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A Comprehensive Study of the Properties of Polypropylene Glycol 1025 (PPG1025) using a Combination of Two Theoretical Models, the Simha–Somsenki (SS) Model and the Cahen–Hilliard (CH) Equation

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Abstract: In this study, the thermal and physical properties of polypropylene glycol PPG1025 were investigated using a combination of the modified Simha–Somcynsky cell theory and the Cahn–Hilliard equation, with the aim of analyzing the effect of temperature and molecular weight on specific volume, density, surface tension, and energy difference coefficient. Experimental data was used within the Wolfram Mathematica environment with the Newton–Raphson algorithm to obtain accurate solutions to nonlinear equations and reduce the error ratio. The results showed that the specific volume increases with rising temperature while the density and surface tension gradually decrease, and the fraction of voids within the polymer structure increases. The limiting energy coefficient and site occupancy index also showed regular changes reflecting the flexibility and stability of the PPG1025 molecular network within the studied temperature range, confirming the efficiency of theoretical models in predicting polymer behavior.

Keywords: : Thermophysical Modeling, Gradient Energy Coefficient, Surface Tension Analysis, Molecular Packing, Void Fraction, Thermal Expansion Behavior, Density–Temperature Relationship

1. Introduction

Polymers have emerged as some of the most significant materials in both industry and science due to their structural diversity and adjustable properties. These long-chain molecules, made up of repeating units known as monomers, exhibit a range of physical and chemical characteristics that can be altered through variations in molecular structure, monomer type, and molecular weight [1][2]. Their applications span from everyday items to advanced technologies, including consumer goods, aerospace innovations, laser printing, and medical devices. Among these, polypropylene glycol (PPG) stands out as a versatile and widely used oligomer, characterized by its customizable viscosity suitable for various systems, along with its high flexibility and compatibility with a range of materials. PPG is frequently utilized in hydraulic fluids, adhesives, cosmetics, insulation foams, and pharmaceutical formulations [3]. A key factor influencing PPG's behavior is its molecular weight, which directly impacts its specific volume, density, surface tension, and thermodynamic properties [4]. Additionally, molecular weight significantly influences PPG's performance at varying temperatures. As the molecular chain length increases, the

extent of packing, free volume, and interface dynamics of the polymer change, leading to a decrease in density. Understanding these parameters is crucial for predicting the polymer's response to heat and pressure, especially in high-performance industrial and medical applications [5]. Within this context, the gradient energy coefficient (κ) is vital for quantifying the energetic penalties associated with polymer density gradients. It is intricately linked to surface tension and phase separation behavior, making it essential for comprehending interface dynamics. To investigate this behavior, the Cahn–Hilliard equation has become a widely accepted theoretical model for explaining the evolution of phase composition in multiphase systems, where the overall free energy is minimized [6]. In this study, a comprehensive thermodynamic model based on the Simha–Somcynsky (SS) equation of state and the Cahn–Hilliard theory has been developed to investigate the thermo-physical properties of PPG with varying molecular weights. This approach allows for the examination of the gradient energy coefficient, surface tension, and other related factors as functions of different temperatures, aiding in the understanding of how mesoscopic thermal performance is influenced by molecular structure [7].

2. Materials and Methods

The Cahn–Hilliard equation is widely used in materials science to describe how composition changes in multiphase systems. It is a conservation law that maintains the overall atomic density as spatial variations occur. This equation plays a crucial role in modeling phase separation and interface evolution in heterogeneous systems [8].

