A REACTIVE CORE-SHELL NANOPARTICLES SYNTHESIS, PROPERTIES AND APPLICATIONS IN RUBBER MATERIALS

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Abstract

This review article provides a concise overview of the utilization of reactive core-shell nanoparticles in polymer materials. The unique core-shell structure of these nanoparticles offers improved compatibility, dispersion, and controlled release within the polymer matrix. The incorporation of reactive core-shell nanoparticles has demonstrated significant enhancements in the mechanical properties of polymers, such as increased strength and toughness. Moreover, the ability to tailor the surface functionality enables precise control over thermal stability, flame retardancy, electrical conductivity, and optical properties. The review also highlights the importance of optimizing interfacial interactions and discusses potential applications in emerging fields. Overall, this review emphasizes the significant contributions of reactive core-shell nanoparticles in advancing the properties and performance of polymer materials.

KEYWORDS**:** Reactive core-shell nanoparticles; polymer composites; mechanical properties; applications.

1. Introduction

Over the past century, it has become increasingly evident that small entities possess not only beauty but also remarkable power. As a result, nanotechnology has emerged as a promising frontier in the realm of science and technology, heralding a new era of advancement. The concept of nanotechnology was initially brought to the forefront by Nobel laureate Richard P. Feynman during his renowned lecture at the California Institute of Technology on December 29, 1959. In this seminal talk, Feynman proposed a range of potential nanomachines that could surpass the functional efficiency of existing manufactured devices by harnessing the unique behaviors exhibited by matter at the nanometer scale. It was in the 1970s that Norio Taniguchi first coined the term "nanotechnology," defining it as the manipulation, separation, consolidation, and deformation of materials at the atomic or molecular level. In the 1980s, another visionary, K. Eric Drexler, emphasized the technological significance of working at the nano scale. At this minuscule dimension, the properties of particles diverge significantly from those observed at larger scales, leading to unprecedented opportunities and possibilities for scientific exploration and technological innovation.

In recent years, the field of nanotechnology has revolutionized various industries by enabling the development of advanced materials with enhanced properties. Among the various nanomaterials, reactive core-shell nanoparticles have emerged as a promising class of materials with diverse applications in the realm of polymer materials [1]. These nanoparticles possess a unique structure where a reactive core is encapsulated within a shell, allowing for precise control over their properties and functionality. The integration of reactive core-shell nanoparticles into polymer materials has opened up new possibilities for tailoring the properties and performance of polymers, thereby expanding their application potential. These nanoparticles exhibit exceptional reactivity due to their high surface area, which arises from the large interface between the core and shell materials [2]. The core-shell structure enables the nanoparticles to selectively interact with the polymer matrix, leading to improved compatibility and interfacial adhesion, which are critical factors in enhancing the overall performance of polymer-based materials. One of the key advantages of using reactive core-shell nanoparticles is their ability to impart multifunctionality to polymer materials. By carefully selecting the core and shell materials, as well as incorporating functional groups or additives, these nanoparticles can introduce a wide range of desired properties into polymers, such as enhanced mechanical strength, thermal stability, electrical conductivity, flame retardancy, and optical properties [3, 4]. This tunability makes them highly versatile and adaptable for various applications across diverse industries. The applications of reactive core-shell nanoparticles in polymer materials are extensive and span several sectors. In the automotive industry, these nanoparticles can be utilized to develop lightweight and high-strength composites, leading to improved fuel efficiency and reduced environmental impact [5]. In the field of electronics, they can enable the fabrication of flexible and stretchable conductive films, which are crucial for the development of wearable devices and flexible displays. Additionally, in the realm of biomedical materials, reactive core-shell nanoparticles can be employed to enhance the biocompatibility and controlled drug release capabilities of polymers, opening up new avenues for drug delivery systems and tissue engineering. However, despite the significant progress made in the utilization of reactive core-shell nanoparticles in polymer materials, there are still challenges and considerations that need to be addressed [6, 7]. These include issues related to scalability, cost-effectiveness, long-term stability, and potential environmental impacts. Continued research and development efforts are required to overcome these hurdles and unlock the full potential of these nanoparticles in practical applications. Given the extensive literature on this topic, our review article specifically concentrates on the molecular design and experimental preparation methods of reactive core-shell nanoparticles. We delve into the intricate relationships between the nanoparticle structure and its resulting properties, while also highlighting the diverse applications of these synthesized materials. In particular, we showcase examples where the incorporation of reactive core-shell nanoparticles has demonstrated remarkable improvements in rubber materials, emphasizing their role in enhancing the performance and functionality of rubber composites.

2. Definition

The prefix "nano" denotes one billionth of a unit of time or length and originates from the Greek word "dwarf," signifying something small. In the conventional sense, a nano material is characterized by having at least one dimension less than 100 nm. When all three dimensions of a material are less than 100 nm, it is referred to as a nano particle. Nano particles hold significant scientific interest as they bridge the gap between bulk materials and atomic or molecular structures. While bulk materials typically exhibit consistent physical properties regardless of their size, this is often not the case at the nano scale. Nano particles display size-dependent properties, such as quantum confinement in semiconductor particles, surface plasmon resonance in certain metal particles, and superparamagnetism in magnetic nanoparticles. As a result, the synthesis of nanoparticles has become an intriguing research topic in recent years.

3. Approaches of synthesis

There are two main approaches for synthesizing nano materials: "Top Down" and "Bottom Up." The "Top Down" approach involves using traditional workshop or microfabrication methods, where external tools are employed to cut, mill, and shape materials into the desired form. Examples of "Top Down" techniques include lithographic techniques (such as UV, electron or ion beam, scanning probe, and optical near field), film deposition and growth, laser-beam processing, and mechanical techniques (such as machining, grinding, and polishing) [8, 9]. On the other hand, the "Bottom Up" approach relies on the chemical properties of single molecules to facilitate the self-assembly of individual components into a desired structure. This includes techniques such as chemical synthesis, laser-induced assembly (such as laser trapping), self-assembly, colloidal aggregation, and 2-photon confocal processing [10]. These approaches leverage the concept of molecular self-assembly, where the understanding and manipulation of the chemical and physical properties of nanoparticles are crucial. Currently, neither the top-down nor bottom-up approach is superior, as each has its own advantages and disadvantages. However, the bottom-up approach has a smaller inherent size limit compared to the top-down approach [11]. Additionally, the bottom-up approach has the potential to become more cost-effective in the future due to its ability to achieve absolute precision, complete process control, and minimal energy loss compared to the top-down approach. The top-down approach in synthesizing nano materials offers several advantages [12]. Scalability: The top-down approach is well-suited for large-scale production as it leverages existing manufacturing techniques and tools used in traditional industries. It allows for the fabrication of nano materials in bulk quantities, making it suitable for industrial applications. Precise Control: With the top-down approach, there is a high level of control over the size, shape, and arrangement of nano materials [13]. External tools and techniques can be used to precisely shape and manipulate materials, resulting in well-defined nano structures. Established Techniques:

The top-down approach often relies on established techniques and processes, such as lithography and microfabrication, which have been extensively developed and optimized over time [14]. This means there is a wealth of knowledge and expertise available to guide the fabrication process. Compatibility with Existing Technology: The top-down approach can be easily integrated into existing manufacturing processes and technologies. It allows for the incorporation of nano materials into existing devices and systems, enabling advancements in fields such as electronics, optics, and medicine without the need for complete reengineering [15]. Versatility: The top-down approach can be applied to a wide range of materials, including metals, semiconductors, polymers, and composites. This versatility allows for the fabrication of diverse nano structures with tailored properties for various applications. Well-Characterized Materials: The top-down approach often utilizes well-characterized starting materials, which can facilitate the understanding and control of the resulting nano structures [16]. This can be advantageous for applications that require specific material properties and performance. Overall, the top-down approach offers excellent control, scalability, and compatibility with existing technology, making it a valuable method for synthesizing nano materials for industrial applications.

