

Computational Dynamics Study for Polymer Blend of Polystyrene, Polypropylene and Natural Rubber

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1. Abstract

This work introduces a sustainable Molecular Dynamics Simulation in studying the miscibility of the polymer blends, which act as a basis for analysis before laboratory experiment. The simulation software use was Material studio version 17.1, using the Forcite and Blend Modules for the computation. Temperature effect is considered on the blend mixtures as free energy of mixing (Gm), the Flory-Huggins interaction parameter (Chi or χ), the mixing energy (Emix) and the phase behaviors were analyzed during the study. The generally accepted measure of miscibility in blend mixtures is when interaction parameter (Chi or χ) is negative or less than 1 and non-miscibility when it is positive or greater than 1 is employed in this study. The results of the simulation showed that PS/PP, PS/NR and PP/NR blends were miscible at 386 K, 267 K and 175 K respectively. The miscibility points led to the evaluation of mixing energies of 0.769 kcal/mol, 0.533 kcal/mol and 0.346 kcal/mol for PS/PP, PS/NR and PP/NR blends respectively. Also, the phase behaviors of the blend mixtures were analogous and have a single critical point. The critical points correspond to an optimal mole fraction of 0.5 for the mixtures at 289 K, 202 K and 134 K for PS/PP, PS/NR and PP/NR blends respectively. The study results implied that PS will be miscible with the PP and NR at all temperatures above 386 K. The favorable interaction observed when PS is mixed with PP and NR is due to the non-polar nature of the polymers. The results achieved are in agreement with the theory.

Keywords: Polymer Blend, Material Studio, Polystyrene, Polypropylene, Natural Rubber.

دراسة الديناميكيات الحسابية لمزيج البوليمر من البوليسترين والبولي بروبيلين والمطاط الطبيعي

المخلص: يقدم هذا العمل محاكاة ديناميكية جزيئية مستدامة في دراسة اختلاط خلاط البوليمر ، والتي تعمل كأساس للتحليل قبل التجربة المعملية. كان استخدام برنامج المحاكاة هو Material studio الإصدار 17.1 ، باستخدام Forcite و Blend Modules للحساب. تم اعتبار تأثير درجة الحرارة على خلطات المزج كطاقة حرة للخلط (Gm) ، ومعامل تفاعل Chi) Flory-Huggins (أو ، وطاقة الخلط (Emix) وسلوكيات الطور تم تحليلها أثناء الدراسة. المقياس المقبول عمومًا للامتزاج في خلطات المزج هو عندما تكون معلمة التفاعل Chi) أو (χ سالبة أو أقل من 1 وعدم الامتزاج عندما تكون موجبة أو أكبر من 1 يتم استخدامها في هذه الدراسة. أظهرت نتائج المحاكاة أن خلاط PS / NR و PP / NR و PS / NR كانت قابلة للامتزاج عند 386 كلفن و 267 كلفن و 175 كلفن على التوالي. أدت نقاط الامتزاج إلى تقييم طاقات الخلط بمقدار 0.769 كيلو كالوري / مول و 0.533 كيلو كالوري / مول و 0.346 كيلو كالوري / مول لمزيج PS / PP و PS / NR و PP / NR على التوالي. أيضًا ، كانت سلوكيات الطور لخلطات المزج متشابهة ولها نقطة حرجة واحدة. تتوافق النقاط الحرجة مع جزء مول مثالي يبلغ 0.5 للمخاليط عند 289 كلفن و 202 كلفن و 134 كلفن لمزيج PS / PP و PS / NR و PP / NR على التوالي. أشارت نتائج الدراسة إلى أن PS سيكون غير قابل للامتزاج مع PP و NR في جميع درجات الحرارة فوق 386 كلفن. التفاعل الإيجابي الذي لوحظ عند خلط PS مع PP و NR يرجع إلى الطبيعة غير القطبية للبوليمرات. النتائج المحققة تتفق مع النظرية.

2. Introduction

It is estimated that plastic wastes produced per year represent 50% - 60% of the produced plastic goods in the same year, that is to say approximately 200 million tonnes per annum around 2020 and 10 – 20 million tonnes end up in the ocean. The plastic wastes represent an outstanding source of polymers, difficult to exploit because of practical, technical, psychological, and economic barriers (Platt, 2006; Nanda and Berruti, 2020; Mazhandu et al., 2020). However, it is also a phenomenal pollution that must be carefully treated. In any case, it is necessary to pay more for the production of a new polymer or treatment of the wastes. Which in other words, a novel material can be achieved by combining (blending) two or more of these polymers to give a unique material with improved properties (Biron, 2017).

Therefore, Polymer blends can be classified as, miscible or immiscible. Miscible blends form solutions and satisfies the thermodynamic criteria for a single-phase system which includes; PPO-PS, PVC-nitrile rubber, PBT-PET etc. while contrary, immiscible blends which is also characteristics of polymer composite and is distinguished by two or more phases that are separated by interfaces. These include toughened polymers or fibers in which elastomer are added, as the second or third phase (Charles, 2002; Zhang et al., 2003 Parameswaranpillai et al., 2014 and Mekonnen, et al., 2015). Examples of the toughened polymer are; high impact polystyrene (HIPS), modified polypropylene, acrylonitrile butadiene styrene (ABS), polyvinylchloride (PVC) etc. (MacKnight, 1989; Schmidt, 2013 Salaeh, 2014).

