based on the determination of moisture loss by drying, so it consists of a balance and a halogen heating system [98].

After performing the compression test, the sample is cut into small pieces and dispersed as evenly as possible in the weighing pan (Figure 41), then it is placed inside the instrument and the initial weight value and the moisture content value are recorded once the test is complete.



Figure 41. Moisture Analyzer HE53 with the specimen evenly distributed in the weighting pan.

2.6.8 Thermogravimetric analysis

To study the thermal stability of a material, thermogravimetric analysis (TGA) was used. This technique monitors the weight loss of the material when subjected to an increase in temperature, or time, in a controlled atmosphere environment [99]. With this technique, it is also possible to measure the moisture content and the amount of volatile material in the sample.

The equipment consists mainly of [100]:

• Very sensitive analytical balance, placed above the furnace and thermally insulated.

- Sample crucible, the crucible material is chosen according to the temperature used to perform the test, in this case the range of temperatures reached is between 0 and 600°C so an aluminium crucible was used.
- Programmable furnace that allows the sample heating rate to be kept under control.
- Gas flushing system, one can choose the speed and type of the desired inert atmosphere, namely nitrogen, air or oxygen.
- Software for data acquisition.

From the analysis, a curve is obtained of the weight loss (%) of the material as a function of temperature. Very often, the derivative of the curve is also shown in order to highlight the weight variations of the analysed sample. Thus, several important information about the material can be derived from this curve, such as: the degradation temperature at 10% (Td_{10%}) defined as the temperature at which 10% of the mass was lost, the maximum degradation temperature (Td_{max}), the value at maximum mass decomposition rate (dW/dT_{max}) and the percentage residue obtained.

The machine used was a TGA/DSC 1 instrument (Mettler Toledo, Columbus, Ohio) and is illustrated in Figure 42.



Figure 42. *TGA/DSC 1 instrument (Mettler Toledo, Columbus, Ohio) [101]. The crucible, containing the sample to be analysed, is placed on top of the balance.*

Atmosphere used was nitrogen (N₂), the flow was set to 30 ml/min. The type of crucible was aluminium 100 μ l. The heating rate programme was set at 10 °C/min.

Temperature range was from 30 °C to 600 °C. The amount of material to be placed in the crucible was between 5 and 10 mg, an attempt was made to keep the weight per sample constant at 7.8 mg.

2.6.9 Cone calorimetry

To study the fire behaviour of the material, a cone calorimeter, Ineltec, BECC, Tona, Spain, depicted in Figure 43, was used.



Figure 43. In the first image is the front view of the calorimetric cone, in the second image is the side view of the calorimetric cone.

This instrument allows several parameters to be monitored when a well-developed fire occurs in a material by assessing flammability from mass loss [102].

The sample is placed under a conical electrical heater, which irradiates the entire surface of the material (Figure 44). Next, ignition occurs by means of an electric spark and finally the flame combustion of the material. The fumes generated by the combustion process are collected by the cone and the concentration of O_2 , CO_2 and CO is measured. During the ignition phase, the ignition time can be measured. This value depends on a number of parameters such as the critical surface temperature for ignition, thermal inertia, critical heat flow and many others. In the second phase, other fundamental parameters can be measured such as [28]:

- Mass loss (%).
- HRR: Heat release rate. Amount of heat released per unit area and time reflecting (KW/m²).
- PHRR: Maximum value of HRR, depends on the intrinsic properties of the material and the conditions under which the test is performed.

- TTPHRR: Time to peak of heat release rate.
- THR: Total heat released. Is the integral of HRR with respect to the time.
- FIGRA: Fire growth rate (FIGRA= PHRR/TTPHRR). Gives information on the flammability of the material. The higher this value, the higher the flammability of the material.
- TTI: Time to ignition.
- Smoke production.
- Production of CO.



Figure 44. *Figure A. Shows the sample before being burnt. Figure B. shows the burning process. Figure C. Shows the residue obtained at the end of the process.*

The standard followed for this test was ISO 5660. The samples had a size of 100 mm x 100 mm $x \sim 10$ mm and were subjected to a heat flux of 50 kW/m².

Chapter 3 Results and discussion

3.1 Intrinsic viscosity

The Table 4 shows the efflux time measurements for the different gelatine and solvent concentrations. Only the measurements necessary to obtain the desired standard are shown.

	С	tp1	tp2	t1	t ₂	t3	t4	t _{avg}	DovSt
	(g/dL)	(s)	(s)	(s)	(s)	(s)	(s)	(s)	DevSt
Gelatine	0.1	16.19	15.93	15.97	16.00	15.97	15.97	15.98	0.015
	0.458	17.94	17.62	17.87	17.88	17.87	17.88	17.88	0.006
	0.7	19.31	19.44	19.31	19.34	19.35	19.34	19.34	0.017
H ₂ O	-	15.84	15.75	15.50	15.50	15.53	15.53	15.52	0.017

Table 4. Efflux time measurements for the different gelatine and solvent concentrations.

Where t_{avg} corresponds to the average time and DevSt to the standard deviation.

In addition, the results obtained for relative $[\eta_{rel}]$ and specific viscosity $[\eta_{sp}]$ calculated with equation (2.11) and (2.12) respectively are given in Table 5.

C (g/dL)	η_r	η _{sp}
0.1	1.030	0.030
0.458	1.152	0.152
0.7	1.246	0.246

Table 5. Relative and specific viscosity for each composition.

Once the values of η_r and η_{sp} have been obtained, the reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) was calculated, with the equation (2.13) and (2.14) respectively.

The Table 6 shows the results obtained for each concentration.

Table 6. Reduced viscosity and the inherent viscosity for each composition.

C (g/dL)	η_{red}	η_{inh}
0.1	0.298	0.294
0.458	0.332	0.309
0.7	0.352	0.314

According to Huggins [84] the intrinsic viscosity $[\eta]$ can be extrapolated from the graph of the reduced viscosity and the inherent viscosity versus concentration of an infinitely dilute solution. Graphically (Figure 45), the following result is obtained:



Figure 45. Reduced or inherent viscosity versus concentration.

By extrapolating the concentration to zero (infinite dilution), the value of the intrinsic viscosity is derived. In this case, the result did not lead to a coincident value for the two straight lines, therefore it was decided to calculate the average value between the two straight lines and use that as the value for $[\eta]$.

The value of the intercept for the reduced viscosity is 28.965 cm³/g while for the inherent viscosity we obtain 29.104 cm³/g. By averaging the $[\eta]$ results to be:

$$[\eta] = 29.0345 \ cm^3/g \tag{3.1}$$

One can now proceed to calculate the average molecular weight M_w (g·mol⁻¹) using the Mark-Houwink equation (2.16), where k= 0.1614 cm³/g and a= 0.8198 [78].

Therefore:

$$M_{w} = \left(\frac{[\eta]}{k}\right)^{\frac{1}{a}} = 563.23 \ g/mol \tag{3.2}$$

Martin Alberto Masuelli and Maria Gabriela Sansone [78] using the same values of k and a at a temperature of 37.4°C obtained an intrinsic viscosity value for gelatine of:

$$[\eta] = 31.35 \ cm^3/g \tag{3.3}$$

Since the properties of gelatine vary greatly depending on the extraction source, it is possible to consider these data comparable.

3.2 Fourier transform infrared spectroscopy

Figure 46 shows the FTIR spectra for the compositions: G5A, G5B, G5C5B, G5T1C5B, G5T2C5B, G5T3C5B and G5T4C5B.



Figure 46. FTIR spectra for each compositions.

OMNICTM software was used to analyse the peaks.

The following references were used to identify the characteristic bands of the functional groups: [103, 104, 105].

With regard to the spectrum analysis of type A gelatine, the characteristic absorption bands of amino acids can be observed, namely:

- A amino band at 3310 cm⁻¹ (N-H stretching)
- B amino band at 2959 and 3074.7 cm⁻¹ (C-H vibration and N-H vibration [106])
- Amide I band at 1651.5 cm⁻¹ (C=O stretching vibration, N-H bending [107] and COO-[106])

- Amide II band at 1548.4 cm⁻¹ (N-H bending, C-O-H [106] and C-N stretching vibration [107])
- Amide III band at 1240 cm⁻¹ (C-N stretching and N-H bending [108])

A comparison with type B gelatine shows that the peak previously obtained in the O-H band at 3310.1 cm⁻¹ shifts to 3301.6 cm⁻¹, which means that the number of OH present increases and is justified by the fact that NaOH is added in solution to change from type A to type B gelatine. Another difference lies in the new peak at 879.3 cm⁻¹, which according to J.H Muyonga et al. [108] corresponds to skeletal stretch. The amine bands I, II and III are not affected by the alkaline environment of the B-type gelatine.

