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Computational Screening of Thermoplastic Starch-Based Biopolymers Blends for Mixing Compatibility

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Abstract

Starch-based composites are among the most studied biomaterials considering their environmental and economic prospects. In this work, a comparative investigation of the mixing compatibility of two thermoplastic starch (TPS)-based blends was conducted. The compatibility investigation was executed with the help of the mixing task of the blends module from Material Studio 5.5 (Accelrys, Inc.). The module task of mixing provides the user with an accurate sampling of the mixing characteristics of the selected binary blends. The Blends module allows the screening for interaction energy between polymer and polymer, between polymer and solvent, as well as between solvent and solvent. The blending characteristics of TPS/Natural Rubber (NR) and TPS/Polycaprolactone (PCL) were studied by screening the monomers of each blend for mixing compatibility. The blending characteristics under study include binding energies distribution (E_{bb}, E_{bs}, E_{ss}), Chi interaction parameter, and mixing energy (E_{mix}). The outcome of the computational screening for the interaction energy between the monomer pairs of TPS/NR and TPS/PCL revealed that caprolactone had the best mixing capacity, illustrated by the similarity between binding energy distributions of the mixture, as well as by the minimal Chi parameter and lowest mixing energy. The TPS/NR blend, on the other hand, had the highest mixing energy and the highest Chi parameter. Moreover, its binding energy distribution displayed the smallest value of similarity. Thus, TPS/NR had the lowest blending capacity.

Keywords

Thermoplastic, Starch, Computational, Screening, Mixing, Compatibility

1. Introduction

We are witnessing, in scientific research, a rising trend focused on the precise and systematic rationalization of various computational data into legitimate chemical investigations. Polymers are ubiquitous materials that play critical roles in various industries, from packaging [1] to biomedical devices [2]. Their properties can be tailored through molecular design, making them highly versatile materials. However, the vastness of potential polymer candidates complicates the material selection and optimization process. Computational screening emerges as a powerful tool to accelerate the discovery and development of new polymers by leveraging computational methods to predict polymer properties and behaviors before experimental validation [3]. The synthesis and characterization of polymers often require significant time and expense. Traditional methods involve trial-and-error approaches, which can be inefficient and slow. Computational screening allows researchers to explore a vast chemical space quickly and cost-effectively [4]. By simulating polymer properties and performance, computational tools can help identify promising candidates, optimize their synthesis routes, and reduce the need for extensive laboratory experimentation [5]. Various studies focusing on computational screening of Thermoplastic starch (a starch-based material obtained by plasticizing starch with agents such as glycerol) and its polymeric blends for various properties have been released lately. Ozeren *et al.* successfully investigated the plasticization process of starch with glycerol. Their computational approach can be used for the analysis of other polymer/plasticizer systems as well as provide a new route for the development of novel classes of plasticizers [6]. Two years later, Ozeren *et al.* managed to extrapolate simulation data for prediction of the tensile properties of thermoplastic starch. The accuracy with respect to the experimental data projection was acceptable in many situations; however, it depended on the extrapolation approach as well as on the particular TPS system [7]. Furthermore, Yamaguchi *et al.* assessed the toughening caused by the development of a core-shell molecular arrangement in starch-based biopolymer composites experimentally and computationally. The researchers performed molecular dynamics simulations for the examination of mechanisms linked to the mechanical and structural characteristics of ternary blends of poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and thermoplastic starch (TPS), as well as of binary blends of PLA/TPS. The dynamics simulation results revealed that PLA/PBS/ TPS blends showed improved mechanical properties compared with PLA/TPS blends. The PLA/PBS/TPS blends with a TPS ratio of 25 - 40 wt% showed higher impact strength than the PLA/PBS blend [8]. Subsequently, TPS plasticization has been studied through both experimental and computational approaches. Results have shown that starch-based systems processed at 140˚C with 15% glycerol (as plasticizer) displayed better tensile properties and wettability. The thermal stability, however, lessened in correlation with an increase in glycerol content. [9]. Finally, Yamaguchi *et al.* executed a study of the phase-separated interface of four environment-friendly polyesters, such as poly(lactic acid), polybutylene succinate (PBS), polyhydroxybutyrate (PHB),

and poly(butylene adipate-co-terephthalate), with TPS using molecular dynamics simulations; it was concluded that PBS, PHB, and PBAT easily spread over TPS and constitute well-matched interfaces, whereas PLA displays lesser compatibility with the TPS. Both PLA and PHB associated with TPS show poor interfacial-fracture energy due to the poor compatibility between PLA and TPS, as well as to PHB having low electrostatic interaction with TPS [10]. The aim of this investigation is to assess the mixing compatibility of TPS-based binary blends (TPS/NR and TPS/PCL) through quick computational molecular screening. This study will also examine the potential accuracy of the computational approach based on the Flory-Huggins mixing theory.