However, there are different simulation packages use for the determination of extend of these blends (Jawalkar et al., 2007). The most common uses of atomistic simulation tools in polymer science and engineering are the prediction of polymer miscibility (Gartner and Jayaraman, 2019). Blends of polymers are desirable since they are easier to produce than novel polymers and circumvent legislative problems. Frequently a pair (or more) of polymers with desirable properties are blended in the hope that the resultant mixture will have improved characteristics (Utracki et al., 2014).

Software's has been developed over the decade for this utilization, examples include Polylab, Material Selector etc. (Wright, 2018; Singh, 2019) but with limitations of number of polymers per batch. However, Materials Studio (MS) can also be utilized to determine the solubility parameters, cohesive energy density and Flory-Huggins interaction parameter of any number of polymers, using molecular dynamics simulation and analyze this to obtain the cohesive energy density. The Mixing Task Options panel in the material studio program allows us to set head and tail atoms in repetition units as noncontact. This means that any atoms indicated as head or tail atoms in the input structures will not be allowed to come into close proximity to any other atoms in the system. Because the non-contact atoms represent the rest of the polymer, you can utilize a monomer to mimic a polymer. (Ahmadi and Freire, 2009; de Arenaza et al., 2012; Erlebach et al., 2020; Material studio modules tutorials 2017).

Therefore, the aim of this work is to use Molecular Dynamics Simulation using Forcite and Blends of Materials Studio 2017, in the framework of the Flory-Huggins model to determine the miscibility of Polypropylene, Polystyrene and Natural rubber as a toughening agent.

3. METHODS

The study of the polymer blends was carried out using Material Studio 2017. The Forcite and Blends modules of the software were employed. The polymer repeat units were imported from the Materials Studio, which has a wide-range collection of predefined structures. The geometries of the repeat units were optimized using Forcite before submitting to the Blend for blend calculations.

3.1 Optimizing the polymer structure using the Forcite module

Forcite is a molecular mechanics unit use for optimization calculations of potential energy and geometry of arbitrary molecular and periodic systems using conventional mechanics. A geometry and energy optimization were first done for each sample using the Forcite module. Optimization was used to achieved the most stable configuration and conformation of the polymer molecules. The task was changed to 'geometry optimization'. The convergence tolerance of energy and force

were set at 1.0×10^{-4} kcal/mol and 0.005 kcal/mol respectively for a maximum iteration of 500. 'Dreiding' forcefield is selected to represent the intra and intermolecular interactions, the charges used was 'charge using QEq' and the quality 'fine'. The convergence limit was fixed at 5.0×10^{-4} e for 50 maximum iterations. Head and tail atoms of the structures are indicated by cyan and magenta color cages around the respective atoms as shown in Figure 3.1

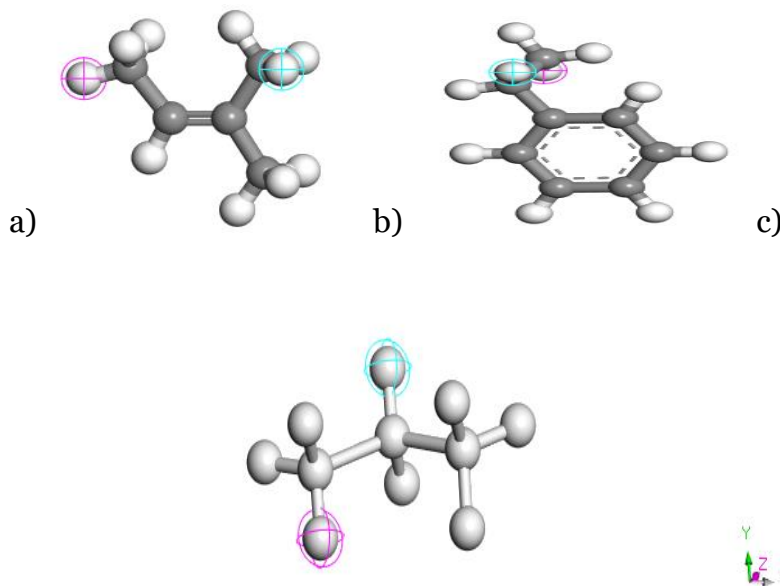


Figure 3.1: Polymer repeat unit of a) NR b) PS c) PP

3.2 Blending the polymers using the Blend module

The Blend module in Materials Studio has been developed to study the miscibility of polymers and solvents, significantly reducing the need for laboratory experimentation. Analysis of the result to predict miscibility, such as Flory-Huggins parameter, mixing energy and phase diagram for the blend mixtures. The module predicts the thermodynamics of polymer mixtures directly from the chemical structure of the components, therefore requires only the components molecular structures and a forcefield as an input to the blend simulation. Its exclusive superiority is the ability to combine Flory-Huggins model and molecular simulation method in calculating the compatibility of polymer mixtures (Abderaman, et al., 2018).