Regarding the analysis of the organo-clay based aerogel, analysing the G5C5B composition, one notices the appearance of new peaks at:

- 3617.7 cm⁻¹, in the free OH band, due to the presence of Al-OH and Si-OH present in the clay [109]
- 1034 cm⁻¹ associated with Si-O stretching vibration [110]
- 917 cm⁻¹ associated with Al₂OH bending [110]
- 622.6 cm⁻¹ is the peak indicating Mg-O-Si [110]
- 519.8 cm⁻¹ reveals Si-O-Al vibration [110]
- 461.4 cm⁻¹ shows Si-O bending vibration group [110]

Usually, strong electrostatic interactions occur between a protein and montmorillonite, and hydrogen bonding can occur between the hydroxyl groups inside the clay cavities and the carbonyl groups in the gelatine [107]. In this case, the addition of MMT did not affect the signal of the amide A bands (3301. 6 cm⁻¹ - 3304.1 cm⁻¹), amide I (1651.2 cm⁻¹ - 1648.9 cm⁻¹), amide II (1546 cm⁻¹ - 1539.2 cm⁻¹) [111].

Regarding the analysis on how the addition of tannic acid impacts the bonds by analysing the absorption spectrum, taking the composition containing one gram of tannic acid first, no difference can be seen in the values of the peaks obtained in the bands corresponding to O-H stretching (from 3304.1 cm⁻¹ to 3304 cm⁻¹) and O-H free (from 3617.7 cm⁻¹ to 3617.1 cm⁻¹). What is actually observed is a decrease in the intensity of these peaks and this may be associated with a decrease in hydrogen bonds in the tannic acid chain due to the interactions occurring between tannic acid and gelatine [112]. Thus, this could account for the fact that a cross-link occurs between the OH groups of tannic acid and gelatine.

Furthermore, as tannic is a polyphenol, a new peak appears at 1076.2 cm⁻¹, which corresponds to C-O-H stretch (phenolic group).

Increasing the tannic acid content in the composition, a new peak appears at 1199.9 cm⁻¹ for T2, 1201.1 cm⁻¹ for T3 and finally 1198 cm⁻¹ for T4. These peaks are in the C-N covalent bond

band, so for these compositions what occurs is the formation of a new bond resulting in the cross-linking of the gelatine by tannic acid [69].

3.3 Thermal conductivity

In polymer foams, it is important to evaluate the thermal conductivity parameter in order to assess its thermal insulation properties. The results obtained for the different samples are shown in Table 7, λ_1 , which is the thermal conductivity along face 1, λ_2 , which corresponds to the thermal conductivity along face 2, and λ_{avg} , which corresponds to the average conductivity.

Gelatine, both acidic and basic, has the lowest thermal conductivity value of 0.037 W/m·K. Jundong Zhu et al. [36] obtained a thermal conductivity value of 0.03937 W/m·K for pure gelatine with a bulk density of 0.029 g/cm³, so it can be concluded that these values are very similar.

The thermal conductivity value increased by 9.6% when clay was introduced into the composition. This is due to the fact that clay being a more conductive inorganic material than gelatine increases its value. Finally, it can be seen that as the tannic acid content increased, the thermal conductivity increased. This is possibly due to the fact that tannic acid acting as a cross-linking agent creates an interconnected network with more solid phase, and therefore less gas phase, which then causes an increase in conductivity. G5T3C5B and G5T4C5B were the specimens with the highest thermal conductivity of 0.045 W/m·K, as shown in the following table.

Sample	λ_1	λ_2	λ_{avg}	
	(W/m·K)	(W/m·K)	(W/m·K)	
G5	0.036	0.037	$0.037 {\pm} 0.0008$	
G5B	0.038	0.037	$0.037 {\pm} 0.0005$	
G5C5B	0.043	0.041	0.042 ± 0.0017	
G5T1C5B	0.044	0.043	0.043 ± 0.0010	
G5T2C5B	0.046	0.044	0.045 ± 0.0014	
G5T3C5B	0.048	0.045	0.046±0.0021	
G5T4C5B	0.047	0.045	0.046±0.0009	

Table 7. Thermal conductivities of various compositions.

3.4 Stabilisation

To work under equal environmental conditions, the different specimens were stabilised in a controlled environment. Stabilisation of the material occurs when the curve of moisture change

as a function of time becomes saturated. Moisture absorption values vary for each composition, with values ranging from 6% to 11%. Compositions containing tannic acid undergo a moisture change of between 8% and 10%, so it can be considered that they undergo a very small weight difference. The curves begin to stabilise once they reach about 72 hours. As can be seen from Figure 47 the curves after 72 h have reached a plateau.



Figure 47. Evolution of moisture absorption in function of the time.

3.5 Density

Table 8 shows the values obtained for the average bulk density (ρ_a) and the standard deviation of each composition.

Sample	$\rho_a \ (g/cm^3)$	Std. Dev.
G5A	0.066	0.003
G5B	0.070	0.001
G5C5B	0.099	0.001
G5T1C5B	0.118	0.001
G5T2C5B	0.134	0.002
G5T3C5B	0.155	0.005
G5T4C5B	0.158	0.005

Table 8. Apparent densities and standard deviation of various compositions.

What is noticeable is that increasing the additive content in a composition increases the bulk density of the material.

3.6 Compressive strength

Table 9 shows the results obtained from the mechanical compression test including Young's modulus (E), yield strength (σ_s) and the corresponding specific values (E_{sp} , σ_{sp}).

As can be seen from Figure 48, the composite aerogel of gelatine-clay and tannic acid has the typical behaviour of a polymer foam when subjected to compression, as already explained in Chapter §2.6.6.

Table 9. Young's modulus, yield strength and the corresponding specific values of various compositions

Sample	E (Mna)	σ (Mna)	E _{sp} (Mna.cm ³ .g ⁻¹)	σ _{sp} (Mna.cm ³ .g ⁻¹)
	(mpa)	(mpa)	(mpa cm g)	(mpa cm g)
G5A	11.49±0.55	0.38 ± 0.06	174.79 ± 8.31	5.73 ± 0.92
G5B	2.10 ± 0.08	0.06 ± 0.005	29.82±1.12	$0.90{\pm}0.07$
G5C5B	2.36±0.16	0.1 ± 0.005	23.86±1.63	$1.00{\pm}0.05$
G5T1C5B	36.92±0.26	0.62 ± 0.10	313.75±2.20	5.29 ± 0.83
G5T2C5B	16.29±0.75	$0.74{\pm}0.09$	121.89±5.61	5.51±0.64
G5T3C5B	18.52±0.96	1.03 ± 0.05	119.57±6.21	6.63 ± 0.30
G5T4C5B	23.11±8.12	1.13±0.13	146.03±51.33	7.11±0.83



Figure 48. Compressive stress-strain curves of various compositions.

Acid gelatine has very good mechanical properties with regard to both Young's modulus (11.49 MPa) and yield strength (5.73 MPa). When switching to basic gelatine, the Young's modulus decreased by about 82% while the yield strength decreased by about 84%. This is due to the fact that the NaOH causes hydrogen bonds to break and thus there is a decrease in mechanical properties. The change from an acidic to an alkaline environment was carried out in order to obtain a crosslink between the gelatine and tannic acid, as composite aerogels containing tannic acid possess much higher compressive mechanical properties than the individual components.

The addition of clay slightly increases the Young's modulus from 2.10 MPa to 2.36 MPa and also the yield strength from 0.06 to 0.1 MPa, the effect however is not very pronounced as the interaction between clay and gelatine is only electrostatic.

When the tannic acid content was 1%, the best mechanical properties in terms of elastic modulus were obtained as compared to all other compositions. Going to a tannic acid concentration of 2%, the elastic modulus value decayed and then increased again as the TA content increased, while the yield strength increased as the concentration of the elements present increased. Similar behaviour was observed by Zangh Xiaoquing et al. [50] by performing a tensile test on gelatine and tannic acid films, whereby increasing from 1 % to 3 % TA decreased the modulus of Young decreased and then increased again to 6 % and 10 %.

This may be due to the fact that increasing the concentration of tannic acid leads to an increase in the density of the material and thus its viscosity. When a viscous material is frozen, the rate of ice growth decreases due to the resistance caused by the viscosity. What has been noticed is a different directionality of ice accretion in the microstructure, which has resulted in two different microstructures and therefore lower mechanical properties. This different directionality of accretion can be seen in Figure 49.



Figure 49. Aerogel anisotropy due to different ice growth directions.
Despite this, the E values always remained higher than in the G5C5B and G5B compositions. This means that the role of the acid tannic as a cross-linker had a reinforcing effect, creating a stronger and more resistant structure.

