



Chemical Structure Modification of Polystyrene (PS): A Short Review

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Article's Information	Abstract
Received: 06.04.2024 Accepted: 16.05.2024 Published: 15.12.2024	Polystyrene (PS) is a polymer that finds extensive usage in several applications such as electronics, packaging, and healthcare. Its chemical structure may be changed to alter its features and capabilities. This leads to improve the performance of the material to be suitable for specific applications. We discuss the recent PS chemical structure modification in this short review. The review focuses on methods of modification such as functionalization, grafting, and copolymerization. It also investigates the impact of various modification options such as PS's mechanical strength, photo-stability, and surface features. It also looks at the wide range of approaches in which modified PS materials are used. We talk about the field's prospects and problems going forward. This is including as improvements in modification methods, incorporating sustainable practices and investigation of new applications. Moreover, it is tackling important scalability, regulatory compliance, and end-of-life issues. By focusing on innovation and resolving future issues, we hope to shed light on the adaptability and potential of modified PS materials through this review.

Keywords:

Polystyrene;
Chemical modification;
Copolymerization; Grafting;
Functionalization;
Properties enhancement.
Chemical change.

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1. Introduction

One of the most widely used and adaptable polymers in contemporary industry is polystyrene (PS), which has uses in a wide range of industries including consumer products, building, packaging, electronics, and healthcare. Every element of daily life and several businesses, including construction, furniture, packaging, electrical and electronic, transportation, and agriculture, have made extensive use of plastic materials. Approximately 325 million tons of plastic are produced worldwide each year [1]. According to estimates, about 25% of municipal solid trash in landfills located in countries

like the US, Germany, and Australia is composed of plastics [2]. Polystyrene (PS), like other polymers, is extensively utilized due to its favorable mechanical characteristics and affordable price. PS is a common ingredient in food containers, disposable plates, cups, cutlery, compact disks, and insulation for building materials, packing foam, and cassette boxes. In 2013, the global PS production was estimated to be 21 million tons [3]. PS is a manufactured insulating material with strong mechanical qualities and high buck resistivity. As a result, it finds extensive application as a dielectric window and spacer in the fields of high-voltage

technology and pulsed power systems [4]. However, the development of high voltage and high capacity of the power system has been hampered by surface flashover at the vacuum/dielectric contact. The theory of secondary electron emission avalanche suggests that the surface flashover process is closely related to the surface charge dynamics [5]. Polymer charging may occur as a result of extrinsic factors like secondary electron multiplier, corona discharge, flaws close to the triple junction, etc. Surface conduction or other decay mechanisms cause surface charges to decay concurrently with charging [6]. The practical performance of polymers is determined by a range of thermal and morphological parameters, including the lamellar and spherulitic microstructure, melting behavior, and glass transition, all of which are influenced by the stereochemistry of polymers. The recently created syndiotactic polystyrene has low dielectric constants and a high melting temperature, making it an attractive thermoplastic for engineering applications compared to its isomers. This stereo-regular and crystallizable material has garnered more interest than its isotactic and atactic equivalents, which have been the focus of much research over the previous few decades [7]. The material's great interest has therefore prompted a number of studies into its conformation, configuration, crystal structure, and crystallization dynamics. The dynamic industrial field of polymer characteristics improvement by mixing with others continues. [8]. As seen in Figure 1, polystyrene is available in three different forms, syndiotactic, atactic, and isotactic. Every shape has distinct qualities that are determined by the configuration of the polymer chains that make it up. The polymer chains are very uniform and organized in a crystalline structure in the syndiotactic form [9].