4. Types of nanoparticle

Nanoparticles in the nanoscale dimension can be categorized into different groups: pure solid nanoparticles, composite or core-shell particles, and hollow particles. Solid nanoparticles are commonly encountered, while core-shell and hollow nanoparticles possess distinct characteristics. Core-shell nanoparticles consist of a core material with a concentric coating of a different material, depending on the intended application of the particles. These nanoparticles exhibit highly functional properties that differ from both the core and shell materials. The properties of the particles can be modified by changing the constituent materials or the core-to-shell ratio [17]. By coating the core particle with a shell material, the reactivity decreases, while thermal stability, overall particle stability, and dispersibility of the core particle increase. Core-shell materials are also economically advantageous, as precious materials can be coated onto inexpensive ones, reducing the consumption of precious materials compared to using pure materials of the same size [18]. If the core material can be removed through dissolution or calcination, the particle is transformed into a hollow nanoparticle. The core of reactive core-shell nanoparticles can take on different configurations, ranging from a single sphere (Fig. 1A) to an aggregation of multiple small spheres (Fig. 1B). Another intriguing possibility is the presence of a small sphere trapped within a hollow shell, resulting in a rattle-like or yolk-shell structure (Fig. 1E). Additionally, the shell structure can manifest as smaller spheres attached to a larger core sphere (Fig. 1C), allowing for diverse and intricate core-shell architectures. Complex core-shell structures can be achieved by incorporating multiple shells (Fig. 1E) or by combining various basic structures (Fig. 1D). In addition, reactive core-shell nanoparticles can exhibit reactive functional groups on their surface (Fig. 1G). This configuration introduces a new level of versatility, as the presence of these reactive groups enables further chemical modifications and interactions with the surrounding polymer matrix. By incorporating such reactive functionalities, the core-shell nanoparticles can actively participate in chemical reactions, leading to enhanced reactivity and tailored properties in the resulting polymer materials. Figure 1G illustrates the potential for surface functionalization, highlighting the exciting opportunities for expanding the scope of applications and functionalities of reactive core-shell nanoparticles in polymer composites. These versatile arrangements provide a rich array of possibilities for tailoring the properties and functionalities of reactive core-shell nanoparticles within polymer materials. [19, 20].

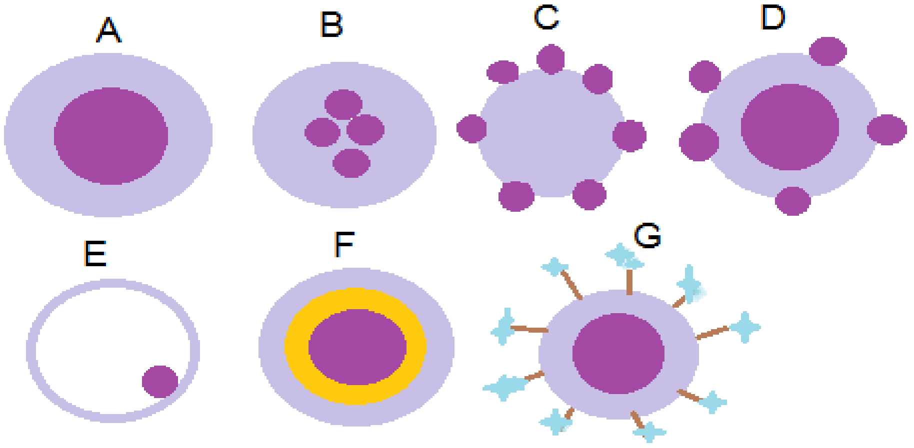

Fig 1. Schematic representation of different types of core–shell particles.

5. Classification of core-shell nanoparticles

Core-shell particles find diverse applications in various industrial fields, including biology, modern electronics, and the coating industry. However, classifying all core-shell materials based on their specific industrial applications can be challenging. Instead, we can categorize core-shell materials based on their material properties, considering whether the core or shell particles are composed of inorganic or organic materials. In this section, we will focus on discussing different types of composite (core-shell) particles and their industrial applications. Composite materials can be classified into four main groups based on their material properties: (i) inorganic-inorganic, (ii) organic-organic, (iii) inorganic-organic, and (iv) organic-inorganic core-shell materials. Fig. 2 illustrates these different types of core-shell materials [21 – 23].

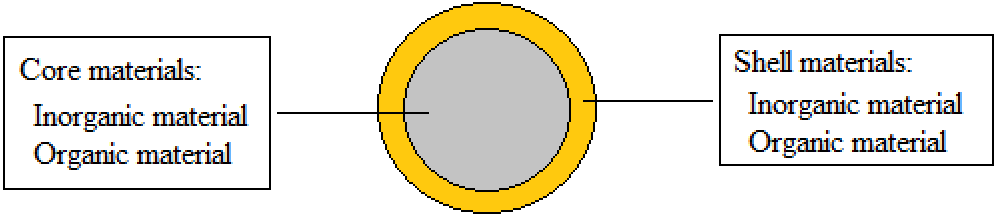

Fig 2. Types of cores and shells nanoparticles.

5.1 Organic-Inorganic core-shell material

These types of particles consist of a core made of organic or polymer material and a shell made of inorganic materials. The shell materials typically studied include metals, metal oxides, or silica. The incorporation of such inorganic coatings provides these particles with high resistance to corrosion and abrasion [24]. synthesized gold-coated polyurethane core-shell particles at the microscale for biocatalytic activity in pepsin digestion applications. Polymer cores with inorganic shell particles are also utilized in the synthesis of hollow particles **[25 – 28]**. Once the core-shell particles are formed, the core polymer can be easily removed either by using a suitable solvent or through calcination, resulting in hollow particles. The inorganic coating on the organic or polymer material enhances the colloidal stability of the core material [29].

5.2 Inorganic-organic core-shell nanoparticle

These types of particles are composed of a metal, metal oxide, or silica core, with a shell made of polymer or other organic materials. Polymer-coated inorganic particles have a wide range of applications, including catalysis, additives and pigments in paints, cosmetics, and inks [30]. In the field of biology, magnetic nanoparticles with polymer coatings are of particular interest. These particles are used for magnetic separation of biochemical products and cells, as well as for controlled drug release within the body [31]. Inorganic-organic composite particles with various functional groups on their surfaces are highly sought after for biological applications, as they can be easily tailored to serve as conjugates [32]. Polymer-coated nano silica particles enhance colloidal stability and are widely used in optical devices, sensors, and electrical devices [33]. Coating TiO_2 nanoparticles with cellulose improves the pigment properties of the particles. Polymer-coated inorganic particles also find applications in dentistry as brace materials and fillers [34].