The local free energy density $\alpha(\rho, \nabla\rho, \nabla^2\rho, \dots)$ is expressed as:

$$\alpha(\rho, \nabla\rho, \nabla^2\rho, \dots) = \alpha_0(\rho) + k_1\nabla^2\rho + k_2(\nabla\rho)^2 \tag{1}$$

In this expression, $\alpha_0(\rho)$ represents the free energy of a homogeneous system, while the gradient terms account for the contributions from heterogeneities in the mixture. The coefficients k_1 and k_2 are determined as:

$$k_1 = \left(\frac{\partial\alpha}{\partial(\nabla^2\rho)}\right)_0, k_2 = \frac{1}{2}\left(\frac{\partial^2\alpha}{\partial(\nabla\rho)^2}\right)_0 \tag{2, 3}$$

These coefficients describe how variations in density affect the system's energy landscape, evaluated at zero gradient. This mathematical representation is essential for modeling polymer mixtures, alloys, and other multicomponent systems undergoing phase separation [9].

The total Helmholtz free energy A of the system over a volume V is given by:

$$A = \int [\alpha_0(\rho) + k(\nabla\rho)^2]dV \tag{4}$$

The first term on the right hand side of eq 4 is the homogeneous part of the energy and the second term is the contribution to the energy from spatial composition gradients. The gradient coefficient which cost is the generation of these gradients so it strongly affects the interface structure [10].

To get the surface tension, which is a crucial property of an interface, the previous energy equation is divided by the interfacial area and integrated across the interface in one dimension:

$$\gamma = \int_{-\infty}^{\infty} [\Delta\alpha + k(\nabla\rho)^2]\,dx \tag{5}$$

Here, $\Delta\alpha$ represents the free energy difference between two coexisting phases (e.g., liquid and vapor). The resulting expression gives the Helmholtz free energy per unit area across the interface, with density gradients driving the structure [11].

To model equilibrium, Euler's equation is applied to the energy functional I:

$$I - \left(\frac{d\rho}{dx}\right)\left[\frac{\partial I}{\partial(d\rho/dx)}\right] = 0 \tag{6}$$

Continuation of Cahn–Hilliard Theory: Surface Tension Derivation

Starting from the earlier equation:

$$\Delta\alpha - k\left(\frac{d\rho}{dx}\right)^2 = 0 \tag{7}$$

This equation can be rearranged to:

$$\Delta\alpha = k\left(\frac{d\rho}{dx}\right)^2 \tag{8}$$

Solving for dx, we isolate the differential:

$$dx = \left(\frac{\Delta\alpha(\rho)}{k}\right)^{-1/2} d\rho \tag{9}$$

This expression shows the spatial increment dx in terms of the density function and energy. Substituting $\Delta\alpha(\rho)$ as a function of ρ, we obtain:

$$dx = k^{-1/2}\Delta\alpha(\rho)^{-1/2}d\rho \tag{10}$$

Now, inserting equation (13) into the surface tension expression:

$$\gamma = \int_{-\infty}^{\infty} 2\,\Delta\alpha(\rho)dx \tag{14}$$

we get the surface tension in terms of a density integral:

$$\gamma = 2\int_{-\infty}^{\infty} [k\Delta\alpha(\rho)]^{1/2}\,dx \tag{15}$$

This result allows us to compute the surface tension based on the local free energy difference across a density gradient [10].

Let Ω denote the domain over which the Cahn–Hilliard equation is solved, with $\partial\Omega$ representing its boundary. In this section, we first address the binary system before introducing the multicomponent model and the stress-enhanced diffusion case[11].

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In the binary case, the Cahn–Hilliard equation is interpreted as a diffuse interface model. Here, c is the mass fraction of one component in a two-component system. The total free energy of the system, based on Ginzburg–Landau[11]. formalism, is given by:

$$F(c) = \int_{\Omega} \left[f(c) + \frac{K}{2} \mid \nabla c \mid^2 \right] dV \qquad (16)$$

This equation describes the system's energy as a combination of a bulk free energy density f(c) and a gradient energy term representing interface effects [12][13].

