Influence of copper oxide nanoparticles on UV aging resistance and thermal degradation of sulfonated poly (1,4-phenylene ether ether sulfone) (SPEES) membrane

Abstract

The purpose of this study is to synthesize multifunctional membranes based on poly (1,4-phenylene ether ether sulfone) (PEES). PESS has good thermal, optical, electrical and antimicrobial properties. Copper oxide nanoparticles reinforced in PEES matrix. These reinforced membranes have a unique structure and properties that influence the thermal stability and UV protection compared with neat PEES. The PEES chain structure and composition of the copper oxide were shown to be associated with the degradation behavior. Since PEES is a hydrophobic polymer, it does not have good interaction with copper oxide nanoparticles resultant polymer chain was functionalized with H_2SO_4 to improve the hydrophilic nature and better dispersion of copper oxide nanoparticles in PEES. The of concentration of copper oxide nanoparticles was varied in sulfonated PEES matrix. The weight loss upon degradation was positively correlated with the concentration of copper oxide nanoparticles. The concentration of nanoparticle ratio varied, which dramatically changed UV shielding properties of PEES. Copper oxide has potential electron correlation effects, high temperature superconductivity, spin dynamics, and antimicrobial properties. Therefore, sulfonated poly (1,4-phenylene ether ether sulfone) (SPEES) copper oxide membrane has improved thermal and optical properties.

Key words: PEES, SPEES, copper oxide, thermal stability, optical studies

1. Introduction

The simplicity, energy efficiency, and high separation operation of membrane technology has made it a critical platform in dealing with the most critical issues in water purification, biomedical engineering, and energy conversion systems. The classical membranes are mostly tailored to size exclusion or diffusion-based selective separation, but suffers from these problems: fouling, weak selectivity, and are not robust enough to work in severe conditions. In an effort to overcome these shortcomings, the idea of multifunctional membranes has been of considerable interest in the past few years.

Multifunctional membranes are novel materials that have been designed to incorporate multiple functionalities in a single membrane system, allowing them to go beyond traditional separation processes. Such membranes can be engineered to possess more than one property, including antimicrobial response, catalyzed degradation, increased hydrophilicity, mechanical stability, thermal stability and stimuli-responsiveness. Such a wide range of functionalities is not only capable of enhancing the effectiveness of the membrane but also increasing the duration of operation by reducing fouling and degradation.

Multifunctional membranes have been used in water treatment systems with combined separation and degradation properties, so it is possible to remove organic contaminants, heavy metals, and pathogenic microorganism. These membranes are also under investigation as wound dressing materials, drug delivery systems, implant coating, in the biomedical field because of their biocompatibility and antimicrobial properties. Moreover, multifunctional membranes has importance in energy applications, including proton exchange membranes fuel cells, to enhance ion transport without damaging the structure in high-temperature and oxidative conditions.

Polymer-based high performance membrane with excellent optical, thermal properties, chemical resistance, electrical and antimicrobial properties.These multifunctional properties as made excellent place in the material science.Synthesis of polymer nanocomposites is relevant due to the global rise in lightweight, durable, and high-efficiency materials in sectors such as electronics, biomedical engineering, energy storage, and environmental protection from temperature, ultra violet rays, microbial infections, nosocomial (hospital-acquired) bacteremia, and the growing issue of antibiotic resistance. A primary focus has been on polymers nanocomposite that has not only excellent physical properties such as hydrophilicity, thermal stability, UV resistant membrane. Biomaterial demand is increasing day by day in human life due to various factors such as accidents and lifestyle.

Poly(1,4-phenylene ether ether sulfone) (PEES) is a thermoplastic polymer that has made place between high performance polymer. It has excellent thermal stability, excellent film-forming properties [1],high proton conductivity, mechanical strength[2], antimicrobial properties and resistance to chemicals [3]. These attributes make PEES an excellent choice in various fields, especially in filtration,[3] and electronics [4]. High performance coating, artificial heart, pacemaker, blood tubes, and various devices are used in medical science for those joints, sutures, bone plates, antibacterial coating and medical devices [5-6].