5.3 Organic-Organic core-shell nanoparticle

In the case of these particles, both the core and shell are composed of polymers. Coating one polymer with another polymer modifies certain properties of the particle. For example, when polymethylmethacrylate (PMMA) is coated with antimony trioxide and polyvinyl chloride (PVC), it enhances the toughness and strength of the PVC material [35]. Similarly, when a polymer is coated with another polymer along with an inorganic salt, it can increase the thermal sensitivity and catalytic activity of the material [36].

5.4 Inorganic-inorganic core-shell nanoparticle

Among the all different types of core-shell nanoparticle inorganic-inorganic core-shell particles are most important. For these types of material both core and shells are made of inorganic materials as depicted in Fig. 3. These types of particle are widely used for commercial purpose mainly for improvement in semiconductor, catalyst, quantum dots, optical bioimaging, etc. Among the different inorganic-inorganic composite particles metallic core-shell particles are having more important. For these types of particles core and shell both are made of metal, metal oxide, semiconductor, any other inorganic compound, or silica.

Metal coated with silica core-shell particles have wide application in optical sensing and optical properties are changes with the silica thickness. modified the coating method to control uniform silica coating on nano silver (Ag) core particle [37]. synthesized silica coated gold particle and synthesized the silica coated Ag particles by sol-gel method and studied the different properties of those particles [38]. Silver/silica particles can be used in fluorescence imaging and again the region of emission is depends on the thickness of the silica [39]. Coating of Fe_2O_3 on MgO and CaO particles can enhance the capability of toxic material adsorption form the environment like SO_2 and H_2S compare to pure MgO and CaO [40]. Magnetic nanoparticle with different inorganic coating have lots of important, these types of particle used for magnetic resonance imaging (MRI) contrast agent, magnetic separation of oligonucleotides, and other biocomponents, and magnetically guided site specific drug delivery system [41]. Gold coating on any particle increases the chemical stability by protecting the core material from oxidation and corrosion and increased the biocompatibility and affinity via amine/thiol terminal groups [42].

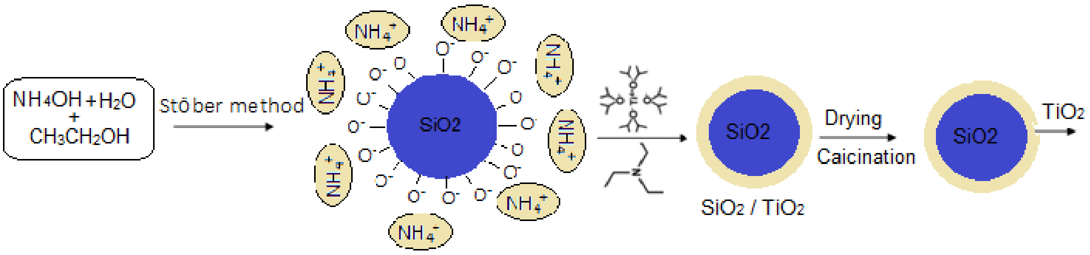

Fig 3. Nitrogen-doped SiO_2/TiO_2 inorganic-inorganic core-shell nanoparticles .

Among the different inorganic core-shell particles, semiconductor core-shell particles are most important. The core of these types of particles is made of either semiconductor material, semiconductor alloy and shell is made of metal, metal oxide or silica and in some case both core and shell are made of semiconductor material or semiconductor alloy [43]. These types of particle either binary with core and shell or tertiary i.e., core with double shell coating. The most common binary structures are well known as quantum dots are mainly core and shell are made of alloy material. These types of particles are used for luminescence and fluorescent bioimaging [44]. Another important inorganic core-shell particles, the core is made of one or more lanthanide group elements whereas, shell is made of silica or any other lanthanide group elements. This type of particles shows high luminescence and has a potential application in the field of electronics and bioimaging [45].

6. Importance of core-shell particles

Increasingly, there is a growing interest in the investigation of core-shell structured nanoparticles. These composite nanoparticles consist of cores and shells with different chemical compositions. They exhibit unique properties that combine the characteristics of diverse materials. This makes them highly attractive for various applications, especially when the surface functions can be tailored to meet specific requirements [46]. The properties of core-shell particles, in general, differ from those of the individual core and shell materials. Coating the core particle serves multiple purposes, such as surface modification, enhancing functionality, improving stability and dispersibility, and controlling the release of the core material. The presence of the shell material can alter core particle properties, including surface charge, functionality, and reactivity. Core-shell particles find wide-ranging applications in fields such as biomedical, pharmaceutical, catalysis, and electronics. In the biomedical field, core-shell particles are extensively utilized for bioimaging, controlled drug release, targeted drug delivery, cell labeling, and as replacements and supports for tissues [47]. They have diverse applications, including fluorescent diagnostic labels, catalysis enhancement, prevention of photo degradation, improvement of photoluminescence, creation of photonic crystals, and enhancement of chemical and colloidal stability [48].

6.1 Synthesis of core-shell particles

Classification of Synthesis Techniques for Core-Shell Particle Formation and Challenges in Achieving Uniform Coating. The synthesis techniques for core-shell particles can be categorized into two types based on the availability of the core particle. Firstly, core particles can be synthesized separately and then incorporated into the system for the coating of the shell material. Secondly, the core particles can be synthesized in situ within the reaction medium, followed by the coating of the shell material [49, 50]. In this review, the focus is on the synthesis of core-shell particles where the core particle is first synthesized in the reactor using suitable reagents. After the complete formation of the core, additional reagents are introduced to form the shell particle in situ [51, 52]. The core surface is modified to selectively deposit the shell material, resulting in the formation of the core-shell particles. The preparation of core-shell particles involves a multistep synthesis procedure, with a crucial step being the maintenance of uniform coating and control over the shell thickness. Various methods have been employed by different research groups for the synthesis of core-shell particles, including precipitation, polymerization , layer-by-layer adsorption techniques [53 – 58]. Despite several attempts by researchers to control the thickness and achieve uniform coating of the shell, it remains challenging. The main difficulties include agglomeration of core particles in the medium, the preferential formation of separate shell particles instead of coating the core, incomplete coverage of the core surface, and the inability to generalize a method for a wide range of materials. In recent years, achieving uniform coating with proper thickness for core-shell particle synthesis has become a challenging research topic. Overcoming these difficulties requires controlling the reaction rate and modifying the surface of the core particles to enable selective deposition of the shell material. Surface-active agents are commonly used by research groups for the purpose of core surface modification [59-61]. These surfactants or polymers can alter the surface charge and selectivity of the core particles, allowing for the selective deposition of the shell material and the formation of uniformly coated core-shell particles [62].

