

Mixed Matrix Membranes of Polysulfone/Polyimide Reinforced with Modified Zeolite Based Filler: Preparation, Properties and Application

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Electronic Supplementary Information

Abstract In this work, polysulfone/polyimide (PSf/PI) mixed matrix membranes were fabricated by reinforcement of modified zeolite (MZ) particles through solution casting method for investigation of antibacterial activity against two gram negative bacteria (*Salmonella typhi*, *Klebsella pneumonia*) and two gram positive bacteria (*Staphylococcus aureus*, *Bacillus subtilis*). The modified zeolite particles were incorporated to PSf and PI matrix and the influence of these particles on thermal, mechanical and structural properties was evaluated. The morphological evolution was investigated through scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis, which revealed good compatibility between organic polymer matrix and inorganic filler. Mechanical stability was investigated by tensile testing while thermal analysis was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). This revealed improvement in thermal properties with increasing filler concentration from 1 wt% to 10 wt%. Structural analysis was successfully done using X-ray diffraction analysis (XRD) and Fourier transform infrared (FTIR) spectroscopy. Solvent content of fabricated mixed matrix membranes was observed to decrease while moving from more hydrophilic to less hydrophilic solvent. However, addition of filler content enhanced the porosity of fabricated membranes. The synthesized mixed matrix membranes exhibited good antibacterial activity and the highest activity was shown by PSf/PI/MZ mixed matrix membrane. Therefore, the combination effect of PSf, PI and MZ sufficiently enhanced the antibacterial activity of mixed matrix membranes.

Keywords Modified zeolite; Polysulfone/polyimide blend membrane; Mixed matrix membrane; Thermal analysis; Antibacterial activity

Citation: Muntha, S. T.; Siddiq, M.; Kausar, A.; Khan, A. Mixed Matrix Membranes of Polysulfone/Polyimide Reinforced with Modified Zeolite Based Filler: Preparation, Properties and Application. Chinese J. Polym. Sci. 2018, 36(1), 65–77.

INTRODUCTION

Mixed matrix membrane (MMM) comprises solid-solid arrangement composed of dispersed inorganic phase reinforcing into polymer matrix. The inherent separation characteristics of inorganic particles result in higher permeability and selectivity of MMM. The major inorganic phases in the polymer membranes are the non-porous and porous fillers^[1–5]. Porous inorganic filler has molecular sieve effect while the nonporous inorganic filler causes increase of tortuous pattern of matrix. Organic-inorganic nanocomposites are being studied massively due to their wide spread potential and extraordinary properties. Organic-inorganic nanocomposites generally consist of organic polymer incorporated with nanoscale inorganic building blocks^[6–10].

Polysulfone (PSf), a thermoplastic polymer, is well known for its stability and toughness at elevated temperatures. Membranes can be manufactured easily with PSf, and such membranes can be employed for various applications

including gas separation, waste water recovery and hemodialysis^[11]. Polyimide (PI) is among the class of thermoset polymers. It is well known for its good chemical resistance and thermomechanical properties^[12]. Materials manufactured from polyimide are flexible, light weight and resistant to chemicals and heat. Significant place has been taken by blend membrane in development of membrane science for growth of polymer structure. The blending of PSf and PI may reduce the possibility of plasticization and thus offer beneficial characteristics to blend membrane.

Zeolites (Z) are aluminosilicates. They are constituted by AlO_4 and SiO_4 tetrahedra that results in formation of ring structure. They are well defined mesopores and micropores and form 3-dimensional network which connects channel system^[13–15]. The exceptionally high porosity of zeolites provides them with larger surface area. The phase separation between inorganic filler and polymer matrix can be minimized by modification of inorganic filler. The modification can alter the properties of zeolite such as hydrophobicity and polarity, thus making it a new candidate for direct applications^[16].

The PSf membranes and derivatives are extensively being used as functional materials in medical, industrial and

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Received July 21, 2017; Accepted August 17, 2017; Published online October 30, 2017

biochemical fields due to their physical properties. The connecting ether oxygen of polysulfone provides toughness while chain rigidity is attained from relatively immobile and inflexible SO₂ and phenyl groups. Much attention has been gained by combination of polymer materials with zeolite particles due to enhanced mechanical, thermal and antibacterial properties. The enhanced antibacterial activity may result due to defence provided by polymer hosting, although the procedure behind functioning of mixed matrix membranes on bacteria is not completely elucidated. Three common methods are known such as, production of reactive oxygen species (ROS) by mixed matrix membrane, uptake of ions from mixed matrix membrane followed by DNA replication and disruption of adenosine triphosphate (ATP) production, and mixed matrix membrane direct damage to cell membrane^[17]. Antibacterial polymers can be used in food contact applications such as food packaging. Such packaging can reduce or retard the growth of bacteria present in packed food or packing material.

Several researchers have fabricated zeolite reinforced polymer membranes. Amooghin *et al.* studied the aminosilane grafting effect on NaY zeolite-Matrimid mixed matrix membrane for CO₂/CH₄ separation. The obtained results exhibited an increased CO₂ permeability for 15 wt% filler loading. The related CO₂/CH₄ selectivity was revealed to increase considerably from 36.3 to 57.1^[18]. Hydrogen bonding was reported as the mechanism for strong attachment between polymer matrix and inorganic filler. Fathizadeh *et al.* fabricated polyamide reinforced by zeolite nanocomposite membrane (NCM) for salt rejection application. Interfacial free energy and contact angle were reported to increase with addition of zeolite nanoparticles (Nps) to the polyamide matrix^[19]. The flux of nanocomposite membrane was 1.8 times higher than that of neat polyamide membrane. Rezakazemi *et al.* prepared polydimethylsiloxane/zeolite MMM for gas permeation studies. Higher permeability was evaluated for MMM as compared to neat polymer membrane^[20]. Better adhesion of zeolite to polymer was reported by SEM. Nik *et al.* fabricated ammine functionalized zeolite-polyimide MMM for gas separation application. Compared to neat polyimide membrane, zeolite-incorporated membrane revealed increased selectivity and permeability. Moreover, the optimum zeolite concentration was observed to be 25 wt%^[21]. Taurozzi *et al.* studied the antibacterial effects of polysulfone/silver nanocomposite membrane. Due to moderate release of silver through nanocomposite, effective reduction of intrapore biofouling was observed for porous membrane^[22]. Liu *et al.* reported strong cytotoxic effect of graphene oxide against bacteria. The bacterial cytotoxicity was attributed to both oxidative stress and membrane. Membrane stress was induced by graphene nanosheets through damaging and disrupting cell membranes, leading to cell death^[23].

In the present study, PSf/Z, PSf/MZ, PSf/PI/Z and PSf/PI/MZ MMM were fabricated through solution casting technique. Polyimide was fabricated through condensation polymerization of 4-aminophenyl sulfone and pyromellitic dianhydride. Blending of PSf and PI was performed through solution casting technique. The amine modification of zeolite was performed and amine modified zeolite (MZ) was

incorporated into PSf matrix for membrane preparation. The stability of fabricated samples toward heat was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The morphological characteristics were explored through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Structure was explored through X-ray diffraction analysis (XRD) and Fourier transform infrared microscopy (FTIR). The tensile study was performed to investigate the mechanical stability of fabricated membranes. The porosity and solvent content of fabricated membranes were determined for various solvents. Antibacterial effects of fabricated mixed matrix membranes against gram negative bacteria (*Klebsella pneumonia*, *Salmonella typhi*) and gram positive bacteria (*Staphylococcus aureus*, *Bacillus subtilis*) were also discussed. Gram negative bacteria cannot retain the crystal violet stain used in bacterial differentiation method. Their cell envelopes are composed of thin peptidoglycan cell wall sandwiched between outer bacterial membrane and inner cytoplasmic cell membrane. Gram positive bacteria retain the crystal violet stain due to thick peptidoglycan layer in their cell wall.

EXPERIMENTAL SECTION

Materials

Polysulfone (average $M_n \sim 2.2 \times 10^4$) was procured by Aldrich. Dimethyl acetamide (DMAc, 99.5%), 1,1,1-trichloroethane and zeolite A-3 granular were supplied by Daejung. 4-Aminophenyl sulfone, pyromellitic dianhydride (PMDA, 97%) and (3-aminopropyl)-trimethoxysilan (APTMS, 99%) were purchased from Aldrich.