Poly(1,4-ether ether sulfone) (PEES)is a material that has aromatic backbone,two ether and sulfone linkages provides moderate polarity with limited inherent hydrophilicity. The hydrophilic behavior of PEES can be modified through chemical modification by various acidssuch as sulfur trioxide, acetyl sulfate, and sulfuric acidwhich promote improved surface wettability and water affinity. Such enhancement in hydrophilicity is improved applicability of PEES in membrane and biomedical systems where effective interaction with aqueous environments is required[7-9].

Recently, copper oxide nanoparticles shows wide range of application such as catalytic systems, sensing devices, gas sensing technologies, pollution degradation due to its resistance to photo corrosion, high oxygen-carrying capacity, electrical and optical and solar energy transformation. Further studies as aantibacterial, anti-viral, anti-inflammatory, and antifungal agent for application for both biomedical and environmentaluses [10-11].

The properties of copper oxide nanoparticles primarily depend on the size of nanopowder, their morphology, and the specific surface area of the prepared materials, and synthesis methods. When these nanoparticles use as filler in polymer matrix, it enhance polymer matrix properties. The thermal, opticalincluding their ability to emit, absorb, and scatter light depends upon copper oxide nanoparticles size, desperation into polymer matrix. Copper oxide and SPEES may combine the qualities to create a new material with unique physical and chemical properties [12].

In this study, we focus on the ethanol-based solution casting method. Functional and morphological studies were done by using FI-IR, SEM, and thermal degradation of polymer nanocomposite was investigated by the help of TGA and DSC. We found that SPEES-copper oxide nano material has better thermal degradation, UV resistant and glass transition temperature (Tg) than neat SPEES.

2. Materials and Methods

Pure poly (1,4-phenylene ether ether sulfone) was obtained from Sigma-Aldrich. Copper oxide nanoparticles synthesized byVedayukt India private limited, Jamshedpur, India. Synthetic grade dichloromethane (Purity>99.9%) and sulfuric acid (H_2SO_4) (Purity>99.9%) were purchased from Merck, India.

2.1 Sulfonation of pure poly (1,4-phenylene ether ether sulfone)

Dichloromethane was used as a dissolving agent for poly (1,4-phenylene ether ether sulfone) pellets. PEES-dichloromethane mixture was stirred again washed with methanol to get PEES in a powdered form and dried at 60 ^{o}C during 12 h. H_2SO_4used as sulfonation agent and stirred with conc. H_2SO_4 during 5h and precipitated in cold deionized water. Sulfonated PEES was washed several times in cold deionized water and dried in 60 ^{o}C at 12 hrs [5].

2.2 Nanocomposites film formation:

Sulfonated poly (1,4-phenylene ether ether sulfone)(SPEES) and copper oxide nanoparticles were combined in different amounts like 2%, 4%, and 6% by weight in table 1. The ethanol solution casting method was used to help the nanoparticles better. Copper oxide nanoparticles were mixed with ethanol and this mixture was sonicated for 30 to 50 minutes to spread the nanoparticles evenly in the SPEES matrix. This sonicated mixture was then added to the SPEES ethanol solution. The mixture was stirred continuously for 5 hours. Just before pouring it in a petri dish, the solution was sonicated again for 3 minutes to stop the nanoparticles from clumping together and to keep them evenly spread in the SPEES matrix. The resulting membrane was then dried at 70 degrees Celsius.

Table -1 Different concentrations of copper oxide reinforced SPEES membranes

Sample Code	**Copper Oxide Loading (%)**
SP	00
RR01	2
RR02	4
RR03	6

3. Results

FT-IR spectra in the 400 to 4000 cm^{-1} range were used to characterize the functional groups that were present in the SPEES and SPEES/cerium oxide membranes. Figure 1 shows the SO_3H group of H_2SO_4 and O-H stretching was observed at3363for neat SPEES that is shift 3383 and 3382 for the nanocomposite membrane.A sharp peak of C–C aromatic bond stretching was observed at 1583 cm^{-1}in the case of SPEES copper nanocomposite.1634 Sharpe peak for neat SPEES, but its intensity reduces in polymer nanocomposite.A peak at 553 cm^{-1} confirmed the presence of Cu-O. A peak at 1042 shows the confirmed presence of S=O stretching for SPEES that shifted to 1103 for nanocomposite membrane. The long polymeric chain was bending in the polymer, as evidenced by a peak of 869 cm^{-1}.