2. Theory and Material

2.1. Mixtures Compatibility

The compatibility characteristics of TPS-based polymer blends were computed with the help of the Blends module. The screening of monomers, facilitated by the Blends module, provides a simplified yet effective approach, as the interactions between monomers serve as indicators of full polymer chain compatibility within this computational framework, allowing efficient prediction of polymer blend behavior [11]. The principle behind the Blends module calculations is expressed by a combination of the Flory-Huggins model and methods of simulations applied to molecules [12]. The ultimate aim is to calculate the compatibility of binary mixtures. These binary systems are evaluated in all sizes, ranging from small systems to relatively huge molecular models. Blends module algorithms establish the distinction between the two constituents of the system by assigning individual roles: one component is assigned the base (b) role, and the screen (s) role is assigned to the second [13].

2.2. Binding Energies

When two molecules are in relative spatial proximity, a phenomenon of intermolecular interaction will take place. The quantity of interaction energy between the two chemicals is termed binding energy. Blends algorithms combine binding energy parameters with coordination numbers during the compatibility investigation to generate the mixing energy (E_{mix}) and chi parameter [14]. Estimation of binding energies requires careful consideration and judgment of the high molecular orientation applied to the two constituents during screening [15]. An extensive number of molecular orientations is provided by the module, which subsequently estimates the energies of interaction related to every configuration. After screening for the binding energy, the Blends algorithm executes the sampling of those configurations considered to be energetically satisfactory [16]. The sampling method utilized here is an altered version of the molecular Silverware algorithm [17]: it is called excluded volume constraints. Excluded volume constraint sampling methods are employed to prevent spatial overlap between particles or molecules [18]. In this approach, a proposed configuration is generated and checked

for particle overlap; configurations exhibiting overlaps are rejected, and new ones are sampled [19]. Here, the constraint is applied based on the excluded volume associated with each molecular configuration. In this sampling technique, the two molecules are joined together in order to establish a proximity of their van der Waals surfaces. Four distinct possible pairs will be generated after any base-screen combination. The binding energy value of each individual pair is expressed as:

- Base-base pair (E_{bb})
- Screen-screen pair (E_{ss})
- Base-screen pair (E_{bs})
- Screen-base pair (E_{sb})

Let us consider a binary mixture made of component A and component B. The binding energy of the interaction between those molecules is calculated using the excluded-volume constraint method. In this method, the calculation of the binding energy is initiated with two chemical compounds that are a representation of the condensed state [20]. After the estimation of binding energies is completed, the module automatically establishes the coordination numbers as well [21]. Once those parameters have been generated, the Blends algorithm performs the calculations of the mixing energy (E_{mix}) based on the equations derived from the Flory-Huggins model.

2.3. Flory-Huggins Model

The efforts to understand the thermodynamics of polymeric solutions are represented by the Flory-Huggins theory. The theory provides a more precise investigation compared to the ideal solution theory. The ideal solution theory presents various conditions of limited ability [22]. Two of the most important limitations of the theory are the large size of polymeric systems compared to solvents, as well as the possibility of chemical interaction between different molecules. The Flory-Huggins model stands out as, without a doubt, the best and least complicated theory for the assessment of binary mixtures thermodynamics of phase separation and mixing [23].

According to the model, the free energy of mixing of the binary system is expressed by the general equation:

$$\Delta G/RT = \Phi_b/n_b \ln \Phi_b + \Phi_s/n_s + \chi \Phi_b \Phi_s \quad (1)$$

where: ΔG = free energy of mixing per mole;

Φ_b = volume fraction of component A;

Φ_s = volume fraction of component B;

X = interaction parameter;

T = absolute temperature;

R = gas constant.

The combinatorial entropy is expressed by the first two elements. Due to their negative mathematical contribution, they provide favorable conditions for a mixed state, which is preferred over the pure components [24]. The term at the end ex-

presses the free energy generated due to interaction. A reliable sign of the attainment of a mixed state is the negative value of the chi interaction parameter.

If the parameter of interaction is positive, a mixed state is inferred to be disfavored [25]. Moreover, when there is equilibrium between both conditions, the algorithm will generate different phase diagrams. The following equation represents the χ interaction parameter:

$$\chi = E_{\text{mix}} / RT \tag{2}$$

where E_{mix} = mixing energy.

