USES OF ADDITIVES IN POLYURETHANES TO ENHANCE THERMAL CONDUCTIVITY

A DISSERTATION

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IN

CHEMISTRY

(Physical specialization)

Submitted by-

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I, Ritik Rana, hereby certify that the work which is being submitted in this major project report entitled, **USES OF ADDITIVES IN POLYURETHANES TO ENHANCE THERMAL CONDUCTIVITY** , in the partial fulfilment for the award of the degree of Master of Science in Chemistry (Physical specialization) at **Delhi Technological University** is an authentic record of my own work carried out by me under the supervision of Prof. Raminder Kaur (Department of Applied Chemistry).

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CERTIFICATE

I, hereby certify that the project dissertation titled, USES OF ADDITIVES IN POLYURETHANES TO ENHANCE THERMAL CONDUCTIVITY , which is submitted by, RITIK RANA [2K22/MSCCHE/32], Department of Applied Chemistry, DELHI TECHNOLOGICAL UNIVERSITY, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the students under my supervision. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

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SUPERVISOR- Dr. Raminder Kaur

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ABSTRACT

Because of the extraordinary qualities of polyurethanes (PU), they are adaptable polymers that are extensively employed in a variety of sectors. However, their utility in heat transfer-intensive applications is limited due to their low thermal conductivity. Researchers have discovered a new way of adding chemicals called additives to polyurethane materials to increase their thermal conductivity to get around this restriction. The additives employed for this aim and their modes of action are thoroughly described in this review.

The potential of a variety of additives, including graphene, carbon nanotubes, metal powders, boron and aluminum nitride, and nanostructured materials, to enhance the thermal characteristics of polyurethanes has been studied. These additives can be distributed throughout the polyurethane matrix to promote heat transmission since they have a high inherent thermal conductivity. To achieve consistent dispersion and optimal thermal performance, surface modifications and functionalization processes are utilized to improve the compatibility and interfacial adhesion between additives and the polymer matrix.

To improve heat conductivity even more, synergistic effects between various compounds or between additives and the polyurethane matrix are being investigated. The influence of processing methods on the dispersion and orientation of additives within the polyurethane matrix is also covered, including melt compounding and solution mixing.

To get the appropriate balance of thermal conductivity and other crucial characteristics in polyurethane materials, the review emphasizes the significance of appropriate formulation design and optimization. Improvements in processing methods and the synergistic effects of different additives have led to notable progress in raising polyurethanes' thermal conductivity and increasing their potential uses in heat transfer devices, insulation materials, and thermal management systems, etc.

Overall, this review paper highlights interesting directions for further research in this area and offers insightful information in the field of additives for improving polyurethanes' thermal conductivity for its different applications.

TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER-1

INTRODUCTION

The presence of remarkable mechanical qualities, processing ease, and adaptability, polyurethanes (PU) have attracted a lot of interest from a variety of sectors. Their very low thermal conductivity, however, has proven to be a hindrance in situations when effective heat transmission is necessary. A great deal of work done to solve this problem is adding different chemicals called additives to increase the heat conductivity of polyurethane materials.

This introduction lays the groundwork for an in-depth analysis of the techniques used and the developments in the use of additives to improve polyurethanes' thermal conductivity. It describes the significance of thermal conductivity in a variety of applications, such as insulating materials and thermal management systems, and emphasizes the crucial role additives play in getting beyond polyurethanes' inherent limits in this area.

The importance of comprehending the mechanisms driving the improvement of heat conductivity in polyurethane composites will be studied. It presents important ideas that affect the thermal performance of polyurethane-based materials, such as filler dispersion, interfacial interactions, and manufacturing methods. To obtain the best possible thermal conductivity increase, it also highlights the necessity of conducting a thorough inquiry into different additives, considering their kinds, characteristics, and compatibility with the polyurethane matrix.

The foundation for a thorough assessment that attempts to shed light on the status of research on additives for improving polyurethanes' thermal conductivity is laid out in this paper. This study aims to contribute to the development of polyurethane-based materials with enhanced thermal characteristics and broader application in many industrial sectors by clarifying the obstacles, prospects, and current developments in the field.

One of the most common and adaptable groups of polymers, polyurethanes (PUs) are used in practically every aspect of contemporary life. Polyurethanes are an important component of many different sectors, from the foam in our mattresses to the protective coatings on our cars, since they improve comfort, safety, and efficiency. Knowing the composition, characteristics, techniques, and uses of polyurethanes is more important than ever as we go through a time of swift technological development and mounting environmental concerns. Starting from Otto Bayer's accidental discovery of polyurethanes in the 1930s and continuing to the present, when they are one of the most frequently used groups of polymers, the review studies the historical development of polyurethanes. It focuses on the turning points and significant discoveries that have influenced the development of polyurethane technology, including breakthroughs in raw materials, catalysts, and processing machinery [1].

CHAPTER-2

Polyurethanes-

Polyurethane is a polymer composed of organic units joined by urethane links(-NHCOO-). It is formed by a chemical reaction between a polyol (an alcohol with hydroxyl groups). Polyurethanes are a class of versatile materials with great potential for use in different applications, especially based on their structure-property relationships. Their specific mechanical, physical, biological and chemical properties are attracting significant research attention to tailoring polyurethanes for use in different applications. Enhancement of the properties and performance of polyurethane based materials may be achieved through using additives in polyurethane and through changes to the production process or the raw materials used in fabrications or by using advanced characterization techniques.

One of the most adaptable and extensively utilized polymers in a wide range of industrial applications is polyurethanes (PUs). These applications include coatings, adhesives, elastomers, sealants, and flexible and stiff foams. Their outstanding mechanical qualities, robustness, and adaptability have solidified their place as essential materials in a variety of industries. With the dawn of a new century marked by quickening technical progress and changing social demands, it is becoming more and more important to investigate polyurethane chemistry and its wide range of uses [2].