Another feature that can be observed from the graph is that the elongation at break decreased when tannic acid was present in the sample, this is typical behaviour of a cross-linked polymer material [50].

The values of E_{sp} and σ_{sp} make it possible to compare the different samples by normalising the influence of density. In this case, the composition G5T1C5B always remained the best in terms of elastic modulus whereas the composition G5T4C5B had the highest yield strength value, as previously obtained for the non-normalised value.

Finally, the standard deviation value obtained for the composition G5T4C5B is too high, which is why more specimens are planned later on to decrease this value.

3.7 Moisture content

The results obtained from the moisture content analysis are shown in Table 10.

Sample	Weight (g)	%MC
G5A	0.939	15.44
G5B	0.979	17.26
G5C5B	1.801	9.29
G5T1C5B	1.251	12.47
G5T2C5B	1.200	14.69
G5T3C5B	1.666	14.71
G5T4C5B	1.717	15.03

Table 10. Moisture content of various compositions.

The moisture content increased from acidic to basic gelatine (from 15.44% to 17.26%) which was attributed to the fact that OH groups are hydrophilic groups, so the higher the content of these groups, the greater the material's ability to retain water. The lowest moisture absorption value was obtained for composition G5C5B. This can be justified by the barrier effect caused by the silicate groups in the clay [113].

The addition of TA caused a decrease in %MC as compared to the base value of G5B. Gelatine has carbonyl groups in the chain, these groups are hydrophilic, so due to the hydrogen bond formed by the reaction of the hydroxyl (OH⁻) groups of TA and the carbonyl groups of the gelatine, there is a reduction in the moisture absorption of the material [113]. As the

concentration of tannic acid increased, there was an increase in %MC. This result is reasonable as TA has many hydroxyl groups that can combine with water.

3.8 Thermogravimetric analysis

Table 11 shows the values of the results of the thermogravimetric analysis (TGA) of the aerogel samples. The degradation temperature at 10% (Td_{10%}), the maximum degradation temperature (Td_{max}), the value at maximum mass decomposition rate (dW/dT_{max}) and the percentage residue obtained are reported.

Samula	Td10%	Td _{max}	dW/dT_{max}	Residue
Sample	(°C)	(°C)	(%/°C)	(%)
G5A	255.15	324.0	0.61	26.6
G5B	194.45	314.0	0.44	34.0
G5C5B	287.92	322.7	0.20	62.0
G5T1C5B	261.93	316.0	0.16	58.6
G5T2C5B	231.41	312.0	0.14	61.3
G5T3C5B	202.81	282.7	0.16	60.6
G5T4C5B	245.69	268.0	0.17	59.3

 Table 11. Results of the thermogravimetric analysis of various compositions.

Figure 50 shows the graph of mass loss as a function of temperature for each composition. It can be seen that the first weight loss is in the 30-140 °C range. This was attributed to the release of water associated with the OH and COOH functional groups. Subsequently, in the 250-400 °C temperature range, the greatest weight loss occurred due to degradation of the gelatine. At these temperatures, the hydrogen bonds between the different molecules and also between functional groups belonging to the same molecule are broken. In addition, the degradation of gelatine is also associated with the breaking of the triple helix that characterises its structure and also the breaking of peptide bonds. Finally, for samples containing tannic acid, a final weight loss occurred between 400°C and 500°C and was attributed to the products of the crosslink that occurs between tannic acid and gelatine [112].

For samples containing tannic acid, it can be seen graphically that the percentage of mass lost during the first step is between 5% and 9%, during the second step between about 20% and 22%, and finally in the last step between 9% and 13%.

Another feature that can be observed both graphically and from the values in the table is the percentage residue. It can be seen that the addition of clay increased the residue by 82%, as it



is an inorganic material that does not degrade at the temperatures reached by the instrument. The addition of tannic acid had little influence on the value of the percentage residue.

Figure 50. Graph of mass loss as a function of temperature for each composition.

Figure 51 shows the graph of the aerogel degradation rate as a function of temperature. Considering the height of the peaks and the values in the table, one can see a large decrease in the decomposition rate of aerogels when tannic acid was present. This means that TA caused a delay in the degradation rate of the material. The values obtained are between 0.14 %/°C and 0.17 %/°C and it can be assumed that there is not a great difference between the different TA concentrations. The maximum degradation temperature of the TA-containing aerogels was lower than in G5C5B, as tannic acid has a maximum degradation temperature of about 258°C, which is lower than in gelatine [114]. Nevertheless, the decomposition rate decreased by 30% with reference to G5T2C5B.

To see the effect of NaOH, it is necessary to observe how the values change from acidic to basic gelatine. The Td_{max} underwent a 3% decrease as the NaOH reacted with the gelatine by a chain scission process. Although the maximum degradation temperature was slightly lowered, the degradation rate was reduced by 28%.



Figure 51. Graph of decomposition rate as a function of temperature for each composition.

With regard to $Td_{10\%}$, it can be seen that the highest value is attributed to composition G5C5B (287.92 °C). By adding tannic acid to the composition, the value of $Td_{10\%}$ decreases compared to that obtained previously. This effect is congruent with the values obtained for the maximum degradation temperature. For the samples containing tannic acid, the best result was obtained for composition G5T1C5B with the value of $Td_{10\%} = 261.93$ °C.

3.9 Cone calorimetry

Using the calorimetric cone, the fire behaviour of bio-based aerogel samples was studied. The parameters of time to ignition (TTI), peak of heat release (PHRR), time to peak of heat release rate (TTPHRR), the total heat release (THR) and the fire growth rate (FIGRA) were used to compare the different compositions. All these results are shown in Table 12.

Sample	Weight	Residue	TTI	PHRR	TTPHRR	THR	THReff	FIGRA
	(g)	(%)	(s)	(kW/m^2)	(s)	(MJ/m^2)	(MJ/g·m ²)	(kW/m ² · s)
G5A	4.24	7.2	0	305.1	30	12.13	2.86	10.17
G5B	4.14	11.5	1	260.9	42	7.89	1.90	6.21
G5C5B	7.53	48.5	4	95.7	33	6.96	0.92	2.90
G5T1C5B	9.49	46.7	8	64.4	30	7.53	0.79	2.15
G5T2C5B	9.68	48.5	7	75.5	30	8.63	0.89	2.52
G5T3C5B	12.09	43.8	9	65.3	36	8.6	0.71	1.81
G5T4C5B	10.51	40.6	12	79.7	36	12.72	1.21	2.21

 Table 12. Cone calorimeter results of various compositions.

Figure 52a also shows the graph of the heat release rate (HRR) as a function of time. Pure gelatine shows a sharp peak, which means that the sample pyrolysed at the same time and that the HRR only depended on the total fire load [102]. Moving from G5A to G5B the PHRR decreases by 14.5%. This was due to the formation of a char layer due to the presence of NaOH in G5B, which deprotonates at high temperatures, producing a structure with a high carbon content and also releases small molecular substances during combustion [32].

The addition of clay to the composition significantly lowered the peak from 260.9 kW/m² to 95.7 kW/m^2 . This effect is justified by the slow degradation of the clay and the ability to create a char layer during the combustion. The curve shows the pattern of an HRR curve of thick charring, meaning that the sample showed an initial increase in HRR and then decreased when a stable char layer was formed.

Samples containing TA showed much lower peaks than the previous compositions due to the intumescent characteristic of TA, as it reduces radicals and oxidants to maximise the unburnt solid [42] and the formation of a char when exposed to heat. The lowest PHRR was associated with the sample containing 1% tannic acid with a value of 64.4 kW/m², followed by an increase for the other concentrations. G5T1C5B and G5T2C5B showed the characteristic curve HRR corresponding to thick charring with additional peak at the end of burning. The second peak can be attributed either to char breaking or to an increase in pyrolysis. The graph of G5T3C5B and G5T4C5B shows a distorted graph, as before the test, the samples were broken as shown in Figure 52c and this caused changes in the area and/or distance to the heated element of the cone.



Figure 52. (a) Heat release rate vs. time; (b) Zoom of the initial part of the heat release rate vs. time curve; (c) Broken G5T3C5B, left, and G5T4C5B, right, samples prior to testing.

Table 12 also shows the THR values of the aerogel samples analysed. The lowest value was found for sample G5C5 were THR= 6.96 MJ/m^2 .

To eliminate the influence of mass differences and thus be able to better describe the combustion mechanism, the THR_{eff}, the THR/mass, is analysed. The lowest values were recorded for the composition of TA1 and TA3 with values of 0.79 MJ/g·m² and 0.71 MJ/g·m², respectively. The total reduction from pure basic gelatine to G5T3C5B corresponded to 62.63%.

