

**Miscibility Studies On Polymer-Plasticizer Systems for Composite  
Propellants: A Combined Experimental and Molecular Simulation  
Approach**

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In

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*Submitted by*

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## CERTIFICATE

This is to certify that the project report entitled “**Miscibility Studies On Polymer-Plasticizer System for Composite Propellants: A Combined Experimental and Molecular Simulation Approach**” is the bonafide work done by Avtar Singh, (2K14/PTE/14), in the partial fulfillment of the requirements for the award of the degree ‘Master of Technology (Polymer Technology)’ and submitted to the Department of Applied Chemistry and Polymer Technology, Delhi Technological University, Delhi. This project was not submitted earlier at any other University or Institute for the award of any degree.

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## Declaration

I Avtar Singh hereby declares that the thesis entitled “**Miscibility Studies On Polymer-Plasticizer Systems for Composite Propellants: A Combined Experimental and Molecular Simulation Approach**” is an authentic record of research work done by me under the supervision of **Dr. S Radhakrishnan**, Scientist, Energetic Material Research Group, High Energy Materials Research Laboratory, Pune, and **Dr. D. Kumar**, Professor Delhi Technological University, Delhi. This work has not been previously submitted for the award of any degree or diploma of this or any other University/Institute.

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## Abstract

Recent developments in rocket propellants demand composite propellants to have high energy, sufficient structural integrity and low temperature capability to qualify for application in propulsion system. Polymer-plasticizer contributes to all the above three important characteristic of propellants. Polymers and plasticizers need to be screened rigorously to achieve most suitable combination. In the present investigation, experimental and simulation studies have been performed to predict the miscibility of polymer and plasticizer. Solubility parameter is the measure of miscibility or compatibility of any two material of interest, which is evaluated by Gee's equilibrium swelling experiments for cross-linked polymers and intrinsic viscosity measurements for linear polymers. Molecular dynamic simulations using COMPASS force-field have been used to evaluate solubility parameter of polymers, HTPB, SPG-255, NBR, HTPB-b-polycaprolactone block copolymer and plasticizers, NG, DEGDN, TEGDN, DOA, BuNENA, TMETN, and BTTN. Flory-Huggins interaction parameter  $\chi$  is also calculated for identifying right combination. Simulated and experimental data proved that energetic plasticizers are not compatible with HTPB. Similarly most suitable plasticizers for SPG-255 and NBR are BuNENA and TMETN where as BuNENA and DOA can be suitable plasticizers for HTPB-b-CP copolymer. Overall, thesis work finds its usefulness in identifying the most suitable plasticizer for a given polymer, which is an initial step for achieving successful propellant formulations.

Keywords: Modeling and Simulation, Molecular Dynamics, Solubility parameter, Miscibility, Energetic materials.

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## Abbreviations

$[\eta]$	Intrinsic Viscosity
$\chi$	Flory Huggins interaction parameter
$\delta$	Hildebrand Solubility parameter
$\mu$	Viscosity
$\rho$	Density
R	Universal Gas Constant
$T_g$	Glass Transition Temperature
$v_e$	Crosslinked Density
$\sigma$	Tensile Stress
$\emptyset$	Volume fraction
UCST	Upper Critical Solution Temperature
NBR	Nitrile Butadiene Rubber
GAP	Glycidyl Azide Polymer
HTPB	Hydroxy Terminated Polybutadiene
DOA	Diethyl Adipate
NC	Nitrocellulose
BTTN	1,2,4-Butanetriol Trinitrate
NG	Nitroglycerin
DEGDN	Diethyleneglycol Dinitrate
TEGDN	Triethyleneglycol Dinitrate
BuNENA	n-Butyl-Nitratoethylnitramine
TMETN	Methyltrimethylolmethane Trinitrate
SPG-255	Poly Functional polycaprolactone
HTPB-b-CP	Block Copolymer of HTPB and polyaprolactone
PVC	Polyvinyl Chloride
SBR	Styrene Butadiene Rubber



## **1. Introduction**

### **1.1 Background on Polymeric Materials**

Polymeric materials are extensively explored to design and develop new type of material with tailor made properties. Molecular structure plays a key role and responsible for the properties that are exhibited by any material. Polymer molecules consists large number of repeating units of same or different types. There is a large scope on these materials to exploit their properties by altering molecular structure by introducing functional group or co-monomers. Apart from chemical approach, physical mixing and blending with different polymers and ingredients provide various opportunities to develop new materials with specific characteristics. The implementation of this material concept requires different knowledge about thermodynamic phase behaviour, rheology, processing, cross-linking, reinforcement of fillers [1].

Polymer composites, blends, gels, adhesives, paints etc are multi-components systems. Each component of system contributes to final properties of system. Hence the contribution of each component needs to be optimized. The component's miscibility plays a vital role in the development of new formulation of multi-components systems. The thermodynamic miscibility and compatibility of polymers with other materials is one of the important phenomenon need to be understood in depth.

### **1.2 Role of Polymers/Plasticizers in Rocket Propellants**

Polymer and plasticizer are two most important ingredients for making composite propellants. Composite propellants consists polymeric binders, plasticizer, curator, burn rate modifiers, solid fillers like oxidizers and metallic fuels etc. Polymeric binder makes a cross-linked network to withhold all ingredients inside matrix of composite, play a vital role in maintaining the structural integrity. Similarly another important ingredient, plasticizer have specific role to improve flowablity or proccessibility of uncured propellant and visco-elastic properties of cured propellant. This is achieved due to comparatively smaller molecule of plasticizer when enters into polymer, it increases free volume in system which results decrease in viscosity and glass transition temperature of system[2]. Generally main role of plasticizer is as the processing aid; it helps to reduce processing viscosity of polymer and increases flexibility. For example, PVC has glass transition temperature higher than the room temperature hence non flexible and brittle material at room temperature, once the PVC is plasticized, its  $T_g$  reduces and it become flexible at room temperature [3]. Hence, it can be said that the polymer and plasticizer

combination controls the structural integrity and low temperature flexibility of composite propellant. Recent developments demands composite propellants also need to have high energy, sufficient structural integrity and low temperature capability to qualify for application in propulsion system. Polymer-plasticizer contributes to all three important characteristic of propellant. But the contribution of each ingredient can be exploited only when these systems are miscible otherwise immiscible system will not be homogeneous, the phase separation will take place. So, the selection or screening of plasticizer and polymer need to be done rigorously to get most suitable combination. The successful choice of plasticizer is made with regard to mixing, reducing mixing time and energy, crosslinking, increase filler dispersion, energy contribution to final combustion and reducing the batch viscosity [4, 5]. For energetic materials like propellant and plastic bonded explosive (PBX), the miscibility is studied mostly by qualitative experiments. Due to inherent explosive nature of these materials, these experiments are hazardous and costly. Quantitative evolution of miscibility can be done by comparing the solubility parameter of polymer and plasticizer. Hence studies on plasticization is vital in the binder systems that are employed in the rocket propellant industry.

### **1.3 Theory of Plasticization**

Plasticizer is an important additive in polymer processing, it is a low molecular weight material added to tailor properties of polymeric material. Plasticizer interacts with the polymer at molecular level to improve the visco-elastic response of material by increasing the chain mobility. It is an important ingredient for composite material formulations. The main acts of plasticizers can be listed as given below.

- Reduce the polymer process viscosity as processing aid.
- Lowering of rigidity at room temperature by reduction in glass transition temperature of polymer by increasing the free volume.
- Increase of the toughness (impact strength) down to the lowest temperature of serviceability.
- Increases the flexibility of final product that will increase the elongation at break.

Plasticization effect into polymer can be introduced by internal or external plasticization. Plasticization occurred due to molecular structure of polymer is known as

internal plasticization. This can be achieved by chemical methods by changing the molecular structure of polymer in such a way the free volume inside polymer packing increased. Copolymerization is one such method in which introduction of co-monomer units along the polymer backbone alters the packing mechanism. Comparison of SBR with polystyrene is one good example of this type of system. Polystyrene possess  $T_g$  greater than room temperature but when random copolymer SBR (25% styrene, 75% butadiene) is formed the  $T_g$  reduced to  $-60^\circ\text{C}$  [2]. This is due to increase in the randomness and free volume in polymer packing. Similarly side chain on polymer backbone increases free volume due to which internal plasticization effect observed in polymer, this can be achieved by adding some chemical reactants during polymerization which only attached to the backbone as side chain.

**External Plasticizers:** External plasticizers are mostly used for commercial purpose. This is because they provide more satisfactory combinations of properties and allows the manufacturer more formulating flexibility than internal plasticizers, which were introduced during the polymerization process. External plasticizers are high boiling point liquids, of low vapor pressure which, without chemical reaction, interact with the polymer, mainly at elevated temperature, by means of their salvation power. The plasticization efficiency of plasticizers is estimated by calculated  $T_g$  of system by following eq.1.1 [3].

$$\frac{1}{T_g} = \frac{w_1}{T_{gpolymer}} + \frac{w_2}{T_{gplasticizer}} \quad 1.1$$

Here  $T_g$  is glass transition temperature of polymer plasticizer system.  $w_1$  and  $w_2$  are mass fraction of polymer and plasticizers,  $T_{gpolymer}$  and  $T_{gplasticizer}$  are glass transition temperature of polymer and plasticizers respectively.

Role of plasticizer can be better realized by understanding the interaction among poly-polymer and polymer-plasticizer interactions. It is the intermolecular interaction of polymer which prevents the plasticization of itself. When the interactions among the polymer molecules are stronger than plasticizer-polymer interaction, the plasticization will not happen. These types of interactive forces are also known as non-bonded interactions; these are due to dispersion forces, induction forces, dipole-dipole interactions and hydrogen bonding.

Plasticizer need to show some specific characteristics for utilization in plasticization. General requirements are low volatility, light stability, no odor, thermal stability and other more important criteria are given below:

**Compatibility:** Plasticizer should be compatible with polymer during processing and during life cycle of final product over a range of temperature of use. The balance of compatibility should not disturb by exposure of common things like air, water, sunlight etc.

**Solvent power:** Plasticizer should exhibit the high degree of solvent power for polymer. Good plasticizer should be able to dissolve amorphous and crystalline region of the polymer these types of plasticizers known as solvent plasticizers where as secondary plasticizers exhibit poor solvent power, they are not capable of penetrating inside the crystalline region.

**Permanence:** It is the tendency of plasticizer to remain inside plasticized material during the life cycle of product. It depends on molecular size of plasticizer and diffusion rate in polymer. Larger will be plasticizer size, lower will be vapor pressure i.e. less volatile, lesser diffusion rate, hence higher permanence. Small size molecule will have high diffusion rate, higher volatility hence permanence will be less.

**Efficiency:** Plasticizer efficiency is relative term for a given polymer, how much desirable properties achieved by using a part of plasticizer in system. It is desirable to use lesser quantity of plasticizer to get maximum plasticization effect.

In selection of plasticizer, the selection cannot be based on one single requirement. Choice of plasticizer is compromise of solvent power, permanence, compatibility and efficiency. All above mentioned requirement cannot be in single plasticizer; it is shown in diagram in Fig. 1.1 [2].

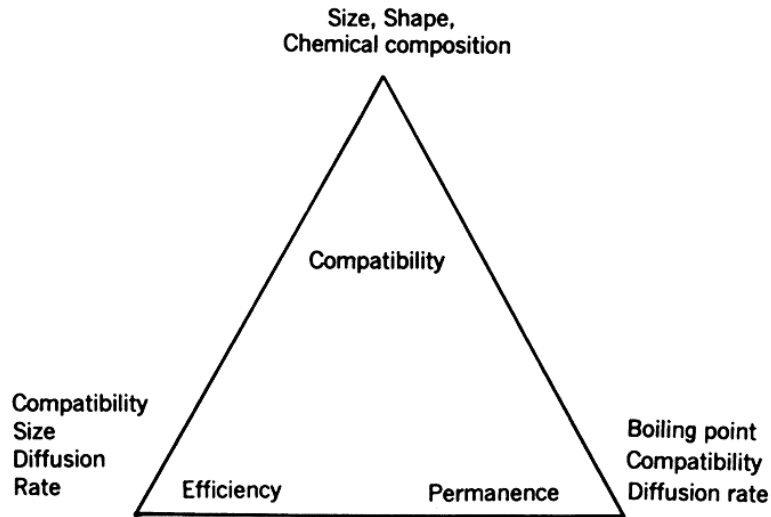


Fig 1.1: Boyer's diagram for relationship between properties of plasticizer.