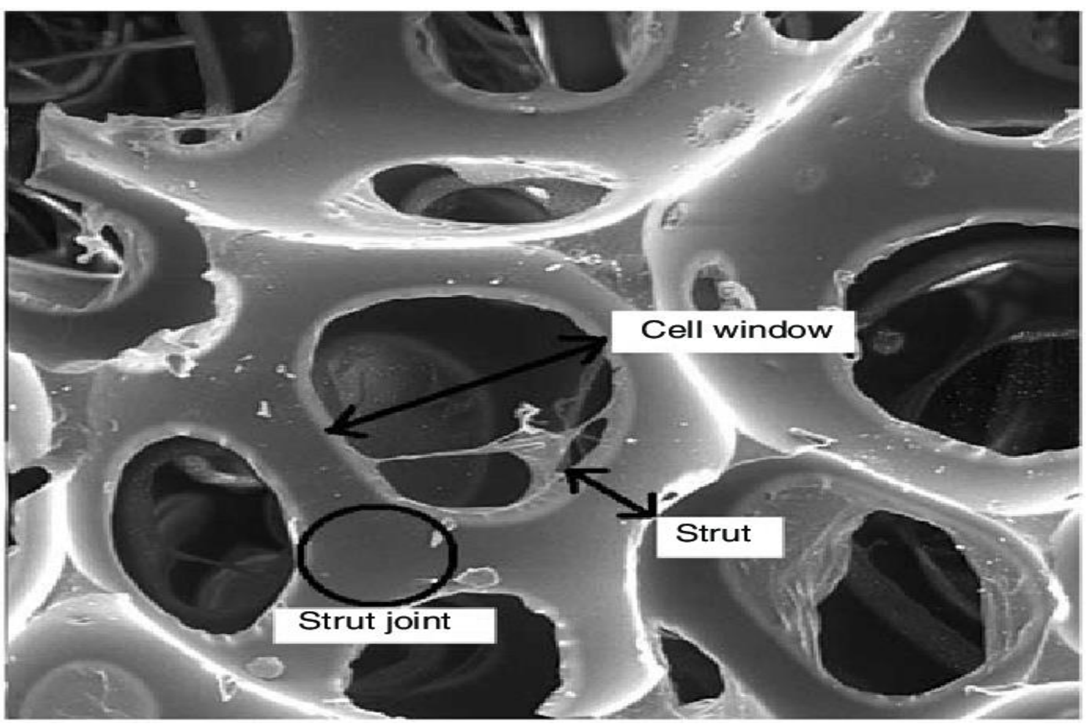

Figure 2.1 structure of polyurethane

Composition-

It is mainly composed of two components-

1. **Polyols-**
   They are compounds having multiple hydroxyl groups. Polyols serve as the reactive backbone of the polyurethane structure, reacting with isocyanate to form polyurethane polymer.

There are two main types of polyols-

1.Polyester polyols- these are the type of polyols which are formed by the condensation reaction of diols (compounds with two hydroxyl groups) with dicarboxylic acids.

They have wide range of applications-

1.coatings and paints

2.Flexible Foams

3.Adhesives and sealants

4.Fibers and Textiles

5.Composite materials

(G Avar, U Meier-Westhues, H Casselmann, and D Achten, 2012)

2.Isocyanate- They are the compounds containing the functional group –NCO. The most used isocyanates are –1. toluene diisocyanate (TDI)

2.Methylene diphenyl diisocyanate (MDI)

3.Hexamethylene diisocyanate (HDI) [3]

History of Polyurethane

The polyurethane was discovered in year 1937 by Ott Bayer and his coworkers at the laboratories of I.G Farben in Leverkusen, Germany. The initial works focused on polyurethane products obtained from aliphatic diisocyanate and diamine forming polyurea, till the interesting properties of polyurethane obtained from an aliphatic diisocyanate and glycol, were realized. by polyether polyols because of their availability in low cost, better hydrolytic stability and easiness in handling

Poly isocyanates were commercially available in the year 1952..

Figure 2.2 Ott Bayer

During World War II, in 1940 due to the demand for polyurethane in military applications, such as coatings, adhesives and insulation materials, it gained more attention.

A Post-war expansion(1950s-1960)-

After World War 2, polyurethane research was expanded rapidly, driven by the demand of durable materials in various industries. In 1952, Dr. Otto Bayer patented the reaction process for producing polyurethanes, known as the Bayer process.

Advancements and Diversification (1970s-1990s)

In the 1970s and 1980s, progress and advancements are seen in polyurethane and develop new formulations with enhanced properties like thermal stability, flame retardancy and environmental sustainability. To reduce the use of ozone- depleting blowing agents' environment friendly foam formulations were discovered.

The spray polyurethane foam was developed which tends to be very useful in construction industry as it provides efficient thermal insulation to buildings.

Modern innovations (2000s-present)-

At this phase of time, the researchers focused on advanced applications, bio-based materials and sustainability.

To reduce reliance on fossil fuels, the bio-based polyols were derived from renewable resources, like castor oil and soyabean oil.

Advances in polymer science and nanotechnology have led to the development of high-performance polyurethane materials with tailored properties [1].

Properties of polyurethanes

Polyurethanes are versatile polymers with a wide range of physical, chemical, biological and chemical properties which makes them suitable for diverse applications across various industries. Some important properties as discussed below-

Flexibility and Elasticity-

Polyurethanes exhibit a wide range of flexibility, from soft and flexible elastomers to rigid and stiff foams. This versatility allows to produce materials that can conform to various shapes and withstand repeated deformation without losing their structural integrity. The flexibility and elasticity of polyurethanes makes them suitable for various applications.

Flexible polyurethane foams-

These foams are soft, pliable and resilient, provide cushioning and comfort in applications like padding upholstery and mattresses. They can conform to the shape of the body or object they support and quickly return to their original shape after deformation.

Elastomeric polyurethanes-

also called thermoplastic polyurethanes. They exhibit high elasticity and have a high dependency on temperatures. They are used in footwear, seals, gaskets, belts, shoes and medical devices where flexibility, abrasion resistance and durability are essential scenarios.

Spray Polyurethane Foams-

Closed-cell SPF provides rigid insulation with some flexibility, while open-cell SPF offers softer, more flexible insulation suitable for irregular surfaces.

Medical Devices- For good comfort to the patient's elasticity and flexibility are very helpful during surgeries and operations. Biocompatible polyurethanes are used in medical devices and implants like surgical instruments, prosthetics and catheters [2].

Strength and durability-

Polyurethanes have high tensile strength, tear resistance, and abrasion resistance which makes polyurethane materials durable and long lasting in complicated environmental conditions.

Tensile strength- Polyurethanes have high tensile strength which makes them suitable for applications where structural integrity and resistance to mechanical stress is required.

The overall combination of high tensile strength, durability, and resistance to mechanical and chemical factors makes polyurethane reliable and versatile for use in diverse industrial purposes like automotive, construction, healthcare and aerospace.

Flexural Strength- the good flexural strength of polyurethanes enables them to resist bending and deformation under applied loads. This property is mainly useful in composite materials and automotive parts [2].

Abrasion Resistance-the nature of polyurethanes resistant to abrasion makes them suitable for applications that need friction. This property is valuable in automotive components, industrial coatings, conveyor belts and machinery parts.

Biological Resistance-some of the applications need the property where the exposure to fungi, bacteria or another microorganism is needed. This property of biological resistance of polyurethanes makes them useful for medical devices, outdoor equipment and agricultural purposes.

(Hans-Wilhelm Engels, * Hans-Georg Pirkl, Reinhard Albers, Rolf W. Albach, Jens Krause, Andreas Hoffmann, Holger Casselmann, and Jeff Dormish, 2013)

Biomedical applications of polyurethanes

Because of its superior mechanical, biocompatible, biodegradable, high flexural endurance, and fatigue resistant qualities, polyurethane (PU) has emerged as a material of choice for biomedical application development. We're going to talk about a few of the major biomedical uses of polyurethanes [2].

