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Research article

Unravelling the Effect of Chain and Branch Content on Viscosity of Polyisobutylene-Mineral Oil Blends by Modelling and its Tribological Properties

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A B S T R A C T

The viscosity index is a fundamental property of lubricating oils and greases that significantly affects their lubrication performance under diverse temperature conditions. This study aims to investigate the influence of chain length and branch content on the viscosity of polyisobutylene (PIB)-blend mineral oil. To achieve this objective, mathematical models are employed to predict the specific volume, Vander Waals volume, structural factor, friction factor, molecular weight, and specific viscosity of lubricant blends and their correlation with macromolecular structure. Furthermore, analytical techniques such as Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance (NMR), and CHNS elemental analyzer are utilized to forecast the appropriate molecular structure of mineral-based oil. The purpose of this research is to comprehend the impact of the macromolecular structure of lubricants on their viscosity, particularly in the case of polyisobutylene (PIB)-blend mineral oil. Overall, the concentration of PIB was found to directly influence the friction (15.3%) and wear (5.6%) performance of the mineral oil explored following ASTM 4172 standard. The mathematical models and analytical techniques employed used in this study can accurately forecast the specific volume, Vander Waals volume, structural factor, friction factor, molecular weight, and specific viscosity of lubricant blends and their relationship with macromolecular structure.

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1. INTRODUCTION

Modern lubricants are expected to provide not only mobility but also energy efficiency making lubricants indispensable for our civilizations [1–3]. To impart specific desirable properties of base oil, various additives such as dispersant, antioxidant, surface protectants are added to enhance its performance [4,5]. The primary aim of the lubricant's science is to correlate measurable viscoelastic properties, such as viscosity and specific volume, with structural parameters, such as molecular dimensions and intermolecular frictional constants. This correlation helps in understanding the effect of molecular dimension on the physical properties of lubricants and estimating those physical properties theoretically.

Till 1960, several researchers suggested that viscosity (η) is greatly influenced by two factors: one is the structural factor (F), which depends largely on the number of atoms (Z) in the chain's backbone, and the other is the temperature-density dependent friction factor per chain atom (ξ) [6–17]. In 1962, Allen and Fox et al. observed that the polymer dimension plays a significant role in viscosity and influences the structural factor of the lubricants, and the focus of the study shifted to the polymer coil dimension other than chain length [18–22]. Further, Allen and Fox introduced new structural parameters that consisted of the radius of gyration (S), molecular mass (M), chain length (Z), and branch content (Ø). They also concluded that the dimensional factor (X) is a more important parameter than either molecular mass (M) or chain length (Z).

By 1980, several researchers had already shown that the viscosity of the liquid was linearly proportional to the chain length and molecular weight of the monomer [18,23–29]. When comparing polymers with the same branch type and content, the viscosity increases in a linear manner with the weight average molecular mass Mw, until it reaches a critical mass Mc. Beyond this critical molecular mass, typically ranging from 2000 to 60,000 g/mol depending on the polymer, molecular entanglement becomes significant. The Mark-Houwink equation is a widely utilized mathematical expression for describing the relationship between viscosity and molecular mass, and has been effectively applied in modeling polysiloxanes [30].

The specific volumes of polymer structures in different thermodynamic states are directly correlated with their van der Waals volumes and relative packing factors. In polymer physics, the molecular packing factor (MPF) is commonly used, which is approximately equivalent to the atomic packing factor (APF) utilized in crystallography [31]. The APF represents the ratio of the van der Waals volume to the total volume and assumes non-overlapping spheres for atoms with their atomic radii. In contrast, the MPF considers the van der Waals volume, including atomic bond lengths.

The friction between monomers within a lubricant structure is characterized by the monomeric friction factor. This factor is influenced by the type, length, and content of branches, but remains unaffected by the degree of polymerization. In comparison to other polymers, PDMS (Polydimethylsiloxane) exhibits an exceptionally low monomeric friction factor, which partly explains the requirement for PDMS to have a high molecular mass in order to achieve a desirable viscosity [21]. The impact of branching on the monomeric friction factor is two-fold. On one hand, the introduction of branches increases friction, while on the other hand, the free ends of these branches tend to decrease friction [21].