The Simha–Somcynsky theory, abbreviated as Modified Cell Theory (MCT), is one of the most prominent theoretical models used to describe the thermodynamic behavior of polymers in their amorphous or molten states. This theory is based on a compartmentalization concept that assumes that each structural unit in a polymer chain occupies a specific spatial volume known as a "cell," with the presence of small gaps (voids) affecting the bulk properties and internal energy of the material.The model is based on the idea that molecules do not occupy the entire volume of the material, but rather a portion of the void space (the void fraction, h h) varies with temperature and pressure, directly affecting density, surface tension, and compressibility. The theory assumes that intermolecular interactions can be described by cohesive and repulsive forces, allowing for the construction of a semi-realistic equation of state applicable to a wide range of thermal conditions[14], [15], [16].

The equation of state in this model is expressed as follows:

$$P = \frac{C \cdot T}{V - V^{1/3}\left(V^{1/3} - \delta\right)} + \frac{2T}{V^2}\left(B - \frac{A}{V^2}\right) \qquad (17)$$

Where: P is the pressure, T is the absolute temperature, V is the specific volume, C is a parameter related to the molecular degrees of freedom (chain structure), δ is a structural correction factor, and A, B are constants associated with the cohesive and repulsive energy between molecules.

Using modified cell theory (MCT), a detailed theoretical evaluation was performed for one type of polypropylene glycol (PPG) polymer: PPG1025. The analysis included key thermophysical parameters such as reduced temperature T^, specific volume V^, reference pressure P^, and characteristic internal energy ε^. The theoretical surface tension constant was also calculated accurately, which is an important parameter in describing surface tension in surface systems. We also calculated the maximum and minimum relative errors to evaluate the accuracy of the numerical solutions obtained through the development of the modified cell theory. The observations summarized in Table 1 indicate systematic trends in physical properties as a function of molecular weight. These increasing trends are attributed to the effect of chain length on the stability and cohesive energy density of the polymer system.

3. Results and Discussion

The properties of PPG1025 were analyzed using a theoretical framework based on Simha–Somcynsky Modified Cell Theory, along with the Carey–Sima Equation, with the aim of characterizing changes in specific volume, density, surface tension, and energy difference coefficient as a function of temperature.

The analysis was performed over a temperature range from 313.2 K to 473.2 K using experimental data entered into the Wolfram Mathematica environment, where the Newton–Raphson algorithm was used to find optimal solutions to the nonlinear equations representing the theoretical model. The theoretical values of the state variables were calculated and then compared with the experimental results to reduce the error ratio and improve the reliability of the model.

The Carey–Sima equation was applied to extract the specific thermal constants of the material, such as k∗ and ε∗. The surface tension variable was also represented as a function of temperature, reflecting the subtle phase changes undergone by the material. The

characteristic constants summarizing the thermal and physical properties of PPG1025 were then extracted, as shown in Table 1 and Table 2, which show the values calculated in terms of temperature for PPG1025 using the extracted theoretical constants.

Table 1. Thermal and physical constants characteristic of the extracted PPG1025 sample.

Constant	The symbol	Value
Number of repetition units	S	10.3
Proportionality coefficient in the model	C	4.3
Characteristic specific volume	$(10^6 \text{ cc/mol})V^*$	37.3909
Reference surface tension	$(\text{N/m})\gamma^*$	0.0311476
Gradient energy coefficient	$(\text{erg·cm/g}^2)K^*$	0.000066651
Characteristic pressure	$(\text{MPa})P^*$	802.267
Characteristic cohesion energy	$(\text{kK})\varepsilon^*$	340.549
Corrected specific volume	$(\text{cc/gm})V^*$	0.000953518
Characteristic temperature	$(\text{K})T^*$	8559.12
Lowest relative error	Min Err	0.06348
Highest relative error	Max Err	0.49746

Table 2. Values calculated based on the temperature of PPG1025 using the theoretical constants derived.