Mixing energy is defined as the free energy difference due to interactivity occurring between the pure state and blended state. The classical Flory-Huggins model suggests that each constituent molecule occupies a geometric arrangement of the points in space at which the atoms or ions of a crystal occur, *i.e.*, a lattice site. Supposing that a lattice site has a coordination number Z, the mixing energy is defined by:

$$E_{\text{mix}} = \frac{1}{2} z\left(E_{bs} + E_{sb} - E_{bb} - E_{ss}\right). \text{ [26]} \tag{3}$$

where, E_{bb} = Binding energy of Base-base pair;

E_{ss} = Binding energy of Screen-screen pair;

E_{bs} = Binding energy of Base-screen pair;

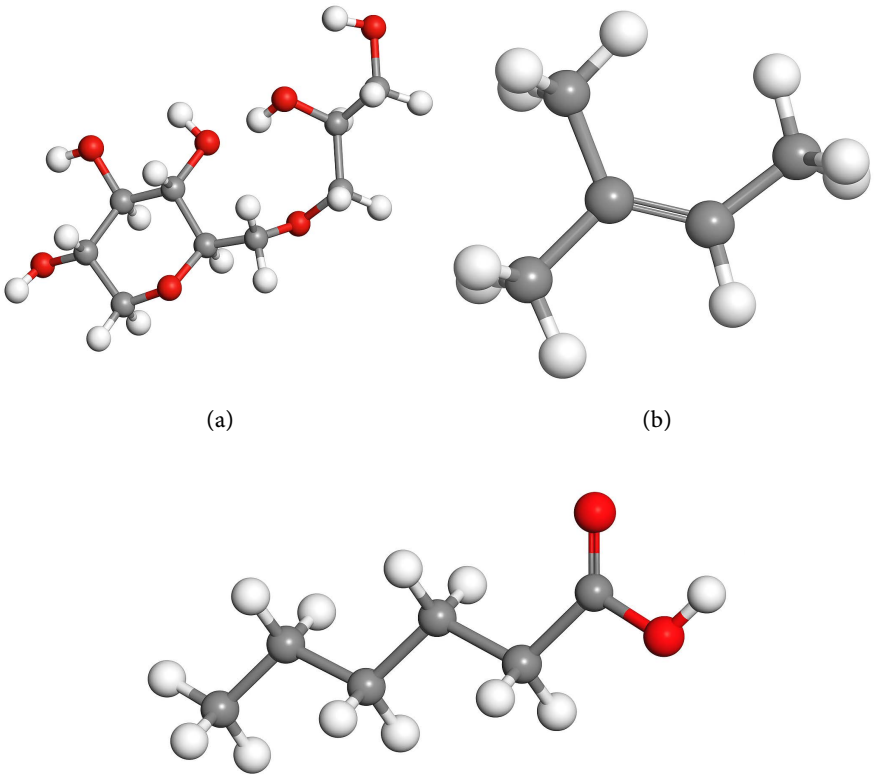
Z = Coordination number for each pair (which is the number of molecules of component B that can be packed around a single molecule of component A within the excluded-volume constraints).

A positive sign of the attainment of a mixed state is the negative value of the chi interaction parameter. If the parameter of interaction is positive, the mixed state is inferred to be disfavored. Moreover, when there is an equilibrium between both conditions, the algorithm will generate different phase diagrams. The combinatorial entropy is expressed by the first two elements. Due to their negative mathematical contribution, they provide favorable conditions for a mixed state, which is preferred over the pure components. The term at the end expresses the free energy generated due to interaction.

3. Calculations

3.1. Geometry Optimization

Three TPS-based polymer mixtures were selected for the compatibility analysis: TPS/NR and TPS/PCL. To begin, the individual structures of the constituting monomers were manually sketched on atomistic 3D windows. Subsequently, energy minimization of sketched structures was carried out through geometry optimization with 500 iteration cycles utilizing the COMPASS force field [27] and SMART algorithm. Energy minimization was conducted using the Forcite module, producing new 3D molecular structures with optimized geometries illustrated in **Figures 1(a)-(c)**, where hydrogen, oxygen, and carbon atoms are depicted as white, red, and grey spheres, respectively.



(a) (b)

(c)

Figure 1. Geometry optimized structure: (a) Thermoplastic starch (amylose + glycerol) [28]; (b) Natural rubber monomer (isoprene); (c) Polycaprolactone monomer.

