Molecular Dynamics Simulation of Polysulfone and Polystyrene-co-maleic Anhydride Blends Compatibility: A mesoscopic, Ewald Approach and Experimental Comparison

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Research Article

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Posted Date: December 10th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-1109742/v1

Molecular Dynamics Simulation of Polysulfone and Polystyrene-co-maleic Anhydride Blends Compatibility: A mesoscopic, Ewald Approach and Experimental Comparison

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23 **Graphical Abstract:**

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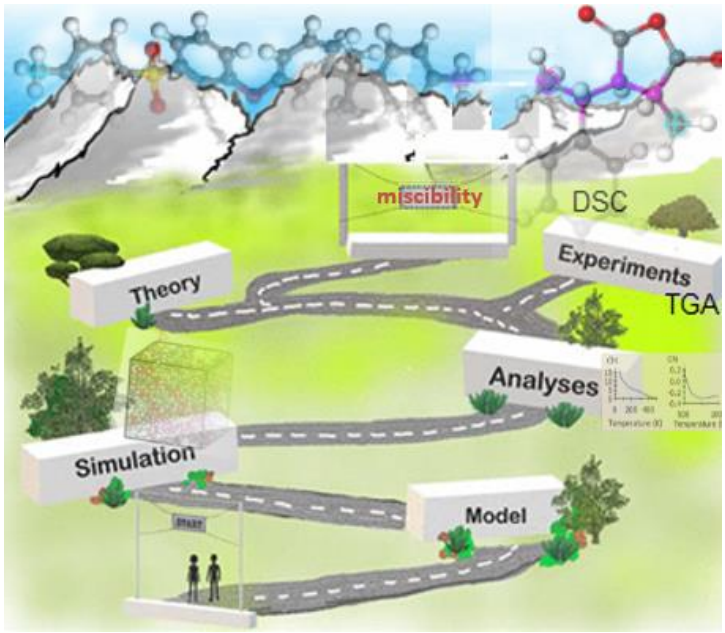

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Highlights

- Amorphous cells built to perform MD simulations NVT-300 ps protocol at various blending ratios
- Schneier theory and thermodynamics study shows that PSF and PSMA is thermodynamically compatible
- The simulation reveals the PSF/PSMA blend is miscible at T higher than 400 K
- Based on the shift of T_g by DSC confirms good interaction between PSF and PSMA

Abstract:

This work aims to use molecular modeling to envisage the compatibility of Polysulfone (PSF) and Poly (styrene-co-maleic anhydride) (PSMA) polymers blend. A blend-module was developed based on the molecular dynamics (MD) technique compared to an experimental study. Molecular dynamics simulations were achieved using the condensed phase-optimized molecular-potentials for atomistic simulation studies (COMPASS) force field with atomic-based electrostatic. The PSF/PSMA blend compatibility facets and thermodynamic Gibb's free energy across ranges of PSF/PSMA blend compositions were calculated. In doing so, the Flory Huggins chi interaction parameter of mixing (χ) and solubility parameters (δ) were computed from 298K and on increasing temperature to predict the miscibility of the polymers blend in the amorphous cell model by atomistic simulations. It was found that the blend-system is miscible using the interaction chi parameter of Florry Huggins at a temperature above 400K. At higher time-step, mesoscopic simulations for PSF/PSMA reached equilibrium and computed free energy. Mixing energy indicated the stability of the PSF/PSMA polymer blend. The results of this work narrate to the Flory Huggins theory enthalpy of mixing for binary blend polymers at 40 and 60 % PSMA. Additionally, the kinetic phase of the miscibility/immiscibility of the PSF/PSMA blend system's miscibility/immiscibility was examined using Differential Scanning Calorimetry (DSC). The result confirms the good interaction between the two polymers through the shift of glass transition temperature (Tg) values within individual polymers Tg. It is crucial to investigate the miscibility of two different polymers for a variety of polymer applications. The MD simulation provides a powerful, accurate computational tool in the estimation of polymer compatibilities.

Keyword: Blend-module simulation; Polysulfone; Poly (Styrene-*co*-maleic Anhydride); DSC analysis; Phase Diagram; Energy of mixing

1 Introduction

Different types of polymer blends have been studied to make new polymer material, such as polymeric membranes, which depend on the polymer-polymer blending's miscibility [1]. There is increasing attention to studying different polymers with their numerous applications in recent years [2, 3]. Studies indicated that Molecular Dynamics (MD) simulations are essential tools, which can avoid countless experimental and human errors in predicting the miscibility or blend compatibility of polymers. [4, 5] [6-8].. In conjunction with MD simulations, Flory-Huggins theory allows the easy way to study the compatibility of the blend polymers. MD simulations have complex systems type simulations that enable the interactions between bonded and non-bonded atoms for the built correct polymers [9, 10]. The interactions can be combined in forcefield files in Material Studio. The simulations can be run using Condensed-phase Optimized Molecular Potentials for atomistic simulations studies (COMPASS), the techniques confirmed by various researchers [6, 11-13]. The simulation systems are very sensitive to parameters set in the forcefield environment. Among the properties of polymers, the interaction parameters can be estimated from numerical paths of the blend polymers, which contain monomers' statistical structure properties to mimic the polymers' behavior [14, 15].

Herein Polysulfone (PSF) common known polymer and has been studied extensively in membrane applications due to its stability and potential in growing membrane technologies. It has been broadly applicable in the area such as ultrafiltration, microfiltration, and its surface modification for nanofiltration and reverses osmosis for water treatment [16]. The modification of PSF can be done by blending with other polymers. However, it is essential to be aware of compatibility or incompatibility to achieve successful blending [17-19]. Poly(styrene-co-maleic anhydride) (PSMA)

versatile copolymer used membrane technology through blending with other polymers to achieve attractive membranes with desirable features such as antifouling, hydrophilicity, and heavy metals rejection and compatibility of PSMA and with polymers has the great technological and scientific interest to researchers to achieve successful fabrication of membranes [20-22].

This study aims to predict the compatibility/incompatibility of the PSF and PSMA by molecular dynamics simulations - forcite blending tool in material studio 2017 software, and comparison with experiments such as thermal properties of these polymers (Differential Scanning Calorimetry (DSC) and thermostability thermogravimetric analysis – (TGA)). Furthermore, this present study reports the MD simulation results obtained from the Discover Amorphous cell module of the material studio 2017. The results obtained using simulations in conjunction with Flory-Huggins theory allows us to foretell the phase behavior of PSF/PSMA blending at various compositions. Thermodynamics analysis and using Schneier's approach of the equation were as well employed to envisage thermodynamic compatibility.

2. Theoretical relations

MD simulations were done with the commercial software Material Studio (2017) from Accelrys Inc. San Diego, CA, USA. The molecular mechanics and dynamics simulation in the discover module and building of amorphous cells were done in this work. The geometric optimization and potential energy estimations of arbitrary periodic and molecular systems using classical mechanics were done with the forcite module's help. Optimization is done to achieve the most stable structural configuration. This optimization is conducted in two-steps in the system, conformation adjustment and energy evaluations.