The mechanism of plasticization is also important phenomena need to be understood in depth to select a suitable plasticizer. There are two classical approaches of plasticization mechanism known as lubrication theory and gel theory. Both give different expectations to make understand plasticization

**Lubrication Mechanism:** Kirkpatrick worked to elaborate lubrication theory, according to him the one part of plasticizer attached to polymer, hence acts as the solvent and other part of plasticizer acts as the lubricant between polymer-polymer molecules and resultant properties like viscosity and flexibility of polymer improves [3]. Another explanation of lubrication theory was given by Clark, according to him the void in molecular lattice of polymer are filled by the small molecules of plasticizers which form a gliding plane to ease the motion or lubricate the motion of polymer molecules. Importance of polarity in plasticization was described by Houwink, he gave the concept of gliding planes formation due to plasticizers between polymer molecules, these planes act as the mobility surfaces and plasticizer molecules between gliding planes act as the lubricants.

**Gel Theory:** According to this theory polymer-polymer molecules have contact points of attraction which form three dimensional honeycomb type networks along the length of molecules, which causes the stability of polymer structure known as gel form. Rigidity of polymer is due to un-plasticized three dimensional networks. Plasticizer molecules come into the network of polymer gel, they reduce the numbers of contact points inside polymer. Reduction in attachment points will loosen the gel network hence polymer

deformation become easier. In general the plasticizers containing long aliphatic chains are more effective than those containing bulky cyclic groups.

Apart from classical theory, Flory proposed free volume theory which is presently accepted as modern theory of plasticization.

**Free volume Theory:** Free volume theory came after classical theory of plasticization. This was postulated by Fox and Flory. According to this theory the friction between polymer molecules is related to free volume between them. Same way glass transition temperature is also related to free volume,  $T_g$  will be lower if free volume will be larger in polymer. It is accepted that at  $T_g$  at a physical state where all materials exhibit same fractional free volume. It means at glass transition temperature, viscosity of all polymers is found to be  $10^{12}$  Pa.s independent of chemical structure of polymer [3].

$$f = V - V_0 \quad 1.2$$

In eq. 1.2  $f$  is the free fraction volume.  $V$  is total volume and  $V_0$  is occupied volume. The evaluation of free volume is a practical challenge. It is calculated indirectly or simulated by molecular dynamic simulations.

#### **1.4 Thermodynamics of Miscibility**

Polymer-plasticizers are mixed by physical blending in extruder, or roll mill or vertical planetary mixer. Due to expenditure of the mechanical energy plasticizers dispersed in polymer. But if plasticized material is not thermodynamically stable, the phase separation may take place. Small molecular size plasticizer will diffuse out from the polymer. That type of behavior results loss in desirable properties of polymeric materials. Thermodynamic stability can be said as compatibility or miscibility. By definition, the miscibility/compatibility describes a single phase system over the entire range under isothermal conditions. The miscibility is governed by concentration dependency of free energy of mixing. One of necessary condition to be fulfilled is that the free energy of mixing should be negative ( $\Delta G_m < 0$ ) for thermodynamically miscible system. In case of polymer blend of two polymers having different glass transition temperature, miscible system will have single  $T_g$  and single phase. The limit of miscibility of plasticizer is the maximum amount of the plasticizer incorporated in polymer and retained in it during storage without external diffusion.

Like dissolves like is earliest concept of miscibility or compatibility. It is later defined as cohesive energy and solubility parameter of individual components. Solubility parameters are a new essence of the rule “like dissolves like” bringing it to a higher level of understanding. Thermodynamic theories and solubility parameter are related to elaborate the compatibility. The development of theory of polymer solution was extended as the theory of miscibility. Phase equilibrium is the most general thermodynamic approach to evaluate the phase state of a complex system.

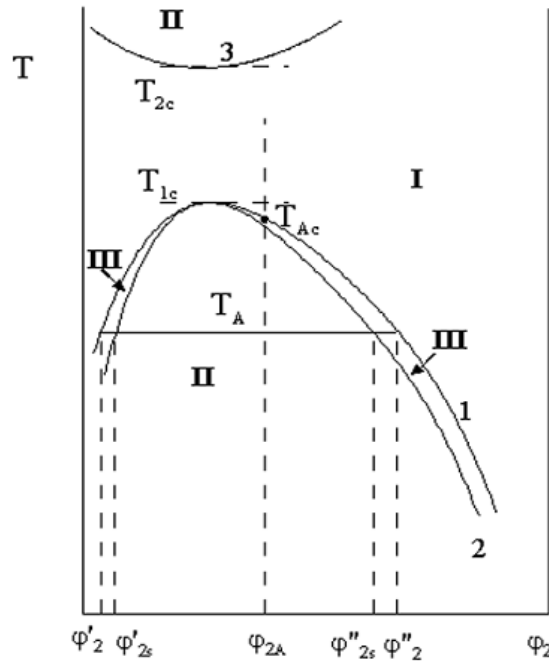


Fig: 1.2 Representation of Phase Equilibrium Diagram, Temperature vs concentration

The phase diagram of the amorphous polymer and plasticizer system is given in Fig 1.2. In this diagram the region II is known as phase separation region, region I is homogeneous & stable, the region III is known as metastable state where the rate of phase separation is very slow due to high viscosity of polymer and plasticizer system.  $T_{1c}$  is known as upper critical solution temperature (UCST), above this temperature the system is completely miscible at all concentration [3].

To understand thermodynamics of miscibility of two components, Gibb’s free energy need to be evaluated as shown in eq. 1.3.

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad 1.3$$

Flory-Huggins, in their theory of polymer solutions used Boltzmann equation of entropy to evaluate  $\Delta G_m$ . According to solution theory of polymers, polymer molecules with several repeating unit is arranged in a two dimensional lattice model. Each polymer

molecules occupies  $n$  square lattices, where  $n$  is number of repeating units in each polymer molecules. Remaining lattices are occupied by solvent molecules. There are number of ways in which polymer molecule can be arranged in the lattice model. According to Boltzmann the number of ways of arrangement solute and solvent in lattice model is related to entropy.

$$\Delta S_m = -k(N_s \ln \phi_s + N_p \ln \phi_p) \quad 1.4$$

The above equation is Boltzmann equation, in which  $k$  is Boltzmann's constant and  $N_s \ln \phi_s + N_p \ln \phi_p$  is number of ways of arrangements and  $\phi$  is volume fraction of solvent and polymer,  $N$  is number of molecules of polymer and solvents.

The enthalpy of mixing a polymer in solution is given by equation 1.5.

$$\Delta H_m = kT\chi N_s \phi_p \quad 1.5$$

Here  $\chi$  is known as Flory-Huggins interaction parameter, it is a measure of solvent power of power of system. It enables us to distinguish between good solvent or poor solvent. Lower value of interaction parameter is indicator of good solvent and high value is indicator of poor solvent [1].

Using equations 1.4 and 1.5, free energy of mixing can be written as following equation.

$$\Delta G = kT(\chi N_s \phi_p + N_s \ln \phi_s + N_p \ln \phi_p) \quad 1.6$$

In this equation last two terms are always negative, hence first term in this equation need to be lowest for miscible system. In other way we can say the interaction parameter can be used to quantify the degree of miscibility of polymer and plasticizer.  $\chi$  is concentration dependent parameter, hence, it cannot be used as universal parameter as indicator of miscibility.

### 1.5 Cohesive Energy and Solubility Parameter

Hildebrand gave a concept of solubility parameter which can be used as replacement of  $\chi$  for quantification of miscibility. This parameter can be directly evaluated for low molecular size materials as square root of heat of vaporization or cohesive energy density. In 1931 Scatchard defined cohesive energy density by energy of vaporization per unit volume. There are physical links between the constituents of a material. These links are due to non bonded interactions among atoms of molecules,



which are due to dispersion forces, polar cohesion and hydrogen bonding. The amount of energy required to overcome these interactions is called cohesive energy. Cohesive energy is one of the fundamental properties of material which can be used to correlate or predict several other properties like glass transition temperature, surface tension, mechanical properties, permeability of small molecules, dielectric constant etc. This energy has three main constituents i.e.  $E_d$ ,  $E_p$  and  $E_h$ , representing contribution of dispersion, polar and hydrogen bonding interaction. Total cohesive energy  $E_{co}$  and cohesive energy density (CED) are given following expressions.

$$E_{co} = E_d + E_p + E_h \quad 1.7$$

$$CED = E_{co}/V = E_v/V \quad 1.8$$

In above equation  $E_v$  is heat of vaporization and  $V$  is molar volume.

Solubility parameter can be determined by using equation 1.9.

$$\delta = \sqrt{CED} \quad 1.9$$

Hildebrand and Scatchard, introduced a new expression for enthalpy of mixing as given in following equation.

$$\Delta H_m = \phi_s \phi_p (\delta_s - \delta_p)^2 \quad 1.10$$

Using this enthalpy of mixing in Gibb's free energy equation 1.3, for negative value of free energy,  $\Delta H_m$  should be close to zero, which is only possible when difference in solubility parameter of two components,  $\Delta\delta = \delta_s - \delta_p$ , is close to zero. Hence any system of two components, the miscible and single phase system will form when  $\Delta\delta < 2.1 \text{ J}^{1/2} \text{ cm}^{-3/2}$  [6, 8]. This approach is very simple and successful for liquids of low molecular weight.

Heat of vaporization is important input for evaluation of solubility parameter. In case of polymer molecules, heat of vaporization or cohesive energy density evaluation is not simple as in case of thermally stable low molecular size liquids. Polymer will decompose before they vaporize. Similar problem is seen in case of energetic plasticizers and most of these materials are thermally labile. These materials are not thermally stable. They decompose rapidly as they are exposed to heat. Direct evaluation of heat of vaporization for energetic plasticizer and polymer is not possible. For such molecules indirect methods like inverse gas chromatography, equilibrium swelling theory, intrinsic viscosity, group contribution and molecular dynamic simulation can be used to determine the solubility parameter [17,20,21, 27, 31].

## 1.6 Interaction Parameter

This interaction parameter is used to describe the compatibility of two components. This parameter is also known as Flory-Huggins interaction parameter. This parameter is related by solubility parameter by following equation.

$$\chi = \chi_s + \left(\frac{V}{RT}\right)(\delta_s - \delta_p)^2 \quad 1.11$$

In this equation  $\chi_s$  is entropy contribution and other term called enthalpy contribution to overall value of  $\chi$ . The enthalpy contribution is function of difference of Hildebrand solubility parameter of polymer and plasticizer. Entropy contribution,  $\chi_s$  is usually taken as constant for given system. Generally its value used for estimation of miscibility is chosen is 0.34. From literature it is clearly understood that the miscible is mostly expressed by entropy contribution of interaction parameter, which is function of  $\Delta\delta = \delta_s - \delta_p$ , the lower value of interaction parameter obtained when  $\Delta\delta$  is lower.

According to Flory-Huggins polymer solution theory, Gibbs free energy is related to interaction parameter as given in equation 1.6.

Interaction parameter can be determined by swelling experiments using Flory-Rehner equation (eq 1. 12), which is function of crosslink density and volume fraction polymer in of swollen state.

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 = -\frac{v_e}{V}V_1\left(\phi_2^{1/3} - \frac{2\phi_2}{f}\right) \quad 1.12$$

Here  $v_e$  is crosslink density,  $\phi$  is volume fraction of polymer in swollen sample.  $V_1$  is molar volume of solvent,  $f$  is functionality of crosslinked polymer.