-

Figure 2.3 (Polyurethane uses in different fields)

Tissue Engineering

Biodegradable polymers have been utilized in tissue engineering for many years because of their biocompatibility, fatigue resistance, and adjustable mechanical characteristics. It has been used in several tissue engineering applications, including bone regeneration, cardiac patches, and fibro cartilage repair. The creation of bromidic qualities that resemble the extracellular matrix's natural state and are appropriate for eliciting cell response is necessary for the construction of PUs as scaffolds for tissue engineering. In this case, several studies have been conducted to create PU scaffolds for tissue engineering uses. To establish their applicability in tissue engineering, Kishan et al. [14] created a tri block poly (ether ester) urethane utilizing a "plug and play" technique. They next investigated their hydrolytic degradation and cyclo compatibility.

Bone regeneration-

PU scaffolds have been investigated as a possible choice for this application since bone regeneration requires processes including migration, proliferation, differentiation of osteo progenitors, and the production of extracellular matrix. For bone tissue engineering, Wang et al. recently created a waterborne, biodegradable PU shape memory elastomer [15]. Firstly, they made PU 3D printing ink, adjusting the viscosity with polyethylene glycol (PEO). For comparison, PU-gelatin 3D printing was also made, and it demonstrated high cell viability, but PU-PEO showed outstanding shape memory capabilities. As a result, PU scaffolds that exhibit superior shape memory and osteogenic effects can serve as designer bone substitutes.

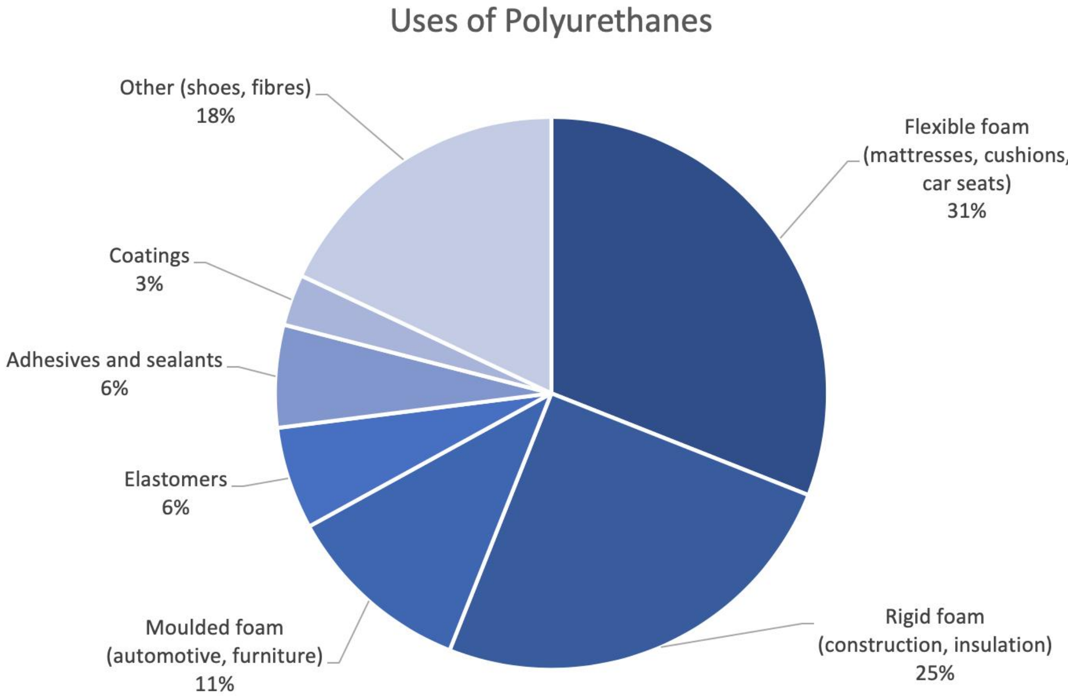

figure 2.4 uses of polyurethanes in different fields

Contact lenses-

Since a few years ago, hydrophilic PU hydrogels have mostly found employment in contact lens applications because of their excellent mechanical, water-absorption, and transparency qualities. The application was initially made public by Blair and Hudgins [19]. of PU hydrogels. In 1980, the work that Gould and Johnson reported was patented [20]. Polyurethane diacrylate has been created for usage in contact lenses. Their creation was stable in boiling water, had good water absorption, and was permeable to ions and gases [2].

Thermal properties of polyurethanes

Thermal properties play a very important role in the use of polyurethanes in different fields. The thermal properties of polyurethanes make them versatile material used in wide range of industries and applications, like automotive components, thermal management systems, and building insulation materials.

1. Thermal conductivity- Generally polyurethane foams have low thermal conductivity due to which they are good insulating materials in buildings, refrigerators etc.

2. Heat resistance- Polyurethanes are resistant to moderate temperatures, exposure to high temperature can cause thermal degradation, which can change mechanical properties, color,

and dimensional stability. Basically, the heat resistance of polyurethanes depends on the types of additives, polyols and isocyanates used.

3. Thermal insulation- due to the low thermal conductivity and closed cell structure of the polyurethanes they exhibit excellent thermal insulation properties. Closed cell polyurethane foams trap air inside the cellular structure and reduce the heat transfer by conduction. The good thermal insulation of polyurethanes makes them suitable for applications requiring temperature control, energy efficiency and thermal comfort [4].

4.Thermal stability- polyurethanes are generally stable at moderate temperatures. Their exposure to high temperature can cause degradation and decomposition. The thermal stability of polyurethane explains that for how much time it is in position of use and predicts their long-term performance.

5.Thermal expansion- the property of thermal expansion of polyurethanes is essential in applications where dimensional stability is important like precise engineering and molding. Thermal expansion depends on factors like density, chemical structure and cross-linking density of the materials [5].

Flame retardancy-

To make the polyurethanes suitable for applications requiring fire safety and resistance, like building materials, electronics and transportation.

Inherent Flammability- Polyurethanes are flammable due to the presence of carbon hydrogen, and oxygen atoms in their structure. When exposed to heat or flames, they can ignite and sustain combustion, releasing heat, smoke and toxic gases.

Flame retardant additives are incorporated into polyurethanes to reduce their inflammability and inhibit the spread of the fire. For example- char formation, gas phase quenching and endothermic reactions [6].

Mechanisms of additives-

- **Char Formation**- when polyurethanes are exposed to heat then some of flame reactants promote the formation of protective char layer. This char layer acts as a barrier, insulating the material and reduces the release of combustible gases.
- **Gas phase Quenching-** the flame retardants act in gas phase by interfering with the chemical reactions involved in combustion, like free radical inhibition. And this reduces the availability of combustible gases and slows down flame propagation.
- **Endothermic reactions**-
  To suppress the flame spread and to reduce the temperature rise during combustion some of the retardants undergo endothermic reactions by absorbing heat and cooling the material.

Biocompatibility of polyurethanes-

Biocompatibility is the ability of material to perform in contact with living tissues without harming. Polyurethanes offer wonderful biocompatibility and versatility for a wide range of medical and biomedical applications, contributing to progress in the field of healthcare, diagnostics, and regenerative medicines.

Measure of biocompatibility of polyurethanes makes them suitable for medical and biomedical applications.