From the Blend module under 'Calculation', the task was changed to 'mixing' which does the binding energy and coordination number calculations, and predicts Flory-Huggins interaction parameter, mixing energy and phase behaviors. The quality was set to 'fine' and the optimized structures of PLA, PS, NR, PET, LDPE and HDPE were inserted in the input section of 'Molecule'. Blend module differentiates the components by using the property role: base or screen. Molecule with screen role is screened against one with base role. PLA was given the property role of base and PS, NR, PET, LDPE and HDPE were given the screen role. 'Dreiding' forcefield was selected, the charges changed to 'charge using QEq' and the quality used was 'fine'. The convergence limit was fixed at 5.0e-4e for 50 maximum iterations.

3.3 Analyzing the blends using Blend module

The analysis option allowed for the study of the free energy (G_m), Flory-Huggins interaction parameter (Chi or χ), mixing energy (E_{mix}) and phase behavior of the generated result.

Analyzing the free energy (G_m) of the blend using Blend module:

Combinatorial entropy contribution is the most significant factor leading to miscibility. One of the important relationships that governs this is the change of free energy of mixing (G_m), given by Equation 1 (Feldman, 2005; White and Wachowicz, 2008). A necessary condition for miscibility to occur is that G_m must be negative ($G_m < 0$). This is a necessary requirement but not a sufficient one (Robeson, 2007). The free energy of mixing of polymers defined by the Flory-Huggins equation (equation 2) strongly depends on the value of the enthalpy of mixing or interaction contribution required for a mutual miscibility of the system. Blend module provide for the study of free energy (G_m) of polymer mixture (Robeson, 2007).

$$G_m = \Delta H_m - T\Delta S \quad 1$$

$$\Delta GRT = A_n A \ln A + B_n B \ln B + AB \quad 2$$

Where;

ΔG_m is the Gibbs free energy of mixing per mole, ΔH_m is the enthalpy of mixing, ΔS_m is entropy factor, T is absolute temperature, ϕ is the composition (volume fraction

of one of the components) n_i is degree of polymerization of component i , χ is interaction parameter and R is the gas constant.

For the analysis of the free energy (G_m) result for each of PLA/PS, PLA/NR, PLA/LDPE, PLA/HDPE AND PLA/PET, temperature range between 298-500 K, temperature steps of 4 and mole fraction between 0-1 were specified.

Analyzing the interaction parameter (Chi or χ) of the blend mixtures using Blend module:

Flory-Huggins interaction parameter is the central measure in the Flory-Huggins theory. According to the Flory-Huggins theory, for two molecules have better miscibility and a favorable interaction at a particular temperature a negative value or a value less than 1 of interaction parameter is required (Robeson, 2007; Abderaman, et al., 2018). It is likely of the two components to show just one phase at this temperature. If interaction parameter is positive or greater than 1, the molecules cannot be mixed, but rather prefer to be surrounded by similar components than each other. The interaction parameter is used to indicate miscibility of polymer blends and the miscibility points (temperature). Blend module allows for this analysis.

For this analysis, temperature range between 298-500 K and 25 steps were specified for each of the PLA/PS, PLA/NR, PLA/LDPE, PLA/HDPE and PLA/PET blend the

Analyzing the mixing energy (E_{mix}) of the blend mixtures using the Blend module:

Generally, it is admitted that a value of the mixing energy (E_{mix}) close to zero indicates miscibility (Abderaman, et al., 2018). The more E_{mix} increases, the less the miscibility. The relationship between Flory-Huggins interaction parameter and mixing energy is given by Equation 3.

$$\chi = \frac{E_{mix}}{RT} \quad 3$$

Blend module was also used to analyze the mixing energy (E_{mix}) of the blend results. The temperature range between 298-500 K and 25 steps were specified for the blend mixtures.

Analyzing the phase behavior of the blend mixtures using Blend module:

Phase diagram in polymer blend is employed to check critical point, which marks the start of coexistence region. The coexistence region is linked by the binodal, indicated by blue lines. While the spinodal, indicated by green lines separates the coexistence region into two regions. In the region between the binodal and the spinodal the mixture is metastable, where the mixture will begin to separate only after a sufficiently large fluctuation. But in the spinodal region the mixture is unstable; any fluctuation will cause the spontaneous separation of the mixture. Similarly, the maximum of the spinodal corresponds to the critical point. In other words, above the binodal region the mixture is stable. Blend module is used for this analysis (Robeson, 2007; Young, 2014).

For the study of the phase behavior of the blend result of each of the blend of PLA with PS, NR, LDPE, HDPE and PET, 25 steps were specified.

4. Results

The blends were carried out at 298 K and the results are presented below. The analysis of the free energy (G_m), interaction parameter (χ), mixing energy (E_{mix}) and phase behavior of the blends are carried out in order to examine the miscibility between the polymers.

4.1 Free energy of mixing (G_m)

The free energy of mixing (G_m) results generated for the blend of PP, PS and NR between the temperature range of 298-500 K, temperature steps of 4 and mole fraction between 0-1 are shown in Figure 3.1-3.3.