Crosslink density of polymer is determined by stress strain analysis of same polymer by using Mooney-Rivlin equation ( eq. 1.13 )

$$\sigma = \frac{F}{A} = 2\left(C_1 + \frac{C_2}{\lambda}\right)\left(\lambda - \frac{1}{\lambda^2}\right) \quad 1.13$$

Here  $\sigma$  is stress,  $\lambda$  is  $L/L_0$ , both are obtained from tensile test on universal testing machine,

When we plot  $\sigma/(\lambda - \lambda^{-2})$  Versus  $1/\lambda$ , intercept at y axis will give value of  $2C_1$  from which we can calculate crosslink density as shown in expression 1.14.

$$2C_1 = 2\rho Rv_e \quad 1.14$$

Using Mooney-Rivlin equation, crosslink density is calculated and same value can be used in Flory-Rehner equation to evaluate the interaction parameter of system [18, 19, 30].

## 1.7 Methods of Evaluation of Solubility Parameter

### 1.7.1 Equilibrium Swelling

Three dimensional polymer networks do not disperse in solvents, but it can absorb large quantity of suitable solvent if submerged in it. Swelling occurs for the same reason that the solvent dissolves simultaneously with an analogous linear polymer to form a polymer solution. Flory said the swollen gel is in fact a solution, although an elastic rather than a viscous one. Thus an increase in entropy is achieved by added volume of the polymer network, the addition of volume is due to spread of solvent into the network. The mixing tendency, expressed as the entropy of dilution, may be augmented or diminished by heat of dilution. As the polymer network is swollen by absorption to assume elongated configurations, and a force similar to the elastic retractive force in polymer as a result develops in opposition to the swelling process. As swelling proceeds, retractive force increases and diluting force decreases and a state of equilibrium swelling is reached in which these two forces are in balance [35].

This method is based on Gee's equilibrium swelling theory. According to this theory, maximum swelling of partially crosslinked polymer takes place in the solvent having solubility parameter value closest to solubility parameter of polymer and it is expressed as swelling ratio[20,25,26].

$$Q = Q_{\max} e^{-aQ(\delta_{\text{solvent}} - \delta_{\text{polymer}})^2} \quad 1.15$$

where  $Q_{\max}$  is the maximum swelling ratio and  $a$  is a constant. The above equation can be rewritten as

$$\pm[Q^{-1} \ln (Q_{\max}/Q)]^{1/2} = |a^{1/2}[\delta_{\text{solvent}} - \delta_{\text{polymer}}]| \quad 1.16$$

By plotting  $\pm[Q^{-1} \ln (Q_{\max}/Q)]^{1/2}$  against  $\delta_{\text{solvent}}$  for a series of solvent,  $a^{1/2}$  and  $\delta_{\text{polymer}}$  can be determined from the slope and the intercept respectively.

The swelling ratio ( $Q$ ) is evaluated at equilibrium

$$Q = 1 + (w_2/w_1 - 1) (\rho_{\text{polymer}}/\rho_{\text{solvent}}) \quad 1.17$$

where  $w_1$  and  $w_2$  are weight of the dry and swollen specimens respectively.  $\rho$  is the density.

### 1.7.2 Intrinsic Viscosity

Polymer molecule in a dilute solution experiences the osmotic action of surrounding solvent, which tends to swell it to a larger average size than it would otherwise assume. A close similarity exists between this molecule expansion and swelling of three dimensional network as discussed in previous topic. In fact the single molecule is assumed as the submicroscopic prototype of three dimensional network. In presence of osmotic action of solvents, the chain of polymer molecules tend to spread less due to elastic reaction consequently develops like retraction forces in swelling polymer. At equilibrium, this elastic force is balanced with osmotic forces which tend to swell the molecule, here it will achieve maximum size in given solvent. The frictional force of polymer molecules in dilute solution is measured as viscosity and it depends directly on the size of the polymer molecule in solution [35].

Intrinsic viscosity measurement method for evaluation of solubility parameter is very much similar to the equilibrium swelling methods but this method is applicable for linear polymers. The dilute solution of polymer is made in such a way each molecule must not interact with other molecules of polymer. This solution is drained through capillary, where the polymer molecule with maximum swollen size exerts large friction while flowing, so highest viscosity. This observation can be seen only when the solubility parameter values of solvent and polymer are closer [22, 34]. Intrinsic Viscosity relation with solubility parameter is analogous as swelling ratio and the expression is given by equation 1.18 [22].

$$\pm[[\eta]^{-1} \ln ([\eta]_{max}/[\eta])]^{1/2} = |k^{1/2}[\delta_{solvent} - \delta_{polymer}]| \quad 1.18$$

$[\eta]$  is intrinsic viscosity of dilute solution of the polymer,  $k$  is constant.

When  $\pm[[\eta]^{-1} \ln ([\eta]_{max}/[\eta])]^{1/2}$  versus  $\delta_{solvent}$  plotted, the straight line will form. The slop of line will give value of  $k$  and intercept at horizontal axis will give solubility parameter of polymer.

### 1.7.3 Inverse Gas Chromatography

The IGC method [21, 31] for determining polymer solubility parameters is based on the principle of Flory-Huggins  $\chi$  parameter.  $\chi$  can be related to solubility parameters by

combining Hildebrand-Scatchard solution theory with Flory theory in equation 1.11. The equation 11 can be rewritten as an expression given in following equation.

$$\left( \frac{\delta_1^2}{RT} - \frac{\chi}{V_1} \right) = \left( \frac{2\delta_2}{RT} \right) \delta_1 - \left( \frac{\delta_2^2}{RT} + \frac{\chi_s}{V_1} \right) \quad 1.19$$

In above equation  $\chi$ ,  $\delta_1$  and  $V_1$  known and  $\delta_2$ ,  $\chi_s$  can be determined graphically.  $\delta_2$  is constant for all the solvents, a plot of  $\{(\delta_1)^2/RT - \chi/V_1\}$  vs  $\delta_1$  gives a straight line. By evaluating intercept of line on axis, solubility parameter can be evaluated.

#### 1.7.4. Hildebrand equation

The heat of vaporization is directly evaluated by using Hildebrand equation. This equation uses boiling point of liquid single input and solubility parameter can be evaluated from heat of vaporization [16].

$$H_v = T_b^2 + 23.7T_b - 2950 \quad 1.20$$

$T_b$  is boiling point of material in Kelvin.

#### 1.7.5 Solvent Spectrum

List of solvent are selected for solvent spectrum method in increasing order of solubility parameter. Polymer sample is dissolved in each solvent, and a range of solvents selected in which sample is soluble. The midpoint of soluble range is taken as the solubility parameter of polymer. This method again is limited to linear and small molecular size polymers [16].

#### 1.7.6. Group Contribution Theory

D.W. Van Krevelen has given the concept of group contribution for determining the physico-chemical properties. This theory is based on semiempirical approach, i.e. empirical but based on a theoretical concept. It is based on additive principle. This principle means many properties if expressed per mole of a substance, may be calculated by summation of either atomic, group, or bond contributions [27].

$$F = \sum N_i F_i \quad 1.21$$

Here  $F$  is additive molar function,  $N_i$  is number of components of type  $I$ ,  $F_i$  is the numerical contribution of the component (atom, atom group, bond), summed over all contributing components. Cohesive energy and molar volume are calculated by

structural contribution of the atoms, groups in same and solubility parameter and cohesive energy can be obtained as shown in eq.1.22

$$CED = \frac{\sum E_i}{\sum V_i} \quad 1.22$$

Here  $E_i$  is cohesive energy of group/atom  $i$ , and  $V_i$  is the molar volume contribution of group  $i$ . From CED,  $\delta$  can be calculated

### 1.7.7 Molecular Dynamics

A molecular Dynamics simulation is powerful computational technique for prediction of condensed phase properties of wide range of molecules. Cohesive energy and solubility parameter of polymers and plasticizers can be evaluated with reasonable accuracy by this method.

## 1.8 Molecular Simulation Methods

### 1.8.1 Background

Prediction of properties of polymers and additives is advantages for developing formulations. The computational techniques are powerful and widely used for material modelling in recent days. The same are also finds important role in energetic materials. These techniques help to predict the behaviour of energetic materials under given environmental conditions. Based on this first hand information of materials, it can be possible to choose suitable material for formulations. The following four are the main computational techniques which can be used for material modelling

- First principles based quantum mechanics
- Classical and quantum mechanics based large scale molecular dynamics simulations
- Mesoscale modelling
- Micro and macro scale modelling

Figure 1.3 illustrate the different levels of computational technique on space and time scale. First principle quantum mechanics (QM) used to simulate the atoms and molecules at electronic structure level in time scale range between femtoseconds to picoseconds. It is used to predict the description of chemical bonds in the system. This information helps to estimate the stability of molecule before actual synthesis of it. QM is most suitable for highly sensitive energetic materials. The information obtained from QM enables to take proactive measures for safety during handling or use.

Molecular dynamics is used to predict static and dynamic behaviour of material at molecular level. In case of classical mechanics based MD simulation, force field is used to predict equilibrium and non-equilibrium properties of condensed phased systems. This method of simulation works at nano-scale and it provides information on atomic positions and velocities from which properties like cohesive energy, heat capacities etc. can be derived[4-15].

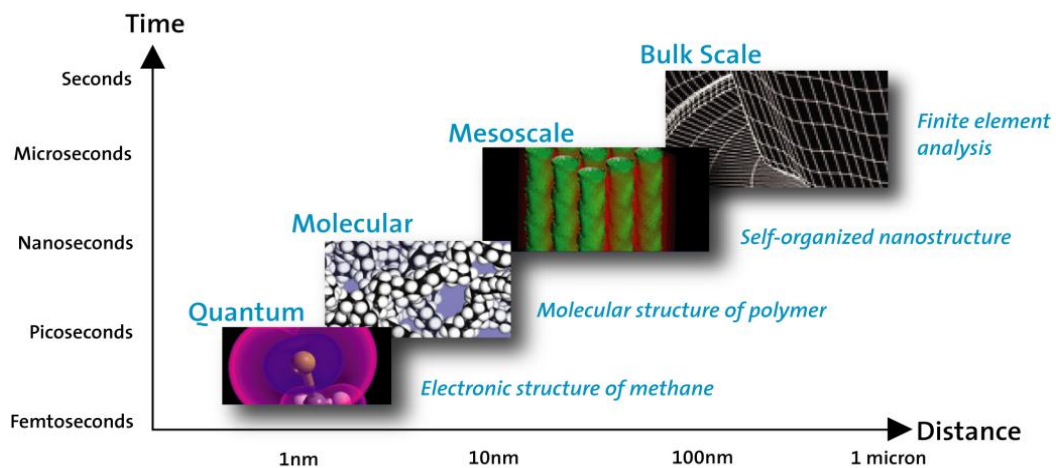


Fig. 1.3: Time and space scale for computational techniques, classification of simulation methods.

Coarse-grain modelling is used for prediction of morphology of materials. Here it is possible to explore on much larger scale, mesoscale, than MD and QM. In this simulation, a bundle of molecules considered as grain or bead which interacts with each other and morphology of system in presence of different grains is estimated.

Last simulation technique at bulk scale is commonly known as finite element analysis. In this simulation the deformation of material is related to internal stress and strain and external forces acting on it. The computational techniques are utilized to develop material the levels used for product development are briefly illustrated in Figure 1.4. Figure 1.4 clearly describes extension of computational techniques from atomic scale ab initio quantum mechanics level to macro scale finite elements methods.

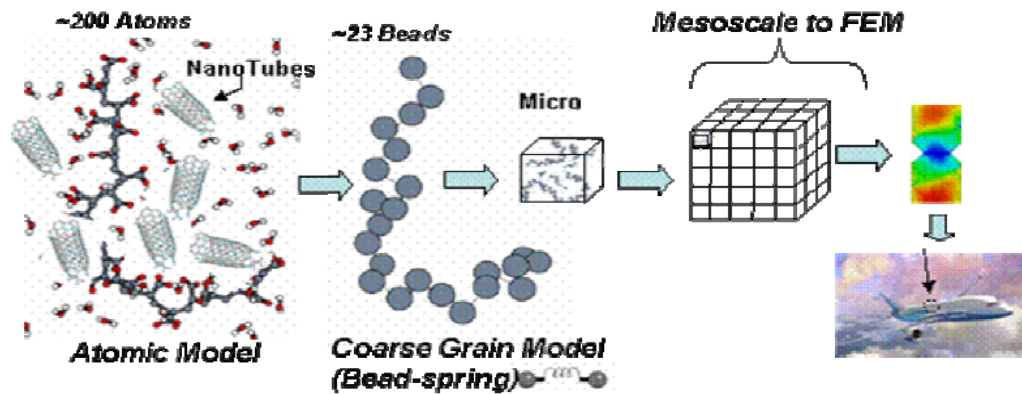


Fig. 1.4: Representation of use of different level of computational techniques for development of product

This work focus on the molecular dynamics simulations and brief background on the same is given here.

