An Overview of Aerogels and its Applications

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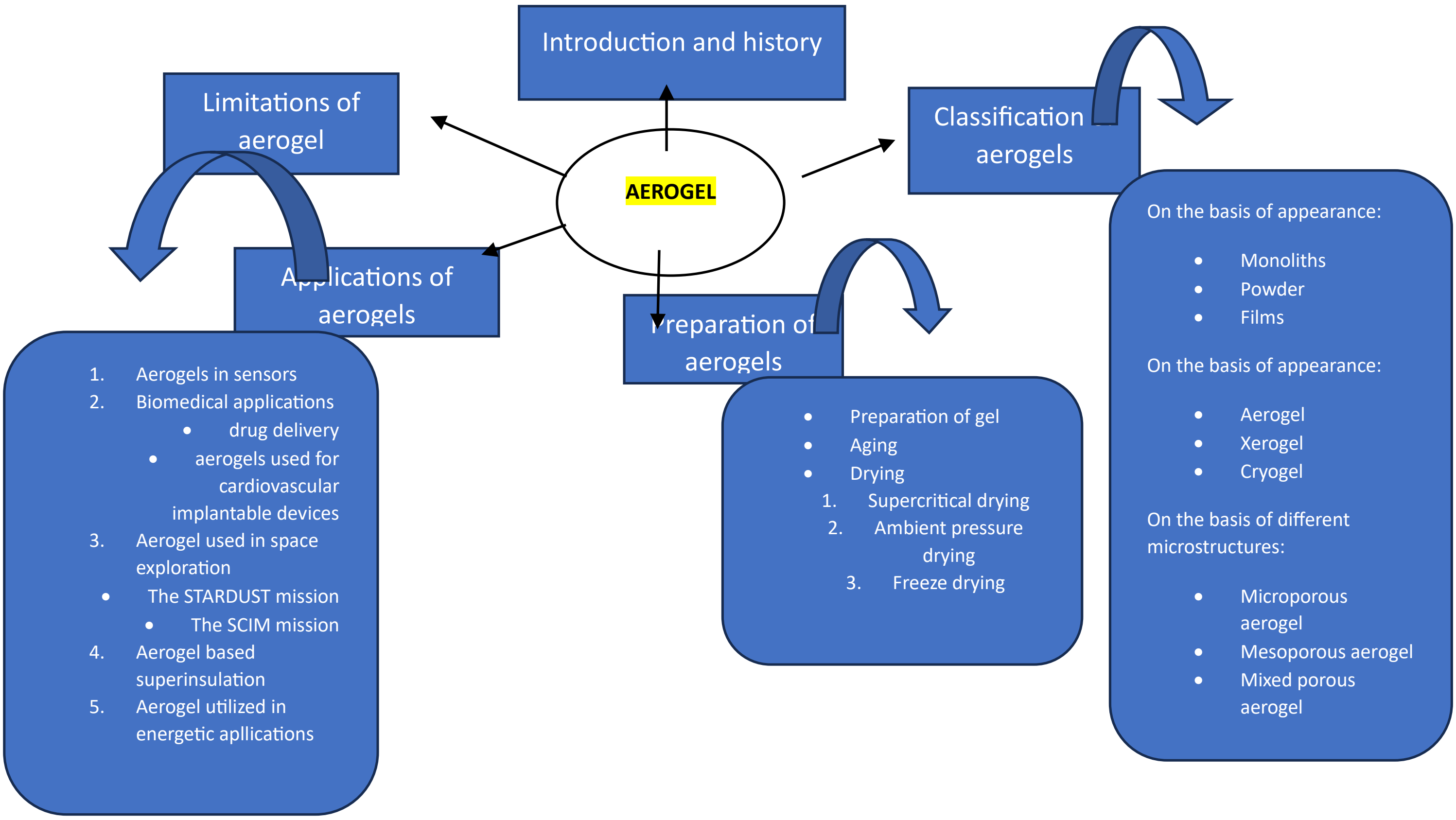
Abstract:

This paper provides a comprehensive overview of aerogels, nanoporous materials with extraordinary properties that have attracted significant interest across various scientific and technological domains. Beginning with their invention by Kistler in 1930, the paper traces the historical developments of aerogels, including key discoveries, advancements, and commercialization efforts. It discusses the classification of aerogels based on physical appearance, preparation methods, and structural characteristics, highlighting their versatility and board spectrum of applications. The preparation process of aerogel through the sol-gel method is detailed, focusing on gel formation, aging, and drying techniques such as supercritical drying and ambient pressure drying. Various applications of aerogels are explored, including their use in sensors, biomedical devices, space exploration missions, superinsulation, and energetic applications. Overall, this paper serves as a comprehensive resource for understanding the history, classification, preparation, applications, and limitations, showcasing their potential for diverse scientific and technological innovations.