The blend-module using Dreiding [23] forcefield was performed in this work. The "Dreiding" forcefield exemplifies intermolecular and intramolecular interaction between polymers. The amorphous cell construction module was done in this work with simulations giving the ability to study molecular systems and poly material type by predicting the model's critical properties. This algorithm is suitable for building longer chains and molecules in two separate steps, first creating an initial guess structure and second structural relaxation to the minimum potential energy state [24, 25]. In this study, Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) forcefield was employed since it allows accurate prediction of the molecules' properties in the broad range, such as conformation, structural vibrational, and thermos-physical properties. These properties are in isolated condensed-phases in a wide range of conditions of pressure and temperature. This is a consistent polymer forcefield (PCFF) used in modeling and simulation for atomistic interaction, and the potential energy total of the system, is the result of the sum of non-bond, bond (valence) and cross term interaction energies as shown in **Eq. (1)**

$$E_{TOT} = E_{valence} + E_{crossterm} + E_{non-bond} \quad (1)$$

The valence interactions energy (E_{valence}) consists of energies of the bond stretching (E_{Bond}), valence angle bending energy (E_{Angle}), dihedral angle torsion energy (E_{torsion}), and out of plane energy interaction or energy inversion (E_{oop} or $E_{\text{inversion}}$). Modern COMPASS forcefield has a new denomination known as Urey Bradley (E_{UB}) that takes into account the interaction between pairs of atom in 1 to 3 configurations that is atom bonded to a common atom. **Eq. (2)** used in the system to obtain Evalence.

$$E_{valence} = E_{Bond} + E_{torsion} + E_{Angle} + E_{oop} + E_{UB} \quad (2)$$

The forcefield's accuracy is done by introducing the correction factor as a bond or angle distortion caused to the nearby atom. This is determined in cross-term interaction energy ($E_{\text{crossterm}}$). This term gives out the dynamic properties of the molecule through vibration frequencies, and later the interaction energy between non bonded atoms ($E_{\text{non-bond}}$) consists of the energy of Van der Waals (E_{vdw}), coulomb energy electrostatic (E_{coulomb}), and energy of Hydrogen bond ($E_{\text{H-bond}}$) shown in **Eq. (3)**

$$E_{non-bond} = E_{H-Bond} + E_{Coulomb} + E_{vdw} \quad (3)$$

In COMPASS, Van der Waals's energy (E_{vdw}) is defined by the electrostatic and potential energy from partial atom charges in a system calculated by the charge equilibration method [26]. The electrostatic interaction was estimated by the Ewald summation method, which is highly accurate in the estimation of long-range molecular interaction [27]. The geometric optimization was done on each polymer PSF, and PSMA and the forcite module were used for this optimization at 5000 steps of energy minimization. The tolerance convergence for force and energy is 0.005 kcal/mol 1×10^{-4} kcal/mol, respectively.

2.1. Blends tool calculation and simulation

2.1.1 Parameters to predict the miscibility

The strength between molecules of the polymer materials is defined by the solubility parameter (The Hilderbrand) – δ [28], which results in blending miscibility. This parameter is calculated by the square root of cohesive energy density (CED), as shown in **Eq. (4)**

$$\delta = \sqrt{CED} \quad (4)$$

The important aspect of the simulation is the polymer molecular weight. Selecting the length of a polymer chain in individual PSF and PSMA polymers, MD simulation was used by performing dynamics to estimate δ. The stable value of δ is obtained at sufficient individual monomers repeating units for running the simulation [29].

In this study, atactic PSF of 20 repeating unit monomer (**Fig. 2**) and isotactic alternate copolymer PSMA of 39 repeating unit monomer (**Fig. 2**) used to construct the amorphous cell weight fraction ratio 1:1 of the blend. Varying the repeating units from 20-80 allows us to build the cell at different weight fraction ratios for the blend. The polymers' densities were employed from the literature study [30], where PSF density set 1.24 g/cm^3 and PSMA density set as 1.08 g/cm^3, and such a system gives out 945 atoms to be investigated for 1:1 polymer repeat unit blend. **Fig. 1** shows the schematic procedure of simulation used to develop the polymer blends and interactions that illustrate the methodology.

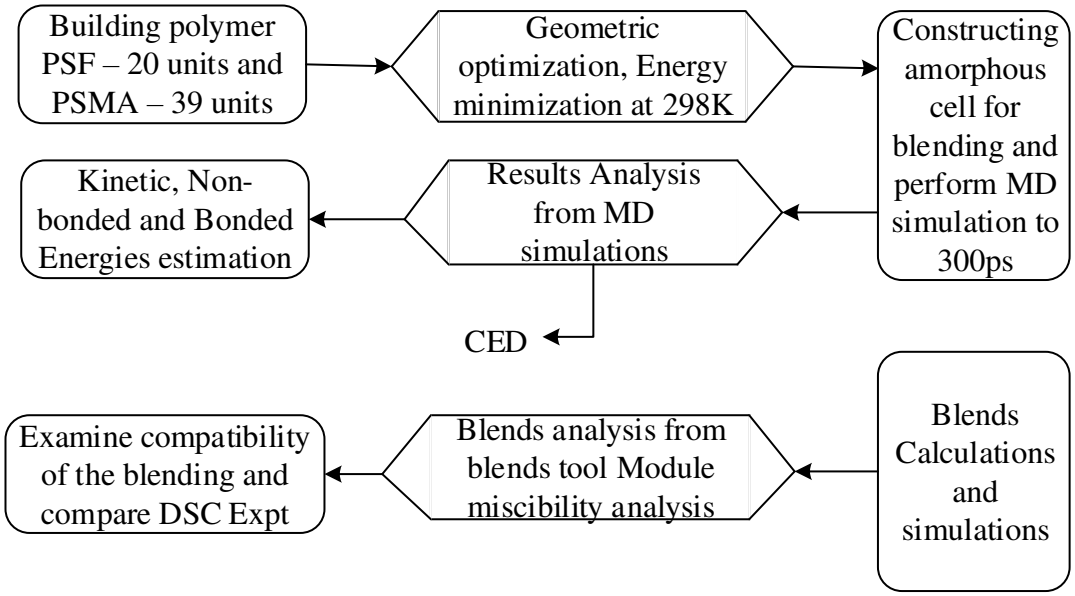


Fig. 1: Schematic procedure for simulation to develop the structure for polymer blends

Polymer molecular weight does not vary with cohesive energy density (CED). However, it is highly related to the interaction of the polymer, and by neglecting intramolecular forces, CED increases with energy (E_{coh}) per mole (V) of the polymer shown in **Eq. (5).** The solubility parameter values are shown in **Table 1,** comparing literature and calculated from the forcite tool – CED.

$$\therefore\ CED = \frac{E_{coh}}{V} \tag{5}$$

It was reported that the CED depends on conversion degree and temperature to achieve the solubility parameter. This shows that there is a linear relationship between crosslinking density and CED. Therefore, the increase in temperature results in a decrease in the solubility parameter, and the temperature has many effects with a polymer having a lesser conversion degree [31].

Thermoset polymer with a higher conversion degree has a lower cohesive energy density and solubility parameter. The cohesive energy density shows a linearly decreasing relationship with the crossslink density. These properties also decrease with increasing temperature and in thermoset polymers with lower conversion degrees show a more significant temperature effect.

Table 1: Solubility parameters and other properties of the polymer

Polymer	Repeating Unit	Molecular weight repeating unit (g/mol)	Density (g/cm^3)	Solubility parameter $(cal/cm^3)^{0.5}$ COMPASS (Charge Eq.)	Solubility parameter $(cal/cm^3)^{0.5}$ Experimental
PSF [a]	20	442.5	1.238	8.27	9.92 [30]
PSMA [b]	39	202.1	1.079	8.01	9.4 [32]

Different researchers have reported other value solubility parameters from the PSF experiment [33-35] and PSMA [36-39]. For this reason, it is important to take into consideration the accurate method of using MD simulation for obtaining interaction between these polymer blends depending on their CED. The blend-module in simulation in predicting miscibility has a superior unique high efficiency taking into account the Flory-Huggins interaction parameter (χ) across a range of temperatures and ideal conditions. This method can envisage the thermodynamics of mixing directly from two polymers' chemical structures (PSF and PSMA). It requires the input of these structures into the blends simulation. This type of simulations' uniqueness depends on combining the modified Flory-Huggins modeling [40-42] with the MD simulation system [43].

The CED computation can enable us to obtain the energy of mixing (ΔE_{mix}) since the Flory-Huggins model of this binary system is based on the thermodynamics of mixing of the polymer/polymer system.