2. Synthesis and Structural Characteristics of Polystyrene (PS):

The usual method for creating polystyrene (PS) is the polymerization of styrene monomers. A naturally existing liquid substance called styrene is used to make a variety of strong, flexible, and light products [10]. As the name implies, the building block of polystyrene is styrene, which is the origin to polystyrene and other well-known copolymers. It is sometimes referred to as ethylbenzene, vinylbenzene, or phenylethane. The production of styrene and its numerous uses constitute a substantial portion of the global economy [11]. By providing more affordable, energy-, and performance-efficient items, it improves people's lives. Polystyrene is a very clear, strong, and stiff resin. It is the most widely used plastic, derived from styrene polymerization. At room temperature, the thermoplastic polymer is solid; however, when heated over 100 °C, it flows. Polystyrene is not soluble in water. Except in a few cases, polystyrene [12, 13]. Styrene may be polymerized to create polystyrene, a polymer. It is frequently utilized in food service establishments for froze cups, plates, and bowls, as well as rigid platters and containers and disposable eating utensils. Styrene undergoes a standard free radical chain reaction to polymerize into polystyrene [14, 15]. Either heat or an initiator will start the polymerization process. Active free radicals are created when initiators break down thermally, and it is these radicals that start the polymerization process [16]. Polystyrene is used in a range of applications, from stiff plastic to foam, from food packaging to electronics protection. Although polystyrene shrinks moderately and has a large range of uses, it flows slowly and can break easily [17].