Considering, Flory's equation, several study further modified the viscosity relationship by introducing two factors: i) friction factor, and ii) the structural factor, which highly depends on not only the chain length (Z) but also on other factors such as the mass (M) and the radius of gyration [32, 33]. J. Zolper et. al. also explored the Berry and Fox equations and mathematically modelled the viscosity relationship with the molecular structure of different types of siloxanes [34–36]. Although it is interesting that research has been carried out with other sets of chemical compounds, mathematical modelling has never been employed for mineral oil based lubricants. The present research shows the first successful attempt of using the Berry and modified Fox equations to model the relationship between viscosity and molecular structure of paraffinic mineral oil (SN 150) blended with a popular viscosity index improver i.e., Polyisobutylene (PIB). Multigrade oil lubricants are designed to maintain their viscosity over a wide range of temperatures, which is important for maintaining proper lubrication in a

range of operating conditions. PIB is an excellent VII because it has a high molecular weight and is highly flexible, allowing it to maintain its viscosity over a wide temperature range. It is also compatible with a wide range of base oils and other additives commonly used in lubricant formulations. PIB is known to enhance viscosity index while its effect on wear and friction is not well understood. To understand effect of PIB on lubricant performance and mechanism of film formation, Tribological tests were performed following ASTM 4172 standards. When it comes to comprehending the influence that chain length and branch content have on the viscosity of a lubricant, the researchers and manufacturers of lubricants will consider this body of research to be of instrumental.

2. MATERIALS AND METHODS

2.1 Base oil and additives

Mineral oil (SN150) and polymer Polyisobutylene (PIB) used in this study were procured and used without any further processing. The base oil are paraffinic in nature and was obtained from Indian Oil Corporation Ltd, while PIB was procured from KUNTAL ORGANICS LLP. Polyisobutylene (PIB) is commonly used as a viscosity index improver (VII) in the production of multigrade oil lubricants. Table 1 and 2 shows the physio-chemical properties of SN150 and PIB respectively.

Table 1. Physico-chemical properties of SN 150 mineral base oil.

Properties	Method	Values
Density @ 15^{0}C (g/ml)	ASTM D 4052	0.8430
K.V. @ 40^{0}C (mm^2/s)	ASTM D 445	33.72
K.V. @ 100^{0}C (mm^2/s)	ASTM D 445	5.56
Viscosity Index	ASTM D 2270	115
Total Acid Number (mg KOH/g)	ASTM D 664	0.002
Pour Point (^{0}C)	ASTM D 97	-21

Table 2. Physico-chemical properties of PIB.

Properties	Method	Values
K.V. @ 100OC (mm2/s)	ASTM D 445	4500-4900
Total Acid Number (mg KOH/g)	ASTM D 664	0.01 Max
Flash Point OC	ASTM D 92	Min 250
Total Sulphur (Wt- ppm)	ASTM D 2785	Max 1.0
Water (Wt- ppm)	ASTM D 6304	Max 40
K.V. @ 100OC (mm2/s)	ASTM D 445	4500-4900

2.2 Sample preparation

Two steps were used to obtain stable blend of PIB in base oil. At first, measured quantity of PIB is added in mineral oil while stirring at 1000 rpm followed by 10 minutes of ultrasonication. No phase separation or cloudiness was observed indicating homogeneous blending. The PIB was blended in 2, 4, 6, 8 and 10 wt.% concentration in mineral oil N150 for viscosity modelling while for tribological testing the concentration was varied by 4,6, and 8 wt%.

2.3 Characterization of mineral oil and its blends

Various analytical techniques such as CHNS analyser, GPC chromatography, and NMR spectroscopy were used to approximate chemical constituents, structure and molecular weight of the mineral oil blends. The CHNS analyser used in this study was FLASH EA 1112 Series manufactured by Thermo Finnigan, while Waters 2410 differential refractometer was used for the GPC analysis. Avance III 500 MHz, (make: Bruker Germany) was used for NMR spectroscopy to approximate molecular structure of the mineral oil. The viscosity of the lubricant blends was determined using Stabinger SVM 3000 viscometer.

2.4 Tribological testing

The tribological performance of PIB enriched mineral oil were studied using 4 ball tribometer (Make DUCOM Instruments) following ASTM 4172 standards. Figure 1 gives schematic of 4 ball tribometer along with tetrahedral arrangement of four balls and method of WSD measurement. The tribometer uses tetrahedral arrangement of three fixed bottom balls submerged in lubricant and top ball rotating at desired speed. The contact point of these balls is submerged under lubricants maintained at desired temperature. The load is applied using a lever mechanism and friction performance is recorded in real time while wear scar diameter is obtained at the end of the test using optical microscope. The matrix of ASTM test is tabulated in table 3.

Table 3. Characteristic values of ASTM 4172B test standards.