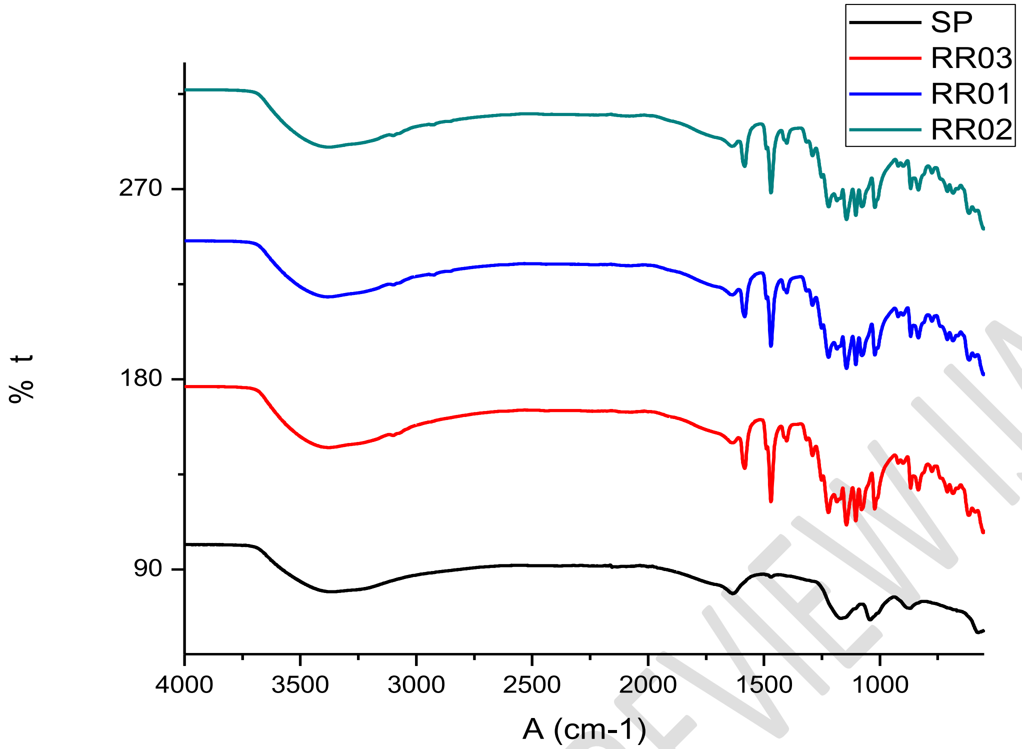
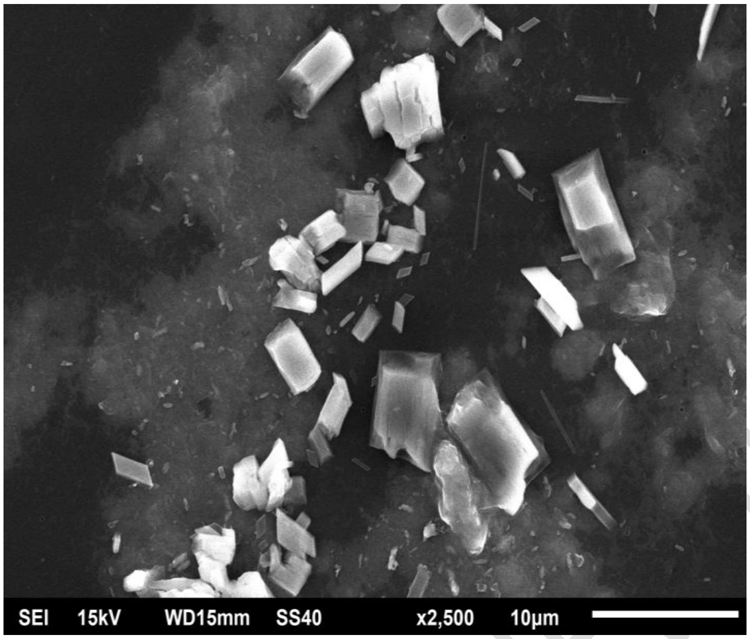