6.2 Mechanism of core-shell particle formation

Various methods are extensively employed for the formation of core-shell particles. Within these methods, the mechanisms of certain approaches have been thoroughly reviewed by different researchers. One example is the formation of organic-inorganic particles, as depicted in Fig. 4.

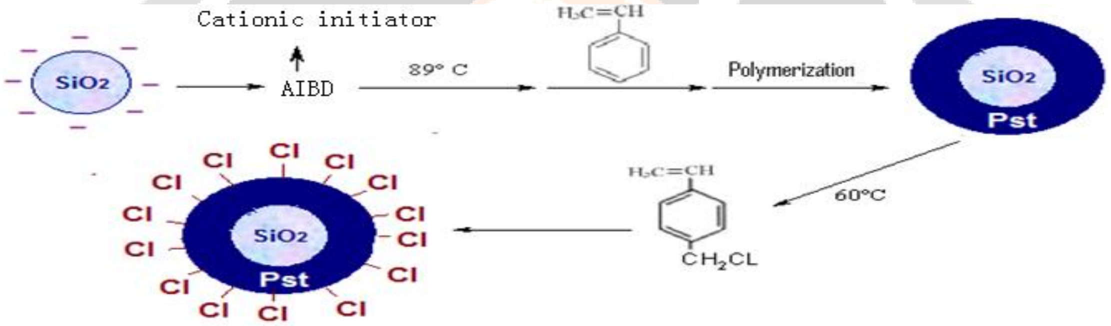

Fig 4. Schematic preparation of functional core/shell polymers [63].

6.2.1 Core synthesis

Core particles can be synthesized either in situ or separately and then incorporated into the reaction system. In the case of separate synthesis, the core particles are prepared independently and introduced into the reaction system as templates with surface modifiers. This allows for selective deposition of the shell material onto the template surface. The main advantage of external core particle synthesis is that the cores are obtained in a pure form with a lower possibility of impurities on their surface. However, in situ synthesis can pose a challenge as impurities from the reaction medium may become entrapped between the core and shell layers. Chemical precipitation reactions in microemulsions or bulk aqueous systems are commonly used techniques for the synthesis of inorganic core particles. The reduction of metal salts by suitable reducing agents is a preferred method for metal core particle synthesis [64]. For metal oxide core particle synthesis, the sol-gel method is often utilized by different research groups [65, 66]. On the other hand, various polymerization techniques are predominantly used for the synthesis of polymeric core particles [67]. Core particles can be synthesized separately and then introduced as templates with surface modifiers or synthesized in situ. External synthesis offers the advantage of obtaining pure core particles with minimal impurities, while in situ synthesis may face challenges related to impurity entrapment. Chemical precipitation reactions, metal salt reduction, and sol-gel methods are commonly employed for the synthesis of inorganic core particles, while polymerization techniques are used for polymeric core particle synthesis.

6.2.2. Shell Synthesis

Shell synthesis refers to the process of fabricating the outer layer or shell of core-shell nanoparticles. In this process, a shell material is formed around a core material to create a distinct structure with unique properties and functionalities.There are various methods available for shell synthesis, depending on the desired characteristics of the nanoparticles and the materials involved. Some commonly used techniques include.

6.2.2.1 Organic/Polymerization method

Polymerization is a crucial mechanism for the formation of polymer shells, which can occur through either radical polymerization or chemical oxidation polymerization. In radical polymerization, two common types are free radical polymerization and atom transfer polymerization. In the case of in situ polymerization, the process begins with the preparation of nano-scale additives that are modified with suitable surface modifiers. These modified additives are then dispersed in the monomers, followed by bulk or solution polymerization**.** A comprehensive review of the processes involved in obtaining inorganic cores and polymer shell particles through polymerization. Different types of polymerization methods for the formation of silica-polymer composite particles**.** Surface modification of silica through bromine attachment, followed by polymer coating with t-butyl acrylate. Various microemulsion methods for forming magnetite cores (Fe_3O_4) and hydrophilic polymeric shell coatings [68]. Synthesizing organic core and organic shell nanoparticles using polymerization methods and characterized them using cryo-TEM, DLS, NMR, AFM, and other techniques. Employing of a direct method for the formation of core-shell particles. They used AAEM (Acetoacetoxyethylmethacrylate) modified ZrO_2 cores as templates and synthesized ZrO_2/PAAEM/PS core-shell nanoparticles through emulsifier-free emulsion polymerization. Synthesizing TiO_2-polymer composite materials via free radical polymerization. For particle synthesis, they utilized poly-(methyl methacrylate) (PMMA) in acrylic acid with 0.5% benzoyl peroxide (PBO_2) for core surface modification [69]. polymerization plays a vital role in the formation of polymer shells. Different types of polymerization methods, such as radical polymerization and chemical oxidation polymerization, are used to achieve core-shell nanoparticle structures. Researchers have explored various approaches, including surface modification, microemulsion methods, and direct polymerization, to synthesize a range of core-shell particles with diverse compositions and properties.

6.2.2.2 Sol-Gel Method

The sol-gel process is a wet-chemical technique, also known as chemical solution deposition, that has gained significant popularity in recent years in the fields of material science and ceramic engineering, particularly for the synthesis of metal oxide particles. This process involves two main steps: hydrolysis of metal salts followed by a condensation process. The sol-gel method is commonly employed for the synthesis of core-shell particles, specifically metal or metal oxide/polymer core-shell structures. The sol-gel process is a versatile technique for the synthesis of metal oxide particles, involving hydrolysis and condensation steps [70]. It is widely utilized for the fabrication of core-shell structures, including metal or metal oxide/polymer composites, and has also been explored for the synthesis of core-shell semiconductor particles by certain researchers.

6.2.2.3. Microemulsion Method

The microemulsion method allows for precise control over particle size and morphology during nanoparticle synthesis. A microemulsion is a mixture comprising an oil phase, an aqueous phase, suitable surfactants, and a cosurfactant. In the microemulsion, surfactant molecules form reverse micelles, while the cosurfactant helps reduce the electrostatic repulsion forces between the charged head groups of the surfactants. To initiate particle formation using this method, reagents are added to the aqueous phase. Within the microemulsion, the micelles serve as centers for nucleation and epitaxial growth of nanoparticles. By adjusting the molar ratio of water to surfactant (R), it is possible to control the particle size and morphology. The microemulsion method is commonly used for synthesizing inorganic core-shell nanoparticles, including those composed of metals, metal oxides, or semiconductors. For example, synthesizing CdS-Ag_2S nanoparticles, gold-coated iron core-shell nanoparticles, using the microemulsion method [71]. Several research groups, have investigated particle formation within the microemulsion system, considering factors such as intermicellar exchange of reactants and the formation of newborn particles in both single and multiple double microemulsion systems [72]. The microemulsion method offers precise control over particle size and morphology by manipulating the molar ratio of water to surfactant, enabling the synthesis of various core-shell nanoparticles with desired characteristics.