Graphical abstract:



History

Aerogels are nanoporous light materials made of an open cell network with several remarkable properties that excite the interest of academics in various scientific and technological fields(Bheekhun et al., 2013). Despite being considered materials of the twenty-first century, they were invented by Kistler in 1930. Aerogels also referred to as frozen smoke, solid smoke, solid air, or blue smoke are low-density solids that possess low heat conductivity, low optical index of refraction, low speed of sound through the material, high surface area, and low dielectric constant [2]. A combination of attributes makes them different across diverse domains, facilitating access to a broad spectrum of applications, with certain ones having already commercialization [3]. Undoubtedly, there has been a resurgence of interest in aerogel materials in recent years. With the unveiling of "coherent expanded aerogels and jellies" in the 1930s, Kistler promptly grasped the potential of these intriguing low-density solids. In addition to being committed to his work as a professor of chemistry, Kistler was a successful businessman. Following his discovery, he pursued industry collaboration after seeing the potential of aerogels as materials. The Monsanto Chemical Corporation commenced production of his aerogels in Everett, Massachusetts in 1940. Marketed under the brand name Santocel. The majority of it was used in thermal applications and as a thickening agent. In the following three decades, as applications and sales volume increased the initial study on the impact of silica aerogels on the human respiratory system was published. Due to Santocel's high production costs and the availability of less expensive silica powders, manufacture of the product ceased around 1970. A major discovery was made in 1968 by Nicolaon and Teichner made the preparation of silica aerogels much easier. The utilization of alkoxide-based precursors, specifically tetramethyl borosilicate (TMOS), instead of waterglass substance previously used by Kistler, greatly aided in the preparation of top-notch monolithic blocks. During the period spanning from the 1940s to the 1970s, academic interest in aerogel materials remained minimal. However, the advent of simpler and safer preparation methods heralded the onset of the first aerogel resurgence in the 1980s, often referred to as the "academic aerogel revolution"[4]

In Sweden, an initial factory for manufacturing silica aerogel blocks with TMOS was established. However, it suffered severe damage in 1984 when an explosion occurred because of a leak in the autoclave in the presence of methanol. But after reconstruction, Air Glass Corporation is presently running the plant. Because of its toxic nature, TMOS must be substituted. Shortly after that, Tewari and Hunt discovered tetraethyl orthosilicate (TEOS) as a safer alternative that would not compromise the quality of aerogels. However, this process is still not sufficiently safe for mass production. Hunt persisted in his pursuit of enhancement and conceived the notion of substituting the alcohol within the gel with liquid carbon dioxide before supercritical drying. This approach was motivated by the fact that CO2 is non-flammable and requires lower temperature and pressure to reach the supercritical state[1].

Hunt and his team explained how they made silica aerogels using a special drying method called ambient temperature supercritical drying (SCD) with supercritical CO2. After further streamlining this procedure, the German Chemical Corporation BASF soon started producing its basogel product range. Simultaneously, the scholarly community began examining these intriguing resources. Therefore, the mid-1980s can be considered the first aerogel renaissance.

In 1985. Jochen Fricke arranged the inaugural International Aerogel Symposium at the ZAE, located in Bavaria, Germany. A few years later, Pekala shared his research on resorcinol-formaldehyde-based silica aerogels. These were the first organic resin-based aerogels with customizable pore structure. The first aerogel based on polyurethane chemistry was reported in 1993. Around that time, Jeff Brinker and Doug Smith created a way to prepare aerogels called ambient-dried aerogels, which made them more suitable for academic researchers. This method has also led to many patents by large chemical companies, such as Hoechst and Dow Chemicals. As a result we call this era the "second aerogel revival," which is marked by a sharp rise in the interest in processing techniques and novel material variants. But it took an additional ten years for the third aerogel renaissance to spark industry interest in these materials. In 2003, Aspen Aerogels and Cabot Aerogel began manufacturing blanket and granular silica aerogel products, respectively on an industrial scale. [4]
In 2004, Brock pioneered the creation of chalcogenide aerogels using reverse micelle synthesis, sol-gel technique, and supercritical fluid drying. In 2006, gradient aerogels did a stellar job at nabbing superfast particles from comets and interstellar space. Then they made a triumphant return to Earth with their cosmic haul. Subsequently, a sequence of innovative aerogels emerged one after another, encompassing CNT aerogel, graphene aerogel, carbide aerogel, and single-element aerogel[5].