Instrumentation

The FTIR spectra were obtained by using Fourier transform infrared (FTIR) spectrometer model Bruker Tensor II Germany. Field emission scanning electron microscopy (FE-SEM) was recorded using a Hitachi S4800 model. Transmission electron microscopy (TEM) was performed by using Hitachi Tecnai G 20 model. The stress-strain behaviors of samples were recorded using Testomeric material testing machine M500-30CT. Thermal stability was studied by METTLER TOLEDO thermogravimetric analyser Switzerland, using 5 mg of sample in Al₂O₃ crucible at a heating rate of 10 K·min⁻¹. XRD study was performed on Shimadzu XRD-6000 using crystal monochromatic Cu K α ($\lambda = 1.5406 \text{ \AA}$, wide angle $2\theta = 5^\circ$ – 50°) at a scanning rate of 8 (°)·min⁻¹.

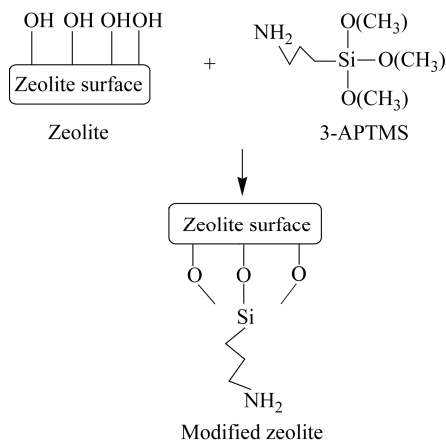
Fabrication of Polyimide

Poly(amic acid) route was followed to fabricate polyimide (PI)^[24]. Equal moles of 4-aminophenylsulfone and pyromellitic dianhydride were taken and dissolved in glacial acetic acid (100 mL). For 18 h, this mixture was refluxed in round bottom flask under nitrogen atmosphere. After 18 h, the mixture was filtered, washed with methanol and obtained precipitates were dried at 80 °C in vacuum oven.

Zeolite Modification

Zeolite (1 mg) was dissolved in 50 mL of 1,1,1-trichloroethane and the resulted mixture was stirred at

room temperature (RT). After 1 h, (3-aminopropyl)-trimethoxysilane (APTMS) was dropwise added to the mixture and it was refluxed at 60 °C for 3 h^[25]. The obtained residues were filtered, washed with methanol and oven dried at 80 °C. Terminal amino groups were provided to zeolite through reaction between methoxy group of silane and zeolite. The reaction for zeolite modification is represented in Scheme 1.



Scheme 1 Schematic illustration for zeolite modification

Fabrication of Polysulfone Membrane

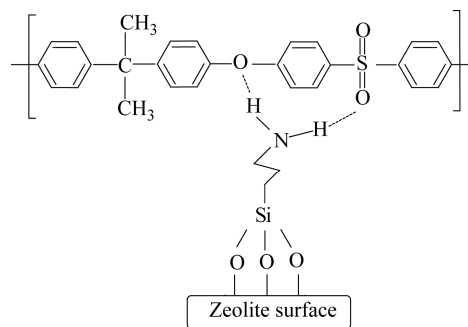
Solution casting technique was followed to fabricate transparent PSf membrane. Polymer solution (10 wt%) was prepared by dissolving PSf beads in DMAc solvent. The solution was vigorously stirred for 4 h. It was carefully poured in glass petri dish and dried at 80 °C in vacuum oven. With help of doctor's blade, membrane was peeled off from glass petri dish.

Fabrication of Polysulfone/Zeolite Mixed Matrix Membrane

Polysulfone/zeolite (PSf/Z) MMMs were synthesized by following solution casting technique. PSf beads (1 mg) were dissolved in 10 mL of DMAc. After complete dissolution of PSf beads in the solvent, varying concentrations of zeolite particles (1 wt%, 5 wt% and 10 wt%) were added to the mixtures followed by stirring for 2 h. The solutions were casted on levelled flat glass plates and dried at 80 °C in vacuum oven. The membranes were peeled off from glass plates with aid of doctor's blade.

Fabrication of Polysulfone/Modified Zeolite Mixed Matrix Membrane

The polysulfone/modified zeolite (PSf/MZ) mixed matrix membranes (MMM) were developed by dissolving 1 mg of PSf beads to 10 mL of DMAc solvent. After homogenous mixing of polymer beads in the solvent, varying concentrations of modified zeolite (MZ) particles (1 wt%, 5 wt% and 10 wt%) were added to the polymer solutions and the reaction mixtures were stirred at RT for 2 h^[26]. The casting solutions were poured in glass petri dishes and oven dried at 80 °C for 3 h to obtain PSf/MZ MMMs. The interaction between PSf and modified zeolite is represented in Scheme 2.



Scheme 2 Schematic illustration for interaction between PSf and MZ

Fabrication of PSf/PI Blend Membrane

In order to develop PSf/PI blend membrane, PSf solution (10 wt%) was prepared by dissolving PSf beads in the DMAc solvent. After homogenous mixing, 0.01 mg of polyimide (PI) was added and casting solution was vigorously stirred for 2 h at RT. The solution was casted on glass petri dish and dried in oven at 80 °C to obtain PSf/PI blend membrane.

Fabrication of PSf/PI/Z Zeolite Mixed Matrix Membrane

PSf/PI/zeolite MMMs were synthesized by solution casting technique. PSf and PI blends were prepared by adding 0.01 mg of PI to PSf solutions. The mixtures were vigorously stirred for 2 h at RT. After homogenous mixing of reaction components, zeolite particles with varying concentrations (1 wt%, 5 wt% and 10 wt%) were added to the casting solutions and the reaction mixtures were stirred for another 2 h. The casting solutions were poured in glass petri dishes and dried in vacuum oven at 80 °C for 3 h to obtain PSf/PI/Z MMMs.

Fabrication of PSf/PI/MZ Mixed Matrix Membrane

PSf/PI/MZ MMMs were fabricated by solution casting method. PI was added to PSf solutions (10 wt%) and reaction mixtures were stirred for 2 h at RT. After 2 h, modified zeolite (MZ) particles with different weight percents (1 wt%, 5 wt% and 10 wt%) were added and mixtures were vigorously stirred for additional 2 h to dissolve the reaction components completely. The casting solutions were poured in glass petri dishes and dried at 80 °C in vacuum oven. The membranes were peeled off from glass petri dishes with aid of doctor's blade. The interaction between PSf, PI and MZ is exhibited in Scheme 3.

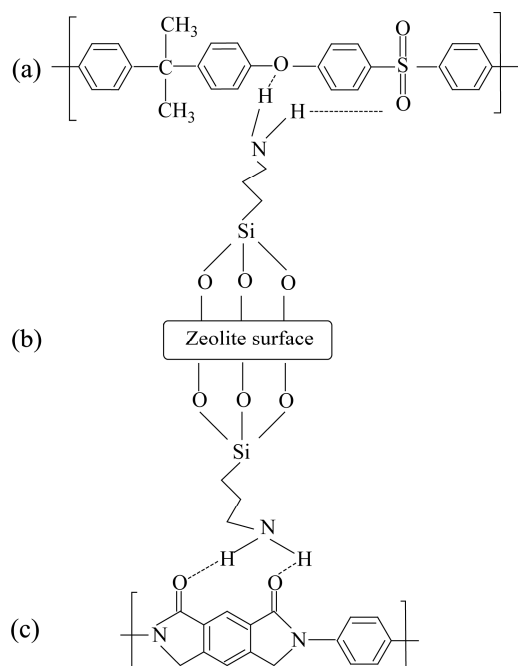
Membrane Property Measurements

In order to determine solvent content, membranes were dipped in various solvents (distilled water, methanol, ethanol, propanol) for 24 h. The membranes were mopped with blotting paper and weighed. Following equation was used to calculate the solvent content of the fabricated membranes.

$$\text{Solvent content} = (W_1 - W_2)/W_2 \quad (1)$$

where W_1 is the weight of wet membrane (g) and W_2 is the weight of dry membrane (g).

For porosity measurement, samples were cut into equal length and width and dipped in various solvents (distilled



Scheme 3 Schematic illustration for interaction between (a) PSf, (b) MZ and (c) PI

water, methanol, ethanol, propanol) for 24 h. The samples were mopped with blotting paper and weighed. Following equation was used to calculate membrane porosity,

$$\text{Porosity} = (W_1 - W_2)/A \quad (2)$$

where W_1 is the weight of wet membrane (g), W_2 is the weight of dry membrane (g) and A is the membrane area (cm^2).