6.2.2.4. Mechanochemical Synthesis

Mechanochemical synthesis is a nanoparticle synthesis technique that involves the combination of mechanical force and chemical treatment. This method utilizes various types of mechanical forces to facilitate the synthesis of nanoparticles. Among these forces, two commonly employed and widely recognized types are described below. The two commonly employed types of mechanical forces used in mechanochemical synthesis are. Ball milling: In this method, mechanical force is applied by placing the reactant materials in a ball mill, which contains grinding balls. The rotational movement of the mill and the collision of the grinding balls with the reactant materials result in the breaking of chemical bonds and the formation of nanoparticles. This process is particularly effective for solid-state reactions and can be used for a wide range of materials. High-energy milling: This technique involves subjecting the reactant materials to intense mechanical force using specialized milling equipment, such as attritors, planetary mills, or vibratory mills. The high-energy impact and shear forces generated during milling cause rapid deformation, fracturing, and mixing of the materials, leading to the synthesis of nanoparticles. High-energy milling is suitable for synthesizing a variety of nanoparticle materials, including metals, alloys, oxides, and composites. Both ball milling and high-energy milling offer advantages such as scalability, simplicity, and the ability to carry out reactions at room temperature or lower, making them widely used in mechanochemical synthesis for the production of nanoparticles [73].

6.2.2.5. Sonochemical synthesis

Sonochemical synthesis is a technique used for nanoparticle synthesis that involves a chemical reaction combined with constant sonication. The application of ultrasonic waves during the reaction improves the reaction rate, disrupts agglomerates, and enhances particle dispersion in the solvent medium. Typically, ultrasonic irradiation within the frequency range of 20 kHz to 1 MHz is employed in sonication methods. The localized cavities formed by ultrasonic irradiation act as microreactors, facilitating the occurrence of the reaction and mechanical effects within a short timeframe. In this synthesis technique, a mixture of reactants in a suitable solution is subjected to ultrasonic waves while maintaining specific temperature and pH conditions. This process leads to the dispersion of nanoparticles in the core material, with the chemical reaction determining the formation of the shell material. The core material is synthesized separately and then added to the reactant mixture. For instance, conducted research on the synthesis of composites such as iron oxide with a gold shell and iron/cobalt alloy nanoparticles using sonochemical synthesis [74]. Similarly, in the presence of inert argon gas synthesized Ag-coated silica particles. Overall, sonochemical synthesis combines chemical reactions with ultrasonic irradiation to enhance reaction rates, disrupt agglomerates, and improve particle dispersion [75]. This technique allows for the synthesis of various nanoparticle composites with different core-shell configurations, enabling the development of tailored materials for specific applications.

6.2.2.6. Electrodeposition

The formation of a shell over the core of nanoparticles can be achieved using an electrical potential method, typically in the presence of charged polymers or inorganic materials. During this process, an electric field is applied, which varies like a wave with positive and negative cycles. It has been observed that metal deposition occurs on the core surface during the negative cycle, while charged polymer deposition takes place during the positive cycle. By controlling the duration of the cycles, the thickness of the shell material can be precisely controlled.The deposition of materials occurs on one of the electrodes involved in the process. The matrix material for the formation of core-shell nanoparticles can either be the electrode itself or the electrolytic medium. A conducted a study on the synthesis of iron oxide shell on iron in silica nanoparticles, utilizing silica gel as the matrix for the nanocomposite [76]. A similar synthesis method for polypyyrole-iron nanoparticles, where the electrolytic medium served as the matrix material [77]. The difference lies in the presence or absence of a matrix material, with PPy-Fe belonging to the class of nano-nanoparticles that can later be dispersed in the desired matrix material [78]. In another study for CuI-Au and CuS-Au core-shell nanoparticles were synthesized using electrochemical atomic layer deposition, demonstrating the versatility of the electrochemical method in producing different types of core-shell nanoparticles [79]. Overall, the electrochemical potential method enables the controlled formation of core-shell nanoparticles by manipulating the deposition process using alternating electrical cycles. The choice of matrix material and the specific deposition technique employed contribute to the synthesis of a wide variety of core-shell nanoparticles with diverse applications.

7. Applications of core-shell nanoparticles

Core/shell nanoparticles are widely used and have a broad range of applications due to the diversity in their size, shape, and composition. In particular, inorganic/inorganic core/shell nanoparticles find extensive use in photocatalysis, where they enhance semiconductor efficacy, catalytic activity, and optical properties. These core/shell nanoparticles can be further classified based on the nature of the surface material, with silica being a commonly used inorganic material. Silica, when employed as a shell material, exhibits various properties such as participating in redox reactions, reducing bulk conductivity, and increasing stability. These characteristics contribute to the inertness of silica and make it suitable for a wide range of applications. For example, CdS/ZnS core/shell nanostructures have been shown to possess higher photocatalytic activity compared to pure CdS or ZnS nanoparticles. The enhance performance of CdS/ZnS core/shell nanostructures in the degradation of organic dyes like methyl orange [80]. This enhanced photocatalytic activity is attributed to the synergistic effects and improved charge transfer within the core/shell structure. Overall, the use of core/shell nanoparticles, especially inorganic/inorganic compositions, offers great potential for applications in areas such as photocatalysis, where their unique properties and structural characteristics contribute to improved performance and efficiency [81]. Indeed, core/shell nanoparticles with inorganic/inorganic compositions are also utilized for enhancing electrochemical properties and sensor-based applications. Here are a couple of examples: Ag/WO_3 Nanostructures: Ag/WO_3 core/shell nanostructures have been employed in sensors and demonstrated improved performance compared to Ag-WO_3 mixtures, pure WO_3, and Ag alone [82]. These nanostructures exhibit synergistic enhancements in sensor working phenomena, such as increased sensitivity to pollution, thermally stability, and shorter recovery time. The altered nature of the material leads to improved sensor performance, making it more effective in detecting and monitoring various pollutants. $SiO_2/Co(OH)_2$ Core/Shell Nanoparticles: $SiO_2/Co(OH)_2$ core/shell nanoparticles have been utilized for adsorption applications, specifically in the removal of harmful chemicals, pigments, colors, and dyes [83]**.** The combination of $SiO_2/Co(OH)_2$ core/shell nanoparticles resulted in an increased adsorption capacity of the dye pollutant from 0.10 mg/mg to 0.39 mg/mg. Remarkably, this improvement was achieved by decreasing the dosage of the particles from 12 mg to 2 mg, highlighting the high adsorption efficiency and potential cost-effectiveness of these core/shell nanoparticles.The utilization of inorganic/inorganic core/shell nanoparticles in electrochemical properties enhancement and sensor-based applications provides several benefits, including increased sensitivity, improved stability, reduced recovery time, and enhanced adsorption capacity. These advantages contribute to the development of highly efficient and reliable sensing devices and pollutant removal systems. Core/shell nanoparticles offer increased sensitivity by maximizing the surface area available for interaction with analytes, leading to more accurate and precise detection. The incorporation of a protective shell enhances the stability of the nanoparticles, ensuring their long-term functionality in demanding environments. Furthermore, core/shell nanoparticles exhibit faster response and recovery times, enabling rapid detection and measurement. In adsorption applications, the synergistic effects of different materials in the core and shell result in higher adsorption capacity and efficiency. Overall, these advancements pave the way for the advancement of cutting-edge technologies in environmental monitoring, industrial processes, healthcare, and other fields, enabling improved performance and reliability. Inorganic/organic core/shell nanoparticles are utilized in various applications such as pigments, drug delivery, and absorption phenomena. These nanoparticles offer several advantages, including increased oxidation stability of the core, enhanced biocompatibility, and electromagnetic shielding. They have also been employed in water treatment [84]. In that study, Fe_3O_4/glucose core/shell nanoparticles exhibited remarkable performance in removing heavy metal ions from wastewater, absorbing up to 93.78% of lead ions. This application highlights the potential of inorganic/organic core/shell nanoparticles for efficient and effective water treatment processes. Organic core in nanostructures enables a wide range of applications, offering flexibility and adaptability. The organic core exhibits a flexible nature, allowing it to withstand certain amounts of pressure, making it useful in the synthesis of construction and building materials. Additionally, the organic core provides thermal and colloidal stability, as well as oxidation resistance, making it valuable in various industries. Organic/organic core/shell nanoparticles introduce a change in rigidity and find extensive applications in the pharmaceutical industry, biosensing, biomaterials, and more. These nanoparticles can also serve as nano-reactors in the future. By altering the volume transition phenomenon within the thermosensitive shell, the catalytic activity of the nanoparticles can be regulated to a significant extent [85]. The volume transition within a thermosensitive network acts as an on-off switch controller, allowing for tunable catalytic activity of nanoparticles with orders of magnitude greater than one. Overall, the utilization of organic/organic core/shell nanoparticles provides opportunities for diverse applications due to their flexible nature, increased rigidity control, and tunable catalytic activity. These advancements open up possibilities in fields ranging from pharmaceuticals to nanoreactors, offering promising avenues for future research and development. Several methods employing both bottom-up and top-down approaches have been developed, refined, and successfully implemented for the synthesis of core-shell nanoparticles. These methods encompass physical, chemical and biosynthetic approaches, either independently or in combination, as illustrated Table 1.