To obtain information on the flammability of the material, it is necessary to analyse the FIGRA data. It can be seen that aerogels containing tannic acid showed the lowest values. For the composition G5T3C5B, the lowest value was found, namely 1.81 kW/m²·s. Thus, TA and NaOH make it possible to decrease the flammability of a material. This is attributed to the fact that these two materials, although easily ingested, form a char quickly that protects the underlying biopolymer [32].

Another very important parameter is the time to ignition. Pure gelatine aerogels burned immediately when the spark was generated, which means that the amount of combustible gas was very high. When clay was added there was a delay in TTI, this means that an intumescent char network is forming. As the acid tannic content increased, the TTI increased, recording the highest value for G5T4C5B of 12 s. The observed flame delay is justified by the fact that sodium hydroxide facilitates the decarboxylation of TA at lower temperatures and this enhances char formation [32].

During the test, it was observed that the aerogels containing both clay and tannic acid were selfextinguishing after about 1 minute, which is because once the organic part of the material has burnt, the intumescent effect of the clay emerges.

Once the combustion process was completed, the residue obtained was determined. Figure 53 shows the residue of the samples. The compositions containing clay showed the highest residue as this material is inorganic and non-degradable at an operating temperature of approximately 800°C. For them, the values were between 40.6% and 48.5%. These results are comparable with the values obtained from the TGA analysis where, in samples containing clay, the percentage residue remained between 58.6% and 62%.



Figure 53. Samples after the combustion process.

In conclusion, although the samples burned easily using a flux of 50 kW/m², the flammability, the THR_{eff} and PHRR was significantly reduced for the compositions G5T1C5B and G5T3C5B.

Environmental impact analysis

Regarding the environmental impact analysis in this project, the factors that have a greater emission of CO_2 on the environment were analyzed.

One source of CO_2 emission comes from transportation. Montmorillonite is sourced from Hoffman Estates, IL, USA, so one would need to consider the emission of kg CO_2 /ton·km due to transportation of this material by land and sea. The gelatine, tannic acid, NaOH, and deionised water all come from Spain, this reduced the emission of kg CO_2 , and thus the emission of this gas into the environment due to the transportation of the material can be considered low.

Another important factor that impacts CO_2 emission is the energy consumption of the equipment used to carry out the project. For this calculation, only the equipment that has been used for the longest time is considered. We then perform the product of the energy consumed per hour (kWh) of each piece of machinery by 0.259 kg of CO_2/kWh [115].

Equipment	Use (h)	Power (kW)	Energy consumption (kWh)	kg of CO2
TGA	16	1.38	22.08	5.72
Cone calorimeter	7	7.00	49.00	12.69
CRYODOS freeze-dryer	390	2.05	799.50	207.07
Vacuum oven	30	2.00	60.00	15.54
Universal testing machine	12	0.60	7.16	1.86
Moisture Analyzer	7	0.40	2.80	0.73
Ultra-Turrax	5	0.50	2.50	0.65
Magnetic stirring	21	0.55	11.55	2.99
Total	488 h	14.48 kW	954.59 kW∙h	247.24 kg CO2

The result obtained is shown in Table 13.

Table 13. Use of the equipment and its corresponding energy consumption.

From this analysis what can be seen is that the largest CO₂ emission was due to the CRYODOS freeze-dryer.

For aerogels production, the freeze-drying process was used, which among the different processes appears to be the most environmentally friendly one since water can be used as a solvent. However, it has a high energy consumption due to the lyophilisation since it involves the operation of a vacuum pump, to maintain the pressure at 0.010 mbar, and a refrigeration system, to maintain the temperature of the aerogels at -80°C.

Budget and/or Economic Analysis

The economic analysis is shown below, dividing consumption into three main areas: labour, materials and equipment used.

• For the calculation of labour costs, the costs associated with the persons who collaborated during the project are considered. Table 14 shows the hours devoted to carrying out the project, the cost per hour of each person, and finally the total cost.

	Hours	Cost €/h	Cost (€)
Junior engineer	750	15	11250
PhD student	120	20	2400
Research Professor	60	30	1800
Full Professor	60	40	2400
Total			17850€

Table 14. Labour costs.

• For the project, 78 cylindrical specimens and 14 square specimens were prepared for the calorimetric cone test. Table 15 shows the quantity in grams of material used, the price of each material and the total cost.

Material	Quantity	Price	Cost (€)
Gelatine	210 g	18 €/kg	3.78
Tannic acid	60 g	130 €/kg	7.8
Sodium hydroxide	46 g	44.70 €/kg	2.06
Montmorillonite	150 g	163.4 €/kg	8.17
Deionised water	4,3 lt	0.79 €/lt	3.4
Ethanol	7 lt	6.28 €/1	43.96
CO_2	40 kg	2.10 €/kg	84
Total			153.17€

 Table 15. Cost of materials used.

• Finally, the cost of the equipment used to characterize the different specimens is considered. For this calculation, the cost estimate for the ePLASCOM research group was analysed considering the time of use or the number of samples analysed. The C-Therm TCi and the FTIR are machines belonging to an external laboratory. Table 16 shows the results obtained.

Equipment	Use	Price	Cost (€)
TGA	16 samples	120 €/sample	1920
Cone calorimeter	14 samples	150 €/sample	2100
Lyophilisation	390 h	4 €/h	1560
Vacuum oven	30 h	2 €/h	60
Cleaner	2 h	20 €/h	80
Universal testing machine	50 samples	12 €/sample	600
Moisture Analyzer	7 samples	60 €/sample	420
FTIR	7 samples	105 €/sample	735
C-Therm TCi	7 samples	10 €/sample	70
Total			7545€

 Table 16. Cost of equipments used.

The price excludes VAT, the cost of waste disposal and the cost of travel to perform the tests.

The higher cost associated with the TGA and calorimetric cone is due to the fact that it was necessary to repeat the tests several times to obtain some reliability of the results.

The Table 17 summarizes the total costs of the project, considering the parameters described above, and the total cost of the project can also be observed.

	Cost (€)
Labour	17850
Materials	153.17
Equipments	7545
Total	25548.2 €

 Table 17. Total cost of the project.

Conclusions

An organic-inorganic composite aerogel based on gelatine, clay and tannic acid was prepared by means of the sol-gel method and obtained by freeze-drying process.

By characterising seven different aerogel samples, an attempt was made to find the optimum composition for the best mechanical, thermal and fire resistance properties.

The thermal conductivity of gelatine decreased when both clay and tannic acid were present in the matrix, from a value of $0.037 \text{ W/m}\cdot\text{K}$, for pure gelatine, to $0.046 \text{ W/m}\cdot\text{K}$ for the G5T3C5B and G5T4C5B compositions.

The bulk density of the aerogels increased with increasing material content, from 0.066 g/cm³ for G5A to 0.158 g/cm³ for G5T4C5B.

The best mechanical properties in terms of elastic modulus (E) were obtained for the composition containing 1 gram of tannic acid, with a value of 36.92 MPa. This is due to the strong interaction that exists between gelatine and tannic acid in an alkaline environment. As the concentration of cross-linking agent increased, Young's modulus decreased, but its value still remained higher than the one of aerogels containing only pure gelatine and the aerogels containing gelatine and clay. As far as the yield strength is concerned, it increased as the tannic acid content increased, reaching a maximum value of 1.13 MPa for the composition G5T4C5B. G5T1C5B was also the stiffest in terms of E_{sp} with the value of 313.75 MPa·cm³·g⁻¹, and G5T4C5B was also the strongest in terms of σ_{sp} with the value of 7.11 MPa·cm³·g⁻¹.

Thermogravimetric analysis showed a large decrease in the degradation rate when tannic acid was present. This effect is justified by the fact that this additive gives better thermal stability to the material due to the creation of a carbonised layer that reduces the fuel exchange between the environment and the aerogel.

The lowest peak of heat release (PHRR) was recorded for composition G5T1C5B with a value of 64.4 kW/m². This pronounced effect was due to the intumescent characteristic of TA and the stable char-forming capacity. The presence of the TA allowed the total heat released to be reduced and also increased the ignition time. The flammability of the material (FIGRA) was also reduced with the presence of TA due to the rapid formation of a char layer that allowed the underlying material to be protected.

It is possible to conclude that one gram of tannic acid is sufficient to achieve a good compromise of mechanical, thermal and fire resistance properties.