Medical devices made up of polyurethanes are catheters, orthopedic implants, wound dressings, vascular grafts and pacemaker leads.

Polyurethanes provide a versatile platform for designing biomaterials with tailored properties to interact with biological tissues. Biomedical applications of polyurethanes include tissue engineering, drug delivery system, and regenerative medicine.

(Halima Khatoon and Sharif Ahmad, July 19, 2018)

Biostability- The good biostability of polyurethanes resists its degradation from enzymatic, oxidative and hydrolytic processes. Biostability is a great feature in polyurethane biocompatibility as it checks that material remains stable and does not degrade or does not have any adverse reactions on getting contact with biological fluids or tissues.

Cell compatibility- The surface chemistry of polyurethanes can be made to promote specific cellular responses and tissue regeneration. Polyurethane biomaterials can support cell attachment, proliferation, and differentiation, making them suitable for cell culture and tissue engineering applications.

Thermal conductivity of polymers

Generally polyurethane materials have very low thermal conductivity. Thermal conductivity of polyurethane foams ranges from 0.015 to 0.030 W/ (m.k) for rigid foams and for flexible foams it lies between 0.25 to 0.35 W/(m/.k).

The thermal conductivity of polyurethanes depends on factors namely temperature, environmental conditions, density, structure, moisture content, and formulation.

(Javier Carlos Quagliano Amado)

Due to low thermal conductivity of polyurethanes, they have many applications where it is used as insulating material but due to low thermal conductivity it also lacks in many areas. So, to enhance the thermal conductivity of polyurethanes additives are used [7].

CHAPTER-3

Additives in polyurethanes to enhance thermal conductivity

To enhance thermal conductivity additives are incorporated into polyurethanes which makes them more effective in application and improves the performance in applications where heat transfer is required. Catalyst addition is typically necessary for the reaction between PUR raw ingredients. The catalyst can speed up the isocyanate–water reaction (blowing catalyst), the isocyanate–polyol reaction (crosslinking or gelling catalyst), or both, depending on its profile.

(Figure 3.1) Polyurethanes additives **Figure 3.2 types of polyurethanes**

Reasons to choose additives to increase thermal conductivity of polyurethanes are-

1. Improves Energy efficiency- By using additives to enhance thermal conductivity of polyurethanes gives better thermal performance, reduce energy consumption, and operating and maintenance expenditures.

2. Enhance heat dissipation- on increasing thermal conductivity of polyurethanes through additives, heat can be transferred more effectively away from heat generating components which improves overall system performance and reliability. In applications like electronic devices, automotive components and thermal management systems, efficient heat dissipation is crucial to prevent overheating and maintain optimal operating temperatures.

3. Increased Heat transfer rate- the faster heat transfer is enabled by the additives to enhance thermal conductivity of polyurethanes which results in reducing thermal resistance and improves overall system performance.

4. Optimized Heat Transfer rate- Additives can be used to increase thermal properties of polyurethanes to meet specific thermal management requirements, ensuring efficient heat transfer and temperature control. Thermal management is important in various industries like heat exchangers, HVAC systems, and thermal interface materials.

5. Expanded Application Capabilities- material with enhanced thermal conductivity can be utilized in new emerging technologies, such as advanced electronics, renewable energy systems and high-performance insulations. By improving the thermal conductivity by additives can also increase the range of applications of where polyurethane materials can be used.

6. Customization and Optimization- Additives customize and optimize the polyurethane formulations to meet specific thermal requirements and performance objectives. By selecting and accorporating the appropriate additives manufacturers can match the thermal properties of polyurethanes to suit the need of diverse applications, industries, and operating conditions.

Additives to enhance thermal conductivity of polyurethanes -

The additives are chosen based on their ability to improve heat transfer within the material and requirement of material according to applications. Lewis bases and tertiary amines, as well as organic metal complexes such as dibutyltin dilaurate and other metal catalysts, are commonly used as catalysts. The trimerization of the isocyanate group and the urethane process are both catalyzed by alkali metal salts of organic acids.

The following are examples of additional additives that are typically used with the polyol component:

Foam stabilizers; blowing agents; hydrolysis stabilizers; flame retardants; antioxidants; UV stabilizers; color pastes; fillers [3].

The additives used to enhance thermal conductivity of polyurethanes are-

Carbon fillers-

By generating conductive networks, improving interfacial contact, enabling phonon transit, offering thermal bridging, and perhaps cooperating with other additives, carbon fillers are essential for raising the thermal conductivity of polyurethanes. When combined, these mechanisms enhance heat transfer characteristics and qualify carbon-filled polyurethanes for uses that demand effective heat dissipation and thermal management [8].

- **Inherent thermal conductivity-**
  Because carbon atoms form strong covalent bonds, carbon-based materials have high heat conductivity by nature. Because of its layered structure, graphite, for instance, has a high conductivity, while carbon nanotubes (CNTs) have a remarkable thermal conductivity along their length.
- **Formation of conductive networks-**
  . Carbon fillers create conductive networks or routes across a polyurethane matrix when they are included into the material. These networks give thermal energy constant paths to follow as it moves from one place to another, facilitating the efficient transmission of heat [9].

- **Interfacial contact enhancement-**
  Due to their wide surface area and high aspect ratio, carbon fillers can make intimate contact with the polymer matrix. By facilitating heat transmission between the polymer chains and the carbon filler particles, this improved contact lowers interfacial thermal resistance and raises thermal conductivity overall.
- **Phonon Transport-**Carbon nanotubes (CNTs) are examples of carbon fillers that effectively transfer heat through materials using quantum mechanical vibrations called phonons. The carbon filler structures allow phonons to propagate, which speeds up heat transmission inside the polyurethane matrix.
- **Thermal Bridging-**
  Examples of carbon fillers that efficiently transmit heat through materials via phonons—quantum mechanical vibrations—are carbon nanotubes (CNTs). The polyurethane matrix's internal heat transfer is accelerated by the phonons that can travel through the carbon filler structures [7].

Figure 3.3 Graphite

Graphite

Graphite acts as an effective additive in polyurethanes to enhance thermal conductivity by forming conductive pathways, reducing interfacial thermal resistance, promoting particle, interactions, and optimizing particle orientation and dispersion within the polymer matrix. This mechanism fills the graphite in polyurethanes suitable for applications requiring efficient thermal management and heat dissipation [10].

- **High intrinsic thermal conductivity-** graphite acts as highly thermally conductive material in its pure form. The high intrinsic thermal conductivity of graphite stems from its crystalline structure, which allows heat to be efficiently transferred through the material via phonon vibrations.
- **Formation of conductive pathways-** Graphite particles that are scattered throughout a polyurethane matrix create conductive pathways that let heat move through the substance. These channels facilitate the transfer of heat energy between channels with low resistance, hence it raises the overall thermal conductivity of polyurethane.

- **Interfacial thermal resistance reduction-**
  In the polyurethane matrix, graphite particles can also lessen the interfacial heat resistance between adjacent polymer chains. Graphite contributes to the reduction of thermal resistance at interfaces by fostering improved thermal contact and interaction between the filler and polymer matrix, therefore improving heat transfer within the material.