Antibacterial Activity Measurements

The antibacterial activity of fabricated MMMs was evaluated against four bacterial strains, namely, *Salmonella typhi*, *Klebsella pneumonia*, *Staphylococcus aureus* and *Bacillus subtilis*. Mueller Hinton agar was used to study zones of inhibition. The morphologically comparable colonies of *Salmonella typhi*, *Klebsella pneumonia* and *Staphylococcus aureus*, *Bacillus subtilis* were shifted and bacteria were

aerobically grown at 37 °C for 18 h. Nutrient agar was disburshed in 25 mm sterilized petri dishes. These petri dishes were sealed in plastic bags and stored at 8 °C. Mueller Hinton agar was suspended in distilled water ($38 \text{ g}\cdot\text{L}^{-1}$) at 121 °C in order to prepare agar media^[27]. It was then cooled to 50 °C. 75 mL of agar media was poured in each 25 mm petri dish. After solidification, it was incubated for 24 h at 37 °C for sterility test. Freshly prepared bacterial stains were seeded with aid of sterile cotton swab. Sterile steel borer (8 mm) was used to make 7 wells per plate. 50 μL of modified zeolite solution prepared in DMSO ($0.5 \text{ mg}\cdot\text{mL}^{-1}$) was poured in relevant well. 0.025 $\text{mg}\cdot\mu\text{L}^{-1}$ per concentration pieces of PSf/Z, PSf/MZ, PSf/PI/Z and PSf/PI/MZ mixed matrix membranes were smoothly positioned over solidified agar in 4 petri plates labelled as (1 = MZ, 6 = PSf/Z, 7 = PSf/MZ, 8 = PSf/PI/Z, 9 = PSf/PI/MZ, P = positive control). Amoxicillin was used as positive control. The samples were incubated for 24 h at 37 °C. Membrane compositions and sample designations are given in Table 1.

RESULTS AND DISCUSSION

Spectroscopic Analysis

For identification of functional groups, FTIR analysis is performed. Figure 1 depicts the FTIR spectra of neat PSf membrane, PSf/PI blend membrane and MZ particles. For the PSf membrane, characteristic peak at 1119 cm^{-1} is associated with sulfonate group ($\text{O}=\text{S}=\text{O}$). Stretching frequencies at 1693 and 1502 cm^{-1} are due to benzene ring stretching mode whereas absorption at 944 cm^{-1} is attributed to antisymmetric C—O stretching vibration. For polyimide, imide ring vibration gives absorption at 1098 cm^{-1} . Peak intensity at 1380 cm^{-1} is associated to C—N—C stretching vibration^[28]. The carbonyl group of imide exhibits absorption band at 1708 cm^{-1} . N—H bending vibration is confirmed by band at 1511 cm^{-1} while medium intensity band at 3394 cm^{-1} is assigned to N—H stretching vibration. FTIR spectrum of MZ indicates appearance of absorption band at 1024 cm^{-1} , related to antisymmetric stretching mode of Al—O. N—H bend gives signal intensity at 1526 cm^{-1} . Sharp

Table 1 Sample code and composition of mixed matrix membranes

Sample name	Sample code	Ratio of PSf/PI	Quantity of zeolite
Polysulfone membrane	PSf	1/0	0
Polysulfone/polyimide blend membrane	PSf/PI	1/0.01	0
Polysulfone/zeolite MMM (1 wt%)	PSf/Z (1 wt%)	1/0	0.01
Polysulfone/zeolite MMM (5 wt%)	PSf/Z (5 wt%)	1/0	0.05
Polysulfone/zeolite MMM (10 wt%)	PSf/Z (10 wt%)	1/0	0.1
Polysulfone/modified zeolite MMM (1 wt%)	PSf/MZ (1 wt%)	1/0	0.01
Polysulfone/modified zeolite MMM (5 wt%)	PSf/MZ (5 wt%)	1/0	0.05
Polysulfone/modified zeolite MMM (10 wt%)	PSf/MZ (10 wt%)	1/0	0.1
Polysulfone/polyimide/zeolite MMM (1 wt%)	PSf/PI/Z (1 wt%)	1/0.01	0.01
Polysulfone/polyimide/zeolite MMM (5 wt%)	PSf/PI/Z (5 wt%)	1/0.01	0.05
Polysulfone/polyimide/zeolite MMM (10 wt%)	PSf/PI/Z (10 wt%)	1/0.01	0.1
Polysulfone/polyimide/modified zeolite MMM (1 wt%)	PSf/PI/MZ (1 wt%)	1/0.01	0.01
Polysulfone/polyimide/modified zeolite MMM (5 wt%)	PSf/PI/MZ (5 wt%)	1/0.01	0.05
Polysulfone/polyimide/modified zeolite MMM (10 wt%)	PSf/PI/MZ (10 wt%)	1/0.01	0.1

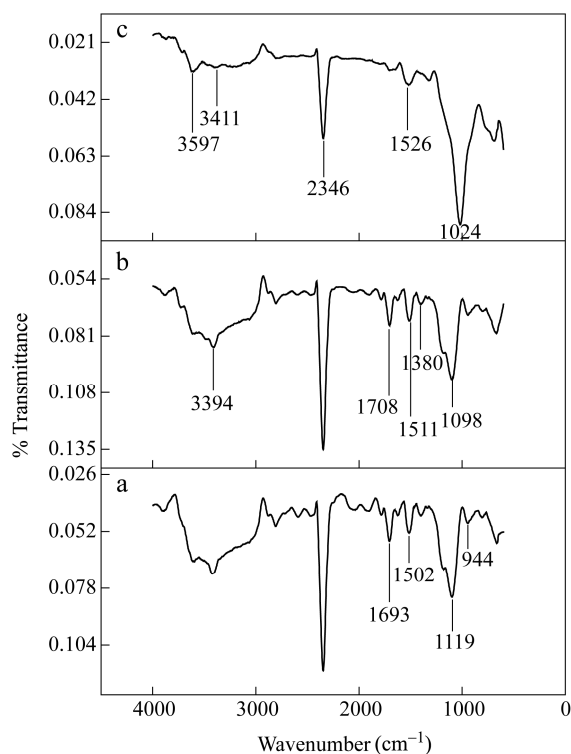


Fig. 1 FTIR spectra of (a) PSf membrane, (b) PSf/PI blend membrane (1 wt%) and (c) MZ particles

peak at 2346 cm^{-1} is related to Si—H bond. N—H stretching vibration is confirmed by small peak around 3411 cm^{-1} . Absorption band at 3597 cm^{-1} is due to residual OH groups.

Molecular interactions are investigated between zeolite and polymer through FTIR spectroscopy as shown in Fig. 2. FTIR spectrum of PSf/Z MMM (10 wt%) exhibits peak for symmetric stretching of sulfonate group ($\text{O}=\text{S}=\text{O}$) at 1146 cm^{-1} while asymmetric stretching of $\text{O}=\text{S}=\text{O}$ group gives signal at 1293 cm^{-1} . Stretching vibration of $\text{C}=\text{C}$ gives a small peak at 1636 cm^{-1} while a characteristic peak for oxygen atom bonded to two phenyl groups appears at 1233 cm^{-1} . The medium intensity peak at 1582 cm^{-1} corresponds to benzene ring stretching mode. Peak for Al—O vibration appears at 831 cm^{-1} while Si—O vibration gives signal at 1146 cm^{-1} . For PSf/MZ MMM (10 wt%), the peak at 1158 cm^{-1} corresponds to $\text{O}=\text{S}=\text{O}$ group because ammine group addition to the system shifts the band to higher wavenumber which is an indication of presence of hydrogen bonding^[29]. Symmetric stretching of C—H bond gives signal at 2852 cm^{-1} . The small peak at 1465 cm^{-1} appears due to C—N stretching vibration. However, N—H wagging gives signal at 668 cm^{-1} . The characteristic peak at 2361 cm^{-1} is due to Si—H bond. The C—H stretch superimposed on N—H stretch gives absorption at 2922 cm^{-1} . No absorbance is observed in OH region due to ammine functionalized zeolite. The intensity of the peak at 2361 cm^{-1} is observed to increase for PSf/MZ MMM as compared to that of PSf/Z MMM, which is an indication of presence of hydrogen bonding and thus it predicts physical interaction between polymer and modified