Classification of aerogels

Aerogels can be classified into various types of lenses. Based on their physical appearance, aerogels can be categorized into three main types: monoliths, powders, and films. Second, considering the method of preparation aerogels fall into four primary types: Pierre's original aerogel definition, xerogels, cryogels, and other related materials within the aerogel spectrum. Finally, from a structural perspective, aerogels can be classified as microporous, mesoporous, and mixed porous aerogels on their specific microstructure[5].

The best way to sort aerogels is by what they are made of. There are two main types of aerogels: single-component aerogels, which are made from one substance, and aerogels, which are made from a mix of different materials. This helps us to understand aerogels better and use them in different ways. Single-component aerogels are made from different types of materials, such as oxide aerogels (which include silica and non-silica) , organic aerogels (made from things like resin and cellulose), carbon aerogels (created from carbonized plastic, carbon nanotubes, and graphene), chalcogenide aerogels, and other types such as single elements or carbide aerogels. Aerogel composites are a mixture of aerogels at a tiny scale, called micro- and nano-aerogel composites. They can also be gradient aerogels meaning that they change gradually from one material to another, or multi-composition aerogels, which contain more than one type of material mixed. The most widely researched and used aerogel type is based on oxidation. This type is common and includes nearly all types of aerogels made mostly from metal-oxygen bonds. Oxide-based aerogels can be performed in many different ways, but three main methods are highly flexible. The first method is called the traditional sol-gel (TS) approach. It's the oldest and most common way to make different types of aerogels even today.

Organic aerogels, which are made from materials like resin and cellulose are often seen as spongy, a special high carbon template (RF aerogel) is heated at a high temperature (usually between 800 to 1200) in the presence of inert gas and at normal air pressure. One of the newest kinds of carbon aerogels is graphene-based. Graphene aerogel is created by using ultrasound to form a gel from a solution of graphene oxide, then drying and heating it to remove water and oxygen. Another fascinating variation in carbon nanotube (CNT) aerogels. Metal and carbide-based aerogels can be produced using a carbothermal conversion method[5]. Considerable efforts have been focused on improving our understanding of aerogel properties, particularly their mechanical characteristics. This endeavor encompasses the stimulation of these properties, such as exploring how the mechanical attributes of hybrid organic-inorganic aerogels change depending on their organic content. There has been significant interest in the luminescent, conducting, or magnetic properties of aerogels, especially for their potential in energy storage applications. Furthermore, more has been ongoing research into the thermal properties of aerogels, particularly with a focus on carbon aerogels. Currently, the main focus of aerogels is how they can be used in various applications. These include storing nuclear waste safely, trapping CO_2 to reduce pollution, creating coatings that repel water, creating sensors to detect chemicals, using them as catalysts in chemical reactions, making molds for metal casting, producing devices that convert sound waves into electrical signals, storing energy, creating materials that burn quickly, releasing a lot of heat(thermites), transporting pharmaceutical drugs safely, insulating materials to keep things cold without catching fire, and studying how liquids behave at extremely low temperatures. Aerogels are now being sold by several companies. Cabot Corp. makes aerogel particulate insulators for windows. Nano Hi-Tech and Okagel also sell insulating products. American aerogel Corp. specializes in open-cell foam materials while Birdair Company uses aerogel inserts in membranes. Aspen Aerogels company produces flexible insulation products, the future success of aerogel depends on how well these companies sell them. We wish them all the best[6].

Preparation of aerogels

Aerogels are typically created through a sol-gel process, which is widely utilized in various types of aerogels. This synthesis procedure involves three essential stages: preparation of gel; aging of gel; and drying of gel.

Preparation of gel: the sol-gel method is commonly to introduce gel formation. To expedite this process, a catalyst is introduced once the requisite precursor has been dispersed in a solvent. For example in the production of silica gel, 0.1 M HCL is incorporated to dissolve the precursor, tetramethoxysilane (TMOS), within an ethanol/water (4:1) blend before catalyzing gelation. The dispersal medium water for hydrogel or aquagel, alcohol for alcogel, or air for aerogel is typically utilized to classify the gels[7].