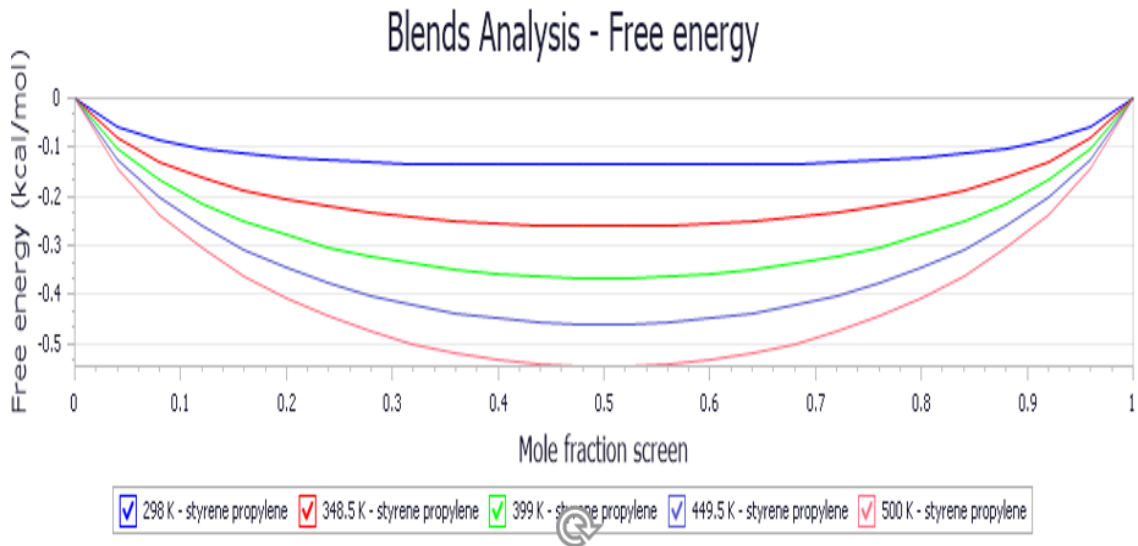


Figure 4.1: Free energy analysis for binary system of PS/PP.

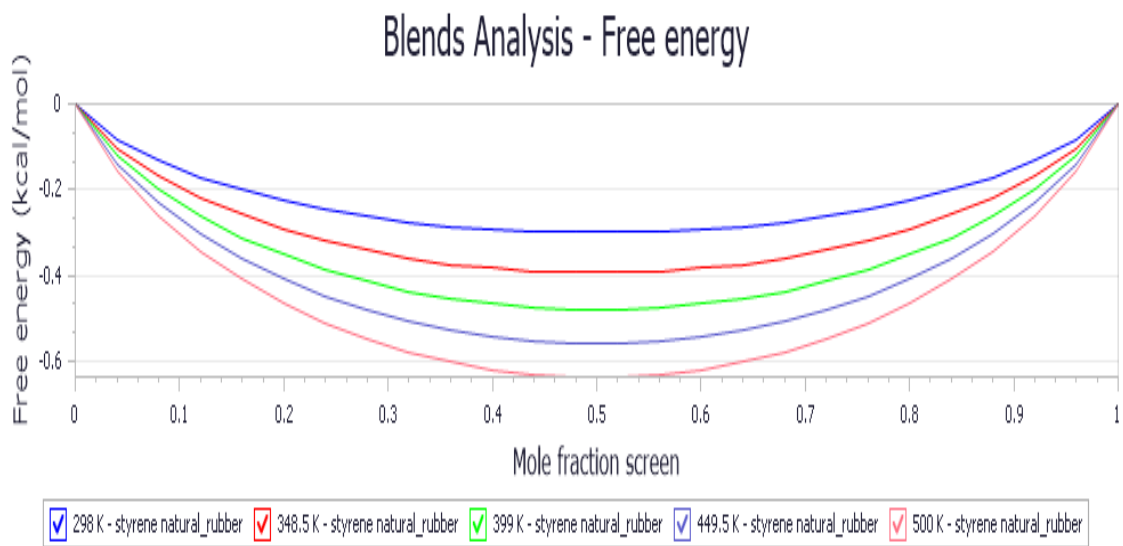


Figure 4.2: Free energy analysis for binary system of PS/NR.