Generally, the energy of mixing is expressed, as shown in **Eq. (6)**

$$\Delta E_{mix} = \Phi_a \left(\frac{E_{coh}}{V} \right)_a + \Phi_b \left(\frac{E_{coh}}{V} \right)_b - \left(\frac{E_{coh}}{V} \right)_{mix} \quad (6)$$

The terms that are in brackets represent cohesive energies of individual pure polymers (a, b) and the polymer blend (mix). However, Φ_a and Φ_b are volume fractions of each polymer in the blending system. The equation

$$\Delta E_{mix} = \Phi_a \left(\frac{E_{coh}}{V} \right)_a + \Phi_b \left(\frac{E_{coh}}{V} \right)_b - \left(\frac{E_{coh}}{V} \right)_{mix}$$

(6) can also be expressed in terms of free energy mixing, as shown in **Eq. (7)**

$$\frac{\Delta G}{RT} = \frac{\Phi_a}{n_a} \ln \Phi_a + \frac{\Phi_b}{n_b} \ln \Phi_b + \chi \, \Phi_a \Phi_b \tag{7}$$

Whereby ΔG is the free energy of mixing (per mole), T is the reference absolute temperature of the simulation (in Kelvin), R is the molar gas constant, and χ is the Flory-Huggins interaction parameter. The beginning two terms in equation **Eq. (7)** Are called combinatorial entropy, this is always negative, thus favoring a mixing state in the pure polymers. Finally, in the last term, the interaction parameter (Flory-Huggins) can be expressed according to case F.H [44], as shown in **Eq. (8)**. When the parameter is positive, the combinatorial entropy disfavors the polymer blend's mixing state and balances these two terms in **Eq. (7),** resulting in different phase diagrams.

$$\chi = \left(\frac{\Delta E_{mix}}{RT \Phi_a \Phi_b} \right) V \tag{8}$$

Generally, this interaction parameter is essential in indicating the polymer miscibility, and it obeys the critical value, as shown in **Eq. (9).**

$$(\chi_{ab})_{critical} = \frac{1}{2} \left(\frac{1}{\sqrt{m_a}} + \frac{1}{\sqrt{m_b}} \right)^2 \tag{9}$$

Whereby m_b and m_a are the degrees of polymerization of individual pure polymer. Therefore, when the blend system's interaction parameter is lower than the $(\chi_{ab})_{critical,}$ then the system is miscible for the whole polymer composition range. Likewise, if the blend system's interaction parameter is slightly higher than the critical value, then the system exhibits the partial miscibility of the polymer blend. Besides, the two phases can exist, containing both compositions. Therefore, for significantly higher interaction

parameter values (χ) than critical, the system becomes completely immiscible. By comparing the values of (χ) estimated from the equation **Eq. (9)** with the atomistic simulation, the compatibility or miscibility behavior of the polymer blends can be predicted [45, 46]. The traditional Flory-Huggins modeling, each component in the blend system, has the lattice site with coordination number Z in which the energy mixing is given by equation **Eq. (10)**

$$\Delta E_{mix} = \frac{1}{2} Z(E_{sb} + E_{bs} - E_{bb} - E_{ss}) \quad (10)$$

Ebb is the binding energy base-base pair, Ebs is a binding energy base-screen pair, E_{sb} is the binding energy screen-base pair, and E_{ss} is the binding energy screen-screen pair. These are energies of interaction between two polymers and, together with the interaction parameter (χ), can generate energy mixing.

The blends-button is selected from the menu toolbar and then the menu's dropdown to select calculation from the module dropdown list. In the setup input section tab, the empty row under the molecule must be assigned to input the structures that have been geometrically optimized by forcite. In the Blends dialogue calculation setup, the quality accuracy has been changed from medium to fine, corresponds to a bin width of 0.2 kcal/mol to 0.02 kcal/mol, respectively. After that, it uses the same dialogue (Blends Calculation) energy tab selected for setup. The forcefield was set to Dreiding and changed the charges to the 'charge using 'QEq' to calculate the Flory-Huggins interactions. Finally, the Run option was selected in the blends calculation dialogue to achieve the polymer's mixing. During the blending simulation, the new file of the PSF mixture was created in Project Explorer. After the simulation was completed, the Blend-Module analysis was selected from the menu bar. The analysis dialogue in the blend-module allows us to examine the interaction parameter (χ), the energy mixing, and the phase

diagrams. This blend-module system was validated by its calculations done in the Material studio [47, 48].

2.1.2 Experimental solubility parameters

2.1.2.1 Schneier theory and Thermodynamics analysis

The enthalpy of mixing Δm reported from Schneier's theory equation **Eq. (11)** can also determine the compatibility of the polymers using experimental parameters from different literature and depending on the density of each polymer $\rho_{a,}$ and ρ_b the solubility parameter of each polymer δ_a , and δ_b the molecular weight of each polymer M_a and M_b and weight fraction for each polymer W_a and W_b. The subscript components "a" and "b" represent two polymers blend, and for this report, specifically, "a" is PSF, and "b" is PSMA. The Schneier equation below is used to obtain the enthalpy of mixing for blended polymers, of which from the calculations, it was reported by Flory-Huggin's theory that for the composite polymers to be compatible, the enthalpy of mixing Δm < 0.01 cal/mol likely for incompatible polymer blend the enthalpy of mixing Δm > 0.01 cal/mol.

$$\Delta \mathrm{H}_m = \left\{ W_a M_a \rho_a (\delta_a - \delta_b)^2 \left[\frac{W_b}{(1-W_b)\mathrm{M}_b \rho_b + (1-W_a) M_a \rho_a} \right]^2 \right\}^{\frac{1}{2}} \qquad (11)$$

In order to obtain the status of thermodynamics compatibility, the Gibbs free energy ΔG_{mix} of blended polymer can be used to determine the thermodynamics compatibility state. Gibbs free energy ΔG_{mix} is dependent on the enthalpy of mixing ΔH_m of the mixed polymers calculated from the above equation, Entropy of mixing ΔS_{mix} , and temperature of mixing T (K) at which mixed polymers become miscible [49]. Different researchers have reported that Gibbs's free energy increase with the increase in compatibility degree. Therefore, the thermodynamics equation **Eq. (12)** is

used to calculate the Gibbs free energy of mixing, and according to the thermodynamics theory [50] for thermodynamic compatible polymers blend, the Gibbs free energy $\Delta G_{mix} < 0$ cal/mol and thermodynamic incompatible $\Delta G_{mix} > 0$ cal/mol.

$$\Delta G_{mix} = \Delta H_m - T\Delta S_{mix} \tag{12}$$

3 Experimental section

3.1. Materials

Polysulfone (PSF) molecular weight about 97,000 g/mole with repeating unit molecular weight 442.52 g/mole. It was purchased from Dalian Polysulfone Plastic Company Ltd (Liaoning province China), Crystal-clear powder form PSMA-5 molecular weight about (1.2 x 10^5) g/mole, MA = 26% wt was purchased from Solvay solexis (Belgium).

Fig. 2 shows the monomers' chemical structure (PSF and PSMA) used in this study.

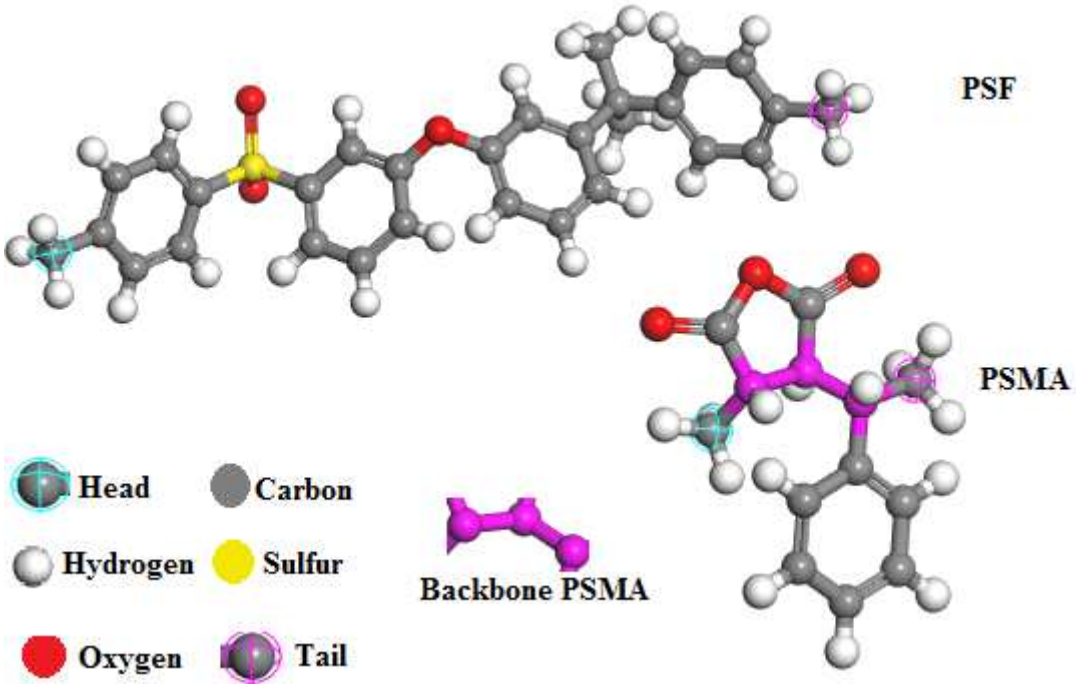


Fig. 2: Chemical structure for PSF and PSMA monomers

3.2. Thermal Properties Analysis

Table 2 indicates the denomination to describe the samples used in this study for thermal properties. The polymer miscibility criterion is to obtain a single glass transition temperature (T_g) in a polymer blend. This is the result of the miscibility at the molecular level of the polymer blends. Additionally, the single T_g can indicate the homogeneity of the polymer chain's distribution in polymer films [51].