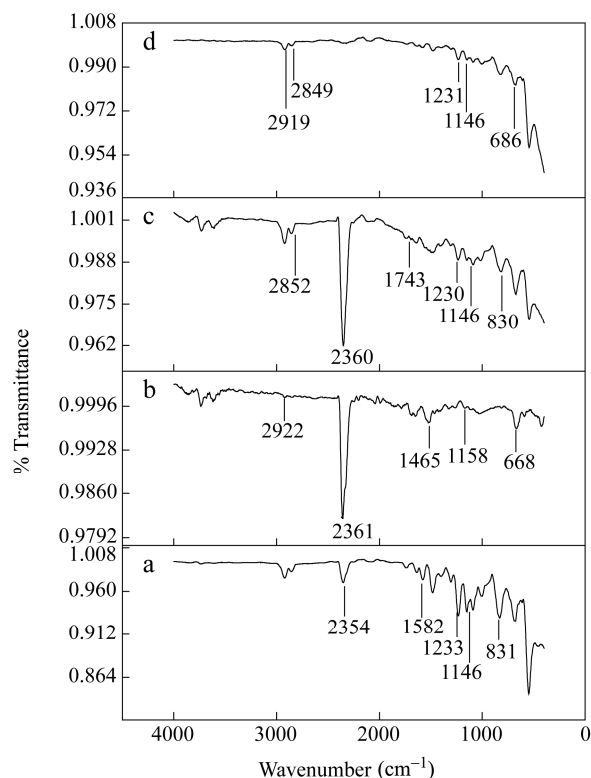


Fig. 2 FTIR spectra of (a) PSf/Z (10 wt%), (b) PSf/MZ (10 wt%), (c) PSf/PI/Z (10 wt%), (d) PSf/PI/MZ (10 wt%) mixed matrix membranes

zeolite. FTIR spectrum of PSf/PI/Z MMM (10 wt%) exhibits symmetric stretching of $\text{O}=\text{S}=\text{O}$ group at 1146 cm^{-1} . The peak at 1230 cm^{-1} is related to C—O bond while absorption at 2852 cm^{-1} is due to C—H bond. The medium intensity peak at 830 cm^{-1} corresponds to Al—O vibration. Carbonyl group of imide gives peak at 1743 cm^{-1} . Imide ring vibration is detected at 1101 cm^{-1} . N—H bending vibration is observed at 1578 cm^{-1} while vibration for Si—H bond is detected at 2360 cm^{-1} . FTIR spectrum of PSf/PI/MZ MMM (10 wt%) exhibits absorption for sulfonate group at 1146 cm^{-1} . The C—O bond gives absorption at 1231 cm^{-1} while absorption for C—H bond is detected at 2849 cm^{-1} . Absorption around 2919 cm^{-1} is observed for C—H stretch superimposed on N—H stretch. Medium intensity peak at 686 cm^{-1} corresponds to N—H wagging. Al—O bond gives signal intensity at 830 cm^{-1} while Si—O gives absorption at 1146 cm^{-1} . The results are summarized in Table 2.

Morphological Investigation

The details about morphology and surface of fabricated composites are observed through SEM. The SEM images of neat PSf membrane, PSf/PI blend membrane (1 wt%), PI, zeolite and MZ are exhibited in Fig. S1 (in electronic supplementary information, ESI). The SEM micrograph of PSf membrane reveals pores of different sizes along with nodules or interconnected cavities on the membrane surface. The surface structure of polyimide imaged through SEM reveals homogenous phase. Smooth morphology is observed

Table 2 FTIR data of fabricated mixed matrix membranes

Sample code	O=S=O (cm ⁻¹)	C—O (cm ⁻¹)	C=C (cm ⁻¹)	C—H (cm ⁻¹)	Benzene ring stretching mode (cm ⁻¹)	Al—O (cm ⁻¹)	C—N—C (cm ⁻¹)	N—H (cm ⁻¹)
PSf	1119	944	—	—	1693	—	—	—
PI	—	—	—	—	—	—	1380	1511
MZ	—	—	—	—	—	1024	—	1526
PSf/Z (10 wt%)	1146	—	1636	—	1582	831	—	—
PSf/MZ (10 wt%)	1158	—	—	2852	—	—	1465	—
PSf/PI/Z (10 wt%)	1146	1230	—	2852	—	—	—	1578
PSf/PI/MZ (10 wt%)	1146	1231	—	2849	—	830	—	—

with distribution of few particles on the surface. The SEM micrograph of the PSf/PI blend membrane (1 wt%) exhibits uniform surface due to homogenous dispersion and appropriate compatibility of both polymers. The SEM images of unmodified and modified zeolite samples are shown in Fig. S1 (in ESI). The unmodified zeolite particles tend to be very closely bound together with little space between them. However, for modified zeolite particles, homogenous smooth surface is observed which reveals crystalline laminar habits. Tubular habit which is an indication of clinoptilolite is also observed^[30].

Figure S2 (in ESI) exhibits SEM image of PSf based MMMs. The addition of zeolite A-3 to PSf membrane in PSf/Z MMM (10 wt%) results in homogenous dispersion however agglomeration can be distinguished from the SEM image. The fillers are strongly attracted towards each other due to weak adhesion between polymer matrix and filler. The SEM image of PSf/MZ MMM (10 wt%) reveals good interaction of organic and inorganic component. The figure shows homogenous distribution of zeolite particles treated with (3-aminopropyl)trimethoxysilane in the PSf hybrid system. Nanosilica particles are also detected because during surface treatment of the zeolite particles with APTMS, some alkoxy groups react with zeolite while others form nanosilica particles in themselves^[31]. SEM image of PSf/PI/Z MMM (10 wt%) indicates void formation due to brittleness and polymer-zeolite interfacial incompatibility. The SEM micrograph of PSf/PI/MZ MMM (10 wt%) reveals homogenous morphology and uniform distribution of MZ particles on the PSf/PI blend surface. Moreover, rod shaped morphology for MZ particles is investigated.

In order to verify the structure of fabricated samples, TEM analysis is performed. The TEM images of neat PSf membrane, PSf/PI blend membrane (1 wt%), PI and MZ are presented in Fig. 3. From the TEM image of the PSf membrane, interconnected cavity channels are revealed. The TEM analysis of polyimide shows that homogenous morphology and ideal bonding between monomers as dark regions are not observed. The TEM image of PSf/PI blend membrane (1 wt%) reveals dense skin and sub-porous layer in the morphology. The TEM image of MZ displays distinctive clinoptilolite morphology occurring as laths and euhedral plates which is characteristic of monoclinic symmetry^[32].

The morphology of fabricated mixed matrix membranes is also investigated through TEM. Figure 4 exhibits the TEM images of PSf based MMMs. The cross-section of PSf/Z MMM (10 wt%) reveals concentricity with outer diameter. The image displays voids on the outer surface as well as

inter-connected pores; zeolite particles are not homogenously distributed along the membrane surface. However, the TEM image of PSf/MZ MMM (10 wt%) shows dense and defect-free membrane along with homogenous and uniform distribution of MZ particles. Interfacial voids are not detected for PSf/MZ MMM which is

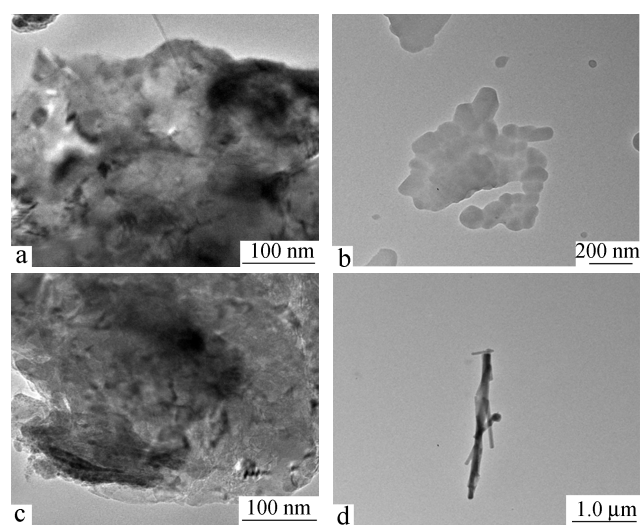


Fig. 3 TEM images of (a) PSf membrane, (b) polyimide, (c) PSf/PI blend membrane (1 wt%), and (d) modified zeolite