Aging of gel: the production of gel does not mark the end of the chemical reaction. This is caused by the possibility that the gel network will continue to expand in the gelation solvent during what is known as an aging process. Unreacted monomers and reactive molecules such as OH exist within the pores of the gelation liquid, which have the potential to undergo condensation on the network , the complete aging process, wherein the gel is immersed in the original sol or another suitable solvent under meticulously controlled conditions, typically spans from hours to days. Aging primarily enhances the mechanical integrity of the delicate network found in the aerogels.

During this process, various phenomena occur among the network particles, with “Ostwald ripening arises from the dissolution of species or molecules within the aggregates from less energetically favorable areas to accumulate at more energetically favorable network sites, such as neck regions or network connection points. Consequently, the network becomes reinforced and coarser. The kinetics of the aging process are significantly influenced by three key variables: pH, time, and temperature. Additionally, as synthetic gels undergo aging, there are notable changes in many textural properties, such as surface area, porosity, and pore size. Extensive research has been conducted on aging to enhance the initial strength of prepared gels. This is widely recognized as a straightforward and dependable approach to reinforcing gel networks[8].

Drying : Drying plays a crucial role in aerogel formation. The two primary drying techniques commonly employed are supercritical drying and ambient-pressure drying. Capillary tension drying under ambient pressure is a continuous process that cannot be stopped. However, this can also be achieved by removing pore liquid above the critical pressure and temperature.

Supercritical Drying: It is the primary and widely adopted method for drying aerogels. During this process, gels are fried at a critical point to mitigate capillary forces. As the liquid evaporated from the gel, the surface tension within the pores led to the formation of concave menisci. Over time, the tension and growing compressive forces surrounding the pores caused the gel body to collapse. To counteract the surface tension and prevent collapse, the gel undergoes supercritical drying in the autoclave. When the temperature and the pressure inside the autoclave reached a certain level, the liquid entered a supercritical state. This allows the molecules to move freely and remove the surface tension. The formation of menisci depends on the surface tension. Subsequently, the fluid is slowly depressurized until the pressure of the autoclave matches the outside air pressure. Methanol is commonly used as a solvent for supercritical drying: high temperature and low temperature. High-temperature supercritical; drying was found to be the best method for reducing gel shrinkage[9].

Ambient Pressure Drying: To lower expenses compared to the costly supercritical drying processes, there is significant interest in ambient pressure drying(APD). APD generally involves two steps: silyation of all hydroxyl (OH) groups is required to prevent water adsorption which can lead to the formation of hydrophobic aerogels. Firstly, this is accomplished by substituting the current solvent with a solvent devoid of water along with a silylating agent such as hexamethyldisilazane(HMDS). This results in the replacement of hydrogen from hydroxyl (OH) groups with an alkyl group such as CH_3. Secondly, drying is conducted through ambient pressure evaporation which involves three stages: initially, after a warming phase, the gel experiences its first drying period where the loss in volume of the gel balances that of the evaporated liquid. This occurs as free water moves continuously to the outer surface due to capillary forces. In the second drying period, known as the falling rate period, diffusive vapor transport becomes predominant, allowing liquid to slowly escape to the exterior.

Freeze drying: Another way to dry aerogels is through freeze drying. This means freezing the liquid inside the pores and then using a vacuum to turn it directly into vapor. One challenge of this method is the long time it takes for the gel network to form properly. Also, a different solvent that expands less and turns into vapor more easily must be used instead of the original solvent.