T (K)	h	ρ (kg/m³)	$\tilde{\gamma}$ (N/m)	$\tilde{K}$ ($\times 10^{-6}$ erg·cm/g²)
313.2	0.091701	985.22	0.031148	5.8588
353.2	0.117849	955.693	0.027971	5.1703
373.2	0.131127	940.714	0.026407	5.0028
393.2	0.144525	925.603	0.024859	4.8186
413.2	0.158036	910.364	0.023329	4.6173
433.2	0.171656	895.003	0.021816	4.3981
453.2	0.18538	879.523	0.020323	4.1606
473.2	0.199204	863.925	0.018849	3.9031

Figure 1 shows the changes in the specific volume of PPG1025 as a function of temperature and under the influence of various pressures ranging from 0.1 to 150 MPa. The graph shows that the specific volume increases gradually with rising temperature, which is expected behavior associated with the increase in thermal energy acquired by the polymer molecules, leading to the expansion of the polymer network and an increase in the interchain distances.

This thermal expansion reflects the elasticity of the material in the liquid state and indicates the polymer's thermal responsiveness within this temperature range, especially for PPG1025-type materials, which are characterized by short chain structures and elastic behavior under thermal influence , On the other hand, the effect of pressure is clearly evident, as increased pressure leads to a reduction in specific volume at the same temperature. This effect is attributed to the convergence of molecules under the influence

of external forces, which reduces the distance between polymer chains. This effect is more pronounced when comparing the low pressure curve (0.1 MPa) and the high pressure curve (150 MPa), where the slope of the curves is greater as the pressure increases, The divergence between the curves at high temperatures indicates that the effect of pressure becomes less pronounced as the thermal energy increases, reflecting the balance between the increased kinetic energy of the molecules and the forces resulting from external pressure , Finally, the high correlation coefficient (ccs ≈ 0.9991) that the theoretical values accurately mimic the behavior of the material, confirming the effectiveness of the theoretical calibration in characterizing the thermal system of PPG1025 under different pressure and temperature conditions.
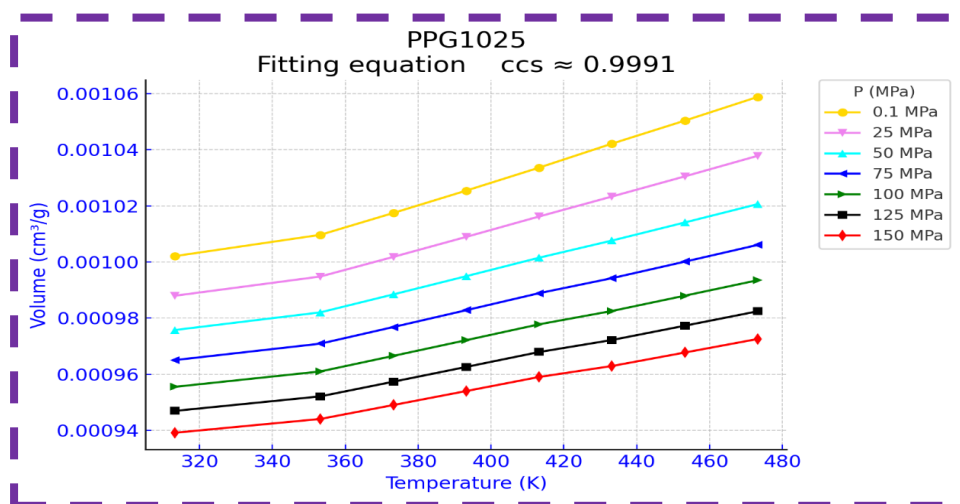

Figure 1. Changes in the specific volume of PPG1025 as a function of temperature and under the influence of multiple pressures.