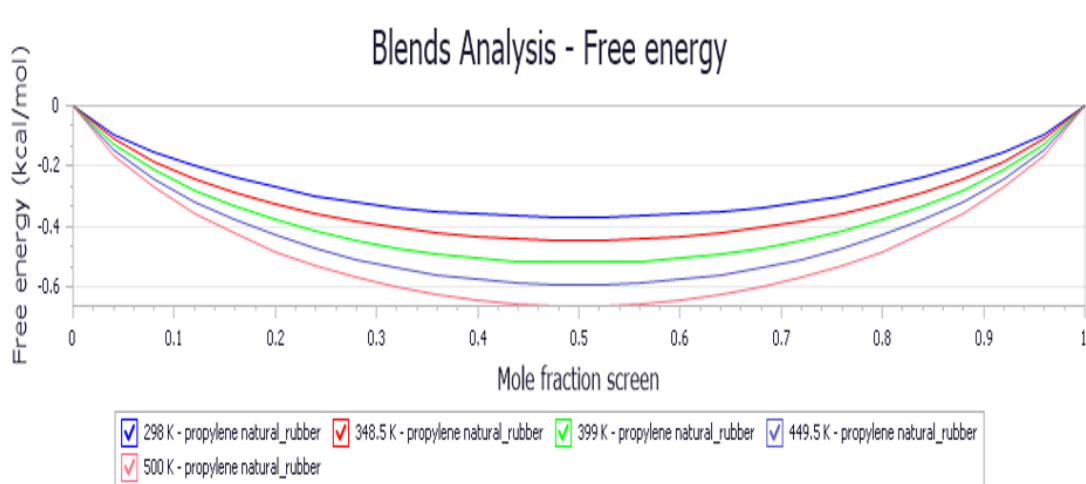


Figure 4.3: Free energy analysis for binary system of PP/NR.

The free energy (G_m) of mixing for the blend of PP, PS and NR in Figure 4.1-4.3 shows that the energy values are all less than zero and the values further decrease as temperature is increase. This result is in line with literature that a necessary condition for miscibility to occur is that G_m must be negative ($G_m < 0$) (Robeson, 2007). This result agreed with the theory of Equation 1, relationship between free energy and temperature.

4.2 Flory-Huggins interaction parameter (χ or Chi)

From Figure 4.4, the interaction parameter (χ or Chi) is plotted as a function of the temperature for mixture of PP, PS and NR. This shows the dependence of interaction parameter (χ or Chi) on temperature.

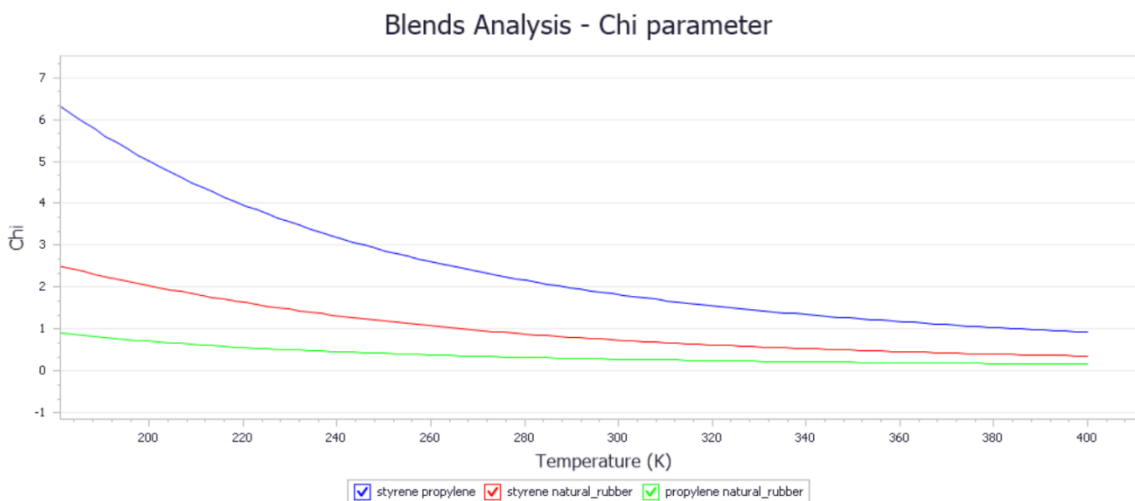


Figure 4.4: Interaction parameter (χ or Chi) analysis.

Miscibility point for PS/PP, PS/NR and PP/NR are found at 386 K, 267 K and 175 K respectively.

According to the Flory-Huggins theory, a negative value or a value less than 1 of Chi (χ) indicates that at this particular temperature the two molecules have better miscibility and a favorable interaction (Abderaman, et al., 2018). If χ is greater than one the molecules cannot be mixed, rather prefer to be surrounded by similar components. From Figure 4.4, it is observed that the Chi (χ) parameter values of blends decrease as the temperature increase. This implies that for a miscible system, increase in temperature decrease Chi (χ) parameter which is measure of increasing miscibility. The result shows that PP/NR had the best miscibility at the lowest temperature of 175 K, followed by PS/NR at 267 K and PS/PP at 386 K accordingly Thus, the results reinforce that of the free energy (G_m), that PP, PS and NR will be miscible.

4.3 The mixing energy (E_{mix})

Figure 4.5 E_{mix} is plotted as a function of the temperature, for mixture of PP, PS and NR.