Figure1 FT-IR of pure SPEES and SPEES/copper oxide membranes

The surface morphology of SPEES-copper oxide nanocomposite was studied by SEM. It is explains the shape, size, dispersion, and compatibility of nanoparticles in a polymer matrix. Good dispersion of a filler in a polymer matrix significantly improves composite performance by improving in thermal properties, optical properties, and antibacterial properties. Figure 2 shows that copper oxide nanoparticles have a pellet form and are well dispersed into the sulfonated poly (1,4-phenylene ether ether sulfone) (SPEES) matrix. It shows good interaction between SPEES and copper oxide nanoparticles.



.

Figure 2.SEM image of SPEES/copper oxide membrane

Thermal analysis is a technique that provides information about how polymer material decomposes with heat. Figure 3 shows SPEES and SPEES-copper oxide membranes start losing weight due to heat occurring at the temperature of 150-300°C. This weight loss occurs due to the removal of absorbed water molecules or solvent. The second stage, located at 300–450°C, resulted from the sulfonic acid groups in SPEES and SPEES-copper oxide in the ion exchange polymer membranes. The third weight loss started at 450°C onwards due to the degradation of polymerbackbones.

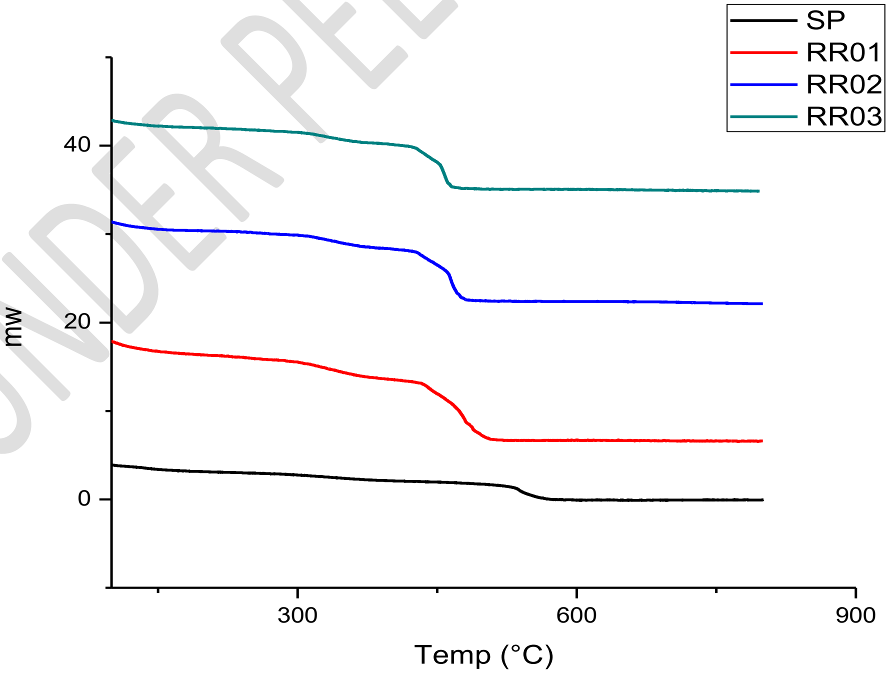


Figure 3. Comparative TGA of pure SPEES and SPEES/copper oxide membranes

DSC analysis gives details about the glass transition temperature (Tg) and melting point of polymer. Tg determined that transition from a hard, brittle, glassy state to a soft, rubbery state. Figure 4 shows that copper oxide nanoparticles were well dispersed in SPEES matrix, and the resultant glass transition temperature (Tg) was increased with copper oxide nanoparticle increase in neat SPEES. 6% copper oxide loading has more Tg than 2%, 4%, and neat SPEES.