Table 2: Description of the samples-polymer concentrations

Name	PSF (% wt)	PSMA (% wt)
T0	100	0
T1	80	20
T2	60	40
T3	40	60
T4	20	80
T5	0	100

3.2.1 Differential Scanning calorimetry (DSC) investigation

The glass transition temperature (T_g) values of pure polymers and polymer blend samples were studied by NETZSCH DSC 200F3 Maia-Germany model instrument to examine the polymer blend and rigidity's miscibility of the polymers. Samples were measured at an average of 8-12 mg, and the thermal scanning was conducted from 20 °C to 220 °C at a heating rate of 10 °C/min under the flow of nitrogen (N_2).

3.2.2 Thermogravimetric Analysis (TGA)

NETZSCH STA449-F3-Jupiter instrument was used to analyze the thermal stability of the polymers. Samples at different polymer concentrations were weighed at an average of 17-19 mg and transferred to Alumina ceramic crucible for thermal analysis. Crucibles are non-reusable with high-temperature stability, a wide range of operating

temperature, and the maximum working temperature for these crucibles is 1750 °C [52]. TGA study was done from 40 °C to 800 °C at a constant heating rate of 20 °C/min, and nitrogen gas was used at a flow rate of 1/ (ml/min):50.

4. Results and Discussion

4.1 DSC Results of PSF/PSMA

One of the most typical experimental methods to evaluate the polymer-polymer compatibility is by determining the polymer blend's Tg value and comparing it with an individual pure polymer (PSF and PSMA). This method can experimentally study the compatibility between the PSF and PSMA polymer. **Fig. 3** shows the results of the DSC for the PSF/PSMA.

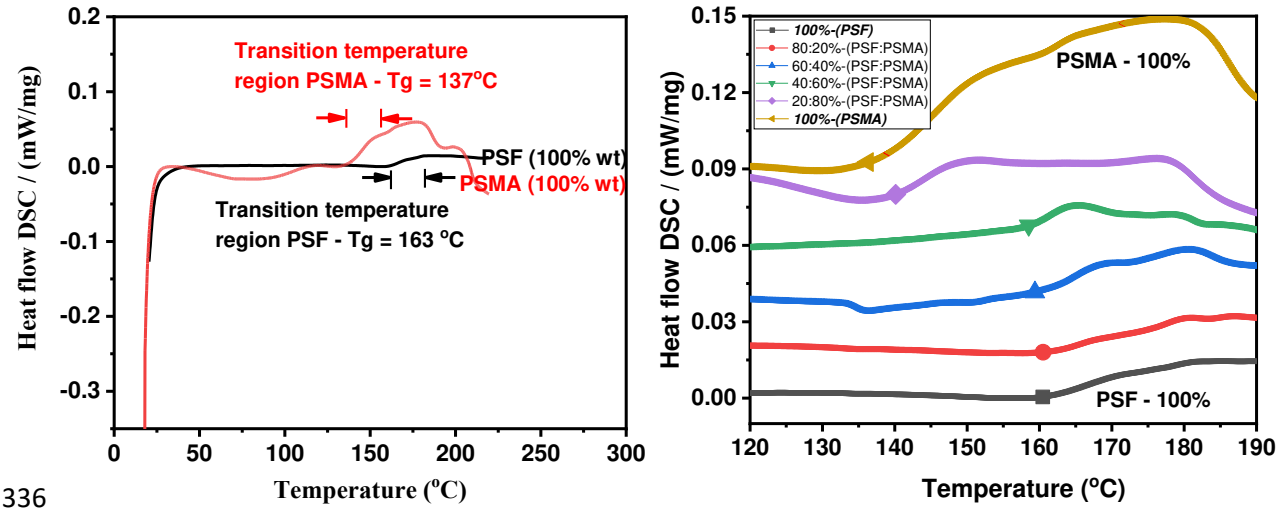


Fig. 3: DSC spectra of PSF/PSMA blending at various concentrations ratio

The criteria behind the polymer miscibility are obtaining the single value of Tg in a polymer blend system, which indicates the miscibility at the molecular state [51]. From **Fig. 3** it is showing that the T_g of individual polymers is different. That is, pure PSF has a T_g of 163 °C, which is higher than pure PSMA having T_g of 137 °C. However, varying polymer concentration of polymer as indicated in **Table 2,** the T_g values change and different from that pure PSF and pure PSMA. These differences

can be due to many van der Waals interactions between two polymers that lose the identity [53].

Furthermore, there is a modeling interaction as the blend's distinct Tg values are in between those of individual polymers (PSF and PSMA). As an increase in the PSF polymer fraction in the blending, Tg's value increases uniformly due to the higher Tg of PSF. The miscibility is observed below 50% of PSMA as it is seen from **Fig. 3** that a single gradual increase of T_g values approaches a similar value to that of PSF. However, above 50 % PSMA, the blend T_g is seen to shift closer to pure PSMA and become immiscible. These results suggest further analysis by MD simulation to understand and compare the miscibility at the edge boundary to avoid overestimations and obtain the equilibrium polymer-polymer interaction and miscibility boundary [54].

4.2 Thermogravimetric Analysis (TGA)

The thermal analysis for the PSF/PSMA data collected from the TGA instrument is indicated in **Fig. 4**.