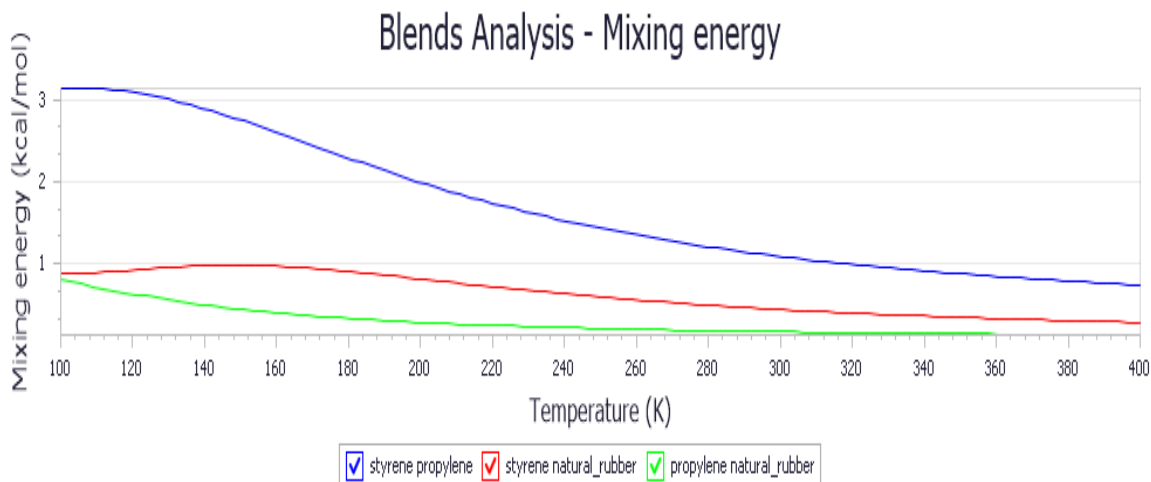


Figure 4.5: Mixing energy (E_{mix}) analysis

The result in Figure 3.5 led to the evaluation of a mixing energy of 0.769 kcal/mol at 386 K for PS/PP, 0.533 kcal/mol at 267 K for PS/NR and 0.346 kcal/mol at 175 K for PP/NR.

A mixing energy (E_{mix}) of a blend mixture close to zero also indicates miscibility (Abderaman, et al., 2018). The more E_{mix} decreases, the more the miscibility. The

analysis of the graph in Figure 4.5 shows that when the temperature increases, the E_{mix} of the blends decreases. This justified the linear relationship between Chi (χ) parameter and mixing energy (E_{mix}) in Equation 2. At the achieved miscibility points of the blends, mixing energy of 0.769 kcal/mol, 0.533 kcal/mol and 0.346 kcal/mol for PS/PP, PS/NR and PP/NR respectively. The mixing energy (E_{mix}) result reinforce that of the interaction parameter (χ), that PP/NR had the best miscibility, followed by PS/NR and PS/PP.

4.4 The phase behavior of the binary mixtures

The phase diagrams of the blends of PP, PS and NR are shown in Figure 3.6-3.8, where the composition of the mixture is given as a function of the mole fraction screen of the other polymers. The phase diagram generally contains three pieces of information: critical points (red), spinodal (green) and binodal (blue). In phase diagrams, a critical point marks the start of coexistence region. However, the mixture is unstable in the spinodal region. Metastable in the region between the spinodal and binodal. But, stable in the binodal region.

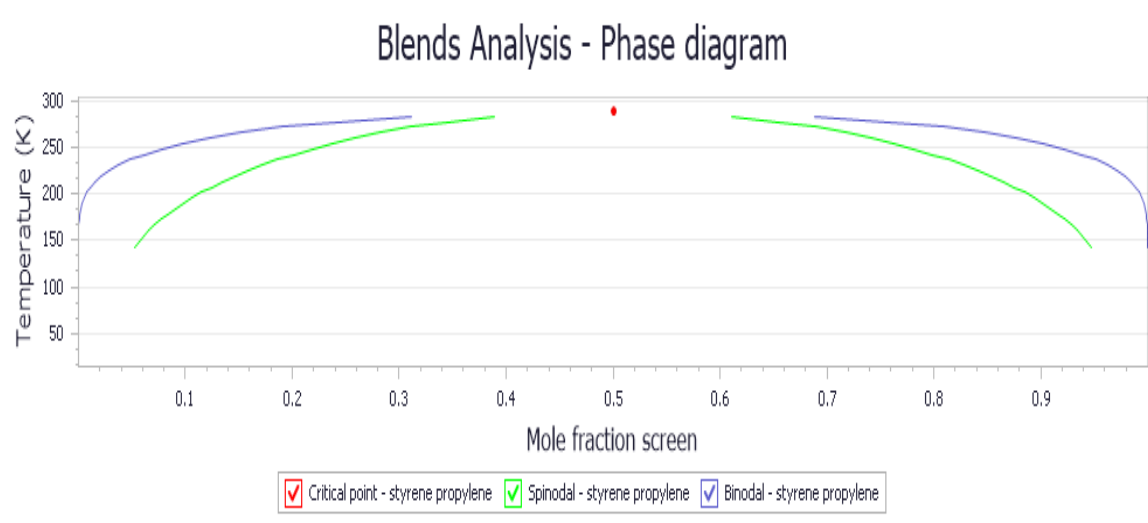


Figure 4.6: Phase diagram for binary system compound of PS/PP.