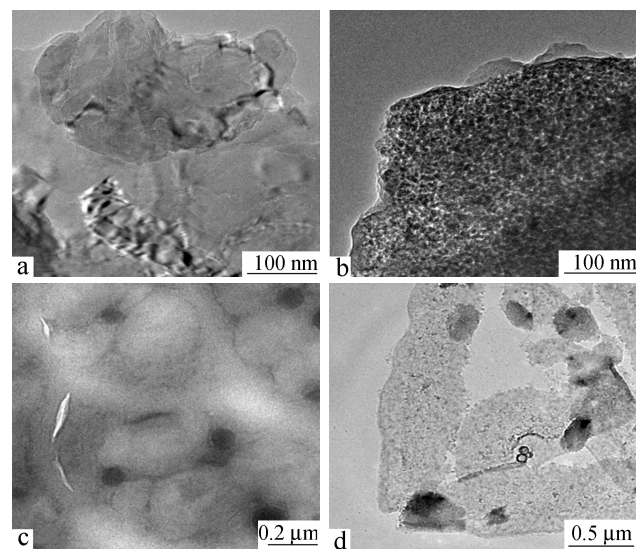


Fig. 4 TEM images of (a) PSf/Z MMM (10 wt%), (b) PSf/MZ MMM (10 wt%), (c) PSf/PI/Z MMM (10 wt%), and (d) PSf/PI/MZ MMM (10 wt%)

an evidence of better interfacial adhesion between MZ particles and polymer matrix. The cross-section morphologies of PSf/PI/Z MMM (10 wt%) and PSf/PI/MZ MMM (10 wt%) reveal no considerable differentiation. Their morphologies display interesting evolution due to better compatibility of PSf and PI. The zeolite particles are uniformly imbedded along PSf/PI blend matrix. The better compatibility between inorganic and organic nature of modified zeolite and glassy polymers (PSf and PI) is the reason for better interaction between polymer and filler surface and thus void formation is not detected.

Mechanical Analysis

In order to evaluate the mechanical properties of fabricated membranes, tensile analysis is performed. Due to better interaction and homogenous dispersion of PSf and PI, Young's modulus is observed to increase for PSf/PI blend membrane (1 wt%) as compared to neat PSf membrane as shown in Fig. 5(a). Similar increase is observed for toughness and tensile strength of blend membrane. Thus, mechanical properties are significantly improved due to blend formation.

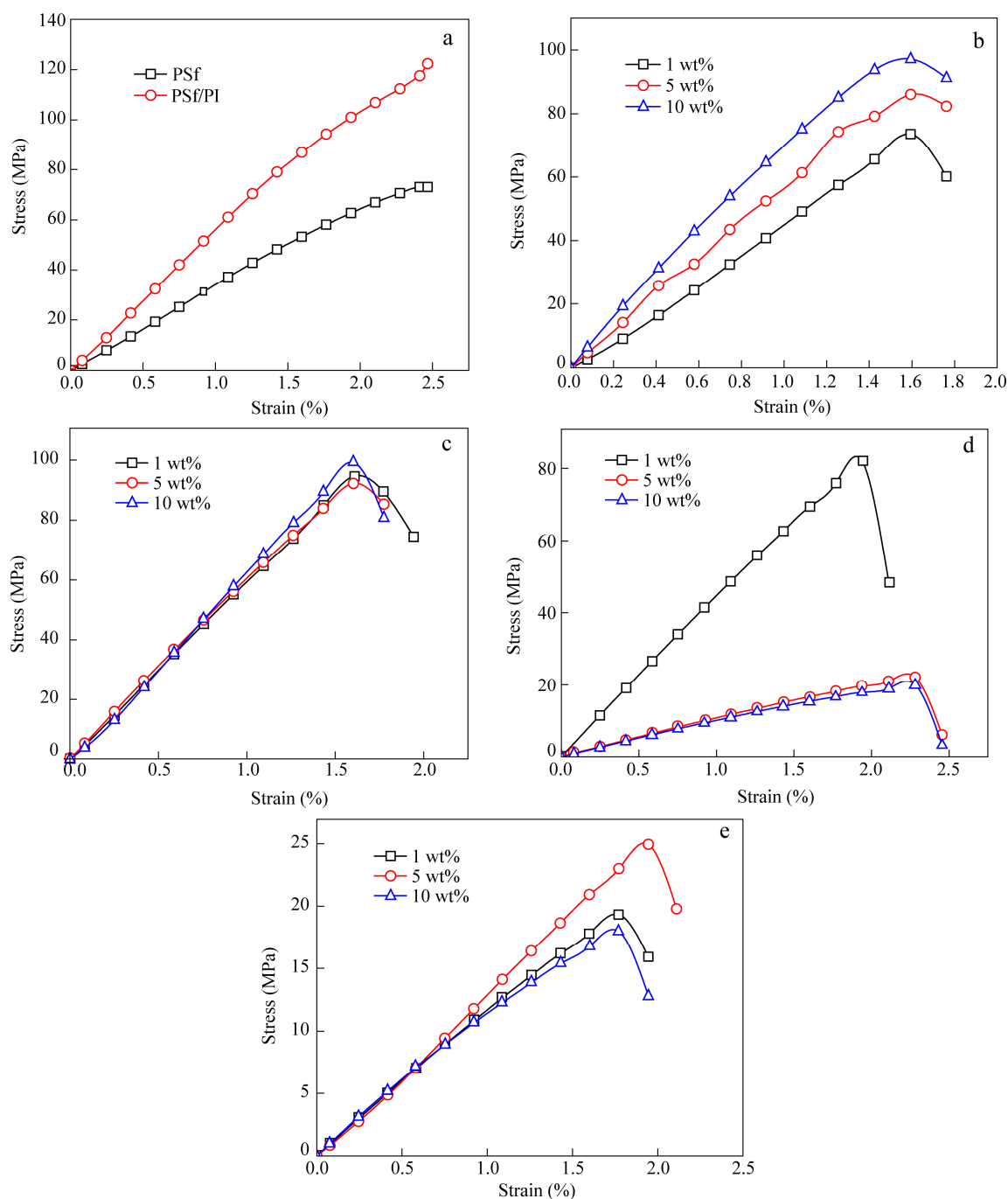


Fig. 5 Tensile overlay of (a) PSf membrane and PSf/PI blend membrane, (b) PSf/Z MMM (1 wt%, 5 wt%, 10 wt%), (c) PSf/MZ MMM (1 wt%, 5 wt%, 10 wt%), (d) PSf/PI/Z MMM (1 wt%, 5 wt%, 10 wt%), (e) PSf/PI/MZ MMM (1 wt%, 5 wt%, 10 wt%)

The tensile overlay of PSf/Z MMMs at different concentrations (1 wt%, 5 wt%, 10 wt%) is presented in Fig. 5(b). The Young's modulus is observed to increase with increasing filler concentration. Therefore, the optimum filler content for PSf/Z MMM is 10 wt%. On the whole, toughness is also increased thus zeolite incorporation into PSf matrix enhances its mechanical properties due to physical adhesion between matrix and filler. The tensile overlay of PSf/MZ MMMs at varying concentrations (1 wt%, 5 wt%, 10 wt%) is shown in Fig. 5(c). The Young's modulus is observed to be almost the same for 1 wt% and 5 wt% MMM but the significant increase is observed for 10 wt % PSf/MZ MMM. Therefore the optimum filler concentration for PSf/MZ MMM comes out to be 10 wt%, for which Young's modulus is evaluated to be 6791 N·mm⁻². Thus, for both PSf/Z MMM and PSf/MZ MMM, the optimum filler concentration is observed to be 10 wt%.

The tensile overlay of PSf/PI/Z MMMs at different concentrations (1 wt%, 5 wt%, 10 wt%) is shown in Fig. 5(d), which reveals decrease in Young's modulus with increasing filler concentration. The decrease may be attributed to the presence of agglomerates at higher concentration which can cause breakage^[33]. The tensile overlay of PSf/PI/MZ MMMs at varying concentrations (1 wt%, 5 wt%, 10 wt%) is shown in Fig. 5(e). While increasing filler concentration from 1 wt% to 5 wt%, Young's modulus is reported to increase; however it is observed to decrease slightly for 10 wt% PSf/PI/MZ MMM. At higher concentration decrease may be attributed to agglomerate formation which limits the reinforcing action of filler and polymer matrix, thus 5 wt% is considered as the optimum concentration for PSf/PI/MZ MMM. The results of mechanical analysis are summarized in Table 3.