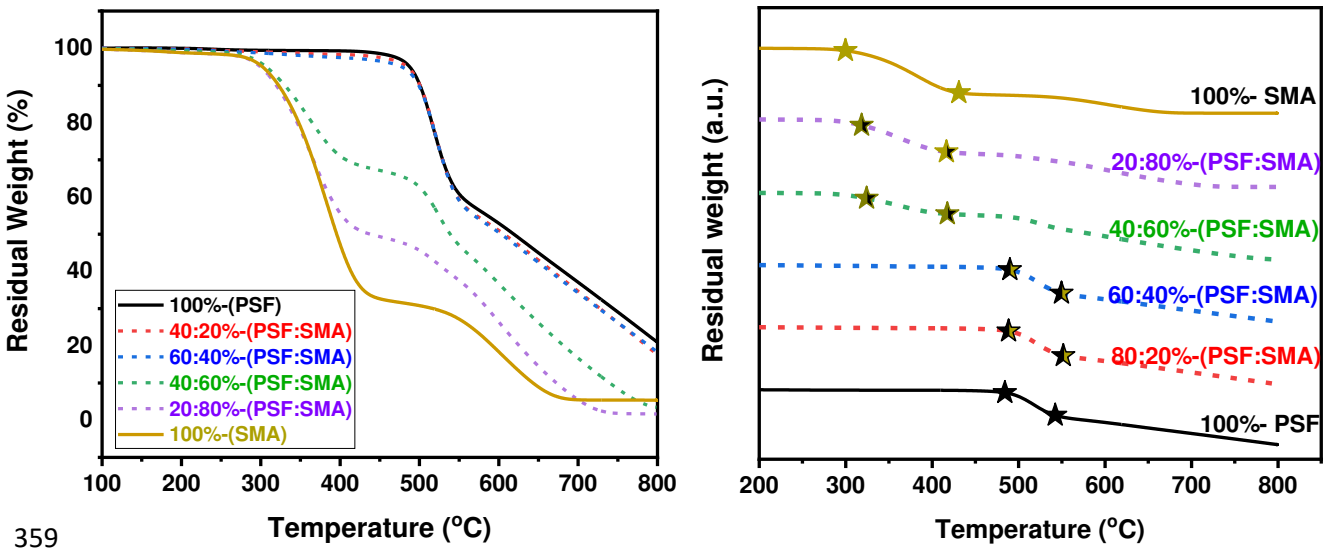


Fig. 4: TGA Analysis of the PSF/PSMA polymer blend

For pure PSF, the degradation onset temperature is seen at **484.9 °C,** and thermal degradation continued up to a temperature of **542.9 °C**. Conversely, pure PSMA is seen to have a degradation onset temperature at **301.8 °C,** and the final degradation temperature was found to be **428.8 °C.** This is attributed to the chemistry nature of the two polymer structures, where cleavage of C=C in benzene (aromatic) ring in PSF will be last, and C-O in maleic anhydride cleaved more easily compared to C=C of PSF [55, 56]**.** The degradation behavior between pure PSF and pure PSMA continued to be seen (PSF/PSMA-polymer blend). The blending of PSMA in the PSF matrix improved thermal stability at a low concentration of PSMA up to 40% of the polymer blend. The stability from 60:40% (PSF:PSMA) blend up to 100% pristine PSF was found to have an onset degradation temperature of **484.9 °C** and a final degradation temperature of **550.8 °C**. This is attributed to the significant part of the blend occupied by highly thermally stable pristine PSF.

Additionally, a further increase of PSMA (20:80%-PSF:PSMA) lowers the thermal stability, and degradation onset temperature was observed to decrease to **316.8 °C,** and final degradation temperature was found to be **414.5 °C.** It is evidently confirmed that the two polymers' interaction at a low concentration of PSMA shows good agreement. As indicated in **Fig. 4**, a single degradation peak in the TGA graph. This confirms the PSF/PSMA blend's miscibility is in the range of 0 to 40% PSMA, as seen in the uniform behavior between the two pure polymers.

4.3 MD Simulations

Structure built in the Material Studio before running simulations was optimized at 5000 steps. **Fig. 5** is shown that profiles were generated during the optimization of these structures. The optimization aims to bring the structures' stable configuration, conformation, and minimal energy evaluation to be used for constructing amorphous cell and blending simulation. It is seen that PSF structure energy was minimized from

2553.4 kcal/mol to 250.3 kcal/mol, whereas for PSMA structure, the energy was reduced from 3603 kcal/mol to -1578 kcal/mol using the conjugate gradient method. This is also done in order to bring its excellent performance and reliability from the initial starting point [57].