Table 1: Showcases a range of synthesis approaches and highlights notable core-shell nanoparticles developed using polymer materials, along with their diverse applications.

core-shell particle	Synthesis method	Uses
SiO_2-St- CMS	Emulsion polymerization	Filler in rubber compositions
SiO_2-PSt-DMAEMA	Emulsion polymerization	Filler in rubber compositions
Fe/Fe_3O_4	By $NaBH_4$ reduction	MRI contrast agents
SiO_2/Fe_3O	electrostatic self-assembly	environmental applications
PBA/St	Emulsion polymerization	Improve mechanical properties
PEHA/St	Emulsion polymerization	Improve mechanical properties
PTT/CSIM	Emulsion polymerization	Improve toughness performance
PTT/GMA	Emulsion polymerization	Improve toughness performance
PS/PMMA	Miniemulsion polymerization	Medical applications
P(St-CPEM)-*g*-P(DMAEMA)	Emulsion polymerization	Catalysis and coatings
Nitrogen-doped SiO_2/TiO_2	Sol-gel synthesis	Photocatalytic efficiency
Fe_3O_4/NH_2–SiO_2	solvothermal reaction	Medical applications
St-MMA-AA	Emulsion polymerization	Improve mechanical properties
TiO_2/Ps	free radical polymerization	Medical applications
Fe_3O_4/C	Hybrids methods	Environmental interest

8. Discussion and analysis

This review article focuses on the exploration of core/shell nanoparticles, encompassing their preparation, classifications, and diverse applications. These nanoparticles exhibit a distinctive composition, consisting of a crosslinked core and a shell that is intimately attached to the core through residual unsaturation linkage. By leveraging this unique core/shell architecture, these nanoparticles offer a high degree of control over their structure, size, and morphology, under the influence of various influential factors. The appropriate selection of salt precursor, solvent media, and surfactant or capping reagent depends on the specific requirements and intended application of the core-shell nanoparticles. Factors to consider include. Salt Precursor: The choice of salt precursor relies on the composition of the core and shell materials. Common options include metal salts (e.g., chloride, nitrate, acetate) for metallic cores and metal alkoxides or chlorides for semiconductor or oxide cores. Compatibility with the desired core-shell materials is crucial. Solvent Media: The selection of a suitable solvent is vital for successful nanoparticle synthesis and stability. The solvent should dissolve the precursor salts and other reagents while providing a favorable environment for nucleation and growth. Water, organic solvents (e.g., ethanol, methanol, toluene), or combinations thereof are commonly used. The choice depends on reaction conditions, desired particle size, and compatibility with the core-shell materials.Surfactant or Capping Reagent: Surfactants or capping reagents control size, shape, and stability of core-shell nanoparticles. They prevent particle aggregation, stabilize the nanoparticle surface, and regulate growth kinetics. Selection depends on the core-shell materials and solvent compatibility. Examples include cetyltrimethylammonium bromide (CTAB), polyvinylpyrrolidone (PVP), and sodium dodecyl sulfate (SDS). Finally steering speed with emulsion polymerization which's very important factor that affect the particle size. For example as illustrated in Table 2.

Table.2. Effect of stirring rate on final particle size of SiO_2-St- CMS particles [63].

Reactive filler	Mass ratio	Stirring speed (rpm)	Particle size (nm)
SiO_2-St- CMS	1 : 0.14 : 0.3	330	114.7 ± 2.2
SiO_2-St- CMS	1 : 0.14 : 0.3	350	99.5 ± 11.8
SiO_2-St- CMS	1 : 0.14 : 0.3	370	91.5 ± 30.8
SiO_2-St- CMS	1 : 0.14 : 0.3	445	90.9 ± 13.8
SiO_2-St- CMS	1 : 0.14 : 0.3	465	45.6 ± 3.7

Note: The particle size was measured by ZetaPALS Particle Sizing Instrument.

Concentration: Optimal concentrations of the salt precursor, solvent, and surfactant or capping reagent are crucial for successful nanoparticle synthesis. Concentrations influence particle size, shape, and yield. Experimental optimization is typically performed, as concentrations may vary depending on the synthesis protocol and desired nanoparticle characteristics. It is important to note that the specific choice of salt precursor, solvent media, and surfactant or capping reagent will vary based on the particular synthesis method, desired nanoparticle properties, and intended application. Referring to relevant literature and conducting preliminary experiments is advisable to determine the most suitable combination for a specific core-shell nanoparticle synthesis. Core/shell nanoparticles have indeed demonstrated significant benefits when used as fillers in elastomer polymers for compost materials. These nanoparticles consist of a core material surrounded by a shell material, and their incorporation into rubber materials offers a wide range of applications.The use of core/shell nanoparticles as fillers in rubber materials aims to improve specific characteristics of the rubber, particularly enhancing the physical properties of polymer materials such as SBV (Styrene-butadiene-vinyl pyridine copolymer) and ACM (BA-MMA-VCA copolymer) (**see** Figure 5). These nanoparticles act as reinforcing agents, enhancing properties such as tensile strength and wear resistance.