### 1.8.2 Theory

Molecular dynamics is governed by classical Newtonian Mechanics. Atoms in this model are represented as ball and bonds between atoms are represented as spring, hence this representation is known as ball spring model. Molecular dynamics allows us to simulate the atoms in a structure will move as a function of time under the influence of computed forces by solving Newton's classical equation of motion. These equations modified to take account of the effect of temperature on system wherever required. Integration of Newton's equation of motion allows to explore constant energy surfaces of system. Most natural phenomena occur under conditions where system exchanges heat with environment. So, molecular systems are exposed to several such conditions in annealing to achieve the equilibrium state [9,27].

Usual procedure of MD simulation stepwise expressed in following list:

1. Chose initial positions of atoms of molecule, not necessary optimized geometry.
2. Choose initial set of atom velocities. These are usually chosen to obey Boltzman distribution for some temperature, the normalized so that the net momentum for the entire system is zero.
3. Compute the momentum of each atom from its velocity and mass.
4. Compute forces on each atom from energy expression, this usually a molecular mechanics force field designed to be used in dynamic simulations.



5. Compute new positions for the atoms a short time later, called the time step. This is a numerical integration of Newton's equation of motion using the information obtained in previous step.
6. Compute new velocities and accelerations for the atoms.
7. Repeat steps 3 and 6
8. Repeat this iteration long enough for the system to reach equilibrium. In this case, equilibrium is not the lowest energy configuration; it is a configuration that is a reasonable for the given amount of energy.
9. Once system has reached the equilibrium, begin saving the atomic coordinates every few iterations, this information is typically saved every 5-25 iterations. This list of coordinates over time is called a trajectory.
10. Continue iterating and saving data until enough data have been collected to give to give results with the desired accuracy.
11. Analyze the trajectories to obtain information about system. This might be determined by computing radial distribution functions diffusion coefficients, vibrational motions, or any other property computable from this information.

### **1.8.3 Force Field**

Force field is used to describe the potential energy surfaces of entire class of molecules with reasonable accuracy. In other words it can be said that the use of force field is to provide the geometrical, energetic, and conformational information which is useful as input for application of rotational isomeric state theory in calculation of the configuration dependent properties of molecules. Sometimes force field is regarded as method of conformational analysis. Basically, it is a set of potential energy functions and it is actually regarded as potential energy surface.

The force fields commonly used for describing molecules employ a combination of internal coordinates and terms (bond distances, bond angles, torsions, etc.), to describe that part of the potential energy surface due to interactions between bonded atoms, and non-bond terms to describe the van der Waals, electrostatic, etc. interactions between atoms. The functional forms range from simple quadratic forms to Morse functions, Fourier expansions, Lennard-Jones potentials[27], etc.

The coordinates of a structure combined with a forcefield create an energy expression. This energy expression is the equation that describes the potential energy surface of a particular structure as a function of its atomic coordinates. The potential energy of a system can be expressed as a sum of valence (or bond), cross-term, and non-bond interactions as shown in following expression.

$$E_{total} = E_{valance} + E_{crossterm} + E_{non-bond} \quad 1.23$$

Here  $E_{total}$  is total potential energy,  $E_{valance}$  is due to bonded interactions,  $E_{crossterm}$  considering angle distortions considered by nearby atoms,  $E_{non-bond}$  due to non-bonded interactions.

Bonded interaction term includes bond stretching, angle bending, dihedral angle torsion, out of plane interactions and Uray-Bradley term which is due to interaction of atom pairs, this expression of bonded interaction is given in eq. 1.24.

$$E_{valance} = E_{bond} + E_{angle} + E_{torsion} + E_{OOP} + E_{UB} \quad 1.24$$

Non-bonded interactions include van der Walls interactions, electrostatic interactions, and hydrogen bonding as shown in following expression.

$$E_{non-bond} = E_{vdW} + E_{ele} + E_{H-bonding} \quad 1.25$$

Non-bonded interactions are dependent on conformation of molecule, so most stable or lowest energy state need to be achieved to accurately evaluate these interactions. The cohesive energy is function of these non-bonded interactions which we will use to evaluate for miscibility study to calculate the solubility parameter of material of interest.

There are several forcefields which are available for Molecular Mechanics and dynamics simulations are given below:

1. COMPASS
2. PCFF: Polymer Consistent Force Field
3. Cvff : Consistent valance Forcefield
4. Dreiding
5. Universal

Choice of forcefield is very critical for MD simulations. COMPASS, Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies, is recently

developed ab initio forcefield. It is derived from polymer consistent forcefield (PCFF). As a validation of COMPASS, molecular mechanics calculations and molecular dynamics simulations have been made on a number of isolated molecules, liquids, and crystals. The calculated molecular structure, vibration frequencies, conformational properties for isolated molecules, crystal cell parameters and density, liquid density, and heat of evaporation agreed favourably with most experimental data.

### **1.9 Origin and Objectives of the Study**

Composite propellant comprises of various energetic and non-energetic ingredients which majorly include binder system (Polymer and plasticizer), oxidiser, metal powder, additives etc. In order to achieve successful formulation, numbers of experiments are to be carried out which involves its processing and further its characterisation. It is worthy to highlight, majority of the ingredients employed in propellant formulation are energetic materials, in combination of fuel and oxidiser, they pose explosive hazard during their handling and storage. Further, random selection of any ingredient may lead to undesired properties of formulation. Apart from explosive hazards, each experiment and product characterization takes about 15-20 days. Hence, experimental research on propellants associated with the handling hazard, lack of cost effectiveness and due to delay on arriving conclusions. Hence, there is an urge to adopt theoretical studies to minimize number of experiments. Further, the theoretical studies may enable developers to select most suitable ingredients for formulation development.

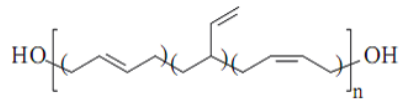
Recent years, several methods have been proposed to predict the solubility parameters by means of computer simulations. Classical molecular mechanics based force field methods are promising for the investigation of structural, thermodynamic and mechanical properties of amorphous polymers and further; it allows the prediction of the miscibility regardless of the availability of polymers to be investigated. One of the most important aspects in MD simulations is the generation of the initial configurations, since they dictate the final properties. Researchers adopt multi-step relaxation procedure and iterative molecular dynamics/molecular mechanics to achieve well-equilibrated most probable structures.

In atomistic simulations, the cohesive energy can be used as criterion to determine whether the cell structure and its energetic consideration properly describe the real

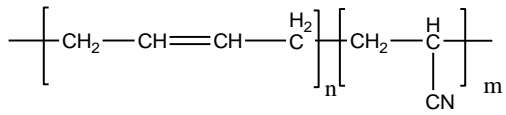
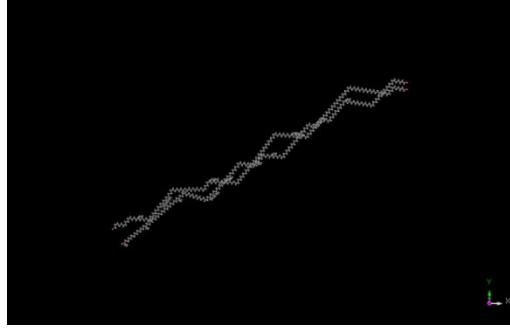
material. Bermejo et al simulated solubility parameter of PVA crosslinked network and also the effect of crosslinkage size on solubility parameter [12]. The solubility parameter of Poly(L-lactide)(PLLA) and Poly(DL-Lactide)(PDLLA), Poly(vinyl phenol)(PVPh) and Polystyrene were studied and analyzed the miscibility state of PLLA and PDLLA with PS & PVPh by Arenaza[9]. Similar work is also reported by Jawalkar, in his study of compatibility of binary blend of PVA and PMMA by MD simulation. Gupta and Alperstein reported miscibility study of pharmaceutical compounds and plasticizing efficiency of methyl-4-hydroxybenzoate in nylon respectively by using MD simulation [8,10,11]. The simulation studies were also extended in solid rocket propellants where prediction of solubility parameter of polymers/plasticizer is a challenging task. Abou-Rachid et al studied the miscibility of HTPB-DOA and immiscibility of HTPB-DEGDN by MD simulations and similarly Gong et al, studied the plasticizing effect of 1,5-diazido-nitrapentane(DIANP) on Nitrocellulose(NC)[6,7]. More recently various energetic plasticizers (NG, BTTN, BuNENA) have been screened for its miscibility with Hydroxy Terminated Polyether (HTPE) by studying the interaction behaviour by MD simulations [7]. To best of our knowledge the most commonly used binder system(which include HTPB, GAP, NBR etc.) were not studied in details, scanty information available for selection of most suitable plasticizer.

The dissertation work aims on the molecular simulations studies to address the screening methodologies for the propellant binder system which details about the polymer-plasticizer compatibility. Molecular dynamics simulation approach based classical physics is adopted to evaluate fundamental properties of polymer and plasticizer. Solubility parameter of polymer and plasticizers is identified as key property that can indicate about the miscibility. Equilibrium swelling and intrinsic viscosity measurements are carried out to determine the solubility parameter experimentally and the results are used for the validation of MD simulations.

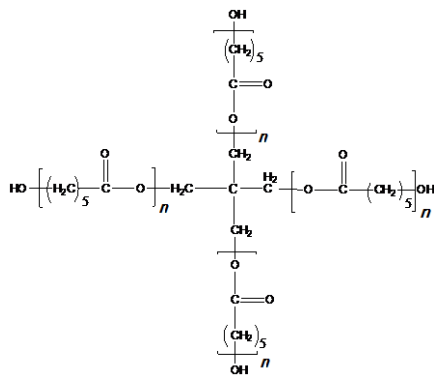
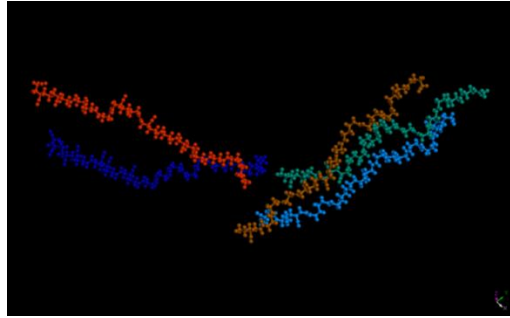
Most commonly used polymers in the propellant binder systems viz. HTPB, SPG-255, NBR, HTPB-b-CP are chosen for this study. Chemical structure and molecular model of polymers and plasticizers which are taken for this study are shown in Fig 1.5. A series of energetic and non-energetic plasticizers are studied for their suitability to the above polymer system.