Glossary

Abbreviations

%MC	Moisture content
ATR	Attenuated total reflectance
Ca(OH) ₂	Calcium hydroxide
CaCO ₃	Calcium carbonate
CHD	Cyclohexane-1,4-diamine
Cl ₂	Chlorine
CO ₂	Carbon dioxide
ECM	Extracellular matrix
FD	Freeze drying
FIGRA	Fire growth rate
FTIR	Fourier transform infrared spectroscopy
H ₂ O	Water
H_3O^+	Hydronium ion
HRR	Heat Release Rate
LOI	Limited Oxygen Index
MMT	Montmorillonite
MTPS	Transient Plane Source
N_2	Nitrogen
Na ⁺	Sodium ion
Na ₂ CO ₃	Sodium carbonate
NaCl	Sodium chloride
NaHCO ₃	Sodium hydrogen carbonate
NaOH	Sodium hydroxide
NH ₃	Ammonia
OH-	Hydroxide ion
PHRR	Peal Heat Release Rate
PI	Polyimide
PU	Polyurethane
PUA	Polyurethane-acrylate
PVA	Polyvinylalcohol
RF	Resorcinol-formaldehyde
SEC	Size exclusion chromatography
SEC-MALLS	Chromatography-multi-angle light scattering
ТА	Tannic acid
TEOS	Tetraeltil orthosilicate
TGA	Themogravimetric analysis
THR	Total Heat Released
TMOS	Tetramethyl orthosilicate
TTI	Time To Ignition
TTPHRR	Time To Peak of Heat Release

Symbols

M _w	Molecular weight	[g/mol]
[η]	Intrinsic viscosity	$[cm^3/g]$
η_{rel}	Relative viscosity	
η _{sp}	Specific viscosity	
η_{red}	Reduced viscosity	
η_{inh}	inherent viscosity	
t	Efflux times	[s]
t_0	Solvent efflux time	[s]
λ	Thermal conductivity	[W/m·K]
D	Thermal diffusivity	$[m^2/s]$
ρ	Density	$[g/cm^3]$
C_p	Heat capacity	[J/g·K]
$\dot{\lambda_s}$	Conductivity through the solid phase	[W/m·K]
λ_g	Heat conductivity in the gas phase	$[W/m \cdot K]$
λ_c	Convection in the gas phase	[W/m·K]
λ_r	Radiation in the foam cells	[W/m·K]
θ	Volumetric moisture content	[%]
V_w	Volume of water	[cm ³]
V _{material}	Volume of material	[cm ³]
θ_{mass}	Moisture content in terms of mass	[%]
m_w	Mass of water	[g]
m _{material}	Mass of dry material	[g]
m_i	Current mass material	[g]
$ ho_a$	Apparent density	$[g/cm^3]$
$ ho_t$	True density	$[g/cm^3]$
$\mathcal{E}_{\mathcal{C}}^{*}$	Maximum nominal compressive	
	strain	
Td _{10%}	Degradation temperature at 10%	[°C]
Td _{max}	Maximum degradation temperature	[°C]
dW/dT_{max}	Thermal degradation rate	[%/°C]
E	Young's modulus	[MPa]
σ_{s}	Yield strength	[MPa]
E _{sp}	Specific Young's modulus	$[Mpa \cdot cm^3 \cdot g^{-1}]$
σ_{sp}	Specific yield strength	[Mpa·cm ³ ·g ⁻¹]

References

[1] Kistler, S. S. (1931). Coherent expanded aerogels and jellies. *Nature*, *127*(3211), 741-741. doi: <u>https://doi.org/10.1038/127741a0</u>

[2] Everett, D. H. (1972). Manual of symbols and terminology for physicochemical quantities and units, appendix II: Definitions, terminology and symbols in colloid and surface chemistry. *Pure and Applied Chemistry*, *31*(4), 577-638. doi: <u>https://doi.org/10.1351/pac197231040577</u>

[3] Leventis, N., Sadekar, A., Chandrasekaran, N., & Sotiriou-Leventis, C. (2010). Click synthesis of monolithic silicon carbide aerogels from polyacrylonitrile-coated 3D silica networks. *Chemistry of Materials*, 22(9), 2790-2803. doi: <u>https://doi.org/10.1021/cm903662a</u>

[4] Liebner, F., Aigner, N., Schimper, C., Potthast, A., & Rosenau, T. (2012). Bacterial cellulose aerogels: From lightweight dietary food to functional materials. In *Functional materials from renewable sources* (pp. 57-74). American Chemical Society. doi: 10.1021/bk-2012-1107.fw001

[5] Ratke, L., & Gurikov, P. (2021). *The Chemistry and Physics of Aerogels: Synthesis, Processing, and Properties*. Cambridge University Press.

[6] Zuo, L., Zhang, Y., Zhang, L., Miao, Y. E., Fan, W., & Liu, T. (2015). Polymer/carbonbased hybrid aerogels: preparation, properties and applications. *Materials*, *8*(10), 6806-6848. doi: <u>https://doi.org/10.3390/ma8105343</u>

[7] Ansari, M. O., Khan, A. A. P., Ansari, M. S., Khan, A., Kulkarni, R. M., & Bhamare, V. S. (2021). Aerogel and its composites: Fabrication and properties. In *Advances in Aerogel Composites for Environmental Remediation* (pp. 1-17). Elsevier.

[8] Hüsing, N., & Schubert, U. (1998). Aerogels—airy materials: chemistry, structure, and properties. *Angewandte Chemie International Edition*, *37*(1-2), 22-45. doi: <u>https://doi.org/10.1002/(SICI)1521-3773(19980202)37:1/2<22::AID-ANIE22>3.0.CO;2-I</u>

[9] Moheman, A., Bhawani, S. A., & Tariq, A. (2021). Aerogels for waterborne pollutants purification. In *Advances in Aerogel Composites for Environmental Remediation* (pp. 109-124). Elsevier. doi: <u>https://doi.org/10.1016/B978-0-12-820732-1.00007-2</u>

[10] Stergar, J., & Maver, U. (2016). Review of aerogel-based materials in biomedical applications. *Journal of Sol-Gel Science and Technology*, 77(3), 738-752. doi: <u>10.1007/s10971-016-3968-5</u>

[11] "The Sol-Gel Process" web source: <u>Aerogel.org » The Sol-Gel Process</u>

[12] Dervin, S., & Pillai, S. C. (2017). An introduction to sol-gel processing for aerogels. In *Sol-Gel Materials for Energy, Environment and Electronic Applications* (pp. 1-22). Springer, Cham. doi: 10.1007/978-3-319-50144-4_1

[13] Nita, L. E., Ghilan, A., Rusu, A. G., Neamtu, I., & Chiriac, A. P. (2020). New trends in bio-based aerogels. *Pharmaceutics*, 12(5), 449. doi: https://doi.org/10.3390/pharmaceutics12050449

[14] Linhares, T., de Amorim, M. T. P., & Durães, L. (2019). Silica aerogel composites with embedded fibres: a review on their preparation, properties and applications. *Journal of Materials Chemistry A*, 7(40), 22768-22802. doi: <u>https://doi.org/10.1039/C9TA04811A</u>

[15] Maleki, H., Durães, L., & Portugal, A. (2014). An overview on silica aerogels synthesis and different mechanical reinforcing strategies. *Journal of Non-Crystalline Solids*, *385*, 55-74. doi: <u>https://doi.org/10.1016/j.jnoncrysol.2013.10.017</u>

[16] Sánchez Soto, M., Cruz Jesús, L. G. D. L., Jokinen, P., Abt, T. M., Cailloux, J., Maspoch Rulduà, M., & Santana Pérez, O. O. (2019). Aerogeles compuestos multicapa a partir de biopolimeros y arcilla. *Revista de la Asociación Española de Materiales Compuestos*, 3(4), 41-47. doi: <u>https://revista.aemac.org/materiales-compuestos/article/view/367/222</u>

[17] Zhong, Y., Godwin, P., Jin, Y., & Xiao, H. (2020). Biodegradable polymers and greenbased antimicrobial packaging materials: A mini-review. *Advanced Industrial and Engineering Polymer Research*, *3*(1), 27-35. doi: <u>https://doi.org/10.1016/j.aiepr.2019.11.002</u>

[18] Rapisarda, M., Malfense Fierro, G. P., & Meo, M. (2021). Ultralight graphene oxide/polyvinyl alcohol aerogel for broadband and tuneable acoustic properties. *Scientific reports*, *11*(1), 1-10. doi: 10.21203/rs.3.rs-256278/v1

[19] Chen, H. B., Chiou, B. S., Wang, Y. Z., & Schiraldi, D. A. (2013). Biodegradable pectin/clay aerogels. *ACS applied materials & interfaces*, 5(5), 1715-1721. doi: <u>https://doi.org/10.1021/am3028603</u>

[20] Budtova, T. (2019). Cellulose II aerogels: A review. *Cellulose*, 26(1), 81-121. doi: https://doi.org/10.1007/s10570-018-2189-1