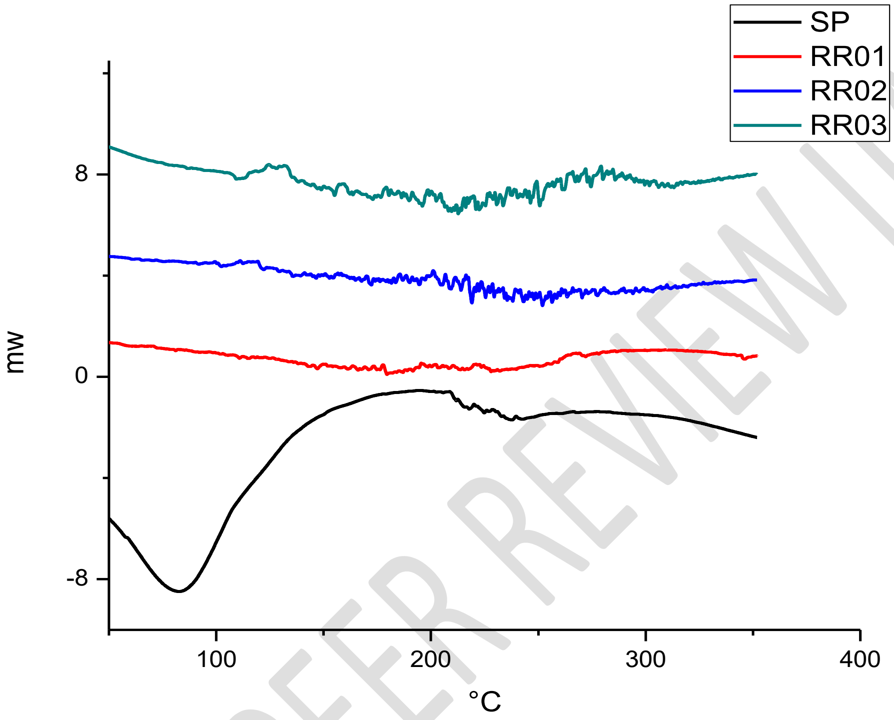


Figure 4. Comparative graph of glass transition temperature (Tg) of pure SPEES and SPEES/copper oxide membrane

UV-absorption lies between 250 to 300 nm. Figure 5 shows the absorption of SPEES and SPEES copper oxide nanocomposite. A slight change was observed in the UV absorption of copper oxide. Absorption of SPEES copper oxide nanocomposite showed a higher absorption peak intensity increase than that of neat SPEES. 2% and 4% loading did not have much effect on the absorption peak, but 6% copper oxide shifted the absorption peak.