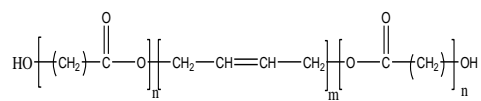
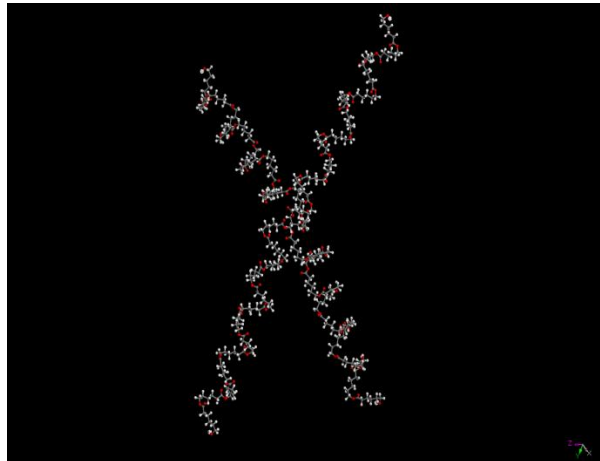
HTPB



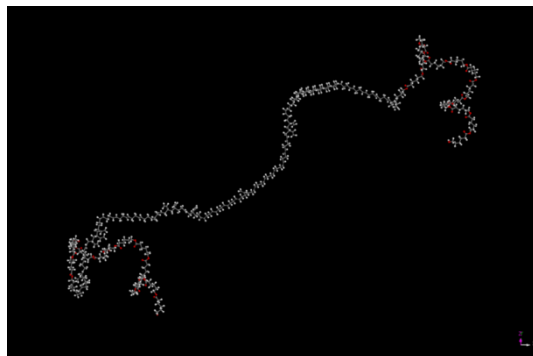
NBR

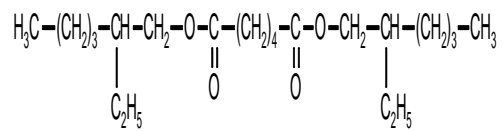


SPG-255

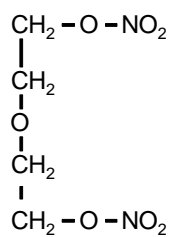
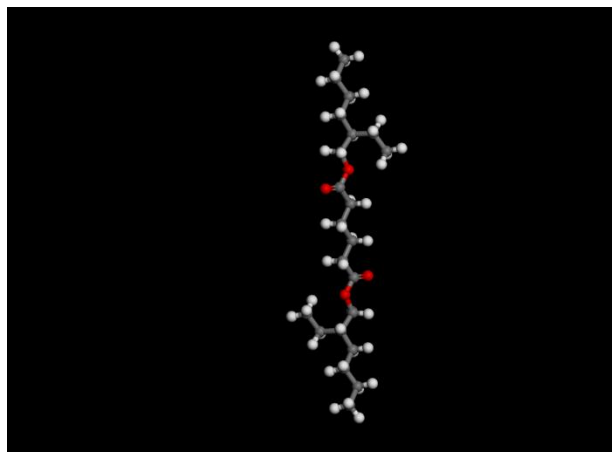


HTPB-b-CP

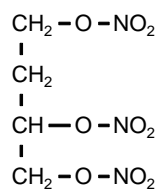
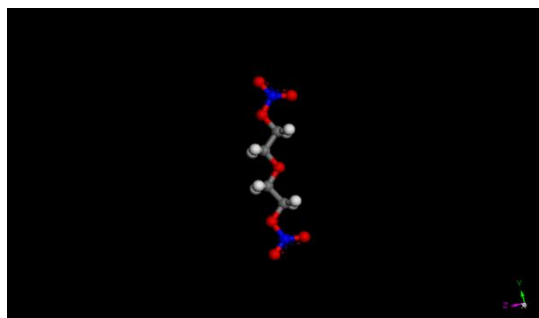




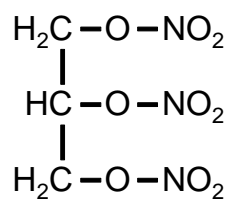
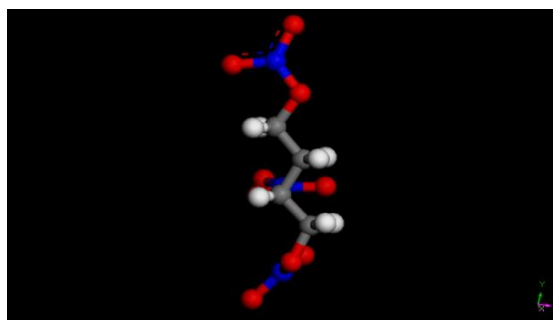
DOA



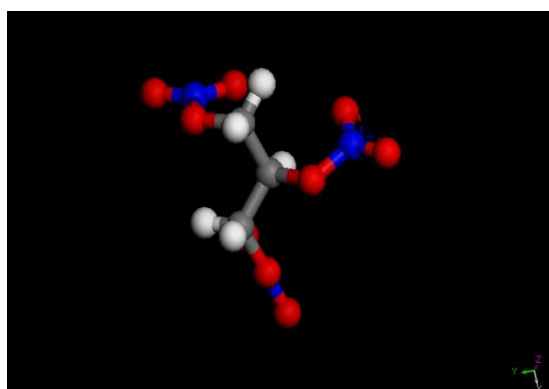
DEGDN

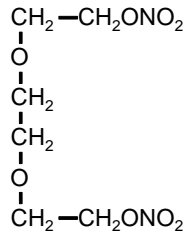


BTTN

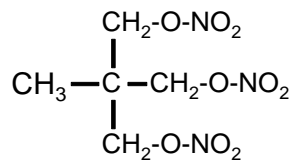
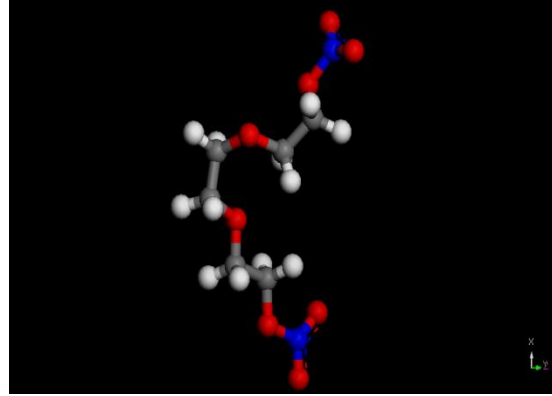


NG

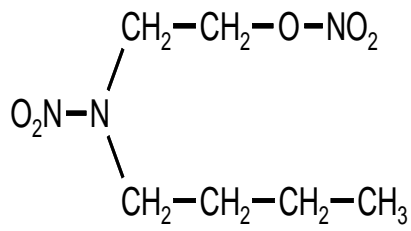
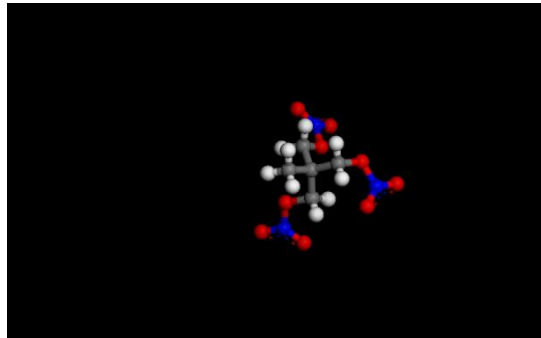




TEGDN



TMETN



BuNENA

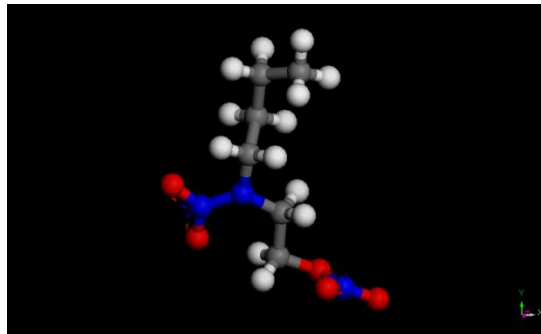


Fig. 1.5 Molecular Structure Model of Polymer and Plasticizers

## 2. Experimental Methods

2.1 **Materials:** HTPB ( $M_w = 2500-2700$ ) is procured from Anabond Pvt Ltd., GAP ( $M_w = 1800-1900$ ) synthesized in HEMRL by EMR division, NBR ( $M_w = 40000-50000$ ), polycaprolactone ( $M_w = 5800-6200$ ), HTPB-b-CP( $M_w = 5600-5900$ ) block copolymer, DOA and BTTN are obtained from SRP division of HEMRL.

Solvents used are n-Pentane, Heptane, Cyclohexane, Carbon tetrachloride, Toluene, Chlorobenzene, Dichloromethane, 1,4-Dioxane, aniline, Nitroethane, NMP, Acetonitrile, Propylene carbonate. All these solvents are used without purification and these are purchased from Merck India. Solubility parameters of the solvents that are used in this study are given in Table 2.1.

Table 2.1: Solubility Parameter of Solvents

Solvents	Solubility Parameter $J^{1/2}cm^{-3/2}$
N-Pentane	14.3
n-hexane	14.93
n-heptane	15.1
Cyclohexane	16.77
Carbon tetrachloride	17.59
Toluene	18.2
Chlorobenzene	19.4
Methyldichloride	19.84
Ethylenedichloride	20.04
1-4 dioxane	20.5
Aniline	21.1
Nitroethane	22.7
N-methyl-2-pyrrolidone(NMP)	23.1
Acetonitrile	24.1
Nitromethane	26
Propylene carbonate	27



## **2.2 Equilibrium Swelling**

For swelling experiments, the iso-cyanate crosslinked polymer sample is taken. A piece of about 0.1 to 0.25g was allowed to swell in solvent in an air tight bottle at room temperature for the duration 10-13 days to reach equilibrium. Weight measurement is done on Mettler Toledo make analytical balance..

## **2.3 Intrinsic Viscosity Measurement**

Intrinsic viscosity is measured by Ostwald viscometer of Technico size A BS/U and size B BS/U. The viscometer and solvent selection is done keeping in mind that flow time of the solvent should be more than 100secs and solubility parameter of solvents should be close polymer solubility parameter which is calculated by equilibrium swelling. To get an accurate value of intrinsic viscosity, four to five concentrations of dilute solutions of polymer are prepared and flow time of the same are recorded.

## **2.4 Solvent Spectrum**

Nitrile butadiene rubber (NBR) of molecular weight ranging 40000-50000, was taken in form of small rubber pieces. The attempt of dissolving the polymer in different solvents of increasing solvent parameter has been done in this study. The solvents in which NBR dissolved are noted

## **2.5 Simulation Method**

Molecular dynamics simulations are carried out in Discover and Amorphous cell modules of Materials Studio 4.3 suite, Accelrys Inc. A well validated condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field is used for the simulation. It is an ab initio force field that enables accurate and simultaneous prediction of gas-phase properties (structural, conformational, vibrational, etc.) and condensed-phase properties (equation of state, cohesive energies, etc.) for a broad range of molecules and polymers. COMPASS is parameterized in two phases: ab initio parameterization and empirical optimization. In the first phase, partial charges and valence parameters were derived by fitting to ab initio potential energy surfaces and the van der Waals parameters were fixed to a set of initial approximated parameters. In the second phase, emphasis was on optimizing the force field to yield good agreement with experimental data. The parameters for covalent molecules are well validated using various calculation methods including extensive MD simulations of liquids, crystals, and polymers. Previous studies on energetic materials confirmed its applicability to nitramines and

hence, COMPASS is chosen for this investigation. The initial configurations are generated in several steps. Amorphous builder is used to construct a cell containing 1000 atoms; accordingly numbers of molecules are selected for each polymer and plasticizer. Thus, in order to avoid surface effects, 3D periodic boundary conditions are used. In all the condensed phase simulation cases, electrostatic interactions are treated using the group based summation, non-bonded interactions are truncated at  $12.50\text{\AA}$ , the Verlet velocity integration method is used with a time step of 1 fs. The constructed cells are subjected to equilibration consisting of various steps. Initially the energy of generated amorphous cell is minimized to convergence value of  $0.001\text{ cal/mol/\AA}$ . In order to bring the polymer model system to the most probable configuration consistent with target temperature and pressure, cell relaxations are performed for the energy minimized cells of polymer models using NVT-MD simulations. The relaxation protocol employed is similar to the Hoffmann's relaxation protocol . Karayiannis et al. modified the above protocol to perform NPT dynamics at the end of the NVT cycles. Berendsen method is used for temperature and pressure control. The final structure is been taken from the relaxation simulation and it is equilibrated by NPT-MD simulations for 1000 ps (Called as Production Run). The specific volume and energy was observed to fluctuate about a well-defined mean over the time scale of dynamics, indicating that the equilibrium density and energy for the given temperature and pressure has been attained and the system is in the most probable configuration.

11 different amorphous systems were modeled, all pure substances. Each pure substance amorphous cell contained a single type of molecule, respectively, two chains of HTPB each containing 50 repeat units (microstructure have 54% trans, 26% cis and 20% vinyl), 16 molecules of DOA etc., to ensure that each system holds at least 1000 atoms in total. The real HTPB molecule has similar microstructure and degree of polymerization. Similarly all other polymer molecules SPG-255, HTPB-b-CP etc. are modeled to predict properties with actual molecular structure. DEGDN, BTTN, TEGDN, TMETN, BuNENA and NG amorphous cell created with 3D periodic boundary conditions.