3.2. Compatibility Calculations

Calculations were executed with the help of the "blends" module. The blends module allows the screening of interaction energy between polymer and polymer, between polymer and solvent, as well as between solvent and solvent. The selection of the monomer to be studied was performed by specifying its head and tail atoms, followed by structure optimization before submission to the calculation tab.

The selected monomers were entered in the first row, and their roles—screen or base—were specified in the second. An overview of the calculation tab layout is provided in **Figure 2**. In this work, TPS served as the base in every blend investigation. The reference temperature was kept at 298 K. Calculation outputs of the mixing task include mixing energy (E_{mix}), binding energies (for the base-base, base-screen, and screen-screen combinations), and χ chi values. The module task of mixing provides the user with an accurate sampling of the mixing characteristics of the selected binary blends. Blends allow the screening for interaction energy between polymer and polymer, between polymer and solvent, as well as between solvent and solvent. For further extrapolations, the blending characteristics of TPS/Natural rubber (NR) and TPS/Polycaprolactone (PCL) binary mixtures of monomers were recorded.

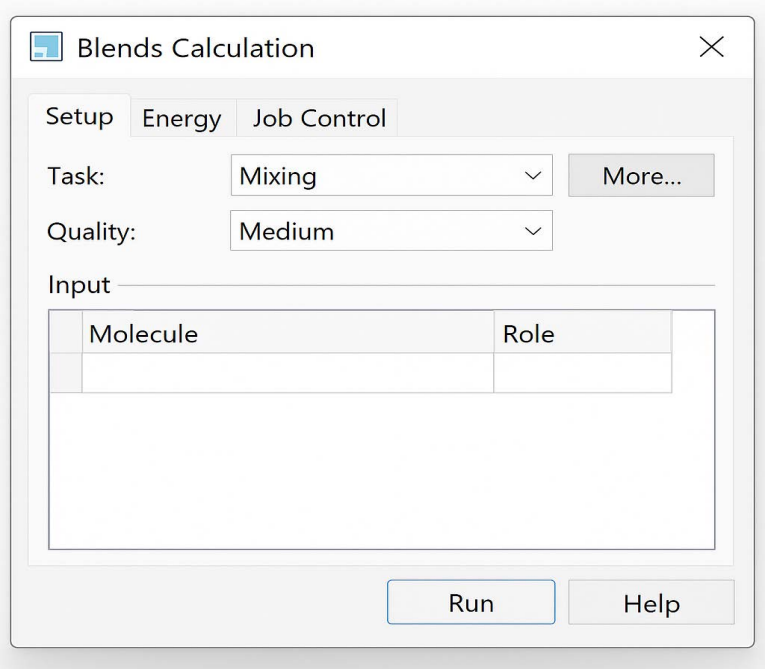


Figure 2. Blends calculation tab in Material Studio 5.5 (Accelrys, Inc.)