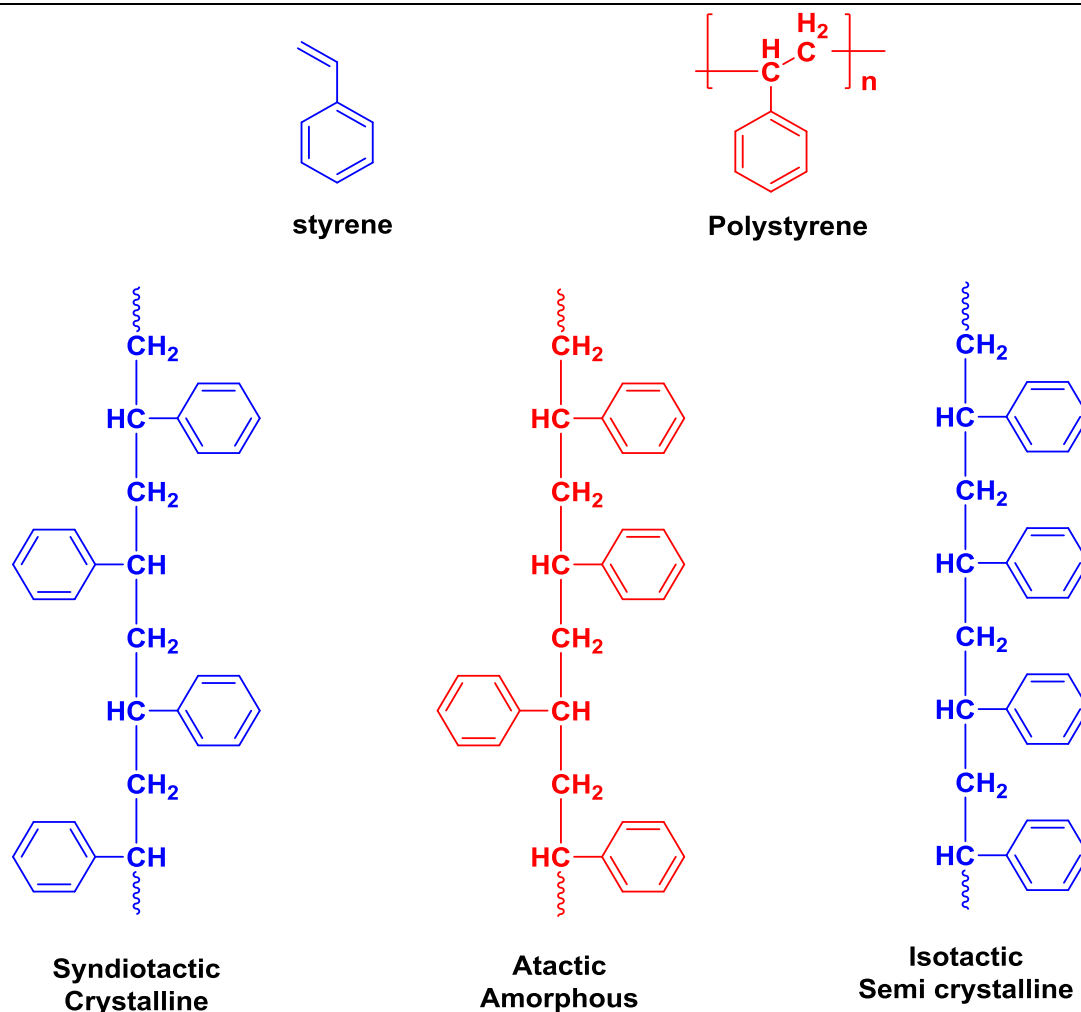


Figure 1: Different structure forms of polystyrene [8].

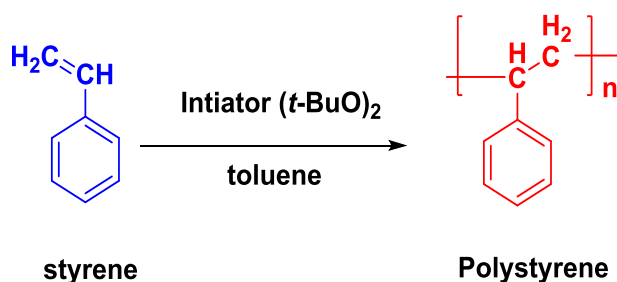


Figure 2: Synthesis of polystyrene [10].

3. Chemical Structure Modification Techniques:

Techniques to modify the chemical structure of polystyrene (PS) provide flexible ways to modify the material properties for various uses [18, 19]. One of the main methods for changing PS chemical

structure is copolymerization. By copolymerizing styrene with other monomers, such as butadiene, methyl methacrylate, or acrylonitrile. Researchers can give PS polymer chains additional properties and applications. For example, acrylonitrile-

butadiene-styrene copolymers, which are renowned for their great impact resistance and toughness, are produced when styrene is copolymerized with AN. Polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) block copolymers are created when MMA is copolymerized. These copolymers have distinct phase separation characteristics and have the ability to self-assemble into a variety of nanostructures [20, 21]. Similarly, blends comprising 0% to 10% styrene-butadiene rubber and 100% to 90% polystyrene

showed better impact characteristics following gamma irradiation at a dosage of 100 kGy. According to FTIR, radiation created a radical in PS's benzene ring that might combine with polybutadiene's double bond to make meta-substituted benzene. Therefore, the increase in Izod impact strength was caused by the chemical bond between the two polymers, especially for the 90/10 PS-polybutadiene mix that was exposed to 100 kGy γ radiation as shown in Figure 3 [22, 23].

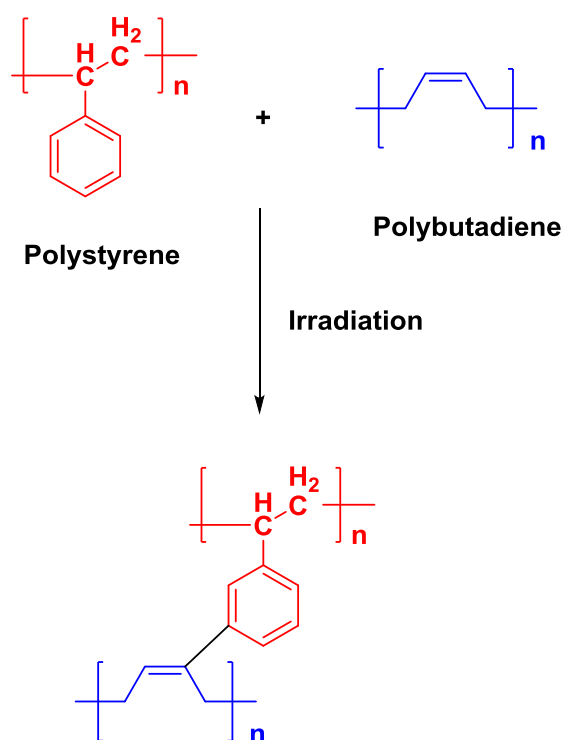


Figure 3: Linking of polystyrene with polybutadiene [22].