Each amorphous system was created using the atom-by-atom approach developed by Theodorou. Initial densities used for a model building were experimental values of

0.94g/cc for HTPB, 0.92g/cc for DOA. A single bond is added per step, under the single substate per state rule, while using a substate width of 20. A random number seed was used to insure a properly randomized distribution of all molecules in the cell.

Model building was followed by constant number of atoms, constant pressure, and constant temperature (NPT) dynamics simulation. An external pressure of 0.0 GPa was imposed, which is a commonly used approximation in density equilibration since the difference between the internal pressure of a system and normal atmospheric pressure can reach four orders of magnitude. The Andersen algorithm was used for temperature control (thermostat), using a collision rate of 1.0, and the Berendsen et al algorithm was used for pressure control (barostat) using a decay cutoff of 0.1 ps. Equilibration was performed until both internal and external energy terms fluctuated around a constant mean value. Pure substances submitted to 1000 ps of NPT MD, using again only the last 250 ps for analysis. In specific cases, when indicated, dynamics simulations were performed for an additional 1 ns duration, and averages calculated over the last 1 ns time. A cutoff distance of 1.25 nm was imposed as the minimal distance at which van der Waals interactions are excluded, using a spline width of 0.10 nm and a buffer width of 0.05 nm. A standard tail correction was applied to CED following this approximation. For Coulombic interactions, which have a more profound effect at long range, calculations were performed by the Ewald summation method with an Ewald accuracy of 10<sup>-2</sup> and an update width of 1.0. The dynamics procedure allowed an equilibration of densities, which converged in all cases to values slightly different from those first imposed. All reported values were obtained from averaging over the last 50 ps of each dynamics run, except for the 1 ns dynamics simulations, where averaging was performed on 1 ns. For Ecoh, a tail correction was applied as described in more details in Ref. [8]. In all cases, when errors are reported, they were calculated from deviations between the three models, using the Student's t-test with a probability level of 95%.

### **Hoffman's relaxation protocol**

For polymers with complex chemical constitutions bearing inflexible groups in the backbone or side groups, sampling well-equilibrated bulk configurations is a major challenge. To create equilibrated structures, the model system is subjected to an equilibration cycle consisting of many, relatively short, NPT and NVT MD stages under the specified conditions of pressure ( $P$ ) and temperature ( $T$ ) aimed at creating a final

structure with realistic density, topology, atomic packing, and low-potential-energy characteristics. According to this procedure, the initially built packing cell is subjected to a static structure optimization using a molecular mechanics (MM). This is followed by a long succession of 5 MD stages (Table 2.2 , consisting of NVT and NPT MD simulations corresponding to temperature annealing and cooling, and compressions-decompressions, as proposed by Hofmann et al. (Hofmann D.; et al. *Macromol. Theory Simul.* 2000, 9, 293). An advantage of the Hofmann et al. method is its speed when taking into account the relaxation times of dense, glassy structures. However, in the present study, this equilibration cycle is extended here by subjecting the resulting configurations to additional molecular dynamics (MD) simulation at a 303 K for 100 ps, affording extra relaxation at all length scales (a shorter version of the modification suggested by Karayiannis et al. (N. C. Karayiannis, V. G. Mavrantzas, and D. N. Theodorou. *Macromolecules* 37, 2978 (2004).

Table 2.2 . Relaxation Protocol.

Stage of equilibration	Ensemble	Temperature (K)	Time (ps)
1	NVT-MD	750	30
2	NVT-MD	600	20
3	NVT-MD	450	20
4	NVT-MD	303	100
5	NPT-MD	303	100

NVT: Constant number of moles/Constant-volume/constant temperature dynamics

NPT: Constant number of moles/Constant-pressure/constant temperature dynamics

### 3 Results and Discussion

#### 3.1 Structure and Chain Packing

Several properties of bulk polymers can now be predicted with greater accuracy using MD simulations. Thus, the approach becomes useful for systems that are difficult to study experimentally or for which experimental data are not available. The polymers and plasticizers which are used in rocket propellant binder applications demands such approaches as these systems suffer from stability and sensitivity issues. Hence, it would be useful to predict the properties of such polymers at the molecular level, to a reasonable degree of accuracy and success, using MD simulations on amorphous polymers. These calculations while predicting the equilibrium configuration of the polymeric chains, would bring polymers sufficient close to their thermodynamically realistic states in order to compute the properties of experimental interest.

Polymer models have been generated in more realistically by simulating the structural features and physical properties. Chemical structures of the investigated polymers and plasticizers are shown in Fig. Amorphous cells were built with minimum two chains to account for intra and inter chain interactions. Chain length was adjusted to match the experimental molecular weight of the polymers that are used in propellant industry. Microstructure of HTPB was considered while constructing HTPB system (54% trans, 26% cis and 20% vinyl). In case of plasticizer models, about 30 to 50 units were taken in the amorphous cells. Quality of the generated results are highly dependent on the final model on which the properties are calculated and hence, built cells were well relaxed and equilibrated using series of molecular dynamic simulations to avoid entrapment of simulated systems in a metastable state of local high-energy minima. These stages (NVT followed by NPT) of MD simulations provides thermal energy to cross-energy barriers between local minima. Molecular Models of NBR and BuNENA at first and last stage of simulation are shown in Figure 3.1 a & b. The final cell densities were carefully analyzed since they are related to physical properties of the material and further density can be employed as the criterion to decide whether the model successfully describes the relevant systems. Densities varied during NPT dynamics simulations and the system was allowed to evolve until the average density remains constant. Representative energy and density profile are shown in Fig 3.2 and Fig. 3.3 respectively.

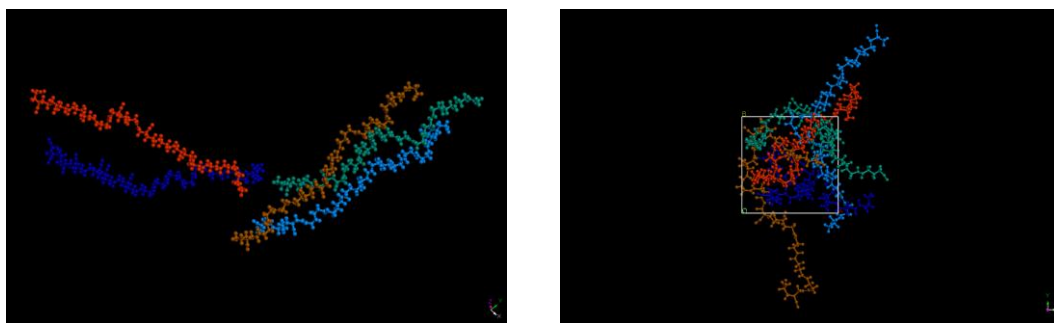


Fig. 3.1 a NBR polymer chain and its Equilibrated final model

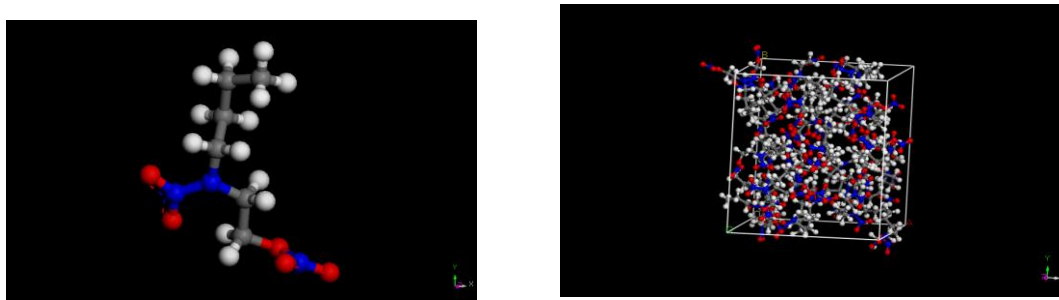


Fig. 3.1 b Structure of Butyl NENA and its Equilibrated final model

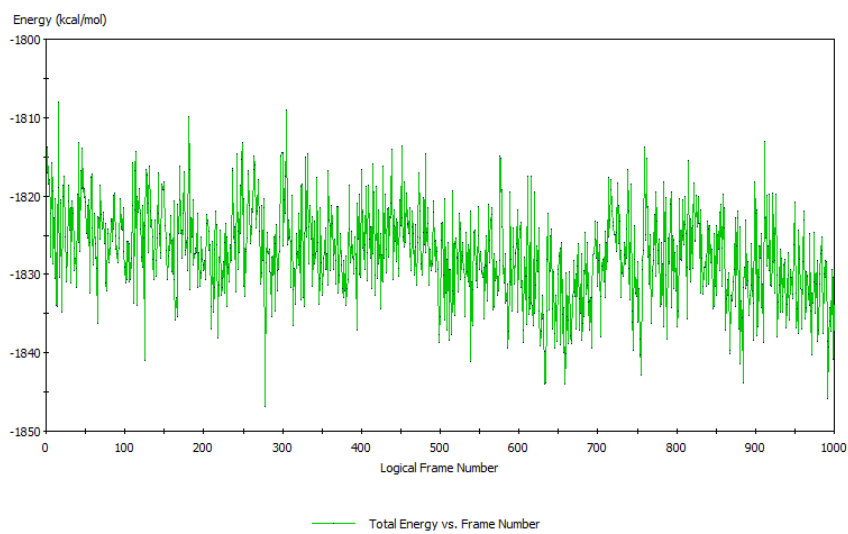


Fig. 3.2 Total potential energy vs frame numbers of simulated BuNENA system

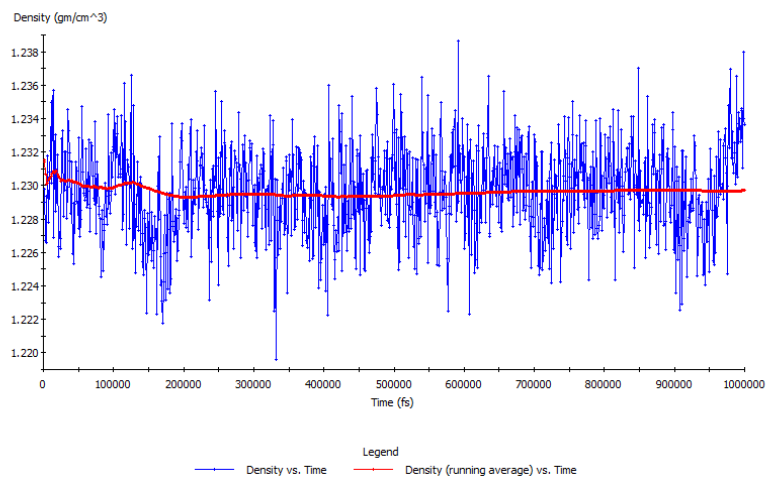


Fig. 3.3 Density vs Simulation Time of BuNENA system

Table 3.1 presents the average densities obtained from the MD simulations and compared with the experimental data. Plot of experimental versus simulated density shows a linear fit with R value of 0.988 (Fig. 3.4) which infers the good agreement in density. However, maximum about 5% deviation in density is seen in HTPB.