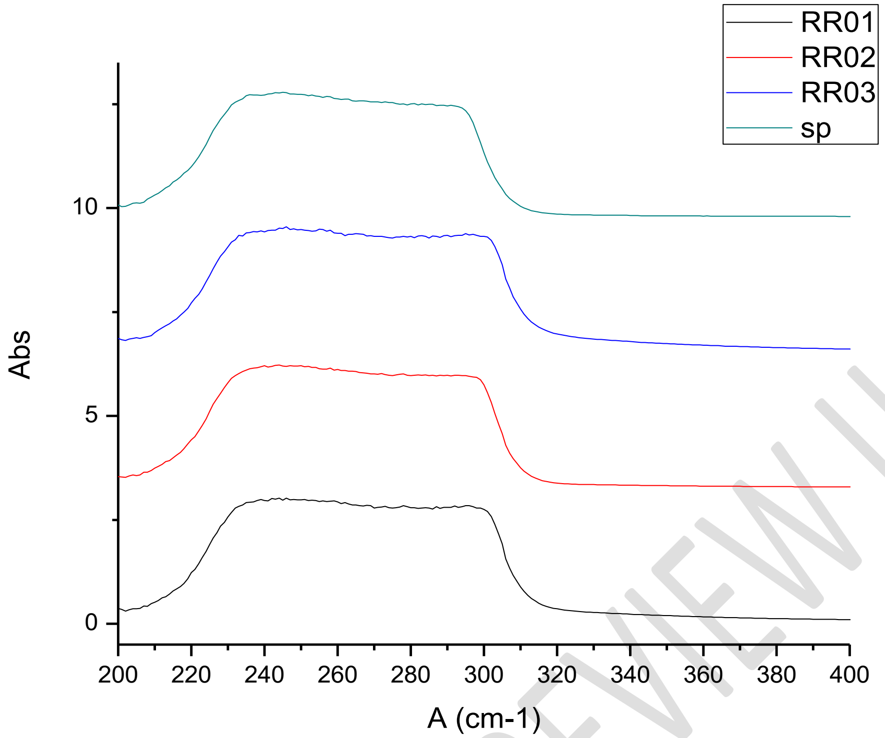


Figure 5. Comparative graph of UV Spectra of pure SPEES and SPEES/copper oxide membranes

4. Discussion

The characteristic C–O–C stretching vibration in the neat SPEES backbone, initially observed at 1167 cm^{-1}, shifted to 1144 cm^{-1} and 1185 cm^{-1} upon the incorporation of copper oxide (CuO) nanoparticles. These shifts confirm a significant chemical interaction between the CuO fillers and the SPEES matrix.

Thermal stability enhanced progressively with CuO loading; specifically, the degradation onset temperature shifted toward higher values compared to the neat polymer (Table 2). This improvement is attributed to the high degree of nanoparticle dispersion and robust interfacial adhesion, which effectively restricts polymer chain mobility. Consequently, the thermal resistance of the composite is significantly bolstered. Notably, the residual char yield decreased as CuO loading increased, suggesting that these nanocomposites are better suited for high-temperature applications.

Table 2 Thermal degradation of pure SPEES and SPEES/copper oxide membranes

Sample Code	**Onset-point**	**Mid-point**	**End-Point**	**Final Weight loss percentage**
SP	342	485	554	100
RR01	359	420	488	99.8

RR02	429	438	471	100
RR03	447	449	472	99.5

Furthermore, the addition of CuO nanoparticles led to an increase in the glass transition temperature (Table 3),further confirming the reduction in chain segmental mobility. Optical analysis (Figure 5) revealed an absorption peak at 244 nmfor neat SPEES, which underwent a bathochromic shift to 282 nm in the nanocomposites. This red shift serves as evidence of strong interfacial interaction and uniform filler dispersion, ultimately enhancing the optical properties of the SPEES-CuO system.

Table 3 Glass transition temperature (Tg) of pure SPEES and SPEES/copper oxide membranes

Sample Code	**Glass transition temperature (Tg)**
AC-SP	82.7
AC-CM 01	91
AC-CM 02	100
AC-CM 03	105

5. Conclusion

This study demonstrates that the incorporation of copper oxide (CuO) nanoparticles significantly enhances the thermal stability of sulfonated poly(ether ether sulfone) (SPEES). Specifically, the 6% loading exhibited superior thermal properties compared to both neat SPEES and the 2% and 4% loadings. This improvement is attributed to the excellent dispersion and strong interfacial interaction of the CuO nanoparticles within the SPEES matrix due to improvement in hydrophilic nature of PEES. 6 % copper oxide nanoparticle concentration has better glass transition temperaturethan 2% and 4% concentration. Furthermore, the 6% loading enhanced UV absorption relative to the pristine polymer.

CRediT authorship contribution statement

Anjali Chhonkar: Writing –original draft, Methodology, Investigation, Visualization Data curation, and Conceptualization. Harikant: Supervision, and administration. GautamJaiswar: Investigation, and Writing –review & editing.

Acknowledgment

The authors wish to thank Jiwaji University, Gwalior, and SAIF, Aligarh Muslim University, analysis on a paid basis.