Another significant alteration method is grafting, which involves attaching polymer chains or functional groups to the PS backbone. A variety of processes, including as anionic polymerization, controlled/living polymerization, and radical polymerization, can be used to produce grafting. Researchers can add additional characteristics including enhanced compatibility, adhesion, and mechanical strength to PS by grafting polymer chains onto the material. Applications for grafted PS materials include surface modification treatments, adhesive formulations, and compatibilizers for

polymer blends as shown in Figure 4 [24]. A novel approach to the synthesis of polystyrene-graft-polythiophene was investigated. In order to achieve this, atom transfer radical polymerization was used to first create poly(styrene-co-acrylonitrile). The Grignard reaction between 2-thienylmagnesium bromide and nitrile groups was then used to construct thiophene groups from the nitrile groups of acrylonitrile units. This process produced a thiophene – functionalized polystyrene macro-monomer [25].

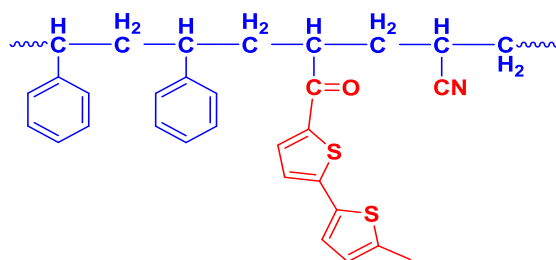


Figure 4: Polystyrene-graft-polythiophene chemical structure.

By employing poly (4-vinylbenzyl-4-oxy-2, 2, 6, 6-tetra-methylpiperidine-1-oxyl-ran-styrene) as the macromediator, nitroxide-mediated photo-living radical polymerization was used to create polystyrene-graft-poly(methyl methacrylate) as shown in Figure 5 [26]. Using a high-pressure mercury lamp as the mediator and a molecular weight of $M_n = 21,700$, the bulk polymerization of methyl methacrylate was carried out at room temperature. The (2RS,2'RS)-azobis(4-methoxy-2,4-dimethylvaleronitrile) was the initiator employed in this procedure. It was present in the presence of 4-

tert-butylphenyl)diphenylsulfonium triflate, which functioned as the photo-acid generator. A controlled polymerization mechanism carried out the polymerization, as seen by the linear increase of the conversion-molecular weight and first-order time-conversion graphs. By using ^1H NMR analysis, it was determined that all of the VTEMPO components supported the controlled PMMA networks. The mole ratio of the VTEMPO at the ends of the chain end to the 1-cyano-3-methoxy-1,3-dimethylbutyl group at the starting chain end of the PMMA was unity [26].

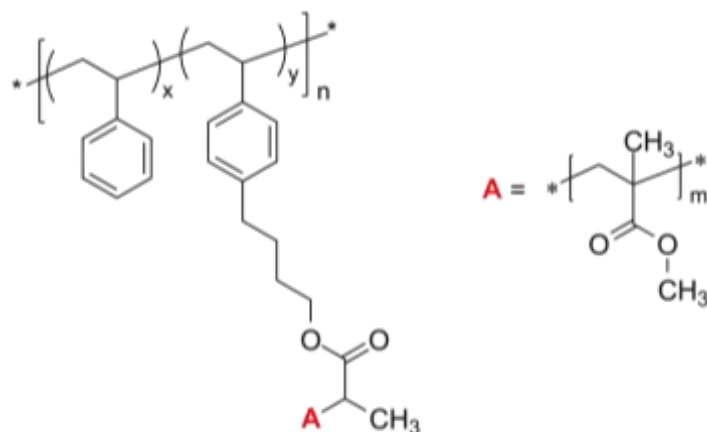


Figure 5: Grafting polystyrene and polymethylmethacrylate [26].