Table: 3.1. Comparison of experimental versus simulated density

Molecule	Density (g/cc)	
	Simulated	Experimental
HTPB	0.875	0.92
DOA	0.8759	0.925 @ 20°C
BTTN	1.5926	1.52
NBR	0.9627	0.98
SPG-255	1.1272	1.15
BuNENA	1.2297	1.22
DEGDN	1.3964	1.385
NG	1.6588	1.592
TEGDN	1.3604	1.327
TMETN	1.4921	1.488
HTPB-b-CP	0.9883	0.94

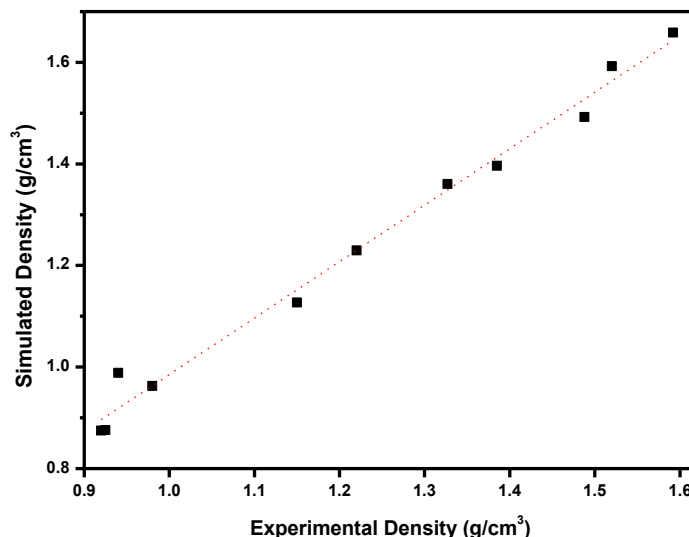


Fig.3.4 Plot of experimental versus simulated density

### 3.2 Prediction of Solubility Parameter

Miscibility between two substances is a consequence of their free energy of mixing  $\Delta G$  being negative. Thermodynamically free energy is function of enthalpy and entropy of mixing i.e.  $\Delta G = \Delta H - T\Delta S$ . Since last term  $T\Delta S$  is positive, sign of  $\Delta G$  is dominated by enthalpy of mixing and according to Hildebrand and Scott enthalpy of mixing is related to difference of solubility parameter as  $\Delta H = \phi_1 \phi_2 (\delta_1 - \delta_2)^2$ . Hence difference of solubility parameter of components is significant figure to determine miscibility. Predicted solubility parameter from the MD simulations is shown in Table 3.2 and it is average of the last 250ps data of production run of NPT-MD simulations. The total solubility parameter is arrived by the contribution from non-bonded van der Waal ( $\delta_{vdw}$ ) and electrostatic ( $\delta_{elec}$ ) interactions. Among the polymer data,  $\delta$  of NBR is very high while HTPB shows  $16.33 \text{ J}^{1/2}\text{cm}^{-3/2}$ . The introduction of 13 units of caprolactone at each hydroxy terminal of HTPB does not significantly alter the  $\delta$  of the virgin HTPB chain. In case of plasticizers, non-polar DOA shows a low value of  $\delta$  while all other posses more than  $20 \text{ J}^{1/2}\text{cm}^{-3/2}$ . Increasing polarity leads to increase in  $\delta$ . It is also observed that contribution from  $\delta_{elec}$  is significant in case of polar plasticizer/polymers. This is also



clearly seen in case of block copolymer of HTPB and caprolactone (HTPB-b-CP) where electrostatic contribution is doubled while no change in van der Waals component.

Table: 3.2 MD Simulated Solubility Parameter ( $\delta$ ) in  $J^{1/2}cm^{-3/2}$

System	Nomenclature	$\delta_{MD}$	$\delta_{vdw}$	$\delta_{ele}$
Polymers	HTPB	16.339	16.286	1.309
	SPG-255	18.314	17.672	4.807
	HTPB-b-CP	16.804	16.549	2.911
	NBR	19.062	17.765	6.907
Plasticizers	DOA	15.916	15.76	2.208
	BTTN	22.645	17.706	14.115
	BuNENA	19.578	16.981	9.742
	DEGDN	21.132	18.197	10.74
	NG	22.747	17.77	14.198
	TEGDN	21.901	19.165	10.597
	TMETN	19.765	16.524	10.839

### 3.3 Miscibility of Polymer and plasticizer

Interaction parameter  $\chi$  is also an important measure for miscibility of system of two components and for relative comparison of different polymer-plasticizer systems. In general, small value of Interaction parameter  $\chi$  indicates that at this particular temperature the molecules have a favourable interaction. It is likely that at this temperature a mixture of two components will show just one phase. If  $\chi$  is large, the molecules both prefer to be surrounded by similar components rather than each other. If the  $\chi$  value is high enough this contribution to free energy overcomes the combinatorial entropy and a mixture of the two components will separate into two phases. Polymer plasticizer Interaction parameter is also known as Flory-Huggins interaction parameter is calculated by following eq 3.1.

$$\chi = \chi_s + \left(\frac{V}{RT}\right)(\delta_1 - \delta_2)^2 \quad 3.1$$

This equation  $\chi_s$  is entropy contribution and the value of the same is usually considered as a constant [28]. The value of the same is taken as 0.34 in the present study. The second term in the above equation is originated from enthalpy contribution to overall value of  $\chi$ . The enthalpy contribution is a function of Hildebrand solubility

parameter of polymer and plasticizer. Hence, enthalpy contribution calculated from the difference between  $\delta$  of polymer and plasticizer is analyzed to reveal the compatibility of polymer with different plasticizers. The calculated enthalpy contribution term and

Table 3.3: Calculated Interaction Parameter of studied Polymer-Plasticizer system

<b>Polymer-Plasticizer system</b>	<b>Interaction Parameter, Enthalpy contribution <math>(V(\delta_1 - \delta_2)^2)/RT</math></b>	<b>Difference of <math>\delta</math> of polymer and plasticizer</b>
HTPB-DOA	<b>0.024</b>	<b>0.42</b>
HTPB-BuNENA	0.734	3.24
HPTB-TMETN	0.828	3.47
HTPB-DEGDN	1.332	4.79
HTPB-TEGDN	2.286	5.56
HTPB-BTTN	2.573	6.31
HTPB-NG	2.387	6.41
SPG-BuNENA	<b>0.109</b>	<b>1.26</b>
SPG-TMETN	<b>0.146</b>	<b>1.45</b>
SPG-DOA	<b>0.930</b>	<b>2.40</b>
SPG-DEGDN	<b>0.454</b>	<b>2.82</b>
SPG-TEGDN	0.939	3.587
SPG-BTTN	1.201	4.33
SPG-NG	1.130	4.43
NBR-BuNENA	<b>0.018</b>	<b>0.52</b>
NBR-TMETN	<b>0.036</b>	<b>0.70</b>
NBR DEGDN	<b>0.250</b>	<b>2.07</b>
NBR-TEGDN	<b>0.597</b>	<b>2.84</b>
NBR-DOA	1.580	3.15
NBR-BTTN	0.831	3.58
NBR-NG	0.790	3.69
HTPB-b-CP-DOA	<b>0.128</b>	<b>0.89</b>
HTPB-b-CP-BuNENA	<b>0.493</b>	<b>2.77</b>
HTPB-b-CP-TMETN	<b>0.606</b>	<b>2.96</b>
HTPB-b-CP-DEGDN	1.070	4.33
HTPB-b-CP-TEGDN	1.896	5.10
HTPB-b-CP-BTTN	2.184	5.84
HTPB-b-CP-NG	2.031	5.94

\* Solubility parameter calculated from MD simulations are used

difference in  $\delta$  are presented in Table 3.3 in a decreasing order of compatibility. The results of the well studied HTPB-plasticizer system clearly reveal the non-suitability of energetic plasticizer for the HTPB polymer. Earlier studies of Greenhalgh et al demonstrated that increasing degrees of immiscibility with increasing difference in solubility parameter between drug/carrier systems[11]. Further it is also reported that the difference in solubility parameter should not be more than  $1.3 - 2.1 \text{ J}^{1/2}\text{cm}^{-3/2}$ , for miscible combination. Based on the experimental facts, in the present study the difference of upto  $3 \text{ J}^{1/2}\text{cm}^{-3/2}$  is considered as a miscible system. Among the screened plasticizers, DOA shows the lowest interaction parameter with HTPB polymer where as BuNENA is the suitable plasticizer for SPG and NBR polymers. On the other hand, HTPB-caprolactone copolymer was investigated to improve the  $\delta$  of polymer so as to make it compatible with energetic plasticizer that posses high value of  $\delta$ . However, from the simulation studies, it is understood that HTPB-caprolactone copolymer(HTPB-b-CP), DOA is appears to be suitable plasticizer than other energetic plasticizers. Nevertheless, BuNENA and TMETN may be explored as plasticizer for the copolymer.

### **3.4 Experimental Evaluation of Solubility Parameter**

In order to validate the simulation data, experimental approaches were also attempted to evaluate the solubility parameter of the few polymers and plasticizers. Equilibrium swelling and intrinsic viscosity studies were carried out for partially cross linked and linear polymers respectively. In addition, Solvent spectrum method is also used for the determination of solubility parameter of NBR.

#### **3.4.1 Equilibrium Swelling Measurement**

The equilibrium swelling experiments were carried out for HTPB, GAP, SPG 255 and HTPB-b-CP copolymers. The recorded data of these polymers are shown in Table 3.4-3.11.

Maximum swelling observed in  $\text{CCl}_4$  solvent for HTPB with the ratio of 6.88. In case of GAP the solvent is NMP and swelling ratio is 6.73. Aniline is observed to be the best solvent for SPG 255 with swelling ratio of 6.05. HTPB-b-CP copolymer exhibited maximum swelling in chlorobenzene with the ratio of 10.8.

Table 3.4: Swelling Experiment 1. Swelling ratio data of Cross-linked HTPB  
(Density of HTPB,  $\rho=0.94\text{g/cc}$ )

Solvent	$\delta$ of solvents $\text{J}^{1/2}\text{cm}^{3/2}$	Density of solvent( $\rho$ ) g/cc	Un-swollen weight of sample $W_1$ (g)	Swollen weight of sample $W_2$ (g)	Average Swelling ratio Q
n-Pentane	14.3	0.626	S1=0.13518 S2=0.22641	S1=0.2336 S2=0.39775	2.11
n-Heptane	15.1	0.684	S1=0.12935 S2=0.21503	S1=0.27355 S2=0.4494	2.51
Cyclohexane	16.77	0.779	S1=0.15119 S2=0.19674	S1=0.5828 S2=0.7575	4.44
Carbon Tetrachloride	17.59	1.594	S1=0.16098 S2=0.20558	S1=1.7629 S2=2.2621	6.88
Toluene	18.2	0.865	S1=0.16518 S2=0.23871	S1=0.976 S2=1.41138	6.34
Dichloromethane	19.84	1.325	S1=0.1761 S2=0.23066	S1=1.1039 S2=1.31677	4.54
Ethylenedichloride	20.04	1.256	S1=0.11362 S2=0.18154	S1=0.58132 S2=0.9374	4.10
1,4 Dioxane	20.5	1.034	S1=0.11759 S2=0.17511	S1=0.40607 S2=0.60375	3.23
Aniline	21.1	1.022	S1=0.16191 S2=0.18501	S1=0.23967 S2=0.25188	1.39
N-methyl pyrrolidinone	23.1	1.028	S1=0.13559 S2=0.15154	S1=0.23059 S2=0.25228	1.62
Acetonitrile	24.1	0.786	S1=0.10359 S2=0.15546	S1=0.1161 S2=0.17145	1.13

Table 3.5:  $[Q^{-1} \ln(Q_{\max} / Q)]^{1/2}$  of HTPB and Solubility parameter of solvents

Solvents	Solubility parameter $J^{1/2}cm^{3/2}$	$[Q^{-1} \ln(Q_{\max} / Q)]^{1/2}$
n-Pentane	14.3	0.7469
n-Heptane	15.1	0.6426
Cyclohexane	16.77	0.3138
CCl <sub>4</sub>	17.59	0
Toluene	18.2	-0.114
Dichloromethane	19.84	-0.3027
Ethylendichloride	20.04	-0.355
1-4 Dioxane	20.5	-0.4842
Aniline	21.1	-0.2516
N-methyl pyrrolidinone	23.1	-0.9427
Acetonitrile	24.1	-1.2611

Table 3.6: Swelling Experiment 2. Swelling ratio data of Cross-linked GAP (Density of GAP =1.266g/cc)