- **Multiple particles contact points-**

  Through direct phonon interactions, graphite particles in polyurethane formulations establish several points of contact with neighboring particles, resulting in effective thermal energy transfer. This process raises the possibility of heat transfer between particles and enhances thermal conductivity overall.

- **Orientation and dispersion control-**

  It is possible to increase the efficiency of graphite particles in improving thermal conductivity by optimizing their orientation and distribution within the polyurethane matrix. The continuous conductive pathways throughout the material are ensured by the proper dispersion and alignment of graphite particles, which improves thermal performance.

Figure 3.4 Aluminum powder

Aluminum Powder

It enhances the thermal conductivity of polyurethanes by dispersing the matrix, forming conductive bridges, enhancing particle contact, acting as a heat sink and potentially synergizing with other additives. These mechanisms improve heat transfer properties and make polyurethane suitable for different applications [11].

- **High intrinsic thermal conductivity-**
  Aluminum has exceptional thermal conductivity qualities that enable heat to go through the material quickly in comparison to many other materials.
- **Particle Dispersion**
  Particles of aluminum are distributed throughout the substance when powdered aluminum is mixed with a polyurethane matrix. These particles facilitate the passage of thermal energy from one location to another by making channels for heat transfer inside the polyurethane matrix.
- **Conductive bridges-**

Conductive links between adjacent polymer chains are created by aluminum particles within the polyurethane matrix. By decreasing thermal resistance inside the material and offering direct paths for heat conduction, these bridges facilitate efficient thermal energy transfer.

- **Enhanced particle contact**-
  Because of their high surface area to volume ratio, aluminum particles are better able to contact the polymer matrix and with one another. By lowering interfacial thermal resistance inside the material, improved particle interaction boosts thermal energy transfer efficiency.
- **Effective heat sink-**
  Within the polyurethane matrix, aluminum particles function as efficient heat sinks, absorbing and dispersing thermal energy away from heat sources. This characteristic keeps the material's temperature distribution consistent and helps avoid localized overheating.
- **Synergistic Effects-**
  To further improve polyurethanes' thermal conductivity, aluminum powder can be used with additional materials like graphite or carbon nanotubes to provide synergistic effects. Combining various additives can enhance overall thermal performance and maximize heat transfer characteristics [12].

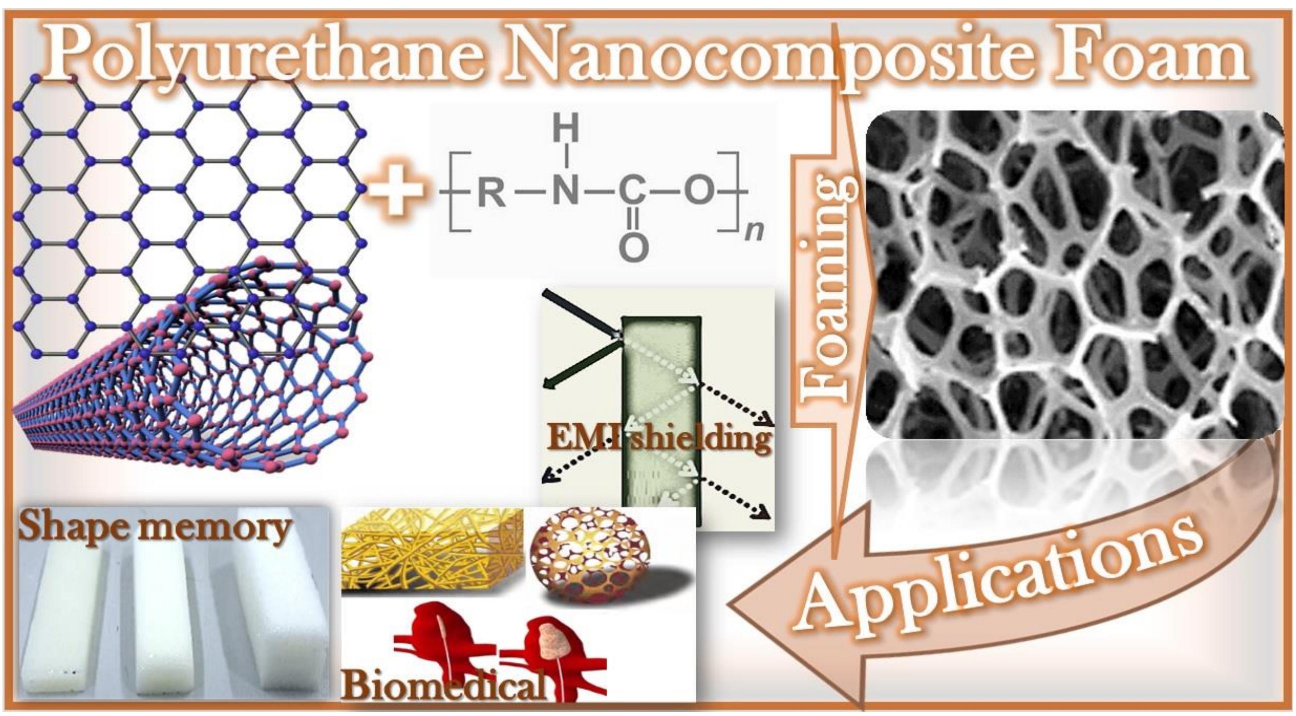

Figure 3.5 polyurethane nanocomposite foam

Carbon nanotubes

Due to the unique structure and exceptional thermal properties carbon nanotubes are highly effective additives for enhancing thermal conductivity of polyurethanes. The collective mechanisms to improve thermal conductivity of polyurethanes for required in applications are forming conductive networks, bridging polymer chains, enhancing contact, scattering phonons, and potentially synergizing with other additives [8].

Intrinsic High Thermal conductivity-

The axial orientation of carbon nanotubes has exceptionally high inherent heat conductivity. This characteristic, which enables effective phonon transport, results from the ordered arrangement of atoms inside the nanotube structure and the strong covalent bonds that bind carbon atoms together.

Network Formation-

Carbon nanotubes may create a three-dimensional network, or percolation structure, when they are scattered inside a polyurethane matrix. This network facilitates the flow of thermal energy from one place to another by establishing continuous channels for heat transfer throughout the material.

Bridging effect-Within the polyurethane matrix, carbon nanotubes function as links between polymer chains. Effective heat transmission down the length of the nanotubes is made possible by the strong van der Waals interactions between the nanotubes and polymer chains, which reduces thermal resistance inside the material.

Contact Enhancement-

Due to their vast surface area and high aspect ratio, carbon nanotubes may interact strongly and intimately with nearby polymer chains and other nanotubes. Because of the decreased interfacial thermal resistance inside the material, this improved contact boosts the efficiency of heat transmission.

Phonon scattering-

The main thermal energy carriers, phonons, can be scattered by carbon nanotubes. The effective conduction of heat and transmission of thermal energy throughout the material is facilitated by phonon scattering at the interfaces between the nanotubes and the surrounding polymer matrix.