Test parameter	ASTM D: 4172B (Characteristic values)
Load, N	392 ± 2
Speed, RPM	1200 ± 60
Lubricant temperature, ^{0}C	75 ± 2
Test duration, min.	60 ± 1

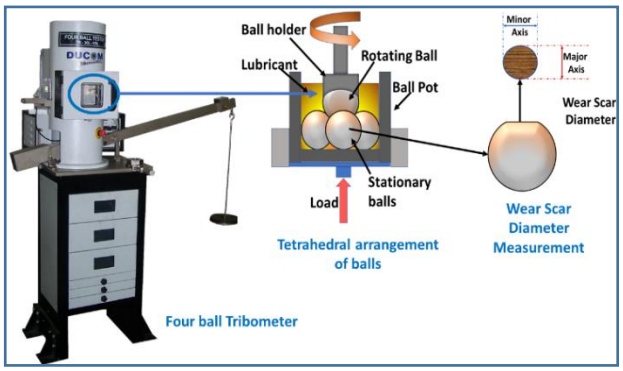


Fig. 1. Four ball tribometer with schematic of tetrahedral arrangement of four balls and method of measuring wear scar diameter.

3. MOLECULAR STRUCTURE OF LUBRICANTS

The mineral base oil can be paraffinic naphthenic or aromatic in nature depending on the degree of processing [37]. Generally, mineral oils are blend of various viscosity grade hydrocarbons and hence their molecular structure is not known. To approximate molecular structure of mineral oil various analytical techniques such as NMR, GPC, CHNS analyser was employed. Table 4 shows the NMR data of mineral base oil consisting of 29.30% of terminal CH3 proton, 62.70% of CH2 proton and 8.00% of the naphthenic proton (Hnaph). The NMR confirms that N150 mineral oil is paraffinic in nature. GPC data of mineral oil is also tabulated in Table 4 which gives the number average molecular weight Mn and the weight average molecular weight Mw.

Table 4. NMR or GPC Data for approximating chemical structure of mineral based oil.

Molecular NMR analysis		GPC analysis		
Terminal groups	**% of total weight**	**Lubricant**	**Mn**	**Mw**
HCH_3	29.30	N-150 mineral oil	495.0	521.0
HCH_2	62.70	PIB	2482	3971
H_{naph}	08.05			

The data obtained from GPC and NMR analysis may be considered sufficient for the approximation of the molecular structure. The approximation of terminal CH_3 and CH_2 groups in mineral based oil are explained below.

The molecular weight of terminal CH_3 groups in N-150 mineral base oil

$$= \frac{\text{Mn} * \text{percentage of total weight}}{100} = \frac{495 * 0.293}{100} = 145$$

Number of terminal CH_3 groups

$$= \frac{molecular\ weight\ of\ terminal\ CH_3\ in\ N150}{molecular\ weight\ of\ CH_3} = \frac{145}{15} = 9$$

Similarly, for CH_2 groups:

Total molecular weight of terminal CH_2 groups

$$= \frac{495 * 0.627}{100} = 310$$

Number of CH_2 groups

$$= \frac{310}{14} = 21$$

Consequently, GPC and NMR analysis show that base oil is saturated paraffinic of order 92% and having 9 terminals CH3 and 21 CH2 groups with a linear hydrocarbon chain. The approximated molecular structure of base oil is shown in figure 2, while figure 3 shows molecular structure of PIB. Table 5 shows the elemental composition of mineral oil obtained by CHNS analyser.

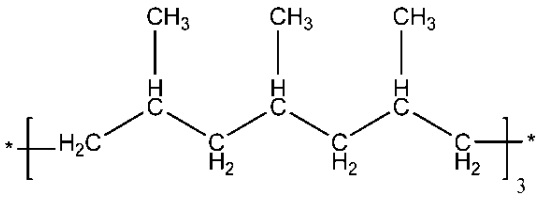


Fig. 2. Approximated molecular structure of N150.

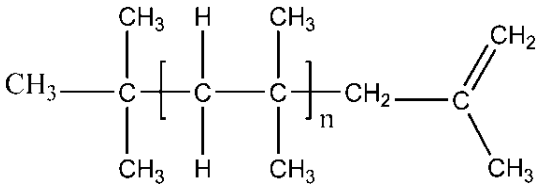


Fig. 3. Molecular Structure of PIB.

Table 5. CHNS elemental analyser data.

Name of elements	% element in N150	Number of elements in mineral oil =(Mn*% of element) / (atomic weight of element)
C	81.011	33.41
H	14.0933	69.74
N	1.4146	0.50
S	1.2652	0.19

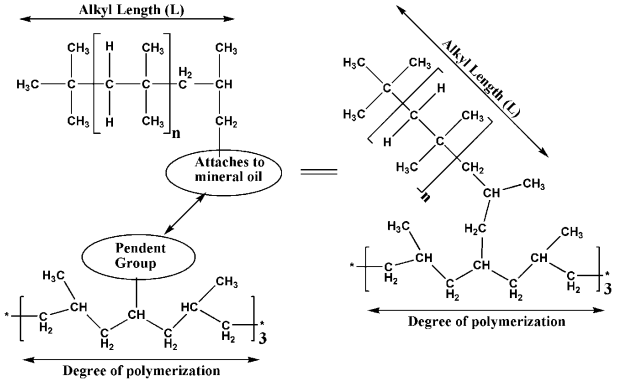


Fig. 4. Schematic diagram of PIB blended in mineral oil.