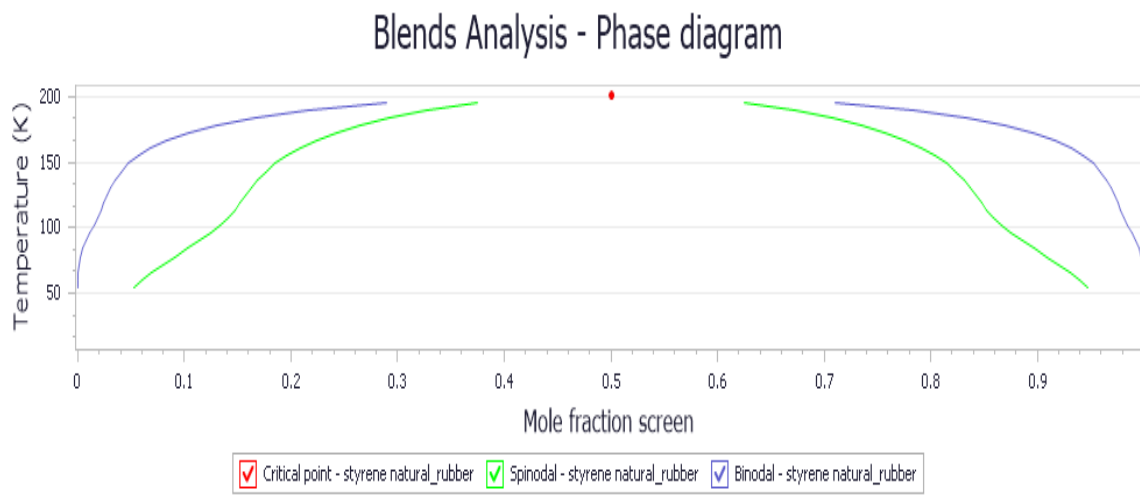


Figure 4.7: Phase diagram for binary system compound of PS/NR.

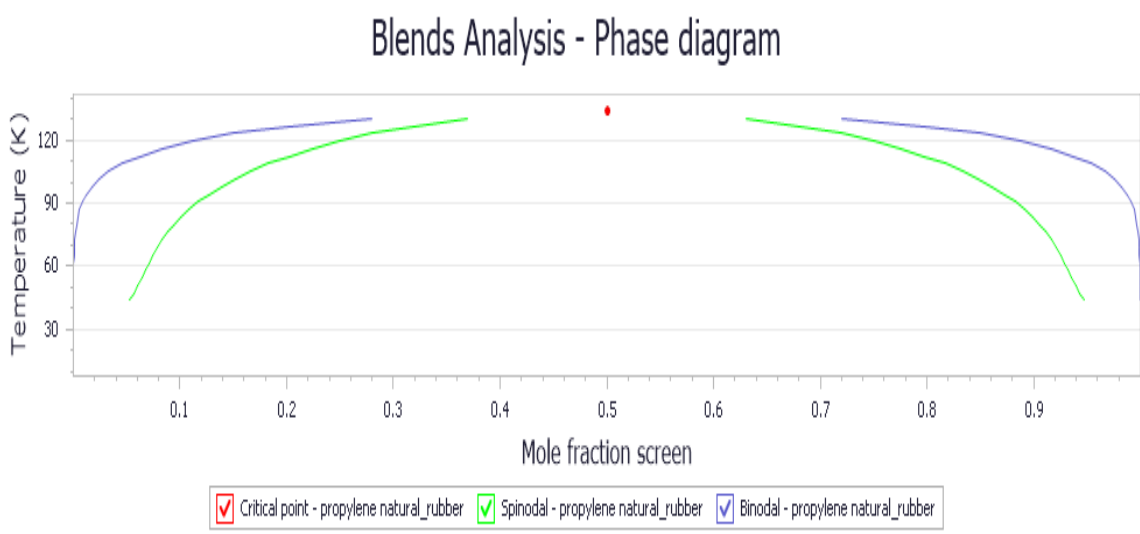


Figure 4.8: Phase diagram for binary system compound of PP/NR.

The results have shown that the critical point temperatures of PS/PP, PS/NR and PP/NR are 289 K, 202 K and 134 K respectively, at an optimum mole fraction of 0.5 for all the systems. Analyzing the phase behavior, it is observed that the blends of PP, PS and NR all have a simple critical point and one coexistence region.

5. CONCLUSION

The study of the miscibility between the blend mixtures of PP, PS and NR by molecular dynamics simulation was carried out using Material Studio 17. The free energy, Flory-Huggins interaction parameter, mixing energy and phase diagrams of blend mixtures were analyzed. Miscibility points for PS/PP, PS/NR and PP/NR

blends were found at 386 K, 267 K and 175 K respectively. The auspicious interaction observed when PS is mixed with PP and NR is due to the non-polar nature of the polymers. The results led to the evaluation of a mixing energy of 0.769 kcal/mol, 0.533 kcal/mol and 0.346 kcal/mol for PS/PP, PS/NR and PP/NR blends respectively. Likewise, the mixtures of PS, PP and NR all have a simple critical point and one coexistence region. The critical points of PS/PP, PS/NR and PP/NR blends are found at 289 K, 202 K and 134 K respectively, at an optimal mole fraction of 0.5 for all the mixtures. Then, it can be said that for a mole fraction of 0.5 and a temperature of 386 K, PS is miscible with all the other polymers (PS or NR).