The process of functionalization entails adding functional groups—either physically or chemically—to the PS polymer strands. Precise control of PS characteristics including solubility, reactivity, and biodegradability is made possible via functionalization. PS chain amination,

hydroxylation, carboxylation, and halogenation are common functionalization techniques. For instance, adding halogen functional groups to PS by halogenation with chlorine or bromine increases its chemical resistance and flame retardancy. Similar to this, PS may be further derivatized and modified by

hydroxylation, which adds hydroxyl groups [27]. Describe the first tracking of polystyrene micro- and nanoplastic particles in animals using molecular imaging as shown in Figure 6 [28]. In order to do this, we altered PS particles with chelator desferrioxamine at four different diameters: 20 nm, 220 nm, 1 μm , and 6 μm . Subsequently, we radiolabeled these particles containing DFO using the radiometal zirconium-89 (^{89}Zr ; $t_{1/2} \sim 3.3$ d) that emits positrons [28]. Next, positron emission tomography (PET) was used to track the

biodistribution of these radioplastics in C57BL/6J mice at 6, 12, 24, and 48 hours following ingestion. The majority of radioplastics are found to persist in the gastrointestinal tract and are eliminated in the stool 48 hours after ingestion, according to imaging data that is corroborated by acute biodistribution studies. The behavior of micro- and nano-plastics in vivo and their potential toxicity is a crucial and developing subject of study, and research suggests that nuclear imaging, and PET in particular, may be a sensitive and practical method [28].

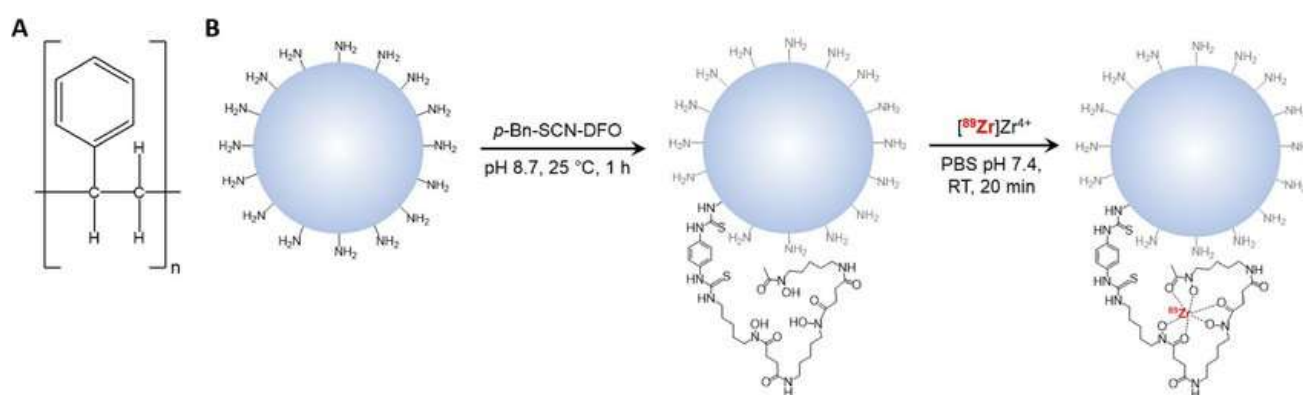


Figure 6: The structure of polystyrene micro- and nano-plastic particles [28].

Researchers have looked into crosslinking, mixing, and the creation of nanocomposite formation as ways to alter the chemical structure and characteristics of PS in addition to these main modification approaches. PS chains that have been crosslinked have increased mechanical strength, thermal stability, and chemical resistance, making them ideal for uses that call for strong materials. Materials with specific qualities and functions can be created by blending PS with other polymers or additives [29, 30]. When compared to pure PS materials, nanocomposites with PS matrices and nanoscale fillers have better mechanical, thermal, and barrier qualities [31]. Block-graft copolymer formation was shown by $^1\text{H-NMR}$ and GPC studies. Grafting was effectively established when the

precursor di block copolymer's initial unimodal GPC peak shifted to increased elution volumes as shown as shown Figure 7. Additionally, as shown in the $^1\text{H-NMR}$ spectra of the polymer acquired after photopolymerization, the signal emerging at around 3.6 ppm related to O-CH₃ protons confirms the existence of grafted MMA units in the polymer [32]. The impact of initiator concentration and irradiation duration on the molecular weights and conversion is an intriguing observation [30]. In result, methods for changing the chemical structure of polystyrene (PS), such as grafting, functionalization, and copolymerization, offer effective means of modifying the material's characteristics to suit particular application needs [33].