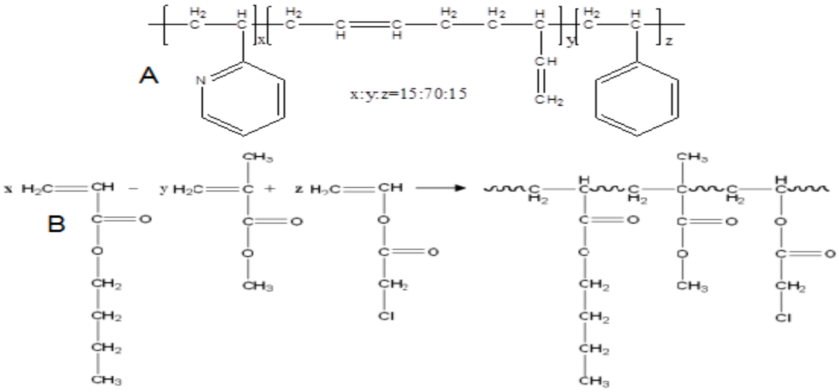

Fig 5. (A) Styrene butadiene-vinyl pyridine copolymer (SBV). (B) Copolymerization of BA, MMA and VCA (preparation of ACM rubber)

The addition of fillers, including core/shell nanoparticles, contributes to the improvement of various physical properties of rubber materials. By incorporating functional core/shell nanoparticles as reactive fillers, a thermo-reversible crosslinking effect can be achieved in the rubber materials. For example as illustrated in Table 3. This means that the crosslinking between polymer chains can be formed and broken reversibly upon the application of heat or other external stimuli. This thermo-reversible crosslinking effect provides advantages such as the ability to reprocess the rubber materials and the potential for self-healing properties.Overall, the utilization of core/shell nanoparticles as fillers in rubber materials offers the opportunity to tailor and enhance the physical properties of the polymer, making them suitable for various applications, including compost materials.

Table.3. Mechanical properties of selected rubber with variable reactive organic-inorganic composite filler content [86].

Components	Shore A Hardness	Tensile Strength (MPa)	Ultimate Elongation (%)	Permanent Deformation (%)
SBV + SiO_2-St	20	1.60	1089	50
SBV + SiO_2-St-CMS	90	4.20	173	5
SBV + SiO_2-St-DVB-CMS	83	5.10	302	50
ACM + SiO_2- St	52	1.10	333	90
ACM + SiO_2- St -DMAEMA	55	3.30	523	75
ACM + SiO_2-St-DVB-DMAEMA	45	1.30	747	120

Note: SBV stands for styrene-butadiene-vinyl pyridine copolymer. CMS stands for chloromethylstyrene. ACM stands for BA-MMA-VCA copolymer. DMAEMA stands for 2-(dimethylamino)ethyl methacrylate.

8.1. Thermo-reversibility of the Rubber Specimen

The study employed two methods, thermo-compression molding and relative torque testing, to investigate the flowability and thermo-reversibility of the crosslinked rubber samples.In the thermo-compression molding method, the procedure involved blending raw rubber with the reactive filler. This mixture was then subjected to thermo-compression using a curing hot press machine (TM-7000). The thermo-compression process was conducted at a specific temperature and pressure (12 MPa) to obtain a sheet with a thickness of 2 mm. The preheating time was set at 10 minutes, and the molding time was 30 minutes. The compression process was carried out in three stages to ensure the absence of any air pockets, which could affect the quality of the crosslinked rubber samples.The second method involved drying the reactive latexes using a freezing dryer. The dried latexes were then blended with reactive rubber materials such as SBV or ACM. Rectangular specimens were cut from the obtained mixture to perform tests such as the swelling degree test and the gel content test. To prepare the specimens for testing, the obtained material was cut into small pieces measuring 5 cm × 5 cm. These pieces were then stacked in 5 or 6 layers and compressed multiple times.Both methods aimed to evaluate the flowability and thermo-reversibility of the crosslinked rubber samples. The thermo-compression molding method allowed for the production of sheet samples, while the relative torque testing method enabled the examination of the swelling degree and gel content of the specimens.These experimental techniques provided insights into the behavior of the crosslinked rubber materials upon heating and their ability to undergo thermo-reversible changes. The results obtained from these methods could contribute to a better understanding of the flow properties and thermo-reversible characteristics of the rubber samples, which are important for their practical applications. Relative torque testing can be performed using a Disk Oscillating Rheometer to assess the flowability and thermo-reversibility of crosslinked rubber samples. The following steps outline the procedure for conducting the test. Prepare a test cell: Set up the Disk Oscillating Rheometer and ensure that the test cell is clean and free from any contaminants. Weigh the sample: Measure seven grams of the crosslinked rubber sample and place it in the test cell. Set the temperature range, set the initial temperature of the test at 120°C. Apply thermo-compression: Begin the test by thermo-compressing the crosslinked rubber sample. Increase the temperature gradually from 120°C to 200°C. Measure the relative torque: As the temperature increases, the rheometer measures the torque exerted by the sample. Record the torque readings at each specific temperature. Calculate relative torque: Calculate the relative torque of the specimen using the formula [t/t0], where t0 represents the torque of the crosslinked sample before heating (maximum torque), and t represents the torque of the sample at a specific temperature during the test. Control temperature: During the torque test, ensure that the temperature is controlled within the desired range (from 120°C to 200°C) to observe any changes in flowability or thermo-reversibility of the crosslinked rubber material. By monitoring the relative torque values at different temperatures, it is possible to determine whether the crosslinked rubber exhibits flowability or undergoes any changes in its rheological properties. This information can provide insights into the material's response to heating and its potential for thermo-reversible behavior as shown Figures (6, 7).

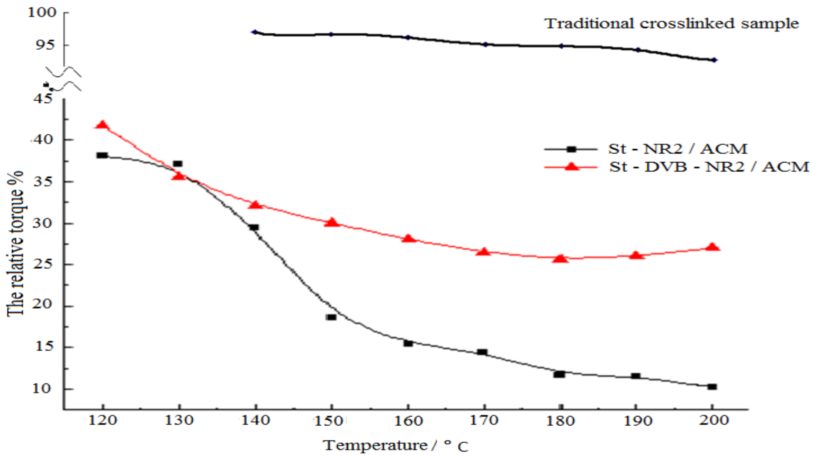

Fig 6. Temperature dependence of the relative torque of thecrosslinked ACM rubbers filled with amino-functionalized PSt particles and DVB crosslinked amino-functionalized PSt particles [86].