Table 5 shows that the percentage of carbon and hydrogen in mineral oil is of order 33.41% and 69.74% respectively. However, the elemental composition of paraffinic carbon or hydrogen in the mineral oil by CHNS analyser is very close to the molecular structure approximated with the help of GPC and NMR analysis. The one termination edge of PIB consists one unsaturated carbon-carbon bond. The unsaturation of PIB is covalently bonded with the paraffinic hydrocarbon chain of N150. However, we made an assumption that each molecule of PIB is attached with only one molecule of mineral base oil. Figure 4 gives the schematic diagram of the PIB blend in the mineral oil N150.

3.1 Mathematical modelling of volume and viscosity

There are several factors that contribute to the calculation of the theoretical specific volume and viscosity. Figure 5 shows the interdependent parameters which needs to be obtained sequentially. First, the specific volume and viscosity are estimated from the molecular structure based on chain length (L), pendent group (J) and degree of polymerization (DP) [19, 34].

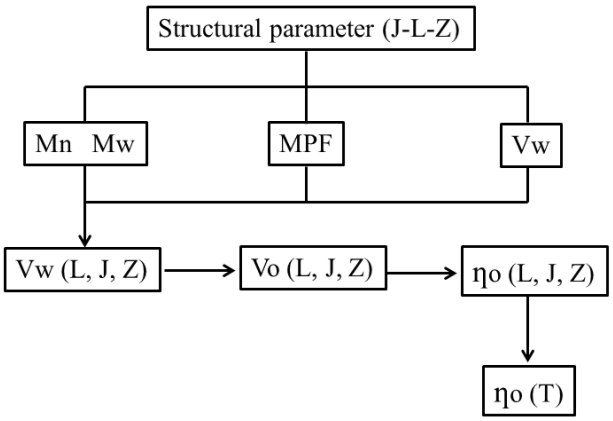


Fig. 5. Steps to model viscosity from structural factors.

The structural volume model uses molecular mass, Van der Waals volume, and molecular packing factor to estimate the theoretical specific volume (V_{0T}). The structural-viscosity model based on Berry and Fox has been used to estimate viscosity (η_{0T}) at atmospheric conditions [38]. Section 3.3 and 3.4 gives all the formulae and their significance in modelling specific volume and viscosity respectively.

4. VOLUME VARIATION WITH STRUCTURE

Several steps are involved in determining the specific volume from molecular structure. The molecular mass (M), van der Waals volume (V_w), van der Waals specific volume (ν_w), molecular packing factor (MPF), and specific volume (V_{0T}) are all computed based on the molecular structure [21,34].

4.1 Molecular length of N150

The total length (Z) of the mineral oil N150 is determined by counting the number of carbon (C) atoms in the backbone. The length of the macromolecular chain (L_m), measured in nanometers, is obtained by multiplying the atomic length by the C-C bond length, which is 0.152 nanometers.

$$\mathbf{L_m = 0.152 * Z}$$

4.2 Molecular mass

The total molecular mass of a compound can be determined by summing up the individual atomic masses of its constituents. The mass equation is written as the sum of the masses of the individual repeating constituents as we have already seen there are three monomers in polymer of mineral oil. Since percentage of PIB is very less in the blend hence we assume that only one PIB attaches to one end of the methyl group of mineral oil. Hence M_1, M_2 represents any two monomers of the mineral oil and M_x represents the mass of the PIB attached with the third monomer.

$$\mathbf{M = M_1 + M_2 + M_x}$$

4.3 Van der Walls volume of the monomer

Given the monomeric mass, the van der Waals volume of a monomer can be calculated by summing up the volumes of its individual

constituents. This is because both the molecular mass and the van der Waals volume are determined by the molecular structure. In the case of the polymer of mineral oil, V_1 and V_2 represent any two of the three unbranched monomers, while Vx represents the van der Waals volume of the PIB attached to the third monomer. Thus, the equation for the van der Waals volume can be expressed as

$$\mathbf{V_w = V_1 + V_2 + V_x}$$

4.4 Van der Waals specific volume

The van der Waals specific volume (ν_w) of a molecule is a measure of the portion of the specific volume that is occupied by the molecule. It is obtained by dividing the van der Waals volume of the molecule by its molecular mass.

$$\boldsymbol{\nu_w = \frac{V_w}{M}}$$

4.5 Molecular packing factor

The molecular packing factor can be determined by comparing the measured specific volume with the calculated van der Waals specific volumes of the constituent molecules. To do this, the specific volume measurements for the monomer are fitted to empirical equations that incorporate specific packing factor values (x, j). These equations use the number average polymer length as a parameter to model the specific volume as a function of the molecular structure [34].