Figure 2 shows the thermal behavior of the surface tension of PPG1025, where a clear decrease in surface tension is observed with increasing temperature. This behavior is fully consistent with the properties of polymeric materials and complex fluids, as an increase in temperature leads to an increase in the kinetic energy of the material's molecules, which weakens the molecular forces of attraction at the surface, thereby leading to a gradual decrease in surface tension. The curve shows that the decrease in surface tension occurs smoothly and regularly across the studied temperature range (313.2 – 473.2 K), indicating the absence of sudden phase transitions within this range, i.e., the material did not exhibit any transitional behavior or structural changes upon heating, indicating the stability of the short-chain polymer structure of PPG1025 in this range.
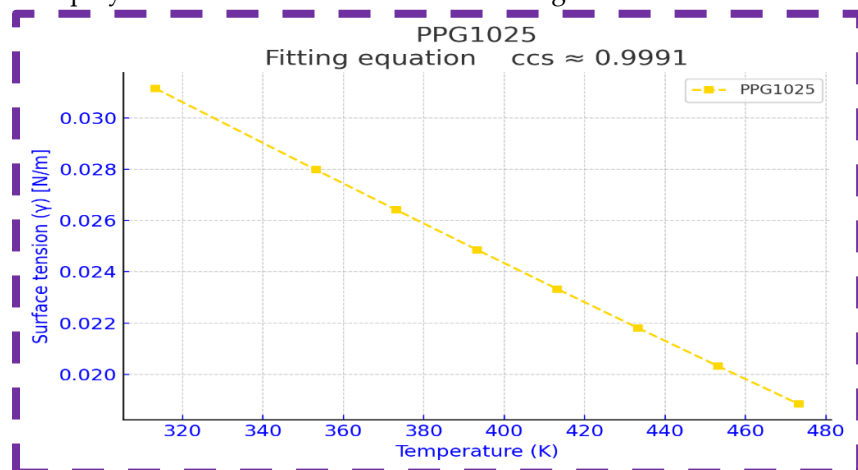

Figure 2. Thermal behavior of surface tension of PPG1025 material.

Figure 3 shows the gradual change in the gap fraction (h) of PPG1025 as a function of temperature. It is clearly observed that the gradual change in the gap fraction increases steadily with rising temperature, which is an expected physical behavior in short-chain polymer materials. This behavior is due to the increase in the kinetic energy of the molecules upon heating, which leads to the widening of the interstitial gaps between the polymer chains, This analysis is based on the Simha–Somcynsky model, which explains the irregular specific volume as resulting from the presence of voids within the polymer network. As the temperature increases, the material becomes less compact and the void fraction increases, as shown by the calculated values. At the minimum temperature T=313.2 K, h=0.091, while the highest value reached h=0.1992 at T=473.2 K.
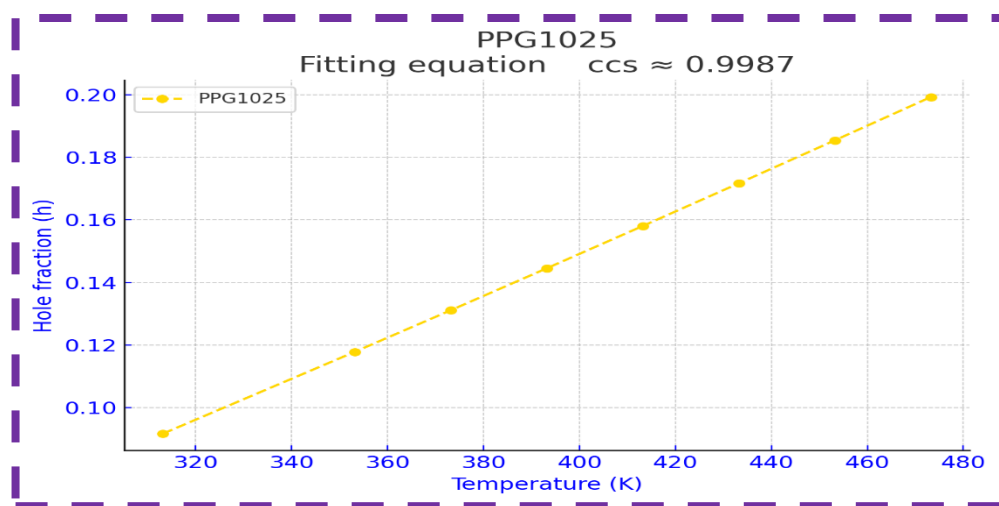

Figure 3. Gradual change in the gap portion (h) of PPG1025 material in terms of temperature.