Synergistic Effects-

Combining carbon nanotubes with additional additives, such metallic nanoparticles or graphene, can have a synergistic impact and improve polyurethanes' thermal conductivity even more. The total thermal performance can be enhanced, and heat transfer qualities optimized by combining various additives [13].

Metallic nanoparticles (gold, silver and platinum)-

To improve polyurethanes' thermal conductivity and equip them for a variety of applications requiring good heat dissipation, such as thermal interface materials, electronic packaging, and heat exchangers, gold, silver, and platinum nanoparticles are useful additions [8].

- **High Intrinsic thermal conductivity**

Because electrons may freely travel throughout the metal lattice, metallic nanoparticles have a high intrinsic heat conductivity. Dispersed across a polyurethane matrix, these nanoparticles function as conduits for effective heat transmission.

- **Increased Particle-Polymer Interface-**
  The polyurethane matrix's surface area and particle-polymer contact are both enhanced by the inclusion of metallic nanoparticles. Better thermal interaction between the metal nanoparticles and the polymer matrix is made possible by this improved interface, which improves thermal conductivity.
- **Percolation Network Formation-**Metallic nanoparticles can percolate into the polyurethane matrix at certain amounts. The material's thermal conductivity is greatly increased because of the network's creation of heat conduction channels.
- **Size and Shape Effects-**

  The impact of metallic nanoparticles on thermal conductivity enhancement might vary depending on their size and form. Smaller or more asymmetrical nanoparticles (such as nanowires or nanosheets) may have better heat conductivity because of less phonon scattering and more phonons mean free pathways.

- **Synergistic Effects-**

  Combining metallic nanoparticles with other additions, such graphene or carbon nanotubes, can improve heat conductivity and have synergistic benefits. The polyurethane matrix's hierarchical network structure may be optimized for heat transmission channels by combining the presence of several nanoparticle kinds.

- **Surface Functionalization-**

  Metallic nanoparticles can be functionalized or have their surfaces altered to enhance their dispersion and compatibility within the polyurethane matrix. Additionally, surface treatments can minimize interfacial thermal resistance and increase thermal conductivity by encouraging improved adherence to the polymer matrix [14].

Phase Change Materials- (Paraffin wax, Fatty acids)

While PCMs by themselves do not directly improve polyurethanes' thermal conductivity, their incorporation into polyurethane-based materials can have positive effects on the management and storage of thermal energy, which can help polyurethanes perform better in a variety of thermal applications [15].

- **Thermal energy storage-**

When a solid changes into a liquid or vice versa, PCMs may absorb or release significant quantities of thermal energy while keeping the temperature almost constant. PCMs can store thermal energy when they are integrated into polyurethane matrices. This may aid in reducing temperature variations inside the material.

- **Heat transfer Enhancement-**
  PCMs can improve overall thermal management in systems that employ polyurethanes, even though they may not directly increase the thermal conductivity of polyurethanes. PCMs can assist in preserving a more stable temperature environment by collecting excess heat at high temperatures and releasing it during low
- **Composite Structure-**
  Together with polyurethanes, PCMs can be included in different types of composite constructions or enclosed within microcapsules. The dispersion of PCMs, the thermal conductivity of encasing materials, and the interaction between the PCM and polyurethane matrix can all have an impact on the overall system's thermal conductivity.
  (Weihua Li1, a, Jinfeng Mao 1， b, Lijun Wang1,c, Luyan Sui1, d, 2011-11-22)

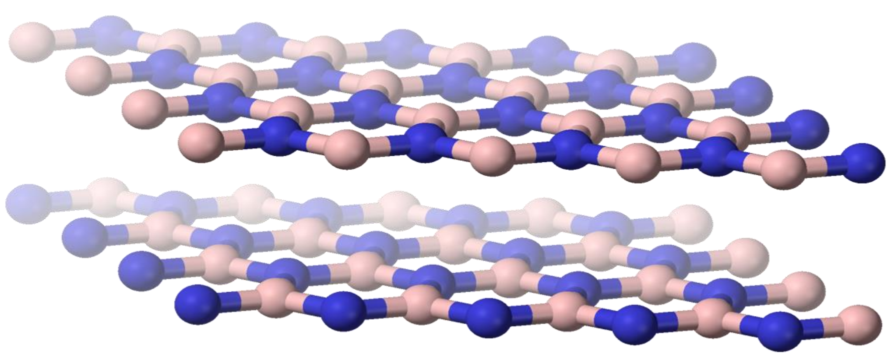

Figure 3.6 Boron nitride nanoparticles

Boron Nitride nanoparticles

For a variety of applications needing good heat dissipation, including thermal interface materials, electronic packaging, and heat exchangers, boron nitride nanoparticles work well as additives to polyurethanes to increase their thermal conductivity [11].

Intrinsic thermal conductivity- The thermal conductivity of metal oxides is often greater than that of polymers. Metal oxide nanoparticles' intrinsic thermal conductivity allows them to function as heat transfer channels when they are scattered inside a polyurethane matrix.

- **Particle-Polymer Interface-**
  The surface area and contact between the metal oxide nanoparticles and the polyurethane matrix are both increased by their inclusion. Better thermal interaction between the metal oxide nanoparticles and the polymer matrix is made possible by this improved interface, which improves thermal conductivity.
- **Percolation Network Formation-**
  Metal oxide nanoparticles can percolate into the polyurethane matrix at certain quantities. The material's thermal conductivity is greatly increased because of the network's creation of heat conduction channels [16].

- **Size and shape effects-** The impact of metal oxide nanoparticles on thermal conductivity enhancement might vary depending on their size and form. Smaller or differently shaped nanoparticles may have higher heat conductivity because of their enhanced phonon, which means free pathways and less phonon scattering.
- **Synergistic effects-**
  To maximize thermal conductivity, metal oxide nanoparticles can be combined with additional additives like conductive polymers or carbon fillers to provide synergistic effects. The polyurethane matrix's hierarchical network structure may be optimized for heat transmission channels by combining the presence of several nanoparticle kinds.
- **Surface functionalization-**
  Metal oxide nanoparticles can be functionalized or have their surfaces altered to enhance their dispersion and compatibility within the polyurethane matrix. Additionally, surface treatments can minimize interfacial thermal resistance and increase thermal conductivity by encouraging improved adherence to the polymer matrix [17].

Figure 3.7 ceramic fillers

Ceramic fillers (alumina, silica)

Ceramic fillers are useful additives that improve the thermal conductivity of polyurethanes. This property makes the materials appropriate for a range of applications that need efficient heat dissipation, including heat exchangers, electronic packaging, and thermal interface materials.

The mechanism of ceramic fillers enhancing thermal conductivity of polyurethanes-

- **High intrinsic thermal conductivity**-
  In comparison to polymers, ceramic materials like silica (SiO_2) and alumina (Al_2O_3) have a higher intrinsic heat conductivity. Ceramic fillers, when incorporated into a polyurethane matrix, offer effective heat transmission channels.
- **Particle polymer interface enhancement-**
- The addition of ceramic fillers increases the surface area and interface between the filler particles and the polyurethane matrix. This enlarged interface facilitates better thermal coupling between the ceramic nanoparticles and the polymer matrix, thereby improving thermal conductivity.