$$\mathbf{MPF} = \frac{\boldsymbol{\nu_w}}{\mathbf{V_{0T}}} = [\mathbf{0.7} + \frac{\mathbf{e}^{\boldsymbol{X}}}{\mathbf{Z}} + \mathbf{j}^{\boldsymbol{X}}]^{-\mathbf{1}}$$

4.6 Specific volume (V_{0T})

The specific volume of a copolymer can be calculated based on the volume fraction (ϕ) of mineral oil in the blend and the specific volume of the monomers. Therefore, the copolymers of the principal mineral oil studied here can be reasonably estimated using the available data range. The molecular packing factor (MPF) is found to be constant for both N150 and PIB-blended N150. In following equation, the subscript "m" represents mineral oil and "p" represents polymer [34].

$$\mathbf{V_{0T}} = \left(\frac{\boldsymbol{\emptyset V_w}}{\mathbf{MPF}}\right)_{\boldsymbol{m}} + \left(\frac{\boldsymbol{\emptyset V_w}}{\mathbf{MPF}}\right)_{\boldsymbol{p}}$$

4.7 Van der Waals volume

The calculation of specific volume for lubricants relies on the van der Waals volume, which can be efficiently determined using the Atomic and Bond Contributions method [39]. This method is both simple and fast, requiring only atomic contributions and information on the number of atoms, bonds, and rings. The van der Waals volume (A^3/molecule) can be calculated using the following formula:

$$\mathbf{V_w}=((\sum \boldsymbol{all\ atom\ contributions}) - \mathbf{5.92}\boldsymbol{N_B} - \mathbf{14.7}\boldsymbol{R_A} - \mathbf{3.8}\boldsymbol{R_{NA}})$$

Where

(RA represents number of aromatic rings, NB represents number of bonds and RNA represents number of Non-aromatic rings). The number of bonds present (NB) can be simply calculated by:

$$N_B = N - 1 + R_A + R_{NA},$$

Where: N is the number of atoms. Individual atoms' van der Waals volume contribution is given in the Table 6.

Table 6. Individual atoms contribution of van der Waals volume [39].

Atom	V_w	Atom	V_w
H	07.24	F	13.31
C	20.58	Cl	22.45
N	15.60	P	24.43
O	14.71	S	24.43

5. VISCOSITY VARIATION WITH STRUCTURE

5.1 The dimensional factor (X)

The Berry and Fox viscosity equation is an empirical model that utilizes a dimensional factor X to estimate the viscosity and molecular entanglement of various polymer classes. The X factor incorporates several parameters, including the radius of gyration ($\langle s_2 \rangle$), polymer length (Z), molecular mass (M), polymer specific volume (V_{0T}), and the volume fraction (∅) of mineral oil in the solution. In undiluted conditions, the volume fraction becomes unity [19,34].

$$\boldsymbol{X = Z\left(\frac{\langle s^2 \rangle}{M}\right)\left(\frac{\emptyset}{V_{0T}}\right)}$$

5.2 The structural factor (F(X))

The Berry and Fox viscosity equation employs the dimensional factor X to compute a structural factor F(X) that captures the

correlation between viscosity and polymer length or molecular mass. The structural factor comprises Avogadro's number N_0 and an exponent a_B that characterizes the viscosity rise with X. As the dimensional factor exceeds the critical value X_c, the exponent in the structural factor increases to model the augmented viscosity of large molecules due to molecular entanglement. To achieve greater accuracy, specific critical factor values and exponents of the structural factor are utilized instead of those reported for the polymers examined collectively by Berry and Fox [21,34,40].

$$\mathbf{F(X)} = \left(\frac{\mathbf{N_0}}{\mathbf{6}}\right)\mathbf{X_c}\left(\frac{\mathbf{X}}{\mathbf{X_c}}\right)^{\mathbf{a_B}}$$

$$\text{For } \mathbf{X < X_c = 5.6 * 10^{-15}: a_B = 1.46}$$

$$\text{For } \mathbf{X \geq X_c = 5.6 * 10^{-15}: a_B = 3.59}$$

5.3 Viscosity calculation

The structural-viscosity model proposed by Berry and Fox can be used to calculate the viscosity of a polymer solution. The model involves calculating the product of the structural factor, F(X), and the monomeric friction factor, ξ0. The equation for viscosity is given by:

$$\boldsymbol{\eta_{oT} = F(X) * \xi_{x\%}}$$

where η is the viscosity of the polymer solution, F(X) is the structural factor calculated using the dimensional factor X, and ξ_0 is the monomeric friction factor.