Figure 4 illustrates the relationship between temperature and density (ϱ) for PPG1025, where we observe that density gradually decreases as temperature increases. This behavior is common in polymeric materials and liquids, and is due to the fact that an increase in temperature causes the material to expand as a result of the increase in the kinetic energy of the molecules, which reduces their cohesion and increases their volume, thereby reducing their density. The regular slope of the curve indicates that PPG1025 responds thermally in a consistent manner without sudden changes, reflecting the stability of the material within this temperature range.
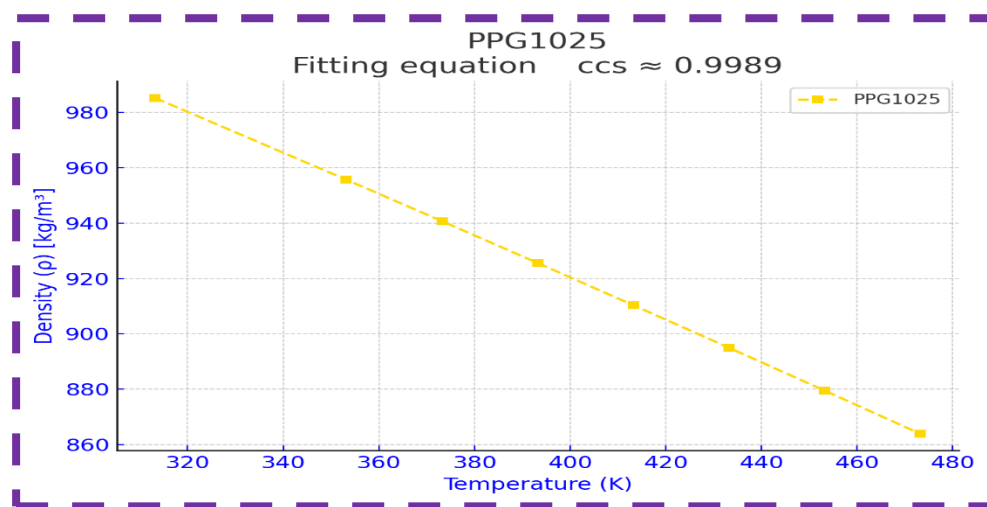

Figure 4. Relationship between temperature and density (ϱ) for PPG1025 material.