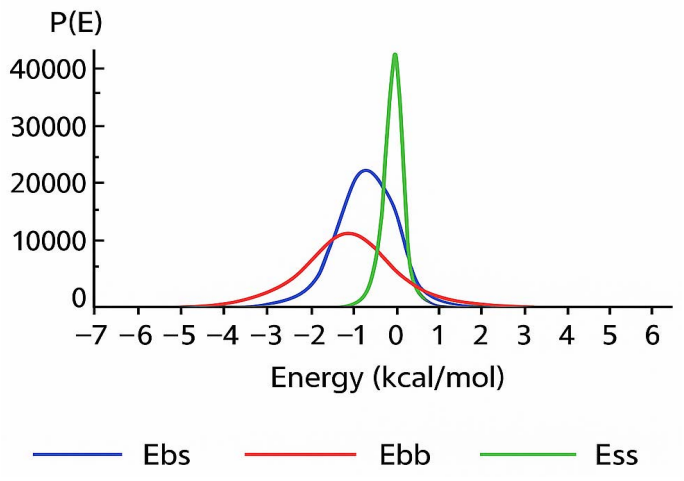
4. Results and Discussion

4.1. Polymer Compatibility

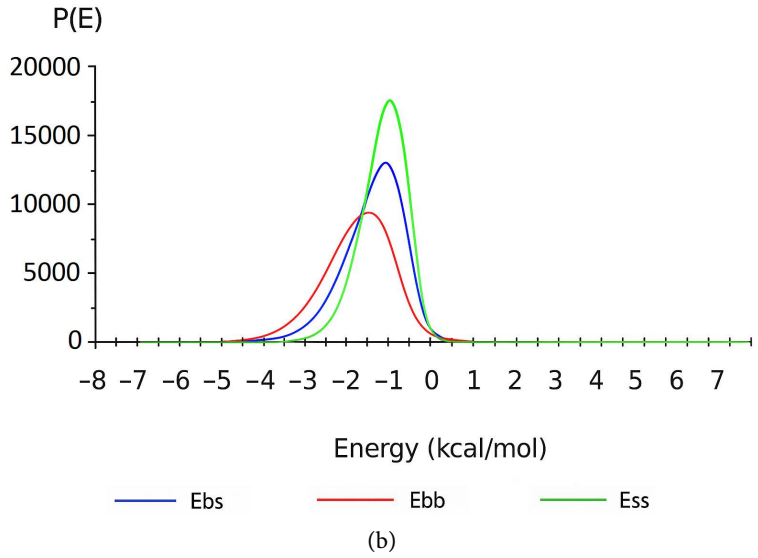
For the data analysis of mixing effectiveness of TPS blends, the following parameters have captured our attention: binding energies distributions (E_{bs}, E_{bb}, E_{ss}), Chi parameter χ, and energy of mixing (E_{mix}).

4.2. Binding Energies Distribution

A strong indicator of structural compatibility between the input monomer pair is the similarity among the binding energy distribution curves for base-base (E_{bb}), base-screen (E_{bs}), and screen-screen (E_{ss}) interactions [29].



(a)



(b)

Figure 3. Plot of binding energy distribution per energy sample P(E): (a) TPS/NR blend; (b) TPS/PCL blend.

From the plots in **Figure 3**, a stronger overlap of binding energy distribution curves is observed for the TPS/PCL mixture (**Figure 3(b)**) relative to the TPS/NR system (**Figure 3(a)**). This suggests that TPS/PCL possesses better structural compatibility, whereas TPS/NR shows the least. This is justified by the fact that TPS/PCL forms compatible blends because of the hydrogen bonding interaction between the ester carbonyl of PCL and the OH groups on starch [30]. Furthermore, it has been observed that the addition of NR to TPS is restricted by phase separation due to poor compatibility between both constituents [31].

4.3. Chi Parameter χ and Mixing Energy (E_{mix})

The χ interaction parameter is a unitless property expressing the difference in energy between solvent-polymer interaction and a polymer-free solvent. Its value can be positive or negative [32]. A χ (chi) value close to zero indicates miscibility, as does an E_{mix} value that is close to zero [33]. Lower χ (chi) and mixing energy values for the TPS/PCL system (**Table 1**) reflect higher compatibility. These results further confirm what has been implied from the binding energies distribution analysis.

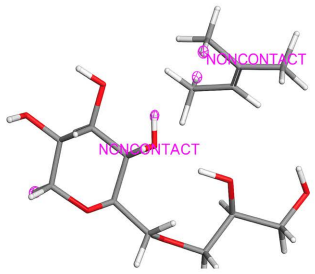
Table 1. Calculated chi parameter and E_{mix} of TPS/NR and TPS/PCL blends.

Polymer Blend	χ Interaction Parameter	Mixing Energy (kcal·mol^{-1})
TPS/NR	5.381	3.186
TPS/PCL	4.429	2.623

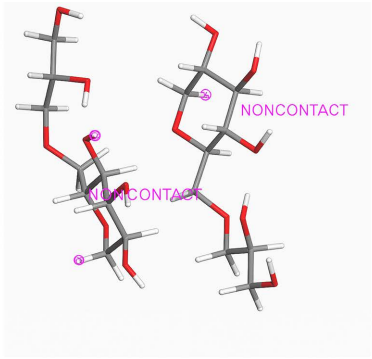
Configurations with the lowest interaction energies

Through the Blends module, pair configurations (base-screen, base-base, and screen-screen) can be organized based on energy to inspect the characteristic bind-

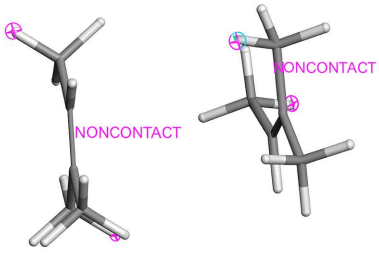
ing and non-binding (non-contact) sites. This is demonstrated in Figure 4(a) and Figure 4(b), where non-binding sites are denoted as *NON-CONTACT*.