5.4 Friction Factor (ξ_0)

The monomeric friction factor is a measure of the resistance of relative motion between monomers in a polymer chain. It is generally low for pure mineral oil, but increases when branched PIB structures are added [28]. To calculate the monomeric friction factor, information on the radius of gyration, specific volume, and viscosity at 40°C and one atmospheric pressure are required. This method is adapted from Ferry's work [41–43].

5.5 Radius of gyration ($\langle s^2 \rangle$)

The Flory Exponent is used to calculate the root mean square of the radius of gyration, which is the second moment around the center of mass of the polymer chain [44–47]. It is a measure of the chain flexibility and is influenced by various factors such as molecular weight and branching.

$$\langle \boldsymbol{S} \rangle = \boldsymbol{bN^{\nu}} \qquad \nu=0.59 \text{ or } 3/5$$

Where N is the number of monomer and b is the total chain length in nanometer.

$$\boldsymbol{\xi_0} = \frac{\mathbf{6V_{0T} * \eta_{oE}}}{\mathbf{N_0}} \frac{\boldsymbol{M}}{\langle \mathbf{s^2} \rangle}$$

The introduction of PIB content has a more significant impact on increasing monomeric friction compared to the addition of alkyl content. This is because PIB creates a more significant barrier to the intermolecular motion of mineral oils. The monomeric friction factor for copolymers with different branch contents is determined by adding the content of pure mineral oil and the branched monomer content. In following equation, the subscript "m" and superscript "p" represent mineral oil and PIB blend, respectively.

$$\boldsymbol{\log \xi_{x\%} = \log \xi_0^m \emptyset_m + \log \xi_0^p \emptyset_p}$$

6. RESULTS AND DISCUSSION

6.1 Volume variation with branch contents

A comprehensive set of mineral oil and PIB molecular evaluations were integrated in this study to establish an approach for predicting specific volume based on the molecular structure. The Molecular packing factor and van der Waals volume of functional monomers are tabulated in table 7. The monomer type includes pure mineral oil and PIB blended functional monomer. The table suggests that there is a correlation between an increase in specific volume and higher alky branch content. Similar observations were also made by Zolper et.al [34]. The empirical value of x and j are used in the calculation of Molecular packing fraction, as discussed in section 4.5.

Table 7. Calculated value of Van der Waals volume and Molecular packing factor.

Van der Waals volume factors		Molecular packing factor of monomers	
Monomer	$\mathbf{V_w}(cm^3/mol)$	**x**	**J**
Mineral oil (B.O)	524.920	1.54	0
PIB blend	3587.02	1.674	-0.2

6.2 Viscosity variation structure

The monomeric friction factors are determined by utilizing the measured values of volume, viscosity, and radii of gyration in the calculation process as detailed in section 3.4.4. The monomeric friction factor for mineral oil and PIB blend is listed in table 8. The blending of PIB in mineral oil enhances the thickening of oil which resulted in increased the viscometric property of the oil. For low branch contents (mineral oil) to achieve higher viscosity as a PIB with high branch content, a significantly higher degree of polymerization is necessary. For example, PDMS (Polydimethylsiloxane) reaches the critical factor at a length of approximately 700 atoms [34]. PAMS (Polyalkylmethylsiloxane) structures, on the other hand, require a longer molecular length to reach the critical factor due to their smaller radii of gyration [34]. These observations can be applied to all species to predict viscosity across a range of molecular lengths and branch contents. Therefore, table 8 shows a high monomeric friction factor for PIB blended mineral oil when compared with neat mineral base oil as discussed in section 3.4.

Table 8, Estimated friction factor for mineral oil and blends.

Monomer	$\log \xi_0$ (m.Pa . s)
Mineral Oil (B.O)	-6.5168
PIB Blend	-5.28759

Table 9 shows the PIB concentration in the base oil and the volume and viscosity obtained from the mathematical equations reported in section 3.3 and 3.4. Due to longer chain length and branch content the friction factor of PIB blend increases with increase in PIB concentration. The viscosity values are very near to experimental viscosity values obtained by Stabinger Viscometer (SVM3000 make Anton Par). It is evident from these results that Berry and Fox equation can give viscosity which is very close to the experimental viscosity values.

Table 9. Intermediate values for viscosity and experimental viscosity values.