Table 3 Mechanical properties of fabricated mixed matrix membranes

Sample code	Young's modulus (MPa)	Elongation at break (%)	Toughness (MPa)
PSf	3565	2.45	98
PSf/PI	5689	3.59	535
PSf/Z (1 wt%)	4906	2.99	191
PSf/Z (5 wt%)	5126	2.25	25
PSf/Z (10 wt%)	6984	1.49	78
PSf/MZ (1 wt%)	6106	2.87	224.58
PSf/MZ (5 wt%)	5943	1.74	77.96
PSf/MZ (10 wt%)	6791	1.80	99.23
PSf/PI/Z (1 wt%)	4433	2.62	142.16
PSf/PI/Z (5 wt%)	1077	2.43	29.58
PSf/PI/Z (10 wt%)	1026	2.73	34.13
PSf/PI/MZ (1 wt%)	1166	1.94	20.48
PSf/PI/MZ (5 wt%)	1389	2.02	23.16
PSf/PI/MZ (10 wt%)	1159	1.85	16.89

Thermal Analysis

The TGA curves of PSf membrane and PSf/PI blend membrane (1 wt%) are shown in Fig. 6(a). From the TGA curve of neat PSf membrane, no weight loss is observed below 150 °C which is an indication of complete solvent removal. The degradation temperature (T_d) is observed at 469 °C and it is associated to main polymer chain degradation^[34]. For PSf/PI blend membrane, degradation

temperature is reported at 475 °C which is slightly higher than the T_d of neat PSf membrane. In order to study the effect of filler on polymer stability, modified zeolite particles at different concentrations are loaded to the PSf matrix. The TGA curves of PSf/MZ MMM at different concentrations (1 wt%, 5 wt%, 10 wt%) are exhibited in the Fig. 6(b). Two step degradation process is revealed where the first step belongs to degradation of some polymer chains while the second step is due to composite degradation. For 1 wt% PSf/MZ MMM, the first step appears at 205 °C with 1% weight loss while the maximum degradation temperature is observed at 504 °C. For 5 wt% PSf/MZ MMM, the first step appears at 176 °C with 1% weight loss while the maximum

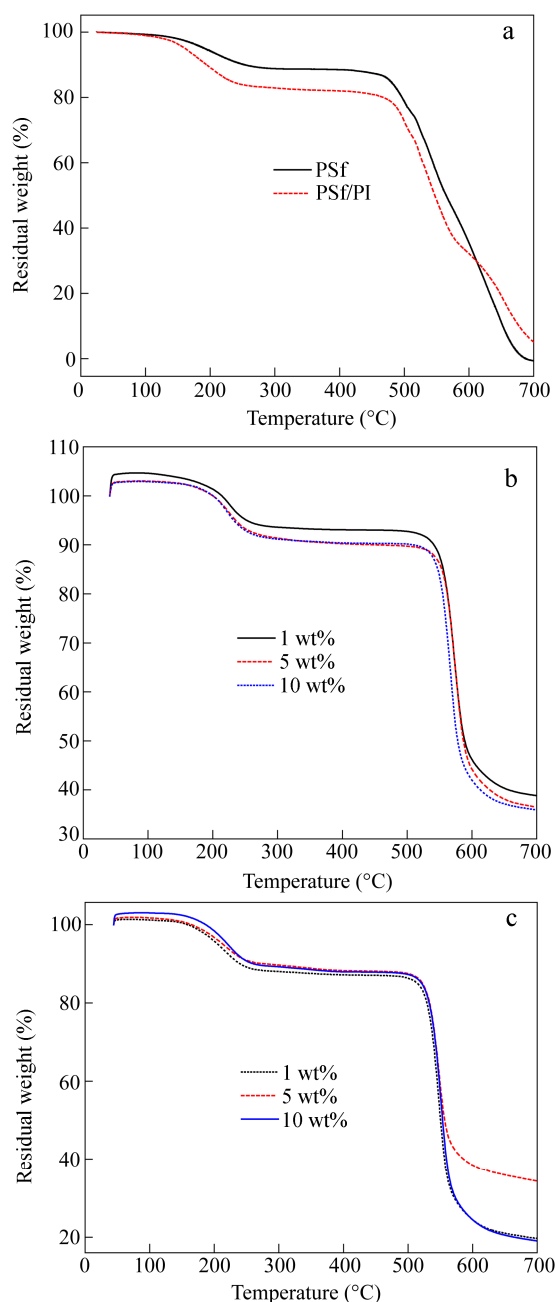


Fig. 6 TGA curves of (a) PSf membrane and PSf/PI blend membrane, (b) PSf/MZ MMM (1 wt%, 5 wt%, 10 wt%), and (c) PSf/PI/MZ MMM (1 wt%, 5 wt%, 10 wt%)

degradation temperature is evaluated to be 513 °C. For 10 wt% PSf/MZ MMM, the maximum degradation temperature is observed to be 531 °C. The TGA curves of PSf/PI/MZ MMMs are shown in Fig. 6(c). The maximum degradation temperature for 1 wt% and 5 wt% PSf/PI/MZ MMM is observed at 478 °C while the maximum T_d for 10 wt% PSf/PI/MZ MMM is reported at 483 °C. The thermally stable PSf/MZ and PSf/PI/MZ MMM are observed to be non-combustible upto 600 °C thus higher temperature is required to completely decompose mixed matrix membranes

due to amine-zeolite mutual interaction. Degradation temperature is observed to increase slightly with increasing filler concentration from 1 wt% to 10 wt% because at the polymer-filler interface, polymer chain mobility is inhibited due to filler attachment or rigidification of polymer chains. Hence, thermal stability of polymer membranes improved significantly by filler addition.

The glass transition temperature of fabricated samples was evaluated through differential scanning calorimetry (DSC) analysis. Figure 7(a) accounts for DSC curves of neat PSf

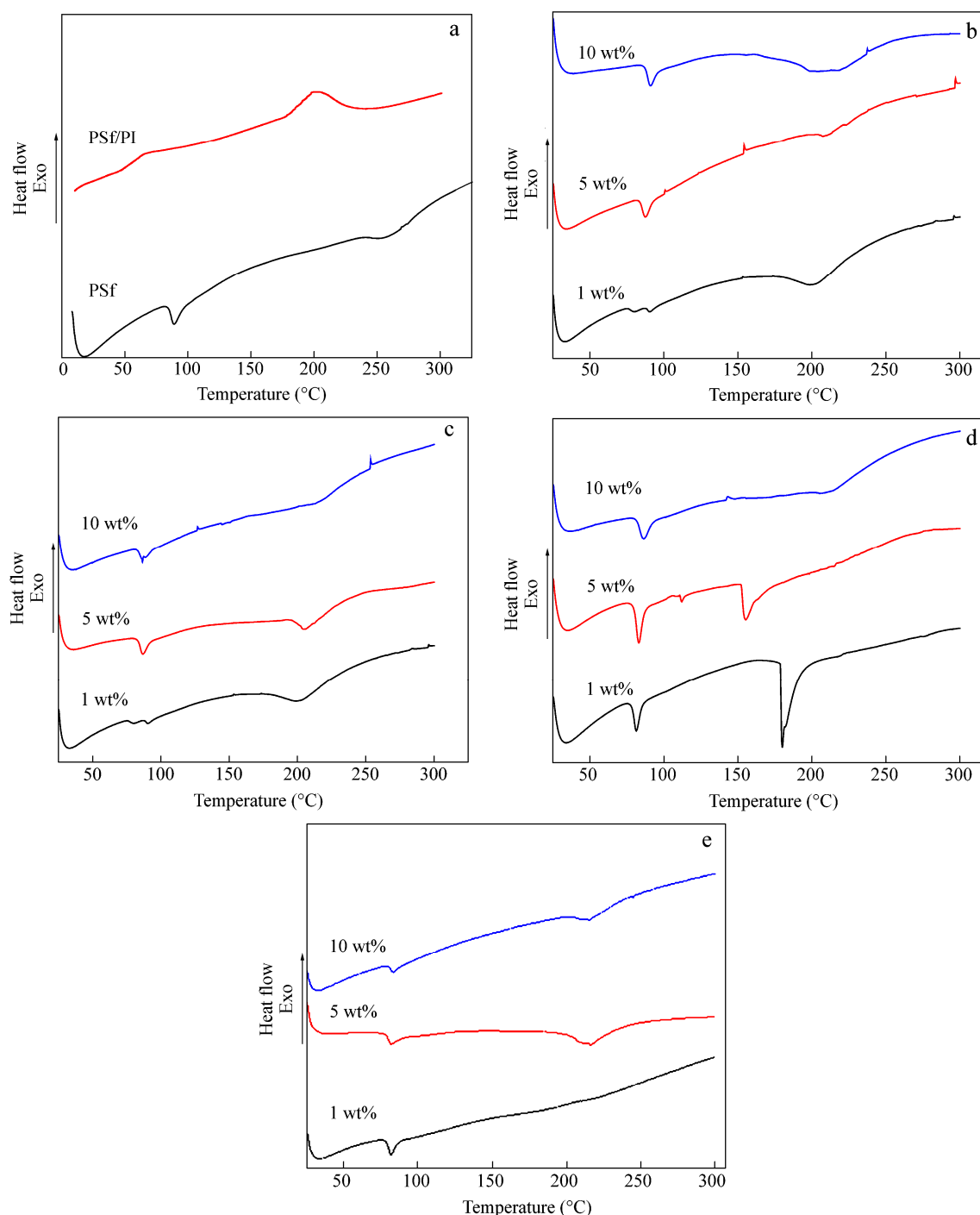


Fig. 7 DSC curves of (a) PSf membrane and PSf/PI blend membrane, (b) PSf/Z MMM (1 wt%, 5 wt%, 10 wt%), (c) PSf/MZ MMM (1 wt%, 5 wt%, 10 wt%), (d) PSf/PI/Z MMM (1 wt%, 5 wt%, 10 wt%), and (e) PSf/PI/MZ MMM (1 wt%, 5 wt%, 10 wt%)