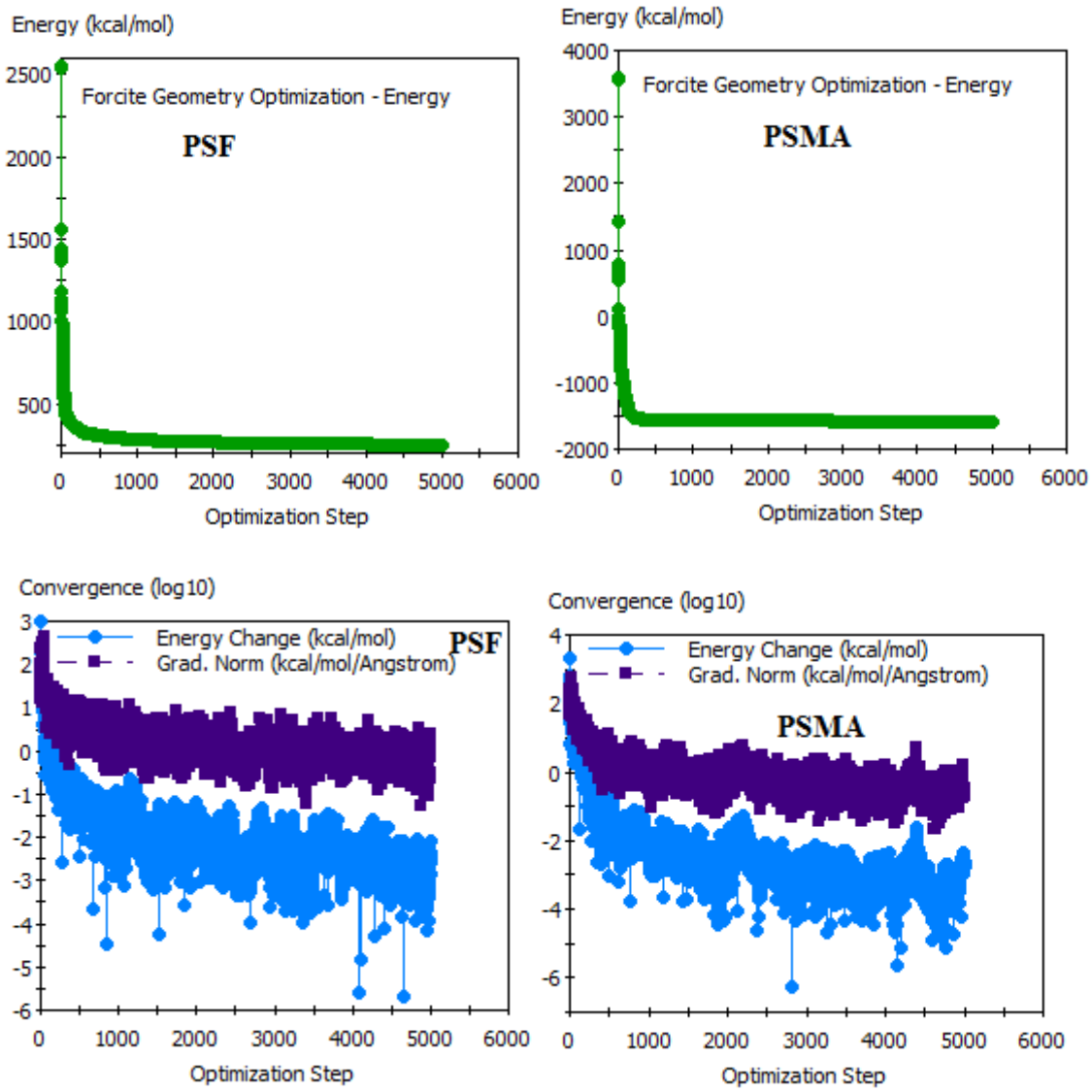


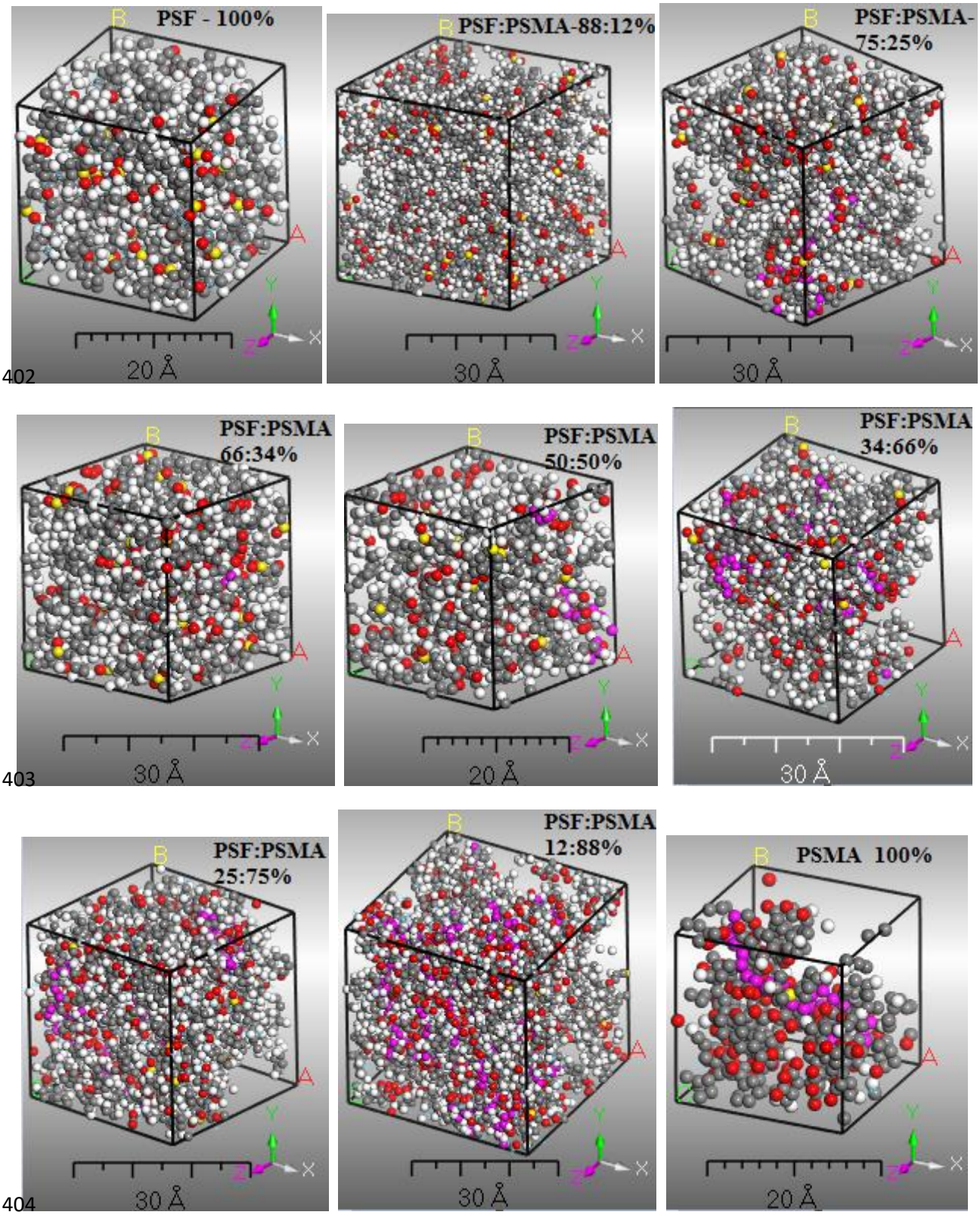
Fig. 5: Energies minimization and convergence profiles generated during optimization

Amorphous cell construction and Dynamics analysis

Unit cells of three-dimensional cubic were constructed having conditions of the periodic boundary in amorphous cell module, as seen in **Fig. 6**. The cells were optimized to minimize energy before running MD simulations. The simulation runs at 300ps, and 298K with NVT ensemble means constant-volume/constant-pressure

400 dynamics, this ensemble dynamics are set in such a way to allow the system to

401 exchange heat with the environment at the controllable temperature.



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405 **Fig. 6: Simulated amorphous cells at various compositions of PSF and PSMA**

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Here Carbon atoms are shown grey; Oxygen atom is shown red in color, Sulfur atoms from PSF yellow in color, and Hydrogen are shown white. For model protocol, different ratios number of chains are constructed in a unit cell. During MD simulation, fluctuation profiles of temperature, non-bonded, potential, and total energies were generated for each unit cell. **Fig. 7** shows an individual pure polymer PSF and PSMA generated profiles (temperature and energies). Further studies on each cell are shown in Supplementary Figure S1

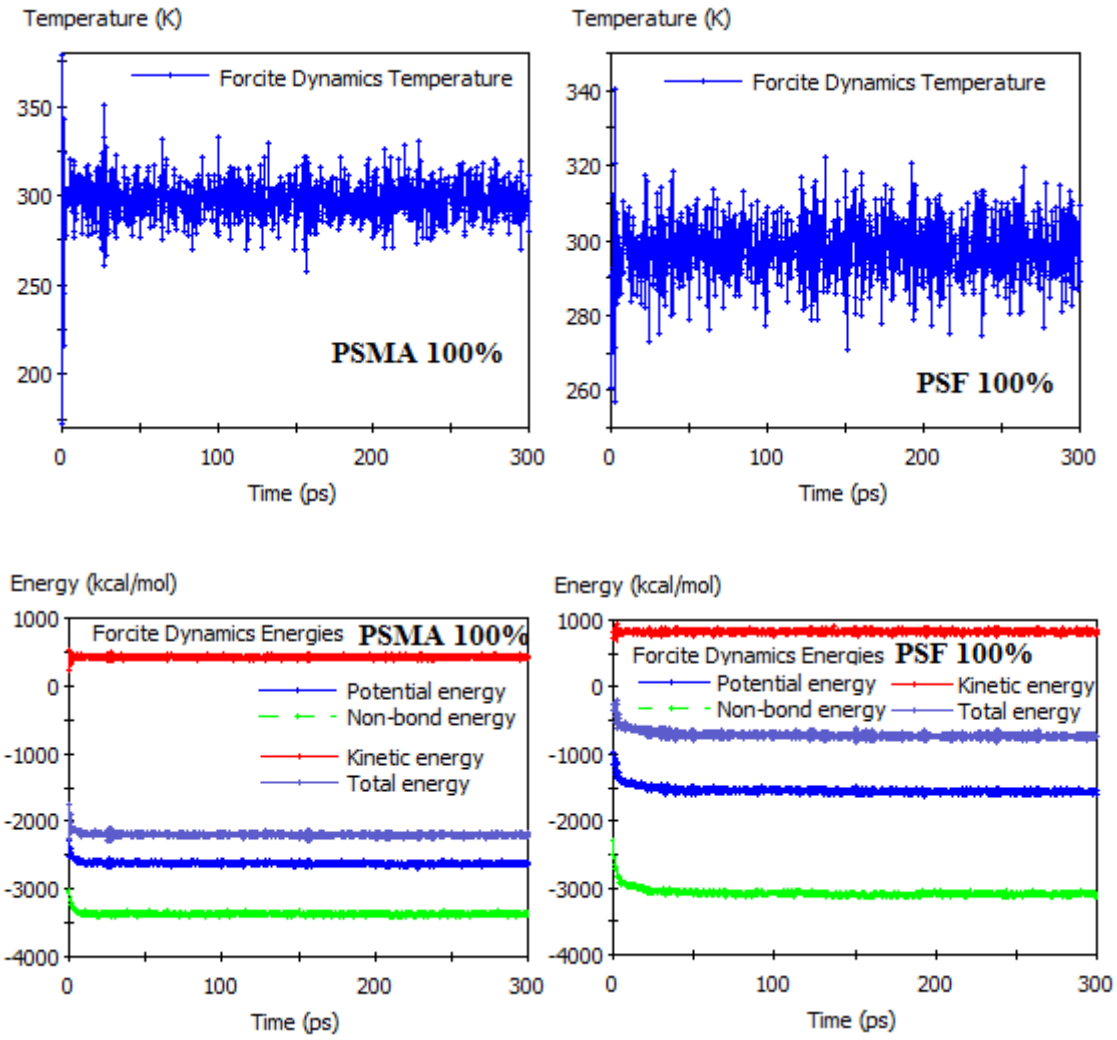


Fig. 7: Fluctuation profiles of temperature, potential, non bonded, kinetic, and total energy plot vs. MD simulation time in ps.

The results show that, for the duration of 300 ps simulation time, there is no significant change in the structures; hence, the time was adequate to attain the state of equilibration protocol. Also, to circumvent the entrapment of the simulated systems in a local metastable state of the minimized energy from geometric optimization, MD simulations were run at NVT ensemble then followed by NPT (constant pressure/content temperature dynamics) so to overcome the energy barrier between the minimal high energy by thermal energy provided [6]. The projected density of each amorphous cell is assumed from 1.24 g/cc to 1.08 g/cc from individual polymers.