Base – screen Non-contact interaction

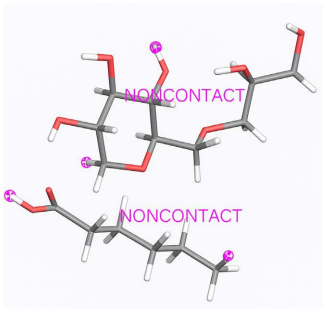


Base – base Non-contact interaction

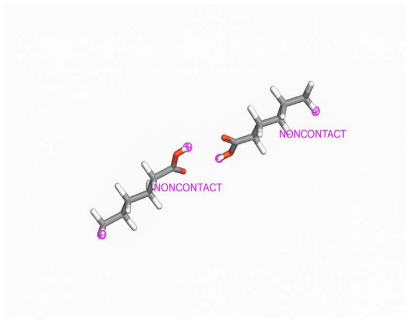


Screen – screen non-contact interaction

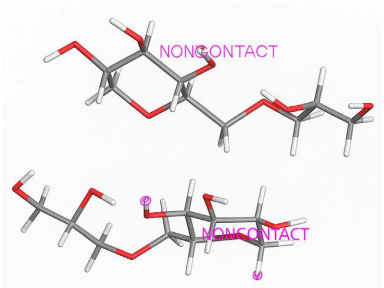
(a)



Base – screen Non-contact interaction



Screen – screen Non-contact interaction



Base–base Non-contact interaction

(b)

Figure 4. (a) Configurations with the lowest energy of interaction for the TPS/NR system, TPS/NR blend; (b) Configurations with the lowest energy of interaction for the TPS/PCL system, TPS/PCL blend.

5. Conclusions

A molecular screening of the interaction energy between the monomer pairs of TPS/NR and TPS/PCL was successfully performed for studying polymer structural compatibility. From the collected data, caprolactone had the best mixing capacity with TPS, whereas natural rubber had the lowest capacity. Poor compatibility of the TPS/NR blend has been reported in existing literature, where it was observed that natural rubber reinforcement of TPS is restricted by phase separation due to poor compatibility of the constituents. This study suggested that an increase in plasticizer (glycerol) content can help to overcome the problem of phase separation. The exact extent to which the use of plasticizer can ameliorate the TPS and NR compatibility is yet to be investigated. TPS/PCL displayed the best mixing potential; the hydrogen bonding interaction that is observed between the ester carbonyl of the caprolactone monomer and the hydroxyl groups present in the starch glucose monomer has explained TPS/PCL compatibility [34]. This high degree of chemical compatibility is also made possible by the elevated content of plasticizer, as well as a very efficient process of TPS plasticization.

Owing to the superior compatibility of the TPS/PCL blend, a diverse range of TPS/PCL-based materials can be developed for applications such as compostable packaging, biodegradable agricultural films, and controlled-release fertilizer coatings [35] [36]. The Flory-Huggins model of investigation for polymeric blending compatibility is a rapid and less costly computational approach compared to the traditional Molecular Dynamics (MD) simulation (although MD simulation might provide a more detailed perspective). The use of monomers as proxies for complete polymer chains, along with the limitations of the selected force field, imposes constraints on the present study. Such approximations should be considered when evaluating the results and planning subsequent studies. The Flory-Huggins approach can facilitate a preliminary comparative analysis of one or several binary blends of polymers by a quick molecular screening of the individual monomers constituting the mixtures.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

[1] Alavi, S., Thomas, S., Sandeep, K.P., Kalarikkal, N., Varghese, J. and Yaragalla, S. (2014) Polymers for Packaging Applications. CRC Press. https://doi.org/10.1201/b17388

[2] Jagur-Grodzinski, J. (1999) Biomedical Application of Functional Polymers. *Reactive and Functional Polymers*, **39**, 99-138. https://doi.org/10.1016/s1381-5148(98)00054-6

[3] Bicerano, J. (1992) Computational Modeling of Polymers. Vol. 25. CRC Press.

[4] Pilania, G., Weis, E., Walker, E.M., Gilbertson, R.D., Muenchausen, R.E. and Simakov, E.I. (2018) Computational Screening of Organic Polymer Dielectrics for Novel Accelerator Technologies. *Scientific Reports*, **8**, Article No. 9258. https://doi.org/10.1038/s41598-018-27572-1

[5] Madhagi, A. and Mohamed, W. (2023) Importance and Application of Computational Studies in Finding New Active Quinazoline Derivatives. In: Al-Kaf, A.G., Ed., *Recent Advances on Quinazoline*, IntechOpen, 90.