Funding detail

We do not have any financial support for this research.

Declaration of interest statement

There are no relevant financial or non-financial competing interests to report.

References

1. Kugarajah V, Sugumar M, Swaminathan E, Balasubramani N, Dharmalingam S. Investigation on sulphonated zinc oxide nanorod incorporated sulphonated poly(1,4-phenylene ether ether sulfone) nanocomposite membranes for improved microbial fuel cell performance.International Journal of Hydrogen Energy. 2021;46(42):22134–22148. https://doi.org/10.1016/j.ijhydene.2021.04.067
2. Purushothaman M, Harikrishnan PA, George J, Rangasmy G, Vaidyanathan VK.Enhancement of antifouling properties, metal ions and protein separation of poly(ether-ether-sulfone) ultrafiltration membranes by incorporation of polyethylene glycol and n-ZnO. Environmental Research. 2023;216(3):114696. https://doi.org/10.1016/j.envres.2022.114696
3. Alqarni SA. Fabrication of poly(1,4-phenylene ether ether sulfone) modified with MWCNTs/reduced graphene oxide–SWCNT nanocomposites for enhanced antimicrobial activities. International Journal of Polymer Analysis and Characterization.2024;29:429–446. https://doi.org/10.1080/1023666X.2024.2378894
4. SalmaU, Hasan MM, Ahmed MJ. A review of recently investigated aromatic, aliphatic, and inorganic polymer backbones as anion exchange membranes for fuel cells. Next Materials. 2025:9:101307. https://doi.org/10.1016/j.nxmate.2025.101307
5. Khan A, Jain RK, Ghosh B, Inamuddin, AsiriAM. Novel ionic polymer–metal composite actuator based on sulfonated poly(1,4-phenylene ether ether sulfone) and PVDF/sulfonated graphene oxide. RSC Advances, 2018;8(45):25423-25435. https://doi.org/10.1039/C8RA03554G
6. Gomez KN, Valero MF. Why Polyurethanes Have Been Used in the Manufacture and Design of Cardiovascular Devices: A Systematic Review, Materials. 2020 Jul 22;13(15):3250. https://doi.org/10.3390/ma13153250
7. Shenvi S, Ismail, isloor AM. Enhanced Permeation Performance of Cellulose Acetate Ultrafiltration Membranes by Incorporation of Sulfonated Poly(1,4-phenylene ether ether sulfone) and Poly(styrene- co -maleic anhydride), Industrial & Engineering Chemistry Research. 2014 53(35):13820-13827. https://doi.org/10.1021/ie502310e
8. Zaidi SMJ. Polymer sulfonation: a versatile route to prepare proton-conducting membrane material for advanced technologies. Arabian Journal for Science and Engineering. 2003:28:183–194.
9. Nisa ZU, Chuan LK, Guan BH, Ahmad F, Ayub S. Investigation of role of coagulation protocol in the synthesis of biochar-based composite of poly(1,4-phenylene ether ether sulfone). Journal of the Indian Chemical Society. 2025;102(1):101562. https://doi.org/10.1016/j.jics.2024.101562
10. Priya M, Venkatesan R, Deepa S, Sana SS, Arumugam S, Karami AM, Vetcher AA, KIM SC. Green synthesis, characterization, antibacterial, and antifungal activity of copper oxide nanoparticles derived from Morindacitrifolia leaf extract. Scientific Reports. 2023;13:18838. https://doi.org/10.1038/s41598-023-46002-5
11. Farooq U, Khan ME, Mohammad A, Alamri AA, Sharma M. Sustainable synthesis of copper oxide nanoparticles: Data-driven photocatalysis, Pt-free hydrogen production, and antibacterial assessment. Catalysts. 2025;15(12):1163. https://doi.org/10.3390/catal15121163
12. Schmidt G, Malwitz MM. Properties of polymer–nanoparticle composites. Current Opinion in Colloid and Interface Science. 2003;8(1):103-108. https://doi.org/10.1016/S1359-0294(03)00008-6