The behavior of the occupied sites ratio for PPG1025 was analyzed using the Simha–Somcynsky model, where y represents the ratio occupied by molecules within the lattice system. It was calculated from the relationship h=1−y, where h represents the fraction of the gap resulting from the lattice not being completely filled. The relationship between temperature and y shows a regular change with increasing thermal effect , As shown in Figure 5, the percentage of occupied sites gradually decreases with increasing temperature, corresponding to an increase in the size of the gap or voids within the material structure. This behavior is observed as a result of increased thermal energy, which causes molecules to be released from their original positions within the network and increases the distances between polymer chains, thereby redistributing the volume of internal sites and decreasing the occupied fraction of the total volume , In the case of short-chain polymers such as PPG1025, the molecular system remains highly flexible, allowing for uniform thermal expansion without sudden changes. As the temperature increases, the network gradually expands and the proportion of molecules occupying sites decreases, so the y ratio gradually decreases while h increases, which explains the inverse relationship between y and temperature in the case of PPG1025 , When comparing the behavior of the occupied site ratio y PPG400 and PPG1025, a fundamental difference in the direction of the relationship with temperature is observed. While PPG400 shows an inverse relationship where y decreases with increasing temperature, PPG1025 shows a direct relationship, i.e., y increases with increasing temperature. When heated, the kinetic energy of the molecules increases and they are released from their network positions, leading to an increase in the distances between the chains and a decrease in the proportion of occupied positions. This results in a clear expansion behavior that causes y to decrease gradually with temperature. In the case of PPG1025, which has a higher molecular weight and longer, more intertwined chains, heating does not immediately lead to disintegration or disruption of the network. On the contrary, the increase in temperature contributes to giving the molecules greater flexibility to rearrange within the network system, allowing a greater number of empty sites to be occupied. This leads to a gradual increase in y with temperature, which explains the observed linear relationship.
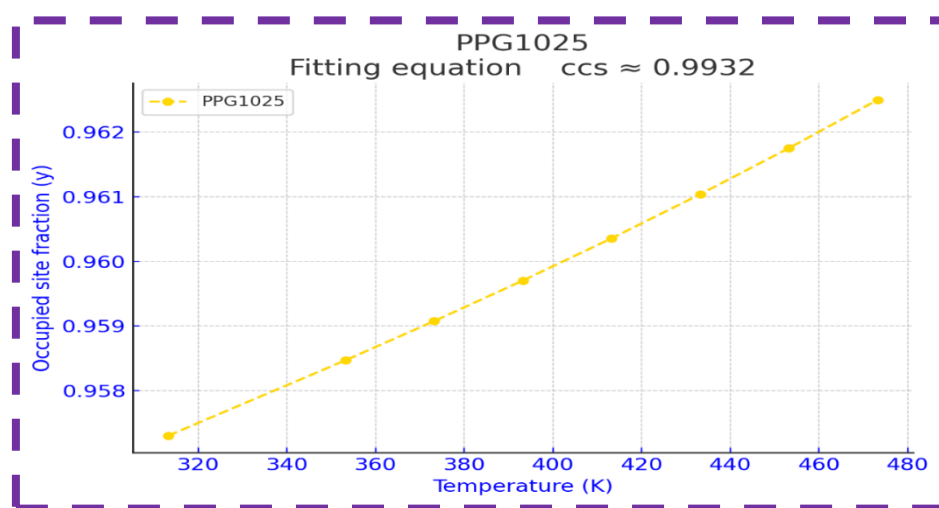

Figure 5. Shows the relationship between temperature and the percentage of occupied sites y for PPG1025.

Figure 6 shows the relationship between temperature and the reduced gradient energy coefficient K~for PPG1025, where the values show a noticeable decrease with the gradual increase in temperature. This behavior reflects the thermodynamic nature of the polymer and expresses the material's resistance to local differences in density or molecular structure within the polymer network , The K~ coefficient is an indicator of the energy required to generate local gradients in the system, whether at the phase boundary or local

fluctuations. The lower the K~ value, the lower the system's resistance to these local changes. This decrease indicates that heating reduces the internal cohesion of the molecules due to increased kinetic energy, which reduces gradients in the system, making the material more "homogeneous" in terms of density distribution. This reflects an advantage in higher molecular weight polymeric materials such as PPG1025, which have a more organized network and greater ability to adapt to thermal changes without sudden collapse of their structure.
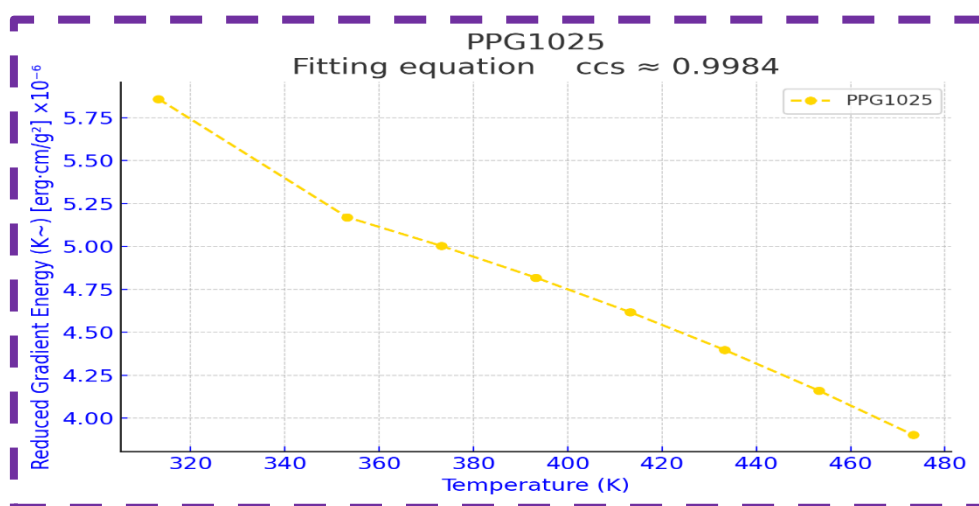

Figure 6. Relationship between temperature and reduced gradient energy coefficient K~for PPG1025 material.