[6] Özeren, H.D., Olsson, R.T., Nilsson, F. and Hedenqvist, M.S. (2020) Prediction of Plasticization in a Real Biopolymer System (Starch) Using Molecular Dynamics Simulations. *Materials & Design*, **187**, Article ID: 108387. https://doi.org/10.1016/j.matdes.2019.108387

[7] Özeren, H.D., Nilsson, F., Olsson, R.T. and Hedenqvist, M.S. (2021) Prediction of Real Tensile Properties Using Extrapolations from Atomistic Simulations; an Assessment on Thermoplastic Starch. *Polymer*, **228**, Article ID: 123919. https://doi.org/10.1016/j.polymer.2021.123919

[8] Yamaguchi, A., Arai, S. and Arai, N. (2023) Molecular Insight into Toughening Induced by Core-Shell Structure Formation in Starch-Blended Bioplastic Composites. *Carbohydrate Polymers*, **315**, Article ID: 120974. https://doi.org/10.1016/j.carbpol.2023.120974

[9] Kshitij, M., Dhal, M.K., Banerjee, A., Prasannavenkadesan, V., Katiyar, V. and Kumar, A. (2025) Thermoplastic Starch Based Melt Processed Films for Packaging Applications: Experimental and Computational Studies. *Materials Today Communications*, **42**, Article ID: 111475. https://doi.org/10.1016/j.mtcomm.2024.111475

[10] Yamaguchi, A., Arai, S. and Arai, N. (2024) Design Strategy for Blends of Biodegradable Polyester and Thermoplastic Starch Based on a Molecular Dynamics Study of the Phase-Separated Interface. *Carbohydrate Polymers*, **333**, Article ID: 122005. https://doi.org/10.1016/j.carbpol.2024.122005

[11] Haider Gilani, S.E., Mehmood, U., Younas, M. and Rasheed, M.H. (2025) Molecular Simulation of Polymer Blend Miscibility: A Predictive Thermodynamic Framework Anchored in Flory-Huggins Interaction Metrics. *Molecular Simulation*, **51**, 999-1007. https://doi.org/10.1080/08927022.2025.2567932

[12] Bae, Y.C., Shim, J.J., Soane, D.S. and Prausnitz, J.M. (1993) Representation of Vapor-Liquid and Liquid-Liquid Equilibria for Binary Systems Containing Polymers: Applicability of an Extended Flory-Huggins Equation. *Journal of Applied Polymer Science*, **47**, 1193-1206. https://doi.org/10.1002/app.1993.070470707

[13] Shih, C. (1992) Fundamentals of Polymer Compounding: The Phase-inversion Mechanism during Mixing of Polymer Blends. *Advances in Polymer Technology*, **11**, 223-226. https://doi.org/10.1002/adv.1992.060110306

[14] Tiller, A.R. and Gorella, B. (1994) Estimation of Polymer Compatibility from Molecular Mechanics Calculations. *Polymer*, **35**, 3251-3259. https://doi.org/10.1016/0032-3861(94)90130-9

[15] Sabattié, E.F.D., Tasche, J., Wilson, M.R., Skoda, M.W.A., Hughes, A., Lindner, T., *et al.* (2017) Predicting Oligomer/Polymer Compatibility and the Impact on Nanoscale Segregation in Thin Films. *Soft Matter*, **13**, 3580-3591. https://doi.org/10.1039/c7sm00048k

[16] de Arenaza, I.M., Meaurio, E. and Sarasu, J. (2012) Analysis of the Miscibility of Polymer Blends through Molecular Dynamics Simulations. In: De Souza Gomes, A., Ed., *Polymerization*, InTech, 33. https://doi.org/10.5772/51327

[17] Blanco, M. (1991) Molecular Silverware. I. General Solutions to Excluded Volume Constrained Problems. *Journal of Computational Chemistry*, **12**, 237-247. https://doi.org/10.1002/jcc.540120214

[18] Meth, J.S., Gam, S., Choi, J., Lin, C., Composto, R.J. and Winey, K.I. (2013) Excluded Volume Model for the Reduction of Polymer Diffusion into Nanocomposites. *The Journal of Physical Chemistry B*, **117**, 15675-15683. https://doi.org/10.1021/jp406411t

[19] Vovchenko, V. (2022) Cooper-Frye Sampling with Short-Range Repulsion. *Physical Review C*, **106**, Article ID: 064906. https://doi.org/10.1103/physrevc.106.064906

[20] Clifton, B.J., Cosgrove, T. and Warne, M.R. (2000) Methods for Calculating Solvent Enthalpy of Vaporisation Values by a Molecular Modelling Technique—Effect of Charge and Method. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **164**, 163-173. https://doi.org/10.1016/s0927-7757(99)00342-8