Sample	∅ %	Volume	F(X)	ξ	$\eta_{theoretical}$	$\eta_{experimental}$
B.O	0	1.153679	110847393	3.04E-07	33.71	33.72
B.O+2%PIB	2	1.152553	105028373	4.01E-07	42.13	39.486
B.O+4%PIB	4	1.151427	99217846	4.98E-07	49.48	46.631
B.O+6%PIB	6	1.15030	93555156	5.95E-07	55.75	55.701
B.O+8%PIB	8	1.14911	89107364	7.12E-07	63.44	66.569
B.O+10%PIB	10	1.14805	85926026	8.38E-07	72.01	78.752

6.3 Viscosity change with additive concentration and temperature

The addition of polyisobutylene (PIB) to lubricant formulations increased the viscosity index (VI) of the resulting lubricant. Viscosity index is a measure of how much a lubricant's viscosity changes with the temperature change. Higher VI indicates relatively stable lubricants, whose viscosity changes less as the temperature increases [48]. When added to a lubricant, PIB molecules form long chains that can expand and contract as temperature changes. This helps to maintain the lubricant's viscosity over a range of temperatures and improves its VI. Table 10 lists the viscosity index of the PIB blend obtained by respective kinematic viscosity at 40 and 100^{o}C. There is a direct correlation between increase in VI attributed to PIB concentration and addition of 10 wt% PIB has significantly enhanced (13.6%) the viscosity index of mineral base oil.

Table 10. Variation of viscosity index with increase of branch content of PIB in mineral oil.

Lubricant Sample	η_{40} (m^2/s)	η_{100} (m^2/s)	VI
Mineral Oil (B.O)	33.72	5.6633	106.726
B.O+2%PIB	39.486	6.299	107.279
B.O+4%PIB	46.631	7.1618	112.874
B.O+6%PIB	55.701	8.1905	116.799
B.O+8%PIB	66.569	9.4083	120.018
B.O+10%PIB	78.752	10.673	121.237

6.4 Friction and wear reduction performance.

Polyisobutylene (PIB) is added to multigrade oils as a viscosity index improver which helps maintain consistent viscosity across a wide temperature range [48]. But tribological performance of PIB is not well understood. This study explores friction and wear reduction properties of PIB following ASTM 4172 test standard. The addition of polyisobutylene (PIB)

to the base oil improved viscosity, leading to enhanced friction and wear reduction performance, as depicted in Figure 6.

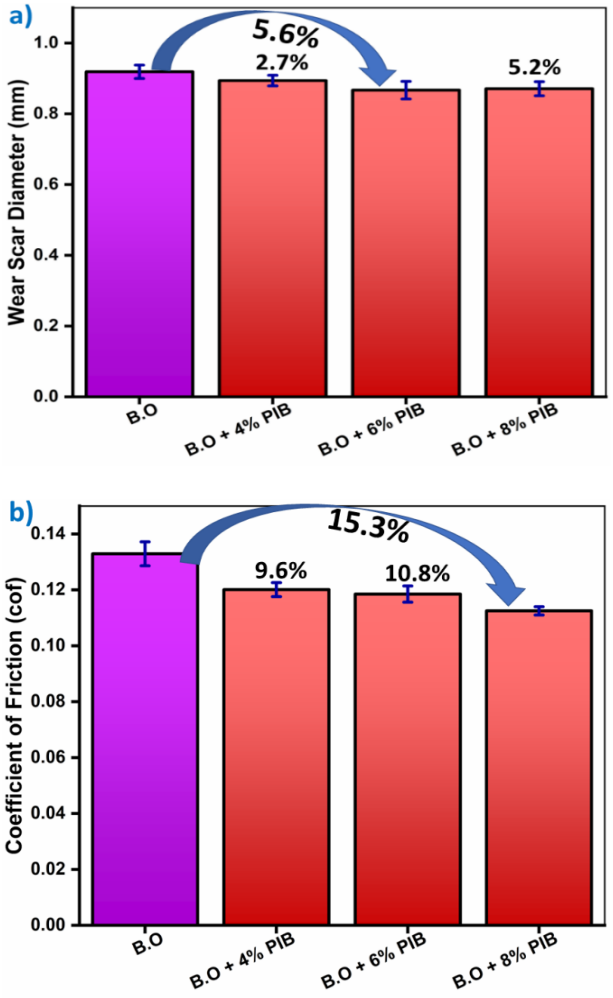


Fig. 6. Friction and wear reduction performance of PIB enriched oil tested following ASTM 4172 standards. Maximum WSD and friction reduction was 5.6 and 15.3 % which could be attributed to increased viscosity of base oil.

The base oil alone exhibited poor surface protection, evident from larger WSD (Wear Scar Diameter), while the addition of 4 wt% PIB marginally improved WSD. The highest WSD improvement of 5.6% was observed with a 6 wt% blend, with no further improvement at higher additive concentrations. Notably, there was a direct correlation between PIB concentration and friction coefficient, at least up to 8 wt% additive concentrations. The highest improvement observed was 15% compared to the neat base oil. The viscosity increase resulting from blending thick PIB polymers likely contributed to the improvements in friction and wear. Interestingly friction reduction is nearly 3 times higher compared to wear reduction. This could be attributed to inability of PIB polymer to make stable protective film on the rubbing surfaces. Figure 7 shows the wear scar diameter of the surfaces lubricated with different mineral oil blends. Worn surface lubricated with neat oil shows longer and deeper grooves (plausibly due to ploughing action) compared to surfaces lubricated with PIB blends. PIB is did provide minor surface protection as evident from wear reduction performances.