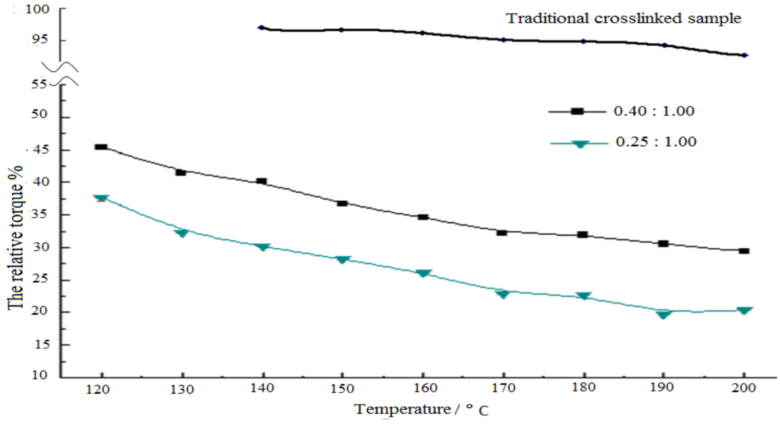

Fig 7. Temperature dependence of the relative torque of the crosslinked SBV rubber filled with reactive filler [63].

Based on the information provided, the relative torque of crosslinked ACM rubber and SBV rubber was repeatedly tested during heating (180℃) and cooling (120℃) cycles. Figures 8 and 9 show that the relative torque of both crosslinked ACM rubber and crosslinked SBV rubber exhibited switchable behavior upon heating and cooling. This behavior indicates excellent reversibility of the crosslinkage formed through the quaternization reaction between rubber chains and filler particles. The results obtained from the testing indicate that there is no significant difference in the thermo-reversibility between the reactive filler crosslinked ACM and SBV rubbers.

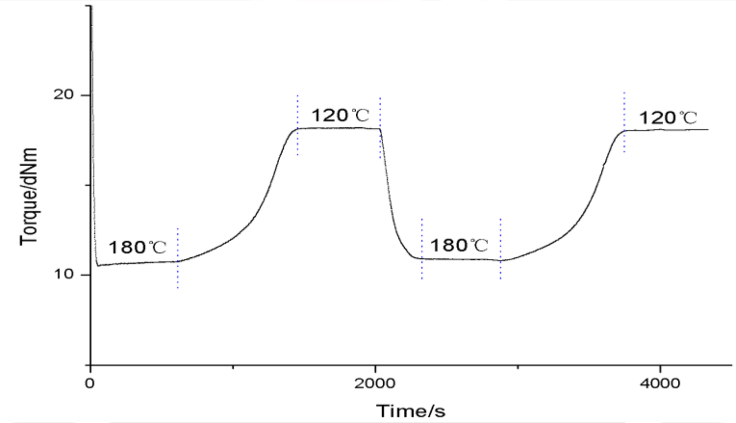

Fig 8. Thermo-reversible cycle of amino-functionalized PSt filler cross-linked ACM [86].

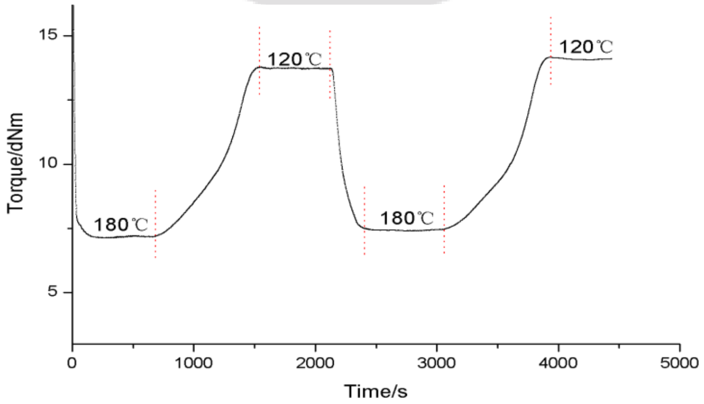

Fig 9. Thermo-reversible cycle of chloro-functionalized PSt filler crosslinked SBV [63].

This implies that the bonding location of chlorine moieties and tertiary amine moieties, whether it is chlorine to the polymer chain/tertiary amine to the particle surface or tertiary amine to the polymer chain/chlorine to the particle surface, does not affect the thermo-reversibility of the crosslinkage formed by the quaternization reaction involving these two types of functional groups. In summary, the testing results demonstrate that both crosslinked ACM rubber and crosslinked SBV rubber exhibit reversible behavior upon heating and cooling. The location of the bonding between the functional groups does not significantly impact the thermo-reversibility of the crosslinkage formed through the quaternization reaction. This information provides valuable insights into the behavior of these materials and their potential applications in various industries.

9. Conclusion and future aspects

In conclusion, this review article has provided a comprehensive overview of the utilization of reactive core-shell nanoparticles in polymer materials. The incorporation of these nanoparticles has demonstrated significant improvements in the properties and performance of polymers across various applications. The core-shell structure offers unique advantages, such as enhanced compatibility, improved dispersion, and controlled release of functional additives within the polymer matrix. One of the key findings highlighted in this review is the ability of reactive core-shell nanoparticles to enhance the mechanical properties of polymers. By reinforcing the polymer matrix, these nanoparticles have shown remarkable improvements in tensile strength, modulus, and impact resistance. Additionally, the core-shell structure provides an effective barrier against crack propagation, leading to enhanced toughness and durability of the polymer materials. Furthermore, the review has emphasized the importance of tailoring the surface functionality of core-shell nanoparticles to achieve desired properties in polymer composites. The ability to functionalize the core and shell independently allows for precise control over properties such as thermal stability, flame retardancy, electrical conductivity, and optical properties. This versatility opens up new avenues for designing advanced polymer materials with tailored functionalities for specific applications. Looking ahead, there are several promising future aspects that warrant further exploration in the field of reactive core-shell nanoparticles. Firstly, the development of novel core-shell systems with enhanced compatibility and interfacial adhesion will be crucial for achieving optimal dispersion and mechanical reinforcement in polymer matrices. Surface modification techniques, such as grafting or coating, can be employed to improve the interfacial interactions between the nanoparticles and polymers, leading to enhanced performance. Secondly, more research is needed to investigate the long-term stability and durability of polymer composites containing reactive core-shell nanoparticles. Understanding the effects of aging, environmental exposure, and processing conditions on the properties of these materials is essential for their successful commercialization and widespread adoption in various industries. Furthermore, the potential applications of reactive core-shell nanoparticles in emerging fields such as biomedical, energy storage, and environmental remediation should be explored. These nanoparticles can be tailored to impart specific functionalities, such as drug delivery, bioimaging, catalysis, and pollutant removal, making them highly desirable for various cutting-edge applications. In conclusion, the integration of reactive core-shell nanoparticles into polymer materials holds great promise for advancing the performance and functionality of polymers. Continued research and development in this area will undoubtedly lead to the creation of innovative polymer composites with enhanced properties, paving the way for exciting opportunities in diverse industries.

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