[21] Chen, C., Yang, H., Yang, X., & Ma, Q. (2022). Tannic acid: A crosslinker leading to versatile functional polymeric networks: A review. *RSC advances*, *12*(13), 7689-7711. doi: 10.1039/D1RA07657D

[22] Liu, Q., Yan, K., Chen, J., Xia, M., Li, M., Liu, K., ... & Xie, Y. (2021). Recent advances in novel aerogels through the hybrid aggregation of inorganic nanomaterials and polymeric fibers for thermal insulation. *Aggregate*, *2*(2), e30. doi: <u>https://doi.org/10.1002/agt2.30</u>

[23] Pojanavaraphan, T., Magaraphan, R., Chiou, B. S., & Schiraldi, D. A. (2010). Development of biodegradable foamlike materials based on casein and sodium montmorillonite clay. *Biomacromolecules*, *11*(10), 2640-2646. doi:<u>https://doi.org/10.1021/bm100615a</u>

[24] Finlay, K., Gawryla, M. D., & Schiraldi, D. A. (2008). Biologically based fiberreinforced/clay aerogel composites. *Industrial & engineering chemistry research*, 47(3), 615-619. doi: <u>https://doi.org/10.1021/ie0705406</u>

[25] Apte, V. (Ed.). (2021). Flammability Testing of Materials Used in Construction, Transport, and Mining. Woodhead Publishing.

[26]"Combustionmechanism"websource:https://www.bbc.co.uk/bitesize/topics/zypsgk7/articles/zcwxcj6

[27] "Flammability of polymers, Zeus industries product" web source: https://www.appstate.edu/~clementsjs/journalarticles/zeus_flammability.pdf

[28] Sánchez-Soto, M., Wang, L., Abt, T., Lucía, G., & Schiraldi, D. A. (2018). Thermal, electrical, insulation and fire resistance properties of polysaccharide and protein-based aerogels. In *Biobased Aerogels* (pp. 158-176). doi: <u>https://doi.org/10.1039/9781782629979-00158</u>

[29] Wicklein, B., Kocjan, A., Salazar-Alvarez, G., Carosio, F., Camino, G., Antonietti, M., & Bergström, L. (2015). Thermally insulating and fire-retardant lightweight anisotropic foams based on nanocellulose and graphene oxide. *Nature nanotechnology*, *10*(3), 277-283. doi: 10.1038/nnano.2014.248

[30] Chen, H. B., & Schiraldi, D. A. (2019). Flammability of polymer/clay aerogel composites:anoverview.PolymerReviews,59(1),1-24.https://doi.org/10.1080/15583724.2018.1450756

[31] Cheng, H. N., Gross, R. A., & Smith, P. B. (2015). Green polymer chemistry: Some recent developments and examples. In *Green Polymer Chemistry: Biobased Materials and Biocatalysis* (pp. 1-13). American Chemical Society. doi:10.1021/bk-2015-1192.ch001

[32] Cheng, Z., DeGracia, K., & Schiraldi, D. A. (2018). Sustainable, low flammability, mechanically-strong poly (vinyl alcohol) aerogels. *Polymers*, *10*(10), 1102. doi: https://doi.org/10.3390/polym10101102

[33] Zhu, J., Zhao, F., Xiong, R., Peng, T., Ma, Y., Hu, J., ... & Jiang, C. (2020). Thermal insulation and flame retardancy of attapulgite reinforced gelatin-based composite aerogel with enhanced strength properties. *Composites Part A: Applied Science and Manufacturing*, *138*, 106040. doi: <u>https://doi.org/10.1016/j.compositesa.2020.106040</u>

[34] Schrieber, R., & Gareis, H. (2007). *Gelatine handbook: theory and industrial practice*. John Wiley & Sons.

[35] Mahapatro, A., & Singh, D. K. (2011). Biodegradable nanoparticles are excellent vehicle for site directed in-vivo delivery of drugs and vaccines. *Journal of nanobiotechnology*, 9(1), 1-11. doi: <u>https://doi.org/10.1186/1477-3155-9-55</u>

[36] Wang, Y. T., Zhao, H. B., Degracia, K., Han, L. X., Sun, H., Sun, M., ... & Schiraldi, D.
A. (2017). Green approach to improving the strength and flame retardancy of poly (vinyl alcohol)/clay aerogels: incorporating biobased gelatin. *ACS applied materials & interfaces*, 9(48), 42258-42265. doi: <u>https://doi.org/10.1021/acsami.7b14958</u>

[37] Kommareddy, S., Shenoy, D. B., & Amiji, M. M. (2007). Gelatin nanoparticles and their biofunctionalization. *Nanotechnologies for the life sciences: Online*. doi: 10.1002/9783527610419.ntls0011

[38] Mariod, A. A., & Fadul, H. (2013). Gelatin, source, extraction and industrial applications. *Acta Scientiarum Polonorum Technologia Alimentaria*, *12*(2), 135-147.

[39] Ziegler, G. R., & Foegeding, E. A. (1990). The gelation of proteins. In *Advances in food and nutrition research* (Vol. 34, pp. 203-298). Academic Press. doi: https://doi.org/10.1016/S1043-4526(08)60008-X

[40] "Denaturation of collagen produces thermoreversible gelatin" web source: https://chembam.com/resources-for-students/the-chemistry-of/gelatin/

[41] Ockerman, H. W., & Hansen, C. L. (1999). *Animal by-product processing & utilization*. CRC Press.

[42] Li, L., Liu, X., Shao, X., Jiang, L., Huang, K., & Zhao, S. (2020). Synergistic effects of a highly effective intumescent flame retardant based on tannic acid functionalized graphene on the flame retardancy and smoke suppression properties of natural rubber. *Composites Part A: Applied Science and Manufacturing*, *129*, 105715. doi: https://doi.org/10.1016/j.compositesa.2019.105715

[43] "Tannic acid powder" web source: <u>https://www.indiamart.com/proddetail/tannic-acid-7925423497.html</u>

[44] "Tannins" web source:https://www.huffpost.com/entry/a-french-thanksgiving_b_5a09eba3e4b0065239218304

[45] "Tannic acid" web source: https://antropocene.it/2019/04/07/acido-tannico/

[46]"Tannicacidstructure"websource:https://www.chemicalbook.com/ChemicalProductPropertyENCB3116328.htm

[47] Anvari, M., & Chung, D. (2016). Dynamic rheological and structural characterization of fish gelatin–Gum arabic coacervate gels cross-linked by tannic acid. *Food Hydrocolloids*, *60*, 516-524. doi:<u>https://doi.org/10.1016/j.foodhyd.2016.04.028</u>

[48] Bahmanzadeh, S., Ruzgas, T., & Sotres, J. (2018). Proteolytic degradation of gelatin-tannic acid multilayers. *Journal of colloid and interface science*, *526*, 244-252. doi: https://doi.org/10.1016/j.jcis.2018.04.112

[49] Peña, C., De La Caba, K. O. R. O., Eceiza, A., Ruseckaite, R., & Mondragon, I. (2010).
Enhancing water repellence and mechanical properties of gelatin films by tannin addition. *Bioresource* technology, 101(17), 6836-6842. doi: https://doi.org/10.1016/j.biortech.2010.03.112

[50] Zhang, X., Do, M. D., Casey, P., Sulistio, A., Qiao, G. G., Lundin, L., ... & Kosaraju, S. (2010). Chemical modification of gelatin by a natural phenolic cross-linker, tannic acid. *Journal of agricultural and food chemistry*, *58*(11), 6809-6815. doi: <u>https://doi.org/10.1021/jf1004226</u>

[51] Scalbert, A. (1991). Antimicrobial properties of tannins. *Phytochemistry*, *30*(12), 3875-3883. doi: <u>https://doi.org/10.1016/0031-9422(91)83426-L</u>

[52] Khan, N. S., Ahmad, A., & Hadi, S. M. (2000). Anti-oxidant, pro-oxidant properties of tannic acid and its binding to DNA. *Chemico-Biological Interactions*, *125*(3), 177-189. doi: https://doi.org/10.1016/S0009-2797(00)00143-5

[53] "Sodium Hydroxide (NaOH)", web source: https://www.chimicaonline.it/composti/idrossido-di-sodio.htm

[54] "Sodium Hydroxide (NaOH) structure", web source: https://www.dutchchems.com/product/sodium-hydroxide/

[55] Król-Morkisz, K., & Pielichowska, K. (2019). Thermal decomposition of polymer nanocomposites with functionalized nanoparticles. In *Polymer composites with functionalized nanoparticles* (pp. 405-435). Elsevier. doi: <u>https://doi.org/10.1016/B978-0-12-814064-2.00013-5</u>