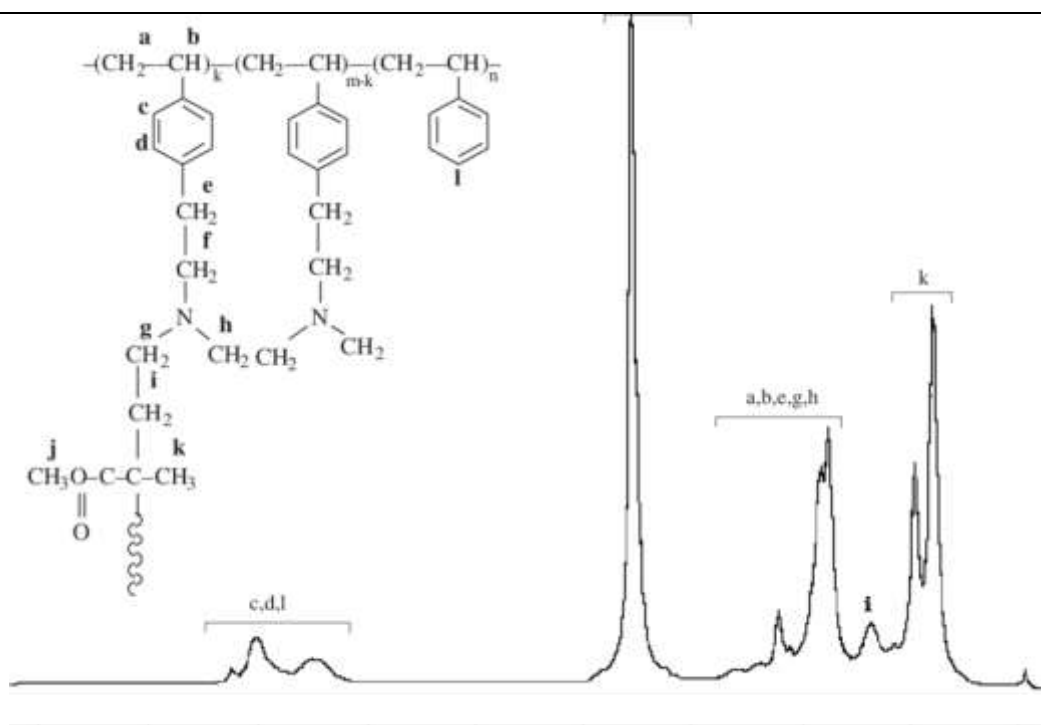


Figure 7: ^1H NMR spectrum of modified polystyrene [30].

4. Effects of Chemical Structure Modification on Polystyrene (PS) Properties:

Because of their many physical and chemical properties, low cost, and suitability for a wide range of applications, polymers are ideal for biological research platforms, organic and flexible electronics, and biomedical devices and materials.¹⁻³ For example, the polymer studied in this paper, polystyrene (PS), has conduction characteristics and dielectric strength that make it a promising insulator for organic electronics applications.⁴ In the realm of biomedicine, polystyrene has proven to be useful as a hemocompatible substance, a bioanalytical experiment platform, an antibacterial surface, and in tissue engineering [34]. However, like other polymers, polystyrene requires functionalization for uses requiring improved wettability, adherence, or covalent immobilization of chemical and biological ligands. Plasma treatment of polymer surfaces has proven an efficient way to achieve these desired properties.^{6–10} Furthermore, wear resistance and hardness are increased by the cross-linking of polymers created by plasma. Nevertheless, intense plasmas should be used