4.4 Flory–Huggins interaction parameter from blend-module analysis

According to the theory of Flory-Huggins, when the interaction parameter (χ) is less than one and up to negative values, two molecules at the particular temperature are miscible, or interaction is favored. Furthermore, if χ is a positive value or higher than one, it indicates that two molecules can not be easily mixed [40, 41]. Likewise, when the interaction parameter value is substantial, the free energy overcomes the combinatorial entropy of mixing, and the molecules will separate into two different phases. This part aims to obtain the value of χ for our two polymers blend (PSF and PSMA). However, the material studio software was capable of producing plots, as indicated in ***Fig. 8*** from the Blend-module analysis dialogue at various temperatures to predict miscibility. The χ value obtained at 298 K particular temperature was 5.014, which confirm immiscible. However, from this result, it shows that the interaction parameter changes continue to change on the increase in temperature where the system becomes miscible from 400 K temperature, and above, at this particular temperature (400 K), the Flory-Huggins interaction parameter was seen to shift to lower values than 1 up to negative values.

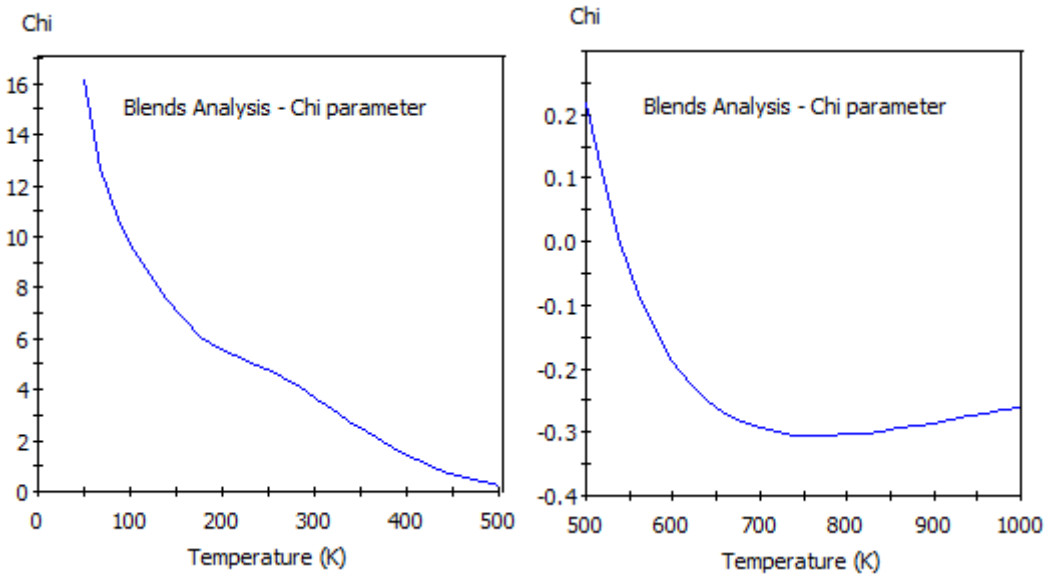


Fig. 8: Flory-Huggins interaction parameter (χ) as a function of temperature (K) for PSF and PSMA polymers blending

Blends combines a modified Flory-Huggins model and molecular simulation techniques to calculate the compatibility of binary mixtures. Two important extensions to the Flory-Huggins model are employed:

Blends incorporates an explicit temperature dependence on the interaction parameter. This is accomplished by generating a large number of pair configurations and calculating the binding energies, followed by temperature averaging the results using the Boltzmann factor and calculating the temperature-dependent interaction parameter.

Blends is an off-lattice calculation, meaning that molecules are not arranged on a regular lattice as in the original Flory-Huggins theory. The coordination number is explicitly calculated for each of the possible molecular pairs using molecular simulations.

These two extensions to the classical Flory-Huggins theory of mixing are considered in the blend simulation.

Also, by substituting the temperature-dependent interaction parameter, χ, in the Flory-Huggins expression, the free energy is known for all compositions and temperatures. From this, the phase diagram of the mixture can then be determined by locating the critical point, the coexisting curve (binodal), and the stability curve (spinodal) in the two-phase diagram.

As with any molecular simulation, the results obtained depend on the accuracy of the forcefield. Blends supports a wide variety of forcefields.

In the traditional Flory-Huggins model, each component occupies a lattice site. Although it is possible to use a fixed lattice coordination number in Blends, in calculating the interaction parameter χ, Blends also provides the option to calculate the coordination numbers for each pair and considered when running blending simulation

In addition to the interaction parameter, it is crucial to analyze the system's mixing energy and free energy to observe the value close to zero, suggesting miscibility. Figure S2 can be used to confirm further on miscibility study of PSF and PSMA. The more decrease of energy mixing to less than zero (negative values) indicates PSF and PSMA are miscible. The free energy plot at the various temperature as a function of the mole fraction of PSMA was generated from the system's analysis. This plot is presented in **Fig. 9**. This plot can be further analyzed using the enthalpy of mixing by Schneier's theory (at 298K), which will be discussed later in this study. However, as the temperature increases, it is free to shift to the negative side at the similar composition of PSMA. This is attributed to the temperature-dependent miscibility behavior, as confirmed earlier in this work.

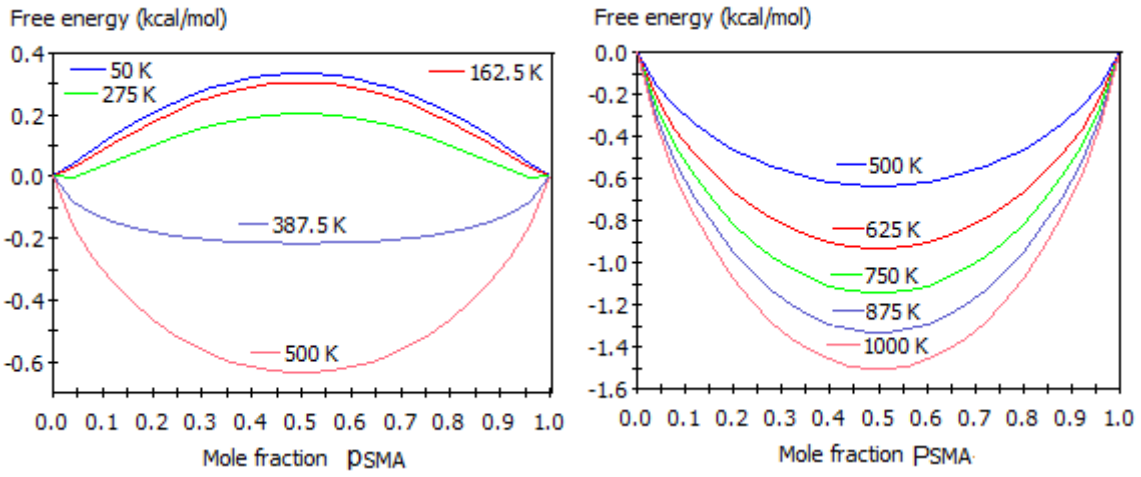


Fig. 9: Free Energy analysis function of mole fraction of PSMA

4.5 Phase Diagram of the PSF/PSMA blend

In illustrating the compatibility between polymers, phase diagrams are essential as they developed from the free energy of the binary system of blend [43, 58, 59]. This part aims from the phase diagram, where we obtain information about the temperature range of PSF/PSMA mixture for miscible and immiscible. An immiscible polymer mixture splits into two phases, wherein the phase diagram, and we can read its composition. **Fig. 10** is the phase diagram obtained from the blend-module analysis.