[56] Massaro, M., Cavallaro, G., Lazzara, G., & Riela, S. (2020). Covalently modified nanoclays: synthesis, properties and applications. In *Clay Nanoparticles* (pp. 305-333). Elsevier. doi: <u>https://doi.org/10.1016/B978-0-12-816783-0.00013-X</u>

[57] Ray, S. S., & Okamoto, M. (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in polymer science*, 28(11), 1539-1641. doi: https://doi.org/10.1016/j.progpolymsci.2003.08.002

[58] Uddin, F. (2008). Clays, nanoclays, and montmorillonite minerals. *Metallurgical and Materials Transactions A*, 39(12), 2804-2814. doi: 10.1007/s11661-008-9603-5

[59] Bello, M. L., Junior, A. M., Vieira, B. A., Dias, L. R., de Sousa, V. P., Castro, H. C., ... & Cabral, L. M. (2015). Sodium montmorillonite/amine-containing drugs complexes: new insights on intercalated drugs arrangement into layered carrier material. *PloS one*, *10*(3), e0121110. doi: <u>https://doi.org/10.1371/journal.pone.0121110</u>

[60] Hun Kim, M., Choi, G., Elzatahry, A., Vinu, A., Bin Choy, Y., & Choy, J. H. (2016). Review of clay-drug hybrid materials for biomedical applications: Administration routes. *Clays and Clay Minerals*, *64*(2), 115-130. doi: <u>https://doi.org/10.1346/CCMN.2016.0640204</u>

[61] Iannuccelli, V., Maretti, E., Montorsi, M., Rustichelli, C., Sacchetti, F., & Leo, E. (2015). Gastroretentive montmorillonite-tetracycline nanoclay for the treatment of Helicobacter pylori infection. *International Journal of Pharmaceutics*, 493(1-2), 295-304. doi: https://doi.org/10.1016/j.ijpharm.2015.06.049

[62] "Deionized water", web source: <u>https://www.chimica-online.it/composti/acqua-distillata.htm</u>

[63]"Ultra-TurraxT25byIKA",websource:https://profilab24.com/es/laboratorio/dispersores/dispersor-digital-ultra-turrax-ika-t-25

[64] "pH-meter series PH20", web source: <u>https://es.vwr.com/store/product/22603637/ph-meter-handheld-ph20#gallery-1</u>

[65] Zhang, L., Huang, Y., Sun, P., Hai, Y., & Jiang, S. (2021). A self-healing, recyclable, and degradable fire-retardant gelatin-based biogel coating for green buildings. *Soft Matter*, *17*(20), 5231-5239. doi: <u>10.1039/D1SM00435B</u>

[66] Fennema, O. (1977). Water and protein hydration. Food proteins. JR Whitaker and SR Tannenbaum, ed. Avi Publ. Co. *Inc:*, *Westport*, *CT*.

[67] Zhao, X., Chen, Z., Che, M., Qiu, S., Huang, R., Qi, W., ... & Su, R. (2020). Tannic acid enhances the removal of chloroform from water using NaOH-activated persulfate. *Environmental Chemistry Letters*, *18*(4), 1441-1446. doi: <u>10.1007/s10311-020-01016-7</u>

[68] Wu, S., Yan, Y., Ni, D., Pan, X., Chen, X., Guan, J., ... & Liu, L. (2019). Development of a safe and efficient gene delivery system based on a biodegradable tannic acid backbone.

Colloids and Surfaces B: Biointerfaces, 183, 110408. doi: https://doi.org/10.1016/j.colsurfb.2019.110408

[69] Zhang, X., Do, M. D., Casey, P., Sulistio, A., Qiao, G. G., Lundin, L., ... & Kosaraju, S. (2010). Chemical cross-linking gelatin with natural phenolic compounds as studied by high-resolution NMR spectroscopy. *Biomacromolecules*, *11*(4), 1125-1132. doi: https://doi.org/10.1021/bm1001284

[70] Leite, L. S. F., Pham, C., Bilatto, S., Azeredo, H. M., Cranston, E. D., Moreira, F. K., ... & Bras, J. (2021). Effect of Tannic Acid and Cellulose Nanocrystals on Antioxidant and Antimicrobial Properties of Gelatin Films. *ACS Sustainable Chemistry & Engineering*, *9*(25), 8539-8549. doi: <u>https://doi.org/10.1021/acssuschemeng.1c01774</u>

[71] Zhao, Q., Mu, S., Long, Y., Zhou, J., Chen, W., Astruc, D., ... & Gu, H. (2019). Tannin-Tethered Gelatin Hydrogels with Considerable Self-Healing and Adhesive Performances. *Macromolecular materials and engineering*, *304*(4), 1800664. doi: <u>https://doi.org/10.1002/mame.201800664</u>

[72] He, M., Sun, H., Sun, H., Yang, X., Li, P., & Niu, Q. J. (2019). Non-organic solvent prepared nanofiltration composite membrane from natural product tannic acid (TA) and cyclohexane-1, 4-diamine (CHD). *Separation and Purification Technology*, 223, 250-259. doi: https://doi.org/10.1016/j.seppur.2019.04.064

[73] Ortiz-Zarama, M. A., Jiménez-Aparicio, A. R., Lourenço, R. V., Amaral-Sobral, P. J., & Solorza-Feria, J. (2016). Rheological characterization of solutions of gelatin with bentonite and tannic acid. *Revista Mexicana de Ingeniería Química*, *15*(3), 819-830.

[74] Shao, G., Hanaor, D. A., Shen, X., & Gurlo, A. (2020). Freeze casting: from lowdimensional building blocks to aligned porous structures—a review of novel materials, methods, and applications. *Advanced Materials*, *32*(17), 1907176. doi: <u>https://doi.org/10.1002/adma.201907176</u>

[75] Shukla, S. (2011). Freeze drying process: A review. *International journal of pharmaceutical sciences and research*, 2(12), 3061. doi: <u>https://doi.org/10.13040/ijpsr.0975-8232.2%2812%29.3061-68</u>

[76] Deville, S. (2008). Freeze-casting of porous ceramics: a review of current achievements and issues. *Advanced Engineering Materials*, *10*(3), 155-169. doi: https://doi.org/10.1002/adem.200700270

[77]" Laboratory Freeze Dryer CRYODOS", web source: https://manualzz.com/doc/6613290/laboratory-freeze-dryer-cryodos [78] Masuelli, M. A., & Sansone, M. G. (2012). Hydrodynamic properties of gelatin-studies from intrinsic viscosity measurements. *Products and applications of biopolymers*, 85-116.

[79] "Precision bath for the VB-1423 SELECTA viscometer", web source: https://www.vidrafoc.com/ba-o-de-precision-para-viscosimetros-vb-1423-selecta.html

[80] "Ubbelhode 1B viscometer", web source: *https://www.directindustry.it/prod/cannon-instrument-company/product-106453-2075339.html*

[81] "Viscosity measuring equipment", web source: <u>https://grupo-</u> selecta.com/wpcontent/uploads/EN_06-water-oil-baths-immersion-thermostats-and-dryblocks.pdf

[82] Chee, S. Y., Wong, P. K., & Wong, C. L. (2011). Extraction and characterisation of alginate from brown seaweeds (Fucales, Phaeophyceae) collected from Port Dickson, Peninsular Malaysia. *Journal of Applied Phycology*, *23*(2), 191-196. doi: 10.1007/s10811-010-9533-7

[83] "Ubbelhode viscometer", web source: https://en.wikipedia.org/wiki/Ubbelohde_viscometer

[84] Huggins, M. L. (1942). The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration. *Journal of the American Chemical Society*, *64*(11), 2716-2718. doi: <u>https://doi.org/10.1021/ja01263a056</u>

[85] "Fourier transform infrared spectroscopy (FTIR)", web source: https://www.mt.com/it/it/home/products/L1_AutochemProducts/ReactIR/ftirspectroscopy.html

[86] "Nicolet 6700 spectrophotometer", web source: <u>https://www.gmi-inc.com/product/thermo-nicolet-6700-ftir/</u>

[87] Hrubesh, L. W., & Pekala, R. W. (1994). Thermal properties of organic and inorganic aerogels. *Journal of Materials Research*, 9(3), 731-738. doi: https://doi.org/10.1557/JMR.1994.0731

[88] Smith, D. S., Alzina, A., Bourret, J., Nait-Ali, B., Pennec, F., Tessier-Doyen, N., ... & Gonzenbach, U. T. (2013). Thermal conductivity of porous materials. *Journal of Materials Research*, *28*(17), 2260-2272. doi: <u>https://doi.org/10.1557/jmr.2013.179</u>

[89] "C-Therm TCi for thermal conductivity analysis", web source: <u>https://www.google.com/search?q=CTherm+TCi+Thermal+conductivity+Analyzer+which+e</u> <u>mploys+the+Modified+Transient+Plane+Source+(TPS)&client=firefox-</u> bd&source=lnms&tbm=isch&sa=X&ved=2ahUKEwiCuNmbqOv3AhWVRvEDHZVMDWg Q AUoAXoECAEQAw&biw=766&bih=697&dpr=1.25#imgrc=uphVDGcrQ-3KUM.