- **Percolation network formation**-
  A percolation network inside the polyurethane matrix can be formed by ceramic fillers at certain concentrations. The material's thermal conductivity is greatly increased because of the network's creation of heat conduction channels.
- **Size and shape effects-**

  The effects of ceramic nanoparticles on thermal conductivity increase are mostly dependent on their size and structure. Because of their smaller size and more phonons means free pathways, smaller or specially shaped nanoparticles (such nanowires or nanosheets) may have better heat conductivity.

- **Synergistic effects-**

  Combining ceramic fillers with additional additives, such metallic nanoparticles or carbon fillers, can improve heat conductivity and have synergistic benefits. The polyurethane matrix's hierarchical network structure may be optimized for heat transmission channels by combining the presence of several nanoparticle kinds.

- **Surface functionalization-**

Ceramic nanoparticles can be functionalized or have their surfaces altered to enhance their dispersion and compatibility in the polyurethane matrix. Additionally, surface treatments can minimize interfacial thermal resistance and increase thermal conductivity by encouraging improved adherence to the polymer matrix [9].

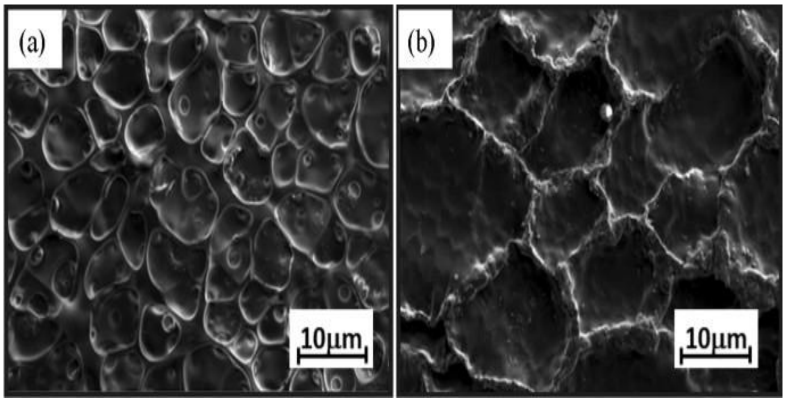

Figure 3.8 Polymer blends

Polymer blends

By mixing different polymers with complimentary qualities and adding nanofillers, polymer blends provide a flexible way to increase the thermal conductivity of polyurethanes. This results in materials with better thermal performance for a range of uses.

Example of polymer blends-

Polyester polyol and 2,4-toluene diisocyanate reacted to form the polyurethane prepolymer, which was subsequently end-capped with phenol. By using 3,30 diamino 4, 40-dihydroxy biphenyl and 2,20-bis(3,4-dicarboxyphenyl) hexafluoro propane dianhydride, soluble polyamide was created in two steps [18].

- **Combining polymers with varying thermal conductivity-**

Blends of polymers are mixtures of two or more polymers with various thermal conductivities. The blend can have better total thermal conductivity than the separate components by choosing polymers with complimentary qualities, such as one with strong thermal conductivity and another with good compatibility with polymers.

- **Synergistic effects-** When two polymers are combined, their synergistic interactions can improve thermal conductivity above and beyond what would be predicted from a straightforward linear combination of their individual characteristics. Improved interfacial contact between the polymer phases, which promotes more effective heat transmission, may be the cause of this synergy.

- **Interfacial engineering-**
  Thermal conductivity may be maximized by engineering the blend's interface between the various polymer phases. To increase heat transmission between the polymer phases, surface alterations or compatibilizers can be utilized to lower interfacial thermal resistance and increase interfacial adhesion.
- **Nanocomposite polymer blends-**
  The addition of nanofillers, such graphene or carbon nanotubes, to polymer blends can improve heat conductivity even further. These nanofillers' high aspect ratio and strong intrinsic thermal conductivity open more channels for heat conduction inside the mix, which improves its thermal characteristics.
- **Tailored Formulations for specific applications-**
  Blends of polymers enable the creation of materials with customized thermal characteristics to fulfill the demands of certain uses. The thermal conductivity of the resultant polyurethane composite may be improved for uses like heat exchangers or thermal management in electronics by modifying the blend's composition and production conditions [13].

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Figure 3.9 Functional additives

Functional Additives

They are also very useful in polyurethanes to enhance thermal conductivity.

1.Surfactants- Better heat conductivity can result from surfactants' ability to enhance the dispersion of filler or nanoparticles inside the polyurethane matrix.

2. Dispersants- Dispersants ensure a more uniform distribution throughout the polyurethane matrix and improve heat conductivity by preventing the aggregation of filler particles or nanoparticles.

3. Compatibilizers- Compatibilizers facilitate better adhesion and decrease interfacial resistance between the various polyurethane composite components, improving heat conductivity in the process.

4.Cross linking agents- To create a more rigid structure that promotes heat transmission and enhances thermal conductivity, cross-linking agents raise the cross-link density of the polyurethane matrix.

5.Surface modifiers- Surface modifiers alter the filler particles' or nanoparticles' surface characteristics to improve interfacial bonding and compatibility with the polymer matrix, both of which increase heat conductivity.

6.Chain Extenders- Further polymer chain development is carried out with the help of chain extenders, which results in larger molecular weight polymers with better heat conductivity.

7.Functionalized fillers- To improve their compatibility with the polymer matrix and interfacial interactions, fillers or nanoparticles can be surface-functionalized with certain groups or molecules, which will increase heat conductivity.

Mechanism of functional additives used to enhance thermal conductivity of polyurethanes-

High thermal conductivity fillers- The polyurethane matrix is combined with functional additions like copper, silver, boron or aluminum nitride particles. Because of their high thermal conductivity, these fillers help the material's internal heat transmission [19].

Particle dispersion- To improve heat conductivity, fillers must be evenly distributed throughout the polyurethane matrix. Heat must be able to pass through the material effectively and unhindered by agglomerates or inadequate filler-matrix interactions. This is ensured by effective dispersion.

Enhanced Interfacial Contact- Strong interfacial adhesion can be promoted by surface treatments or chemical changes of fillers that enhance their compatibility with the polyurethane matrix. By decreasing thermal resistance at the filler-matrix contact, this improves thermal conductivity.

Multifunctional Additives- Certain additives provide mechanical strength or flame retardancy in addition to improving thermal conductivity. It is possible to achieve the required degree of heat conductivity and enhance overall performance by including multifunctional additives.

Optimized Formulation- To obtain the appropriate balance of qualities in the polyurethane formulation, the additives are carefully chosen and combined. To increase thermal conductivity without sacrificing other crucial properties of the material, factors including filler loading, particle size, and compatibility with other components are tuned.

Processing Techniques- The dispersion and orientation of fillers within the polyurethane matrix can be influenced by the processing techniques chosen, such as melt compounding or solution blending, which can ultimately alter the product's thermal conductivity.