Applications of aerogels

Aerogels in sensors: Sol-gel materials have been thoroughly researched for their possible uses in chemical sensing. These materials are attractive for sensing applications because they are porous and have low density. A recent literature search found over 2700 references for “sol-gel sensor”[10]. Aerogels have; lots of surface areas where reactions can happen, and their pores are easy to get into. They are very porous overall. That’s why people think they could be good for making sensors. In a study by Wang and others, they found that when the air gets more humid, the resistance of thin films made from silica nanoparticle aerogels drops a lot. Because of how their pores are set up, these aerogels have a 3.3% difference in behavior depending on whether humidity is going up or down, and they are super sensitive to humidity levels of 40% or more. Wub and Chen-yang conducted research on the potential of aerogels for biosensor applications. They made mesoporous aerogels at room temperature using a method called sol-gel polymerization. They used an ionic liquid as both liquid and the material that helps create tiny holes in the aerogels[11]. The importance of gas sensors has significantly grown across various industries due to the rapid advancement of society. These sectors encompass the detection of explosive and harmful gases for industrial monitoring and public safety purposes as well as the analysis of the gas we exhale for disease diagnosis. Resistive gas sensors are widely favored among gas sensors types because they are cost-effective, easy to process, and simple to operate. in these sensors, sensing typically takes place at the surface of the active sensing materials. When gas molecules adhere to the surface of the active sensing layers, it leads to a change in the sensor’s conductivity. Gas sensors are constantly being studied for their sensitivity, detection limits, selectivity, response and recovery rates and stability. Here are some advantages of using gas-sensing materials based on aerogels.1) aerogels offer ample surfaces for gas adsorption and contain numerous active sites for gas sensing due to their high specific area and surface-to-volume ratios.2) Their interconnected three-dimensional porous structure allows for a steady and rapid transport route for gas diffusion. This often results in aerogels-based gas sensors showing quick response times, low detection limits, and high sensitivity. Moreover, by combining various molecules to create a composite aerogel, a synergistic effect can be achieved, leading to good selectivity and stability in gas sensing applications[12].

Biomedical applications:

- A) <u>Drug delivery:</u> Aerogels offer promising and practical applications in the field of biomedicine, particularly in pharmaceutical settings. Within pharmaceutical applications, aerogels serve as an effective drug delivery system across multiple administration routes, including oral, pulmonary, nasal, and topical routes. By facilitating controlled and modified drug release profiles, aerogels have the potential to enhance therapeutic outcomes significantly. Aerogel-based platforms for therapy can control how bioactive molecules are delivered, making medication more available in the body[13]. When a medicine is delivered to a specific area of the body with a high yield, it is said to be effective. Drug delivery systems are frequently created with the possibility of undesirable side effects that need to be drastically minimized in mind. Because of this, an ideal drug delivery system would identify the intended body location, deliver the medication there, and avoid affecting any other body regions. Thinking about this, the way the drug is released is the first important thing to consider. Usually, we can put release profiles into three different groups. The first type is bolus release, where the drug is released quickly and completely in a short time, usually less than 30 minutes. The second type is sustained release, which means the drug is released over at least 4 hours. Lastly, there's controlled release, where different release patterns can be combined into one system. Usually, we say that a controlled release system system combines sustained release and bolus systems. In an ideal scenario (which is theoretical), the controlled release devices can deliver and release the integrated medication as required. This ensures that the planned treatment strategy is adhered to while delivering the correct dosage of the medication[14].

- B) aerogels used for cardiovascular implantable devices: As the primary cause of death in the United States, cardiovascular disorders and their complications generate significant demand for biomaterials appropriate for cardiovascular implantable devices. Typically, a biomaterial must be compatible with the organ system for the entire lifespan of the device to be used effectively in the human body. In the context of the cardiovascular system, this means the material should be suitable for the patient's blood, especially in terms of immunological responses and blood clotting reactions. Additionally, it should be suitable for blood vessels if the device interacts with them. When an implantable device comes in contact with blood, it quickly attracts proteins from blood, which stick to its surface. Then platelets may stick to and become activated on the surface. When platelets become activated and blood starts to clot, it can lead to the formation of a clot on the surface of a device implanted in the body this clot can greatly affect how well the device works. A perfect polymeric material for implantation in the bloodstream should not lead to platelet activation, an immediate immune response, or the sticking of plasma proteins to its surface. Artificial heart waves, among the most recognized blood implantable devices, are utilized to replace damaged or diseased heart waves. Approximately 300,000 prosthetic heart waves are implanted each year, with mechanical heart valves accounting for roughly 60% of these procedures. Tissue valves dominate the prosthetic heart valve market, serving as the preferred alternative to mechanical valves. despite over a decade of research, polymeric heart waves continue to fall short of expectations. Typically made of polyurethane, they feature soft leaflets and closely resemble natural heart valves. However, due to various issues such as insufficient mechanical strength and material degradation, their overall success rate remains relatively low. Yin and Rubenstein from Oklahoma State University recently began a study to see how different types of aerogels work in the cardiovascular system. In their first tests, they used a special kind of aerogel called X-MP4-T045, which is surfactant-templated polyurea-nanopaencapsulated microporous silica aerogel. They made X-MP4-T045 using tetramethylorthosilicate and a tri-block copolymer called Pluronic P123, following a method called Leventis approach. X-MP4-T045 has a porosity of 50.0% and a mass density of 0.66g/cm3. They examined how it impacts the generation of plasma anaphylatoxins, plasma protein adhesion, platelet activation, blood clotting, and the normal functioning of vascular endothelial cells[15].