cautiously because they can produce surface roughening and modification depths that are too large for some surface-sensitive nanoscale applications. The electrons in plasmas are typically excited by the application of electric fields. These powerful electrons interact with the surrounding gas to create ions, radicals, and excited species through electron-driven ionization and dissociation processes. These reactions ultimately alter the polymer's surface. UV and VUV photons produced by the excited species will penetrate the material up to a few micrometers, changing the chemical and morphological surface of the polymer.¹¹ as well as the operating environment [35]. Polystyrene (PS) surfaces in argon/nitrogen, argon/oxygen, and argon/sulfur hexafluoride environments were treated with plasmas created by electron beams [36]. The resulting modifications to the polymer surface energy, morphology, and chemical composition were analyzed using a suite of complementary analytical techniques, including AFM, X-ray photoelectron spectroscopy (XPS), contact angle goniometry, and reflection electron energy loss spectroscopy (REELS). The plasma treatments only marginally

enhanced the surface roughness, while introducing the predicted chemical alterations nitrogen- and oxygen-based after Ar/O₂ plasma, and fluorine-based after Ar/SF₆ plasma. Fluorinated PS surfaces did not change significantly over time; instead, they became more hydrophobic. However, polymer treated in Ar/O₂ and Ar/N₂ plasmas showed hydrophobic recovery from its initial hydrophilic condition after 28 days of age [36]. The aromatic carbon chemistry of the top 1 nm of these aged surfaces clearly showed that the hydrophobic recovery was produced by the reorientation and diffusion of intact aromatic polymer fragments from the bulk rather than contamination. Nondestructive

depth profiles of aged plasma-treated PS films were reconstructed from parallel angle-resolved XPS (ARXPS) images using a maximum-entropy approach. The essential components of the reconstructed profiles were confirmed by sputter profiles created with 200 eV Ar ions. Both types of depth profiles showed that the electron-beam-generated plasma modifications are limited to the upper 3–4 nm of the polymer surface, but valence band measurements and unsaturated carbon signatures in ARXPS and REELS data indicated that a significant portion of the PS structure was preserved below 9 nm [36].

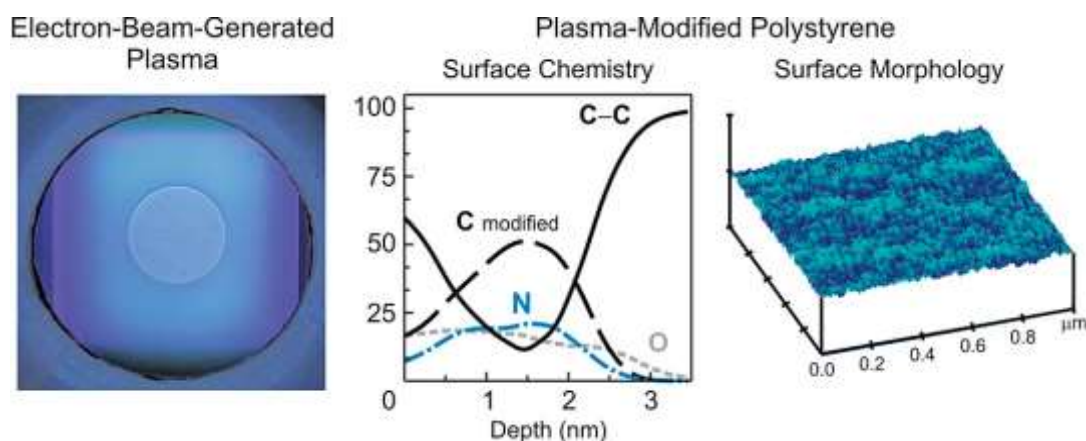


Figure 8: Influence of modification on polystyrene surface properties [36].