REFERENCE

- [1] Abderaman, M. B., Gueye, E. H. O., Dione, A. N., Diouf, A. A., Faye, O., & Beye, A. C. (2018). A Molecular Dynamics Study on the Miscibility of Polyglycolide with Different Polymers. *International Journal of Materials Science and Applications*, 7(4), 126.
- [2] Ahmadi, A., & Freire, J. J. (2009). Molecular dynamics simulation of miscibility in several polymer blends. *Polymer*, 50(20), 4973-4978.
- [3] Biron, M. (2017). Recycling: The First Source of Renewable Plastic. *Industrial Applications of Renewable Plastics*, 67-114. <http://dx.doi.org/10.1016/B978-0-323-48065-9.00003-0>
- [4] Charles, H. (2002). *Handbook of Plastics, Elastomers and Composites*. McGraw-Hill Professional, USA. p. 69 ISBN 0-07-138476-6
- [5] de Arenaza, I. M., Meaurio, E., & Sarasua, J. R. (2012). Analysis of the miscibility of polymer blends through molecular dynamics simulations. *Edited by Ailton De Souza Gomes*, 29.
- [6] Erlebach, A., Muljajew, I., Chi, M., Bückmann, C., Weber, C., Schubert, U. S., & Sierka, M. (2020). Predicting Solubility of Small Molecules in Macromolecular Compounds for Nanomedicine Application from Atomistic Simulations. *Advanced Theory and Simulations*, 3(5), 2000001.

- [7] Feldman, D. (2005). Polyblend compatibilization. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 42(5), 587-605.
- [8] Gartner III, T. E., & Jayaraman, A. (2019). Modeling and simulations of polymers: a roadmap. *Macromolecules*, 52(3), 755-786.
- [9] Jawalkar, S. S., Raju, K. V., Halligudi, S. B., Sairam, M., & Aminabhavi, T. M. (2007). Molecular modeling simulations to predict compatibility of poly (vinyl alcohol) and chitosan blends: a comparison with experiments. *The Journal of Physical Chemistry B*, 111(10), 2431-2439.
- [10] MacKNiGHT, W. J. (1989). Polymer Blends WiLLiAM J. MacKNiGHT and FRANK E. KARASZ University of Massachusetts, Amherst, MA, USA. *Comprehensive Polymer Science: Specialty polymers and polymer processing*, 7, 111.
- [11] Mazhandu, Z. S., Muzenda, E., Mamvura, T. A., & Belaid, M. (2020). Integrated and Consolidated Review of Plastic Waste Management and Bio-Based Biodegradable Plastics: Challenges and Opportunities. *Sustainability*, 12(20), 8360.
- [12] Mekonnen, T. H., Misra, M., and Mohanty, A. K. (2015). Processing, performance, and applications of plant and animal protein-based blends and their biocomposites. In *Biocomposites* (pp. 201-235).
- [13] Nanda, S., & Berruti, F. (2020). Thermochemical conversion of plastic waste to fuels: a review. *Environmental Chemistry Letters*, 1-26.
- [14] Parameswaranpillai, J., Thomas, S., and Grohens, Y. (2014). Polymer blends: state of the art, new challenges, and opportunities. *Characterization of polymer blends: miscibility, morphology and interfaces*, 1-6.
- [15] Platt, D. K. (2006). *Biodegradable polymers: market report*. iSmithers Rapra Publishing.
- [16] Robeson, L. M. (2007). Polymer blends. *A Comprehensive Review*. First Edition. Munich, Germany: Hanser Publishers, ISBN-10: 3-446-22569-2, ISBN-13: 978-3-446-22569-5
- [17] Salaeh, S. (2014). *Processing of natural rubber composites and blends: relation between structure and properties* (Doctoral dissertation, Université Claude Bernard-Lyon I).

- [18] Schmidt, A. (2013). *Handbook of Polymer Synthesis, Characterization and Processing. Edited by Enrique Saldívar-Guerra and Eduardo Vivaldo-Lima. Angewandte Chemie International Edition, 53(2), 358–358. doi:10.1002/anie.201309282*
- [19] Singh, A., Radhakrishnan, S., Vijayalakshmi, R., Talawar, M. B., Kumar, A., & Kumar, D. (2019). Screening of polymer-plasticizer systems for propellant binder applications: an experimental and simulation approach. *Journal of Energetic Materials, 37(4), 365-377.*
- [20] Utracki L.A., Mukhopadhyay P., Gupta R.K. (2014) Polymer Blends: Introduction. In: Utracki L., Wilkie C. (eds) Polymer Blends Handbook. Springer, Dordrecht. https://doi.org/10.1007/978-94-007-6064-6_3
- [21] White, J. L., & Wachowicz, M. (2008). Polymer blend miscibility. *Annual Reports on NMR Spectroscopy, 64, 189-209.*
- [22] Wright, C. J. (2018) Case Study: Practical Introduction of a Materials Selection Software in a Fundamentals of Materials Science Course.
- [23] Young, N. P. (2014). *Thermodynamics and phase behavior of miscible polymer blends in the presence of supercritical carbon dioxide* (Doctoral dissertation, UC Berkeley).
- [24] Zhang, G., Zhang, J., Wang, S., & Shen, D. (2003). Miscibility and phase structure of binary blends of polylactide and poly (methyl methacrylate). *Journal of polymer science part B: Polymer physics, 41(1), 23-30.*