membrane and PSf/PI blend membrane (1 wt%). The DSC analysis of neat PSf membrane reveals glass transition temperature (T_g) at 71 °C while the DSC curve of PSf/PI blend membrane shows characteristic glass transition temperature of 172 °C which exhibits compatibility of both polymers. In order to determine the effect of filler on glass transition temperature of polysulfone membrane and polysulfone/polyimide blend membrane, DSC analysis is conducted for MMM. DSC curves of PSf/Z MMM are shown in Fig. 7(b). The melting temperature (T_m) for 1 wt% PSf/Z MMM is investigated around 200 °C while T_g is evaluated to be 86 °C for 1 wt%, 87 °C for 5 wt% and 91 °C for 10 wt% PSf/Z MMM. T_g is observed to increase with the increase in filler content due to hindrance of polymer chain movement at polymer-filler interface because chain entrance of filler particle causes rigidification^[35]. Similarly increasing trend is observed for T_g values of PSf/MZ MMM with increasing filler content from 1 wt%, 5 wt% to 10 wt% as exhibited by Fig. 7(c). For 1 wt% PSf/MZ MMM, T_g is evaluated to be 85 °C while T_m is determined around 201 °C. For 5 wt% PSf/MZ MMM, T_g is examined at 86 °C while T_m is noticed at 205 °C. For 10 wt% PSf/MZ MMM, T_g is observed around 88 °C. The glass transition temperature values of PSf/Z MMM at different weight percent are evaluated to be slightly higher than those of PSf/MZ MMM. Zeolite modification causes lowering of T_g of fabricated samples due to presence of flexible aminosilane groups. DSC curves of PSf/PI/Z MMM are shown in Fig. 7(d). The DSC analysis of 1 wt% PSf/PI/Z MMM reveals T_g at 81 °C and T_m at 180 °C. For 5 wt% PSf/PI/Z MMM, T_g is evaluated to be at 83 °C while T_m at 155 °C. The DSC analysis of 10 wt% PSf/PI/Z MMM exhibits T_g at 86 °C. The thermal analysis of PSf/PI/MZ MMM reveals the increase in T_g with increasing filler content as shown in Fig. 7(e). The T_g is examined to be at 82 °C for 1 wt% and 5 wt% PSf/PI/MZ MMM while T_g is evaluated to be 84 °C for 10 wt% PSf/PI/MZ MMM. T_m is observed to be 213 °C for 5 wt% and 215 °C for 10 wt% PSf/PI/MZ MMM. Table 4 accounts for thermal properties of PSf based mixed matrix membranes.

Table 4 Thermal analysis of PSf based mixed matrix membranes

Sample code	T_g (°C)	T_m (°C)	T_d (°C)
PSf	71	—	469
PSf/PI	172	—	475
PSf/Z (1 wt%)	86	200	—
PSf/Z (5 wt%)	87	—	—
PSf/Z (10 wt%)	91	—	—
PSf/MZ (1 wt%)	85	201	504
PSf/MZ (5 wt%)	86	205	513
PSf/MZ (10 wt%)	88	—	531
PSf/PI/Z (1 wt%)	81	180	—
PSf/PI/Z (5 wt%)	83	155	—
PSf/PI/Z (10 wt%)	86	—	—
PSf/PI/MZ (1 wt%)	82	—	478
PSf/PI/MZ (5 wt%)	82	213	478
PSf/PI/MZ (10 wt%)	84	215	483

XRD Analysis

For purpose of ascertaining crystallinity of fabricated

samples, XRD analysis is performed. Figure S3 (in ESI) shows the XRD patterns of PSf membrane and PSf/PI blend membrane. XRD pattern of neat PSf membrane demonstrates rigid and amorphous polymer structure. The broad peak is observed in the range of 2θ values of 18°–25°. The addition of crystalline PI into amorphous PSf matrix results in decrease in peak broadening. Peak is observed in the range of 2θ values of 22°–25° for PSf/PI blend membrane. The XRD patterns of PI and MZ particles are depicted in Fig. S4 (in ESI). The diffraction peaks for pure PI are observed at 2θ values of 10.48°, 14.33°, 15.7°, 19.4°, 22.1°, 24.8°, 28.41° referring to d -spacing of 8.43, 6.17, 5.72, 4.55, 4.03, 3.62 and 3.14 Å respectively. The reflection peaks are revealed from the XRD pattern of MZ at 2θ values of 9.9°, 22.4°, 25.8° and 27.8°, which refers to d -spacing of 8.9, 3.9, 3.4 and 3.2 Å. This demonstrates clinoptilolite as major phase of modified zeolite, as confirmed from literature^[36]. The average crystallite size of modified zeolite calculated from Scherrer formula is 12 nm.

$$d = K\lambda/B\cos\theta \quad (3)$$

In Eq. (3), λ is X-ray wavelength, d is average crystallite size, K is Scherrer constant, θ is Bragg angle and B is the full width of the peak at half maxima. The crystal size attained using this formula is considered as average crystal dimension which is perpendicular to reflection plane. The studied samples do not always have uniform size crystals therefore crystal size evaluated from Scherrer equation is 20%–40% accurate.

The XRD patterns of PSf based mixed matrix membranes are shown in Fig. 8. The XRD pattern of PSf/Z MMM

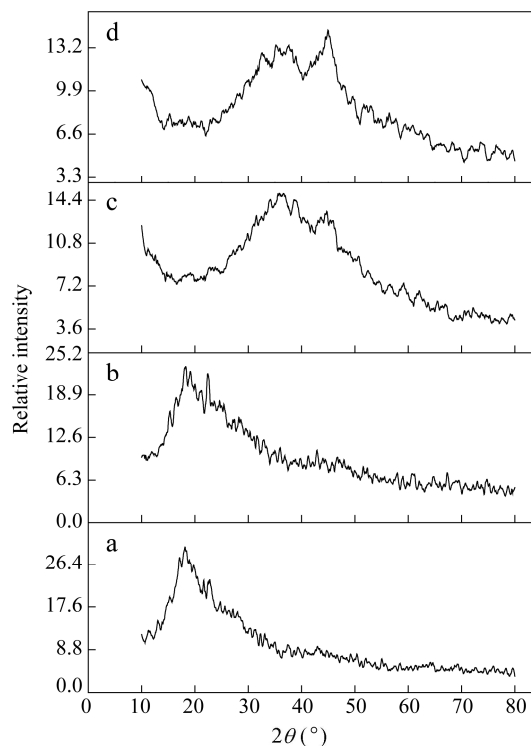


Fig. 8 XRD patterns of (a) PSf/Z MMM (10 wt%), (b) PSf/MZ MMM (10 wt%), (c) PSf/PI/Z MMM (10 wt%), (d) PSf/PI/MZ MMM (10 wt%)

(10 wt%) shows slightly broad peak at 2θ value of 18° . The same band is observed for PSf/MZ MMM (10 wt%) but intensity of the peak is observed to decrease. For PSf/PI/Z MMM (10 wt%), relatively broad band is observed for 2θ values of 34° to 45° while for PSf/PI/MZ MMM (10 wt%), band is observed in the range of 2θ values of 32° to 45° . Thus, the XRD patterns of fabricated mixed matrix membranes confirms their highly amorphous structure. The addition of crystalline PI and MZ does not cause any effect on amorphous nature of polymer membranes.