[21] Jian, W., Zeng, Y., Xiong, H. and Pang, J. (2011) Molecular Simulation of the Complex of Konjac Glucomannan-Borate in Water. *Carbohydrate Polymers*, **85**, 452-456. https://doi.org/10.1016/j.carbpol.2011.03.013

[22] Sariban, A. and Binder, K. (1987) Critical Properties of the Flory-Huggins Lattice Model of Polymer Mixtures. *The Journal of Chemical Physics*, **86**, 5859-5873. https://doi.org/10.1063/1.452516

[23] Flory, P.J. (1942) Thermodynamics of High Polymer Solutions. *The Journal of Chemical Physics*, **10**, 51-61. https://doi.org/10.1063/1.1723621

[24] Fredrickson, G.H., Liu, A.J. and Bates, F.S. (1994) Entropic Corrections to the Flory-Huggins Theory of Polymer Blends: Architectural and Conformational Effects. *Macromolecules*, **27**, 2503-2511. https://doi.org/10.1021/ma00087a019

[25] Elbro, H.S., Fredenslund, A. and Rasmussen, P. (1990) A New Simple Equation for the Prediction of Solvent Activities in Polymer Solutions. *Macromolecules*, **23**, 4707-4714. https://doi.org/10.1021/ma00223a031

[26] Patterson, D. and Robard, A. (1978) Thermodynamics of Polymer Compatibility. *Macromolecules*, **11**, 690-695. https://doi.org/10.1021/ma60064a015

[27] Asche, T.S., Behrens, P. and Schneider, A.M. (2016) Validation of the Compass Force Field for Complex Inorganic-Organic Hybrid Polymers. *Journal of Sol-Gel Science and Technology*, **81**, 195-204. https://doi.org/10.1007/s10971-016-4185-y

[28] Ibrahim, M.M., Moustafa, H., Rahman, E.N.A.E., Mehanny, S., Hemida, M.H. and El-Kashif, E. (2020) Reinforcement of Starch Based Biodegradable Composite Using Nile Rose Residues. *Journal of Materials Research and Technology*, **9**, 6160-6171. https://doi.org/10.1016/j.jmrt.2020.04.018

[29] Xiao, J. (2005) Simulation Investigations in the Binding Energy and Mechanical Properties of HMX-Based Polymer-Bonded Explosives. *Chinese Science Bulletin*, **50**, 21-26. https://doi.org/10.1360/982004-147

[30] Shin, B., Lee, S., Shin, Y., Balakrishnan, S. and Narayan, R. (2004) Rheological, Mechanical and Biodegradation Studies on Blends of Thermoplastic Starch and Polycaprolactone. *Polymer Engineering & Science*, **44**, 1429-1438. https://doi.org/10.1002/pen.20139

[31] Carvalho, A.J.F., Job, A.E., Alves, N., Curvelo, A.A.S. and Gandini, A. (2003) Thermoplastic Starch/Natural Rubber Blends. *Carbohydrate Polymers*, **53**, 95-99.

https://doi.org/10.1016/s0144-8617(03)00005-5

[32] Nagy, E. (2019) Mass Transport through a Membrane Layer. In: Nagy, E., Ed., *Basic Equations of Mass Transport Through a Membrane Layer*, Elsevier, 21-68. https://doi.org/10.1016/b978-0-12-813722-2.00003-0

[33] Materials Studio (2017) Blends Manual. Accelrys Inc., 27

[34] Li, G. and Favis, B.D. (2010) Morphology Development and Interfacial Interactions in Polycaprolactone/Thermoplastic-Starch Blends. *Macromolecular Chemistry and Physics*, **211**, 321-333. https://doi.org/10.1002/macp.200900348

[35] Tutek, K., Kosmalska-Olańska, A. and Masek, A. (2025) Modification of Thermoplastic Starch (TPS) with PLA and PCL via Ring-Opening Polymerization (ROP): Comparative Study of Water Solution and Solvent-Free Approaches. *Industrial Crops and Products*, **235**, Article ID: 121785. https://doi.org/10.1016/j.indcrop.2025.121785

[36] Matzinos, P., Tserki, V., Kontoyiannis, A. and Panayiotou, C. (2002) Processing and Characterization of Starch/Polycaprolactone Products. *Polymer Degradation and Stability*, **77**, 17-24. https://doi.org/10.1016/s0141-3910(02)00072-1