5. Applications of Modified Polystyrene (PS):

Polystyrene (PS) is a versatile and adaptable material with a wide variety of uses across several sectors due to its chemical structure modification capabilities. In industries where customized qualities are crucial for efficiency, such as packaging, electronics, automotive, construction, and healthcare, modified PS materials are used [37, 38]. The packaging industry is one where modified PS is most commonly used. PS-based products are commonly utilized in packaging because of their simplicity of manufacturing, lightweight nature, and ability to withstand heat. Expanded polystyrene, polyvinylidene fluoride polymer, and blend polymers

polyethersulfone have been employed to create the membrane (proton exchange membrane). This membrane was altered by immersing it in diluted sulfuric acid after casting and adding organic sulfonic acid to the mix solution during the building process [39]. FTIR spectra were used to verify the sulfonation. Water absorption, (SO₃H) concentration, ion exchange capacity, and conductivity of proton were the characteristics of the sulfonated membrane. Electrochemical polarization tests and power densities produced from them are used to assess the membrane's efficiency in the Microbial Fuel Cell [40, 41]. Modified PS materials are used in structural components, roofing, and

insulation in the building industry. Expanded polystyrene (EPS) and extruded polystyrene (XPS) are examples of PS foams that are perfect for insulation applications because they are lightweight, have moisture resistance, and provide thermal insulation [42]. Reinforcing fibers and flame-retardant additives, when added to modified PS formulations. This is to improve the structural strength, durability, and fire resistance of building materials as shown in Figure 9. Modified PS materials are also being used in medicine applications including lab equipment, packaging,

and medical devices. Medical goods function better and are safer when made with modified PS formulations that contain biocompatible additives or antibacterial agents, all while maintaining regulatory compliance [42]. A variety of sectors, including packaging, electronics, automotive, construction, and healthcare, use modified polystyrene (PS) products. Chemical structural modification may be used to tailor PS's features, resulting in materials with improved performance characteristics that are tailored to the unique needs of each application sectors.



Figure 9: Various usages of modified polystyrene [42].

6. Future Perspectives and Challenges:

The field of polystyrene (PS) chemical structure modification has enormous potential for future innovation and progress, providing chances to create materials with improved qualities and unique functions. Anticipating the future, a number of viewpoints and obstacles may be seen that will influence the direction of this field's study. Progress in Modification Methods: It is anticipated that future studies will see improvements in modification

methods with the goal of enhancing scalability, accuracy, and efficiency. The creation of customized PS materials with previously unheard-of control over their characteristics and capabilities will be made possible by advancements in controlled/living polymerization processes, innovative catalyst systems, and reaction engineering methodologies. Integration of Sustainable Practices: Research on PS modification will take a different turn as a result of the push for environmental responsibility and

sustainability. It will be critical to work toward more environmentally friendly synthesis processes, make use of renewable resources, and encourage recyclable and biodegradable materials. As environmental concerns develop, sustainable modification techniques like enzymatic grafting and bio-based additions will become more popular. Multifunctional Materials Design: Upcoming studies will concentrate on creating multifunctional PS materials that can concurrently meet the needs of several applications. Researchers want to develop materials with customized combinations of mechanical strength, thermal stability, conductivity, and biocompatibility by combining several modification processes, including grafting, copolymerization, and functionalization. Investigating Emerging Applications: Investigating new application domains will direct scientific efforts toward the creation of PS materials with particular capabilities. Applications including wearable technology, biomedical implants, 3D printing, flexible electronics, and wearable electronics provide special opportunities and problems that call for creative solutions. Changing the chemical structure of PS materials will be essential to their use in these innovative domains. Even with the bright future, a number of obstacles need to be overcome in order to fully use PS modification. Structure-Property Relationship Complexity: The complex interaction of material qualities, manufacturing parameters, and chemical structure makes designing and optimizing modified PS materials extremely difficult.

7. Conclusions

To summarize, One polymer that is widely used in a variety of industries, including electronics, packaging, and healthcare, is polystyrene (PS). Its traits and capabilities may be altered by changing its chemical structure. As a result, the material performs better and is more appropriate for certain uses. In this brief overview, we address the recent alteration of the PS chemical structure. The review focuses on modification techniques such as copolymerization, grafting, and functionalization. Additionally, it looks at the effects of several modification choices on the surface characteristics, mechanical strength, and photo-stability of PS. It also examines the variety of methods that modified

PS materials may be applied in. We discuss the future potential and issues facing the field. This involves utilizing advancements in modification techniques. Through the utilization of chemical structure modification, scholars can persist in pushing the limits of PS materials, therefore generating novel prospects for innovation and tackling forthcoming issues.

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