Membrane Properties

The results for solvent content of fabricated membranes are summarized in Table 5. Increasing trend is observed for the solvent content of membranes in various solvents. It is observed to decrease while moving from water to less hydrophilic solvent as solvent content is dependent on solvent hydrophilicity^[37]. Following trend is recorded for the solvent content of fabricated membranes in different solvent. The optimal results are attained for membranes evaluated with water,

Water > Methanol > Ethanol > Propanol

Table 5 Solvent content of PSf, PSf/PI, PSf/Z, PSf/MZ, PSf/PI/Z, PSf/PI/MZ membrane

Membrane	Solvent content (%)			
	Water	Methanol	Ethanol	Propanol
PSf	0.08	0.02	0.008	0.005
PSf/PI (1 wt%)	0.11	0.04	0.02	0.008
PSf/Z (10 wt%)	0.31	0.04	0.03	0.02
PSf/MZ (10 wt%)	0.67	0.05	0.03	0.02
PSf/PI/Z (10 wt%)	0.84	0.07	0.07	0.05
PSf/PI/MZ (10 wt%)	2.10	1.82	0.91	0.09

The porosity of fabricated membranes was also analysed. The results for porosity of fabricated membranes are reported in Table 6. The lowest porosity is exhibited by neat PSf membrane; however, with addition of nano-filler content in the polymer matrix, steady increase is observed. Thus, membrane's hydrophilic nature is enhanced by addition of the filler. Porous nature of membrane is observed to decrease with decreasing hydrophilicity of solvent.

Table 6 Porosity of PSf, PSf/PI, PSf/Z, PSf/MZ, PSf/PI/Z, PSf/PI/MZ membrane

Membrane	Porosity			
	Water	Methanol	Ethanol	Propanol
PSf	0.9	0.031	0.009	0.003
PSf/PI (1 wt%)	1.02	0.054	0.052	0.049
PSf/Z (10 wt%)	1.17	0.069	0.061	0.057
PSf/MZ (10 wt%)	1.29	0.076	0.064	0.059
PSf/PI/Z (10 wt%)	1.32	0.087	0.075	0.071
PSf/PI/MZ (10 wt%)	1.39	0.092	0.081	0.074

Antibacterial Activity of Nano-zeolite Incorporated Polymer Membranes

The fabricated mixed matrix membranes were evaluated for antibacterial activity against two gram negative bacteria

(*Salmonella typhi*, *Klebsella pneumonia*) and two gram positive bacteria (*Staphylococcus aureus*, *Bacillus subtilis*). The photographic images of zone of inhibition against *Salmonella typhi* and *Klebsella pneumonia* are shown in Fig. 9. Sufficient mean inhibition zone diameter was evaluated against *Salmonella typhi* and *Klebsella pneumonia* for fabricated mixed matrix membranes. MZ, PSf/Z, PSf/MZ exhibited good activity against gram negative bacteria however PSf/PI/Z and PSf/PI/MZ revealed much better activity against gram negative bacteria. Potential increase was observed in death rate of microbes by blend formation. Therefore, the combination effect of PSf, PI and MZ in the present work exhibited sufficient antibacterial activity.

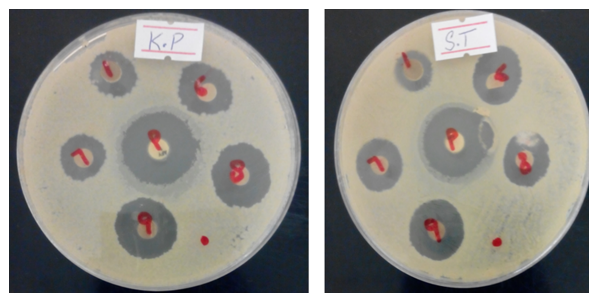


Fig. 9 Antibacterial activity of (1) MZ, (6) PSf/Z (10 wt%), (7) PSf/MZ (10 wt%), (8) PSf/PI/Z (10 wt%), (9) PSf/PI/MZ (10 wt%) against K.P. (*Klebsella pneumonia*) and S.T. (*Salmonella typhi*)

The photographic images of zone of inhibition against *Bacillus subtilis* and *Staphylococcus aureus* are shown in Fig. 10. All fabricated MMMs exhibited good activity against *Bacillus subtilis*, but the maximum activity was revealed by PSf/PI/MZ mixed matrix membrane. Superior structural integration of PSf, PI and MZ was responsible for better antibacterial activity. When observing the zone of inhibition against *Staphylococcus aureus*, no activity was observed for MZ, PSf/Z, PSf/MZ and PSf/PI/Z while PSf/PI/MZ revealed some activity. This may be due to well dispersed MZ nanofiller in the PSf/PI blend matrix. The results sustained and PSf/PI/MZ MMM revealed the best antibacterial activity against gram negative and gram positive bacteria among all fabricated mixed matrix membranes. The differences observed in inhibition zones against bacteria for MMMs are reported in Table 7. The results of antibacterial activity are plotted in Fig. S5 (in ESI).

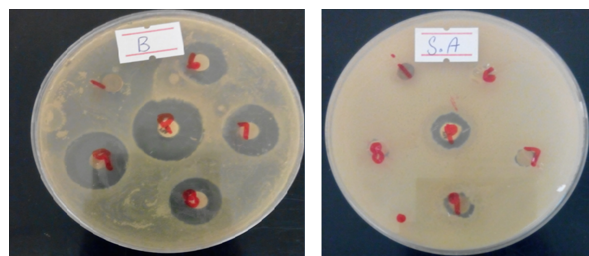


Fig. 10 Antibacterial activity of (1) MZ, (6) PSf/Z (10 wt%), (7) PSf/MZ (10 wt%), (8) PSf/PI/Z (10 wt%), (9) PSf/PI/MZ (10 wt%) against B. (*Bacillus subtilis*) and S.A. (*Staphylococcus aureus*)

Table 7 Differences observed in inhibition zone against *Salmonella typhi*, *Klebsella pneumonia*, *Bacillus subtilis*, *Staphylococcus aureus* for fabricated mixed matrix membranes

Sample	Inhibition zones (mm)			
	<i>Salmonella typhi</i>	<i>Klebsella pneumonia</i>	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>
MZ	13	15	0	0
PSf/Z (10 wt%)	18	18	17	0
PSf/MZ (10 wt%)	15	14	19	0
PSf/PI/Z (10 wt%)	17	20	17	0
PSf/PI/MZ (10 wt%)	19	20	20	2

CONCLUSIONS

The PSf/PI mixed matrix membranes were prepared by incorporating modified zeolite particles through solution casting method. The ammine modified zeolite particles reinforced in varying concentrations from 1 wt% to 10 wt%. The SEM analysis of MZ particles exhibited tubular habit which was an indication of clinoptilolite morphology and these results were confirmed by TEM analysis which showed monoclinic symmetry indicating laths and euhedral plates. The morphological investigations of mixed matrix membranes revealed uniform distribution and better compatibility between inorganic filler and polymer matrix. The tensile overlay of zeolite filled PSf/PI mixed matrix membranes revealed good mechanical properties. The thermal behaviour of fabricated membranes was observed to improve with filler loading. Predominantly in 10 wt% PSf/PI/MZ mixed matrix membranes, strong interaction and fine compatibility of polymers (PSf and PI) and filler (MZ) adequately enhanced the thermal properties. Another distinctive advantage of fabricating mixed matrix membrane increased in glass transition temperature as compared to neat polysulfone membrane. In XRD analysis, the MZ particles were found to have crystalline nature with an average crystallite size of 12 nm calculated by Scherrer formula; however, its addition to polymer membranes did not cause any effect on amorphous nature of polymer membranes. Study of membrane properties such as the solvent content and porosity were found to be dependent on solvent hydrophilicity and thus filler was added to enhance the hydrophilic nature of membrane in order to obtain the optimal results. The fabricated mixed matrix membranes were investigated for antibacterial activity against gram negative bacteria (*Salmonella typhi*, *Klebsella pneumonia*) and gram positive bacteria (*Staphylococcus aureus*, *Bacillus subtilis*). All fabricated membranes revealed good antibacterial activity however the optimal results were exhibited by PSf/PI/MZ mixed matrix membrane. Thus, the combining effects of PSf, PI and MZ greatly enhanced the antibacterial activity as well as improved the thermal, mechanical, morphological, structural and membrane properties.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2021-2>.

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