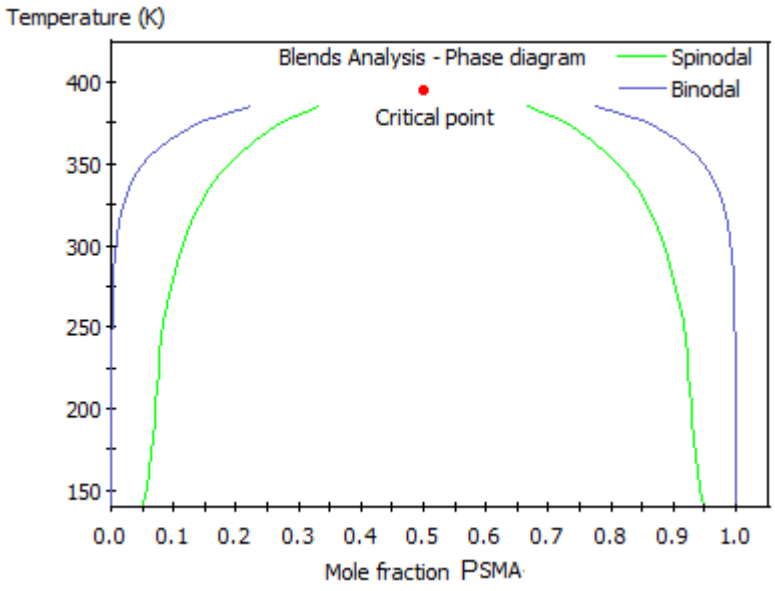


Fig. 10: Phase diagram for the binary system of PSF /PSMA

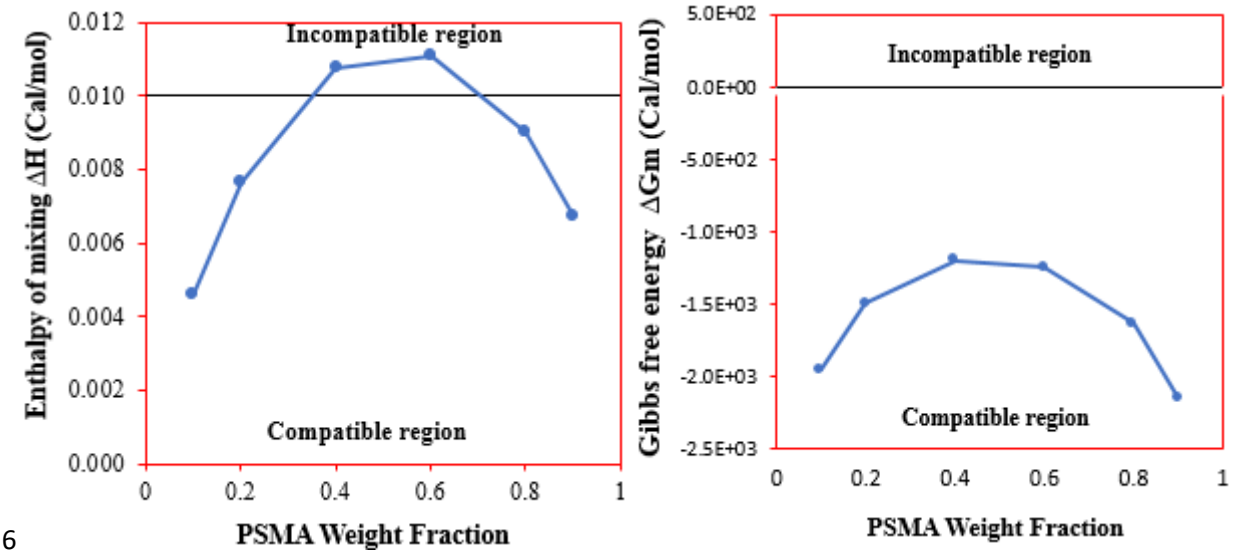
The pieces of information obtained from this plot, such as critical point (in red dot), Binodal (Blue line color), and spinodal (Green line color). Furthermore, these results show that at the critical point, there is a coexistence region for PSF / PSMA and the PSF/PSMA blend by split into two phases, which results in lower free energy, as illustrated earlier. The temperature at a critical point found was 400 K at a mole fraction of 0.5 PSMA. This plot has a single critical point that confirms one coexistence region. However, a complex binary system of polymer blend may have more than one critical point in its phase diagram due to several coexistence regions. Thus, the spinodal is linked to the coexistence region's separation into two phases, whereas the binodal links with the coexistence region in this phase diagram. In the region between the spinodal and binodal, the polymer blend system is metastable. That is, the blend will separate only after sufficiently high fluctuation. The region in the spinodal bounded up to lower temperatures the PSF/PSMA is immiscible, which agrees from the earlier illustration of Flory Huggins interaction parameter and mixing energy. Any fluctuation causes immiscibility as the system is unstable in the spinodal region. Additionally, above the binodal region, PSF /PSMA blend system is miscible and stable.

Recent advances in molecular simulation techniques have improved this situation. Accurate forcefields can be obtained by defining parameters using structural and spectral data. Molecular simulations can be performed on well-characterized systems, leading to a better fundamental understanding of atomic-level interactions. This information can then be used to predict useful physical properties of systems that are less well characterized. Many factors govern mixing processes, including the temperature and the chemical nature of the individual components. Additional factors may be involved for polymers; for example, chain packing, the degree of crystallinity, molecular weight, and chain flexibility. Not all of these factors can be addressed using

520 molecular simulation techniques. However, it is possible to obtain structural data for
521 the individual components in a mixture and to calculate the interaction energy terms
522 required for the thermodynamic expressions.
523

524 ## 4.6 Compatibility by Schneier theory and thermodynamics

525 Solubility parameters from the experimental work together with densities and
526 molecular weight of the repeating units can be used to estimate enthalpy of mixing
527 using **Eq. 11**. Therefore, the enthalpy of mixing obtained using experimental data of
528 solubility parameters from **Table 2** can be plotted against the mole fraction of PSMA,
529 as indicated in **Fig. 11**. It is mentioned that the Schneier theory of compatibility is
530 assumed only at the temperature of the blend system 298 K, and interest lies in the
531 system of compatible solids at room temperature. Hence solubility parameters and
532 density used in the calculation were at 298K [60]. Therefore the result disagrees with
533 simulations; however, only at 40 % up to 60% PSMA blend agree with MD
534 simulation blends. Only 60% of PSMA agree with the DSC experiment, and below
535 40% PSMA as illustrated earlier in this study.



536

537 **Fig. 11: (a) PSF/PSMA Schneier calculation – Enthalpy of mixing (b) PSF/PSMA**
538 **Gibb's Free energy graph - thermodynamic theory of compatibility**

It is seen that the PSF/PSMA polymer blend is partially compatible. From 0.4 to 0.6 PSMA wt/wt, the enthalpy of mixing is higher than the limit of Flory Huggin's theory (**10^{-3} cal/mol**), which changes to the incompatibility on increase further PSMA weight fraction turn to the compatible state. Therefore, from the Schneier equation calculation, the system is partially compatible, which allows further investigation, such as MD Simulations, compared to the experimental DSC approach. In **Fig. 11**. From these **(12,** it is seen that Gibb's free energy is dependent on the enthalpy of mixing calculated from the Schneier equation, the entropy of mixing and temperature at which polymer blend system, higher temperature > 298 K as higher than 400K the system is thermodynamically compatible with an increase pf PSMA polymer composition in the blend system.

5. Conclusion

In this study, the miscibility between PSF and PSMA was intensively examined by MD simulation and the experiment. The energy mixing, Flory-Huggins interaction parameters, amorphous cell, and phase diagrams were studied in this work. The results showed that PSF and PSMA are miscible from a temperature above 400K with an optimal weight fraction of PSMA of about 0.5. In the DSC experiment, the two polymers show a good interaction as the shift of T_g values within the range of individual polymer T_g. Furthermore, based on thermodynamics techniques, experimental data together with MD simulation blending are verified; thus, two polymers PSF/PSMA thermodynamically compatible. In this perspective, membranes such as for water treatment and fabrication of these blends (PSF and PSMA) can be done via thermally induced phase separation method with glycol derivative diluent to dissolve the polymer blends at high temperature.

Acknowledgment

Authors gratefully acknowledge the Tianjin Science and Technology Planning Project (Grant No. 18PTZWHZ00210), National Natural Science Foundation of China (Grant No. 21576209 and 21878230), and Innovative Team in University of Ministry of Education of China (Grant No. IRT-17R80) for their financial support. Also, I would like to thank the School of Materials Science and Engineering, Tiangong University, China, for their kind assistance.

*Declarations

Funding: (Authors gratefully acknowledge the Tianjin Science and Technology Planning Project (Grant No. 18PTZWHZ00210), National Natural Science Foundation of China (Grant No. 21576209 and 21878230), and Innovative Team in University of Ministry of Education of China (Grant No. IRT-17R80)

Conflicts of interest/Competing interests: (No declared conflict of Interest)

Availability of data and material: (Not applicable)

Code availability: (Not applicable)

Authors' contributions: (Not applicable)

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