Figure 7 shows the change in reduced surface tension γ~ for PPG1025 material in terms of temperature, where a steady decrease in values is observed as the temperature increases. Reduced surface tension is a relative representation of surface tension values after normalization to system variables, reflecting the extent to which temperature affects the molecular forces responsible for surface cohesion within the material ,In higher molecular weight polymeric materials such as PPG1025, heating increases the kinetic energy of the molecules, but without causing rapid or direct disintegration of the polymer structure. Instead, van der Waals and hydrogen forces continue to play their role, but with less effect, leading to a gradual decrease in surface tension. This behavior reflects the orderly nature of the PPG1025 network, which exhibits thermal flexibility without sudden collapse or obvious phase transitions , The highest value of reduced surface tension γ~=0.4571 was reached at T=313.2 K, and gradually decreased to γ~=0.2794 at T=473.2 K. This regular decrease highlights the thermal effect on the properties of the surface material.

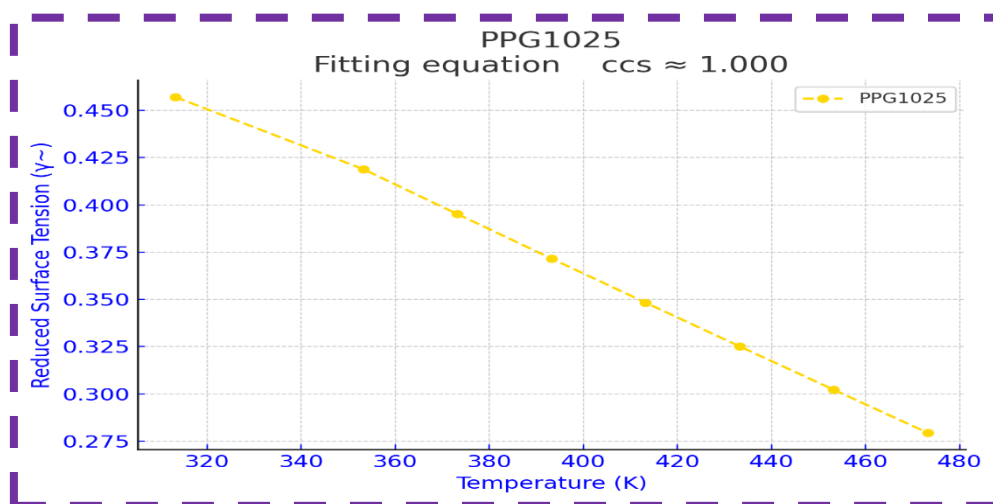**Figure 7.** Thermal change in reduced surface tension γ~ for PPG1025 material.

4. Conclusion

The study successfully demonstrated the effectiveness of combining the modified Simha-Sumsinski cell theory and the Cahen-Hillard model to predict the thermophysical behavior of PPG1025 across a temperature range of 313.2 to 473.2 Kelvin. The results showed that temperature has a significant effect on the main properties: the specific volume increases, while the density, surface tension, and gradient energy coefficient decrease steadily. The void ratio showed a continuous increase, reflecting thermal expansion and reduced molecular packing. The close agreement between theoretical predictions and experimental data, as evidenced by very low relative errors, confirms the accuracy of the proposed model. These results highlight the stability and flexibility of the short-chain polymer structure of PPG1025 under thermal influence, providing valuable insight for its application in industrial and medical systems where precise thermal performance is critical.

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