Aerogel: Used in space exploration

- A) The Stardust Mission: Among the various applications being explored for aerogel, none are as extensive as its use in space exploration. NASA's Discovery Program's fourth mission, STARDUST, is dedicated to collecting samples from outer space and returning them to Earth for detailed laboratory analysis. The spacecraft will complete three orbits around the sun and travel beyond the orbit of Mars, making the realization of a long-standing aspiration. The primary cargo of the STARDUST mission, which aims to gather and preserve samples from a newly discovered comet named Wild-2, consists of aerogel. The sample collector's back will capture fresh interstellar material that the solar system has intercepted from other stars while traveling toward wild-2[16]. Since low-density aerogel is a superior medium for capturing particles at high speeds, it was taken into consideration when designing the stardust mission.

- The SCIM mission: Utilizing aerogel to trap dust particles within the atmosphere, the SCIM(sample collection of the investigation) Mission is set to deploy a spacecraft into the upper Martian atmosphere for sample retrieval, with the intention of later returning the space to earth. The technology developed and produced for the Stardust Mission serves as a cornerstone of the mission's infrastructure. SCIM, designed for collecting and bringing back sample a sample from Mars to Earth, is considered a mission with low risk and low cost. The dust found in the Martin atmosphere provides a global representation of Mars's surface. As a result, this mission will bring back a sample that reflects the entire planet rather than just one specific location. This is a significant advantage of the sample collection strategy. Similar to the Stardust Mission, SCIM will bring back the aerogel to Earth after utilizing it to collect particles[17].

Aerogel-based Superinsulation: Around the world, insulation products are available for many purpose. These include industrial processes, high-quality products and systems, specific markets, and building construction along with heating, ventilation, and air conditioning (HVAC) systems. Typically, an insulation layer helps to reduce energy losses by limiting the transfer of heat between two objects maintained at different temperatures. When insulation is inadequate, additional energy must be supplied to compensate for these losses. The next three categories, which vary in how aerogel is combined with material, system, or part, are commonly used for aerogel-based superinsulation products.

- Monolithic aerogels: Monolithic aerogel are big blocks(>1Cm) made of the same kind of aerogel material throughout.
- Divided materials: Divided materials refer to finely broken-up aerogels, which are like small, random pieces or crumbs of aerogel. Granules usually have diameters below 1cm, while powders are even smaller, typically around 1mm in size.
- Composite materials: Composite materials are made up of aerogel phases that are either the same throughout(homogenous) or different (heterogeneous). These aerogel phases are changed by adding things like fibers, blankets, fleece, or other substances during the manufacturing process[18].

Aerogel utilized in energetic applications: The potential use of aerogels are energy materials is an innovative and intriguing concept. Explosive applications are particularly interested in the even distribution of extremely small energetic particles that aerogels can provide. There are various possibilities, including combining aerogels with explosives to form composite materials, synthesizing aerogels directly from energetic molecules, and developing aerogels that contain both reducer and oxidizer components. Another study presented in ISA5 provides an overview of ongoing research, including experimental findings involving aerogels containing explosives[19].

Limitations of aerogel:

a) Aerogel materials are not used much right now they are expensive to make.

b) They are not very strong.

c) the most expensive and risky part of making aerogels is the supercritical drying process. A major goal in aerogel production is to find a way to get rid of the need for supercritical drying.

d) Aerogels can cause irritation to the eyes, skin, breathing passages, and digestive system[20].

Conclusion:

Aerogel represents a versatile and promising class of materials with a wide range of applications spanning from space exploration to the biomedical field. Despite their remarkable properties and potential, aerogels face limitations such as high production costs, mechanical weakness, and safety concerns. However, ongoing research efforts aim to address these challenges and further expand the practical applications of aerogels. With continued innovation and development, aerogels have the potential to revolutionize various industries and contribute significantly to technological advancement.

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