Synergistic Effects- Adding more additives or combining additives with the polyurethane matrix can have synergistic effects that increase heat conductivity beyond what would be possible with just one addition working alone [20]

CONCLUSION-

IN summary, we investigated the complex field of adding additives to polyurethanes to improve their thermal conductivity. We have learned a great deal about the processes behind the improvement of heat conductivity in polyurethane composites by an extensive inquiry that covered synthesis methods, characterization techniques, processing strategies, and practical applications. It has been demonstrated that adding additives such metal powders, boron and aluminum nitride, graphene, carbon nanotubes, and nanostructured materials may greatly enhance the thermal characteristics of polyurethane materials. Through deliberate dispersion of these chemicals within the polyurethane matrix and optimization of interfacial interactions, scientists have developed materials possessing heightened capacities for heat transmission. As a result, this dissertation has clarified the significance of additives in raising polyurethanes' thermal conductivity and laid the groundwork for further developments in this fascinating and quickly developing topic. Researchers may create polyurethane materials with previously unheard-of thermal characteristics by utilizing additives, opening the door to creative solutions for the challenging problems of the twenty-first century.

References

[1] H. W. Engels et al., “Polyurethanes: Versatile materials and sustainable problem solvers for today’s challenges,” Angewandte Chemie - International Edition, vol. 52, no. 36. pp. 9422–9441, Sep. 02, 2013. doi: 10.1002/anie.201302766.

[2] S. Ahmad, “Polyurethane: A Versatile Scaffold for Biomedical Applications,” Significances of Bioengineering & Biosciences, vol. 2, no. 3, Jul. 2018, doi: 10.31031/sbb.2018.02.000536.

[3] G. Avar, U. Meier-Westhues, H. Casselmann, and D. Achten, “10.24 - Polyurethanes,” in Polymer Science: a Comprehensive Reference: Volume 1-10, vol. 1–10, Elsevier, 2012, pp. 411–441. doi: 10.1016/B978-0-444-53349-4.00275-2.

[4] J. Carlos Quagliano Amado, “Thermal Resistance Properties of Polyurethanes and Its Composites,” in Thermosoftening Plastics, IntechOpen, 2020. doi: 10.5772/intechopen.87039.

[5] Y. M. Ha et al., “Enhanced thermal conductivity and mechanical properties of polyurethane composites with the introduction of thermally annealed carbon nanotubes,” Macromol Res, vol. 25, no. 10, pp. 1015–1021, Oct. 2017, doi: 10.1007/s13233-017-5139-0.

[6] F. Valipour, S. F. Dehghan, and R. Hajizadeh, “The effect of nano- and microfillers on thermal properties of Polyurethane foam,” International Journal of Environmental Science and Technology, vol. 19, no. 1, pp. 541–552, Jan. 2022, doi: 10.1007/s13762-021-03150-3.

[7] A. Navidfar and L. Trabzon, “Analytical modeling and experimentally optimizing synergistic effect on thermal conductivity enhancement of polyurethane

nanocomposites with hybrid carbon nanofillers," Polym Compos, vol. 42, no. 2, pp. 944–954, Feb. 2021, doi: 10.1002/pc.25877.

[8] S. A. Abdullah, L. Frormann, and A. Saleem, "Thermal and electrical conductivities of carbon fibers and carbon nanotubes incorporated polyurethanes composites," in Key Engineering Materials, Trans Tech Publications Ltd, 2010, pp. 349–355. doi: 10.4028/www.scientific.net/KEM.442.349.

[9] V. A. Nieberlein, "Thermal Conductivity Enhancement of Epoxies by the Use of Fillers," 1978.

[10] Z. Luo, J. Yan, and D. Chen, "Preparation of functionalized graphene/thermal conductive polyurethane films," in Journal of Physics: Conference Series, IOP Publishing Ltd, Jan. 2021. doi: 10.1088/1742-6596/1759/1/012020.

[11] S. Akkoyun and M. Akkoyun, "Improvement of thermal conductivity of rigid polyurethane foams with aluminum nitride filler," Cellular Polymers, vol. 40, no. 2, pp. 87–98, Mar. 2021, doi: 10.1177/0262489321988970.

[12] A. Alshaikhi and G. P. Srivastava, "Role of additives in enhancing the thermal conductivity of AlN ceramics," J Phys D Appl Phys, vol. 41, no. 18, Sep. 2008, doi: 10.1088/0022-3727/41/18/185407.

[13] L. Jarosinski, A. Rybak, K. Gaska, G. Kmita, R. Porebska, and C. Kapusta, "Enhanced thermal conductivity of graphene nanoplatelets epoxy composites," Materials Science-Poland, vol. 35, no. 2, pp. 382–389, 2017, doi: 10.1515/msp-2017-0028.

[14] Z. Lu, Y. Wang, and X. Ruan, "The critical particle size for enhancing thermal conductivity in metal nanoparticle-polymer composites," J Appl Phys, vol. 123, no. 7, Feb. 2018, doi: 10.1063/1.5014987.

[15] W. Li, J. Mao, L. Wang, and L. Sui, "Effect of the additive on thermal conductivity of the phase change material," in Advanced Materials Research, 2012, pp. 1302–1306. doi:

10.4028/www.scientific.net/AMR.399-401.1302.
[16] W. Zhou, S. Qi, Q. An, H. Zhao, and N. Liu, "Thermal conductivity of boron nitride reinforced polyethylene composites," Mater Res Bull, vol. 42, no. 10, pp. 1863–1873, Oct. 2007, doi: 10.1016/j.materresbull.2006.11.047.
[17] S. Quiles-Díaz et al., "Enhanced Thermal Conductivity in Polymer Nanocomposites via Covalent Functionalization of Boron Nitride Nanotubes with Short Polyethylene Chains for Heat-Transfer Applications," ACS Appl Nano Mater, vol. 2, no. 1, pp. 440–451, Jan. 2019, doi: 10.1021/acsanm.8b01992.
[18] R. K. Mishra, J. Abraham, N. Kalarikkal, K. Jayanarayanan, K. Joseph, and S. Thomas, "Conducting Polyurethane Blends: Recent Advances and Perspectives," in Polyurethane Polymers: Blends and Interpenetrating Polymer Networks, Elsevier Inc., 2017, pp. 203–231. doi: 10.1016/B978-0-12-804039-3.00008-7.
[19] M. S. A. Rahim, I. Ismail, S. B. Choi, W. H. Azmi, and S. N. Aqida, "Thermal conductivity enhancement and sedimentation reduction of magnetorheological fluids with nano-sized Cu and Al additives," Smart Mater Struct, vol. 26, no. 11, Oct. 2017, doi: 10.1088/1361-665X/aa8d8f.
[20] Y. Xu and D. D. L. Chung, "Increasing the thermal conductivity of boron nitride and aluminum nitride particle epoxy-matrix composites by particle surface treatments," Compos Interfaces, vol. 7, no. 4, pp. 243–256, 2000, doi: 10.1163/156855400750244969.