[90] Venkataraman, M., Mishra, R., & Militky, J. (2017). Comparative analysis of high performance thermal insulation materials. *J. Text. Eng. Fash. Technol*, 2(3), 401-409.

[91] Liu, Y., Wu, H., Zhang, Y., Yang, J., & He, F. (2020). Structure characteristics and hygrothermal performance of silica aerogel composites for building thermal insulation in humid areas. *Energy and Buildings*, *228*, 110452. doi: <u>https://doi.org/10.1016/j.enbuild.2020.110452</u>

[92] Erich, B. J., & Pel, L. (2011). Moisture content measurement. In *Fundamentals of mold* growth in indoor environments and strategies for healthy living (pp. 305-334). Wageningen Academic Publishers, Wageningen. doi: 10.3920/978-90-8686-722-6_11

[93] Van Keulen, J. (1973). Density of porous solids. *Matériaux et Construction*, 6(3), 181-183.

[94] "Universal testing machine (ZwickRoell Z010, 10 kN RetroLine)", web source: https://www.zwickroell.com/products/pre-owned-market/pre-owned-z010-allroundline-10-kn/

[95] Gibson, L. J. (1997). Ashby MF: Cellular Solids: Structure and Properties. *Edition: Cambridge Solid State Science Series*.

[96] Xi, S., Wang, X., Liu, T., Zhang, Z., Zhang, X., & Shen, J. (2021). Moisture-Resistant and Mechanically Strong Polyimide-Polymethylsilsesquioxane Hybrid Aerogels with Tunable Microstructure. *Macromolecular Materials and Engineering*, *306*(4), 2000612. doi: https://doi.org/10.1002/mame.202000612

[97] Gomes, M. G., Flores-Colen, I., Manga, L. M., Soares, A., & De Brito, J. (2017). The influence of moisture content on the thermal conductivity of external thermal mortars. *Construction and Building Materials*, *135*, 279-286. doi: https://doi.org/10.1016/j.conbuildmat.2016.12.166

[98] "Moisture Analyzer HE53, by Mettler Toledo Greifensee, Switzerland", web source: https://www.mt.com/int/en/home/products/Laboratory_Weighing_Solutions/moistureanalyzer.html?cmp=sea_57010123&SE=GOOGLE&Campaign=MT_LABTEC|Moisture|_EN

<u>ROW&Adgroup=MoistureAnalyzerMT&bookedkeyword=moisture%20analyzer%20mettler</u> <u>&matchtype=p&adtext=311389590221&placement=&network=g&kclid= k_EAIaIQobChMI</u> <u>tfie4djt9wIVp5BoCR3lhQrZEAAYASAAEgJtivD_BwE_k_&cq_src=google_ads&cq_cmp=</u> 1627618976&cq_term=moisture%20analyzer%20mettler&cq_plac=&cq_net=g&cq_plt=gp& cq_con=64667758049&cq_med=&cq_pos=&gclid=EAIaIQobChMItfie4djt9wIVp5BoCR3lh QrZEAAYASAAEgJtivD_BwE

[99] Zafeiropoulos, N. E. (Ed.). (2011). Interface engineering of natural fibre composites for maximum performance. Elsevier.

[100] Ebnesajjad, S. (2011). Surface and material characterization techniques. In *Handbook of Adhesives and Surface Preparation* (pp. 31-48). William Andrew Publishing. doi: https://doi.org/10.1016/B978-1-4377-4461-3.10004-5

[101] "TGA/DSC 1 instrument (Mettler Toledo, Columbus, Ohio)", web source: https://www.industry-plaza.com/thermogravimetric-analyzer-tga-p125364890.html

[102] Schartel, B., & Hull, T. R. (2007). Development of fire-retarded materials—interpretation of cone calorimeter data. *Fire and Materials: An International Journal*, *31*(5), 327-354. doi: https://doi.org/10.1002/fam.949

[103] Jones, R. N. (1979). Group frequencies and the chemical bond. In *Infrared and Raman Spectroscopy of Biological Molecules* (pp. 81-93). Springer, Dordrecht. doi:10.1007/978-94-009-9412-6_6

[104] "IR Spectrum Table & Chart", web source: https://www.sigmaaldrich.com/IT/it/technical-documents/technical-article/analyticalchemistry/photometry-and-reflectometry/ir-spectrum-table

[105] "Recursos Educativos de Quimica Organica. Tablas de Espectroscopia", web source: https://www.ugr.es/~quiored/lab/tablas_espec/ir.htm

[106] Ferfera-Harrar, H., & Dairi, N. (2013). Elaboration of cellulose acetate nanobiocomposites using acidified gelatin-montmorillonite as nanofiller: Morphology, properties, and biodegradation studies. *Polymer composites*, *34*(9), 1515-1524. doi: <u>https://doi.org/10.1002/pc.22440</u>

[107] Mu, C., Li, X., Zhao, Y., Zhang, H., Wang, L., & Li, D. (2013). Freezing/thawing effects on the exfoliation of montmorillonite in gelatin-based bionanocomposite. *Journal of Applied Polymer Science*, *128*(5), 3141-3148. doi: <u>https://doi.org/10.1002/app.38511</u>

[108] Muyonga, J. H., Cole, C. G. B., & Duodu, K. G. (2004). Fourier transform infrared (FTIR) spectroscopic study of acid soluble collagen and gelatin from skins and bones of young and adult Nile perch (Lates niloticus). *Food chemistry*, *86*(3), 325-332. doi: https://doi.org/10.1016/j.foodchem.2003.09.038

[109] Kevadiya, B. D., Joshi, G. V., Patel, H. A., Ingole, P. G., Mody, H. M., & Bajaj, H. C. (2010). Montmorillonite-alginate nanocomposites as a drug delivery system: intercalation and

in vitro release of vitamin B1 and vitamin B6. *Journal of biomaterials applications*, 25(2), 161-177. doi: <u>https://doi.org/10.1177%2F0885328209344003</u>

[110] Edraki, M., & Zaarei, D. (2018). Modification of montmorillonite clay with 2mercaptobenzimidazole and investigation of their antimicrobial properties. *Asian Journal of Green Chemistry*, 2(3), 189-200. doi: 10.22034/ajgc.2018.61073

[111] Coronado Jorge, M. F., Alexandre, E., Caicedo Flaker, C. H., Bittante, A. M. Q. B., & Sobral, P. J. D. A. (2015). Biodegradable films based on gelatin and montmorillonite produced by spreading. *International Journal of Polymer Science*, 2015. doi: https://doi.org/10.1155/2015/806791

[112] Menezes, M. D. L. L. R., da Rocha Pires, N., da Cunha, P. L. R., de Freitas Rosa, M., de Souza, B. W. S., de Andrade Feitosa, J. P., & de Souza, M. D. S. M. (2019). Effect of tannic acid as crosslinking agent on fish skin gelatin-silver nanocomposite film. *Food Packaging and Shelf Life*, *19*, 7-15. doi: <u>https://doi.org/10.1016/j.fpsl.2018.11.005</u>

[113] Ortiz-Zarama, M. A., Jiménez-Aparicio, A. R., & Solorza-Feria, J. (2016). Obtainment and partial characterization of biodegradable gelatin films with tannic acid, bentonite and glycerol. *Journal of the Science of Food and Agriculture*, *96*(10), 3424-3431. doi: <u>https://doi.org/10.1002/jsfa.7524</u>

[114] Lisperguer, J., Saravia, Y., & Vergara, E. (2016). Structure and thermal behavior of tannins from Acacia dealbata bark and their reactivity toward formaldehyde. *Journal of the Chilean Chemical Society*, *61*(4), 3188-3190. doi: <u>http://dx.doi.org/10.4067/S0717-97072016000400007</u>

[115] "Factor de emision de la energia eléctrica: el mix eléctrico", web source: https://canviclimatic.gencat.cat/es/actua/factors_demissio_associats_a_lenergia/#:~:text=El% 20mix%20de%20la%20red%20el%C3%A9ctrica%20espa%C3%B1ola%20publicado%20por %20la,259%20g%20CO2eq%2FkWh

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