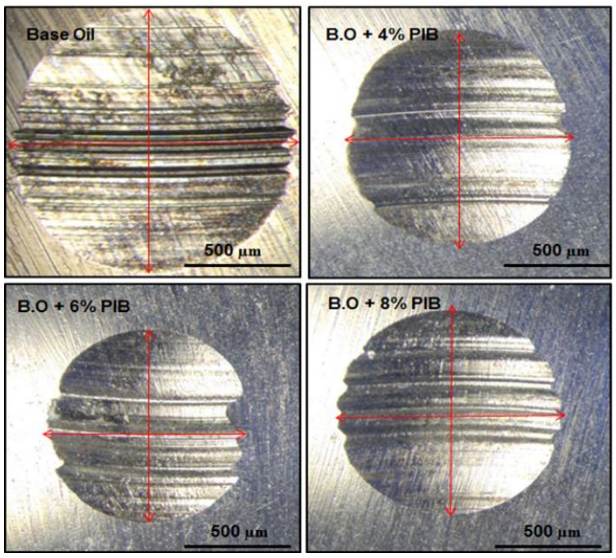


Fig. 7. Wear Scar Diameter (WSD) shows dominant abrasion marks on the worn surface, which could be attributed to inability of lubricant to provide stable surface protection.

PIB works by increasing the molecular weight of the base oil in the lubricant, which leads to an increase in its viscosity at high temperatures. This increase in viscosity helps to reduce the tendency of the lubricant to thin out at higher temperatures, which can reduce its ability to provide adequate lubrication [48]. The reduction in friction and wear of lubricants can be attributed to several factors. Firstly, the increased viscosity provided by PIB helps to maintain a thick film of lubricant between the moving surfaces, which helps to reduce direct contact and subsequent wear. Secondly, PIB can improve the lubricant's ability to adhere to metal surfaces, which further reduces the risk of metal-to-metal contact and wear [48]. Additionally, PIB can also help to reduce friction by reducing the tendency of the lubricant to foam, which can lead to air pockets and reduced lubrication efficiency. The reduction in friction and wear provided by PIB can help to extend the service life of lubricated components and reduce maintenance costs.

7. CONCLUSIONS

This paper presents a modeling system that establishes connections between lubricant properties and their molecular structures. The paper successfully explores the relationship between molecular structure, specific volume, and viscosity of the PIB blended in the group-I mineral oil (N 150) using a combination of several established models. These properties can be predicted by considering molecular features such as branch types, contents, and degrees of polymerization. Further the study explores tribological performance of PIB enriched lubricants. Overall, the conclusions of the study are as follows:

- Increasing the branch contents and chain length in mineral oil decreases the specific volume of the blend for PIB as proved by experimental and theoretical values.
- Increasing branch contents and chain length results in an increase in viscosity and a higher corresponding increment in the monomeric friction factor.
- Berry and Fox mathematical formulae are very effective for modelling viscosity based on molecular structure.
- This Berry and Fox equation is applicable for the mineral oil and copolymer blends as well if enough data on its molecular structure is available.
- A direct correlation between PIB concentration and viscosity index was observed and 10 wt% PIB blend improved viscosity index by 13.6%.
- PIB as an additive also improved tribological performances (wear reduced 5.6% while friction reduced by 15.3%) of base oil which could be attributed to increased molecular weight of the base oil in the lubricant, which leads to an increase in its viscosity at high temperatures.

The future scope of the study involves expanding the research to encompass more complex lubricant systems, including those with functional groups. This expansion would involve investigating how the presence of these additional components influences volume and viscosity variations and integrating them into the model. Furthermore, the developed model can be applied to predict volume and viscosity variations for new lubricant structures that lack experimental characterization. This predictive capability would offer valuable insights into the behavior of novel lubricant materials, enabling researchers to make informed decisions before undertaking extensive experimental investigations. To facilitate practical usage, user-friendly computational tools and software may be developed based on the model. This advancement would empower researchers and engineers to easily predict volume and viscosity variations in lubricant systems by inputting molecular structure and thermodynamic parameters. Moreover, the impact of environmental factors such as temperature, pressure, and humidity on the volume and viscosity variations of lubricants may be explored. Additionally, sustainable alternatives may be considered, and the model may evaluate the potential of utilizing bio-based or recycled lubricant materials, taking into account their environmental implications. In summary, the future research endeavors may involve investigating complex lubricant systems, predicting volume and viscosity variations for uncharacterized structures, developing user-friendly computational tools, and considering the environmental impact and sustainable alternatives for lubricants.

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