Solvent	$\delta$ of solvents $J^{1/2}cm^{3/2}$	Density of solvent( $\rho$ ) g/cc	Un-swollen weight of sample $W_1$ (mg)	Swollen weight of sample $W_2$ (mg)	Average Swelling ratio Q
Cyclohexane	16.77	0.779	S1=247.65 S2=119.2	S1=287.9 S2=140.5	1.28
Carbon Tetrachloride	17.59	1.594	S1=188.29 S2=125.43	S1=296.29 S2=196.4	1.45
Toluene	18.2	0.865	S1=211.67 S2=99.15	S1=328.6 S2=151.92	1.79
Chlorobenzene	19.4	1.306	S1=191.31 S2=138.96	S1=504.8 S2=346.71	2.52
1-4 Dioxane	20.5	1.034	S1=203.33 S2=105.26	S1=783.23 S2=366.49	4.27
Aniline	21.1	1.022	S1=276.89 S2=110.1	S1=1152.38 S2=460.07	4.93
N-methyl pyrrolidinone	23.1	1.028	S1=218.4 S2=104.7	S1=1241.92 S2=588	6.73
Nitromethane	26	1.127	S1=218.91 S2=70.46	S1=744.6 S2=240.8	3.71
Propylene-1-2 carbonate	27.2	1.204	S1=267.58 S2=90.52	S1=952 S2=325.2	3.71

Table 3.7 :  $[Q^{-1} \ln(Q_{\max}/Q)]^{1/2}$  of GAP and Solubility parameter of solvents

Solvents	Solubility parameter $J^{1/2}cm^{3/2}$	$[Q^{-1} \ln(Q_{\max}/Q)]^{1/2}$
Cyclohexane	16.77	1.1407
Carbon Tetrachloride	17.59	1.0267
Toluene	18.2	0.8586
Chlorobenzene	19.4	0.6246
1-4 Dioxane	20.5	0.327
Aniline	21.1	0.2516
N-methyl pyrrolidinone	23.1	0
Nitromethane	26	-0.4011
Propylene-1-2 carbonate	27.2	-0.401

Table 3.8: Swelling Experiment 3. Swelling ratio data of Cross-linked SPG-255 (Density of SPG255=1.15g/cc)

Solvent	$\delta$ of solvents $J^{1/2}cm^{3/2}$	Density of solvent( $\rho$ ) g/cc	Un-swollen weight of sample $W_1$ (mg)	Swollen weight of sample $W_2$ (mg)	Average Swelling ration Q
n-Pentane	14.3	0.626	S1=112.3 S2=80.86	S1=115.31 S2=83.5	1.054
n-Heptane	15.1	0.684	S1=255.78 S2=73.4	S1=262.58 S2=76.51	1.0579
Cyclohexane	16.77	0.779	S1=160.77 S2=68.03	S1=174.17 S2=73.65	1.1224
CCl <sub>4</sub>	17.59	1.594	S1=238.05 S2=138.45	S1=904.18 S2=514.18	2.9883
Toluene	18.2	0.865	S1=250.17 S2=75.69	S1=804.75 S2=242.94	3.9424
Chlorobenzene	19.4	1.306	S1=177.8 S2=140.05	S1=852 S2=668.35	4.33
Dichloromethane	19.84	1.325	S1=126.8 S2=64.7	S1=789 S2=397.7	5.5322
Aniline	21.1	1.022	S1=244.36 S2=84.96	S1=1341.37 S2=465.74	6.047
Nitroethane	22.7	1.045	S1=105.55 S2=82.75	S1=378.2 S2=300.94	3.8722
NMP	23.1	1.028	S1=161.08 S2=67.2	S1=650.36 S2=271.65	4.4
Acetonitrile	24.1	0.786	S1=175.73 S2=147.11	S1=332.2 S2=280.8	2.316
Propylene-1-2 carbonate	27.2	1.204	S1=180.05 S2=76.99	S1=416.1 S2=179.78	2.2637

Table 3.9:  $[Q^{-1} \ln(Q_{\max} / Q)]^{1/2}$  of SPG 255 and Solubility parameter of solvents

<b>Solvents</b>	<b>Solubility Parameter <math>J^{1/2} \text{cm}^{3/2}</math></b>	<b><math>[Q^{-1} \ln(Q_{\max} / Q)]^{1/2}</math></b>
n-Pentane	14.3	1.286866
n-Heptane	15.1	1.283652
Cyclohexane	16.77	1.2248
Carbon Tetrachloride	17.59	0.48567
Toluene	18.2	0.3294
Chlorobenzene	19.4	0.2777
DCM	19.84	0.1313
Aniline	21.1	0
Nitroethane	22.7	-0.3393
N-methyl pyrrolidinone	23.1	-0.26875
Acetonitrile	24.1	-0.64369
Propylene-1-2 carbonate	27.2	-0.6588



Table 3.10: Swelling Experiment 4. Swelling ratio data of Cross-linked HTPB-b-PC (Density of polymer=0.94g/cc)

Solvent	$\delta$ of solvents $J^{1/2}cm^{3/2}$	Density of solvent( $\rho$ ) g/cc	Un-swollen weight of sample $W_1$ (mg)	Swollen weight of sample $W_2$ (mg)	Average Swelling ratio Q
n-Pentane	14.3	0.626	S1=216.5 S2=70.44	S1=328.81 S2=107.36	1.783
n-Heptane	15.1	0.684	S1=267.36 S2=73.32	S1=355 S2=137.46	1.826
Cyclohexane	16.77	0.779	S1=174.26 S2=74.52	S1=713.28 S2=300.59	4.696
Carbon Tetrachloride	17.59	1.594	S1=209.76 S2=64.93	S1=3586.7 S2=1064	10.284
Toluene	18.2	0.865	S1=195.7 S2=70.23	S1=1958.52 S2=688.86	10.68
Chlorobenzene	19.4	1.306	S1=182.93 S2=53.98	S1=2695.6 S2=785.4	10.82
Dichloromethane	19.84	1.325	S1=266.56 S2=110.71	S1=3719 S2=1545.1	10.19
1-4 Dioxane	20.50	1.034	S1=207.69 S2=80.85	S1=2032.8 S2=707.68	8.518
Aniline	21.1	1.022	S1=256.22 S2=81.3	S1=1221.14 S2=368.85	4.358
Nitroethane	22.7	1.045	S1=198.78 S2=81.27	S1=337.54 S2=136.5	1.62
Acetonitrile	24.1	0.786	S1=208.71 S2=62.8	S1=239.11 S2=72.24	1.177
Nitromethane	26	1.127	S1=230.15 S2=81.33	S1=710 S2=109.34	2.013
Propylene-1-2 carbonate	27.2	1.204	S1=219.22 S2=85.79	S1=253.26 S2=98.32	1.114

Table 3.11:  $[Q^{-1} \ln(Q_{\max}/Q)]^{1/2}$  of HTPB-b-CP and Solubility parameter of solvents

Solvents	Solubility Parameter, $(J/cm^3)^{1/2}$	$[Q^{-1} \ln(Q_{\max}/Q)]^{1/2}$
n-Pentane	14.3	1.0056
n-Heptane	15.1	0.9869
Cyclohexane	16.77	0.4215
Carbon Tetrachloride	17.59	0.0727
Toluene	18.2	0.0348
Chlorobenzene	19.4	0
DCM	19.84	-0.0767
1-4 Dioxane	20.5	-0.1675
Aniline	21.1	-0.4567
Nitroethane	22.7	-1.0828
Acetonitrile	24.1	-1.373
Nitromethane	26	-0.9139
Propylene-1-2 carbonate	27.2	-1.4252

Fig. 3.5 shows the relationship between swelling ratio of different polymers and the solubility parameter of various solvents. In all the cases Gaussian distribution is achieved and observed the  $Q_{\max}$  of 6.88 in  $CCl_4$  for HTPB. Similarly, maximum swelling was achieved in NMP, aniline, chlorobenzene for GAP, SPG-255 and HTPB-b-CP respectively. Plot of  $\pm [Q^{-1} \ln(Q_{\max}/Q)]^{1/2}$  against  $\delta_{\text{solvent}}$  for various polymers is shown in Fig. 3.6 Linear fit was achieved in all the cases, solubility parameter of each system is obtained from the intercept. Graphically obtained values of solubility parameters are 17.97, 23.62, 21.33, 18.97  $(J/cm^3)^{1/2}$  for HTPB, GAP, SPG-255 and HTPB-b-CP respectively. Analysis of the results reveals that the solubility parameter increases with increasing polarity of the polymer. Solubility parameter of energetic plasticizer, DEGDN which cannot be estimated by the conventional methods was also achieved by the above swelling method. Polymer of known solubility parameter was swollen in DEGDN to calculate its swelling ratio. The achieved value of DEGDN solubility parameter is 25.38  $(J/cm^3)^{1/2}$ . To best of our knowledge, no experimental report on the solubility parameter of DEGDN is found and it is determined for the first time in this study. Similarly, solubility parameter of DOA is also determined and it is comparable with reported values [5].

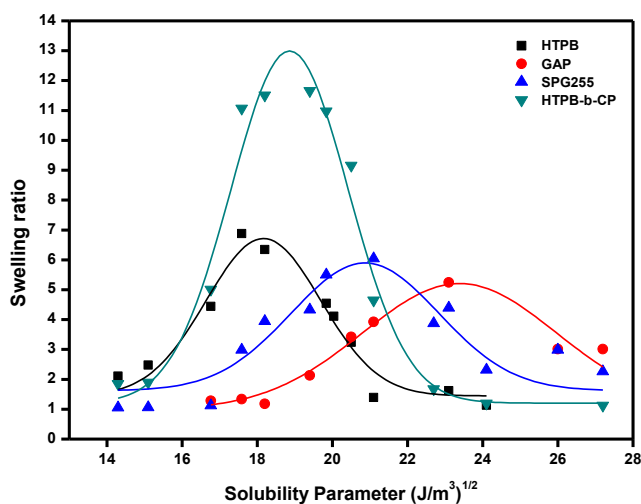


Fig. 3.5 Swelling Ratio Vs Solubility Parameter of Solvents

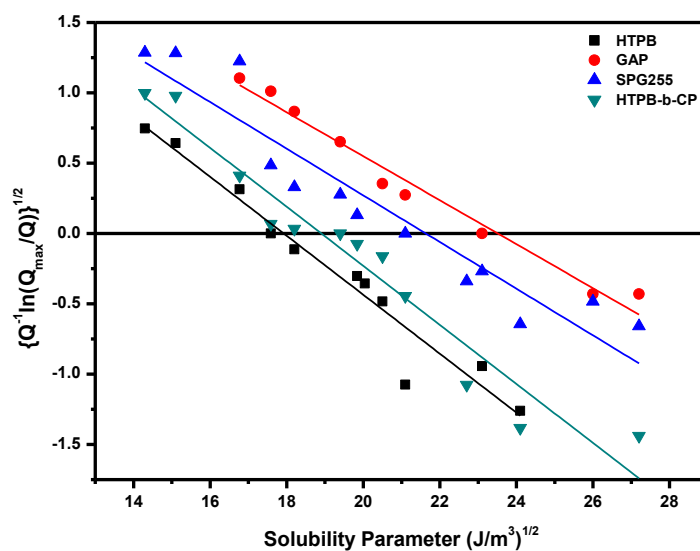


Fig. 3.6  $[Q^{-1} \ln(Q_{\max}/Q)]^{1/2}$  vs Solubility parameter

### 3.4.2 Intrinsic Viscosity Studies

Hydroxy Terminated Polybutadiene (HTPB) solution is made in toluene, heptane, cyclohexane, chlorobenzene and 1,4-dioxane. The flow time, relative viscosity, specific viscosity and intrinsic viscosity values for HTPB in various solvents are shown in Table 3.12-3.16 and the  $[\eta]$  versus concentration plots are shown in Fig. 3.7 – 3.11. Intrinsic

viscosity is obtained as intercept of straight line on vertical axis, is shown in Table 3.17 for different solvents. All measurement of HTPB solution flow time is recorded on viscometer of size A.

Table 3.12: Viscosity data of HTPB-Toluene solution, Solvent flow time ( $t_s$ ): 203.9s

Conc. C (g/dl)	Flow time, t, (s)	Relative Vis. $\eta_r = t/t_s$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
0.5028	220.3	1.080	0.080	0.160	0.0773	0.1538
1.011	235.1	1.153	0.153	0.151	0.1423	0.1408
1.5004	250.1	1.227	0.227	0.151	0.2043	0.1361
2.0102	270.3	1.325	0.325	0.162	0.2817	0.1402
3.0148	313.7	1.538	0.538	0.179	0.4308	0.1429
4.096	363.6	1.783	0.783	0.191	0.5783	0.1412

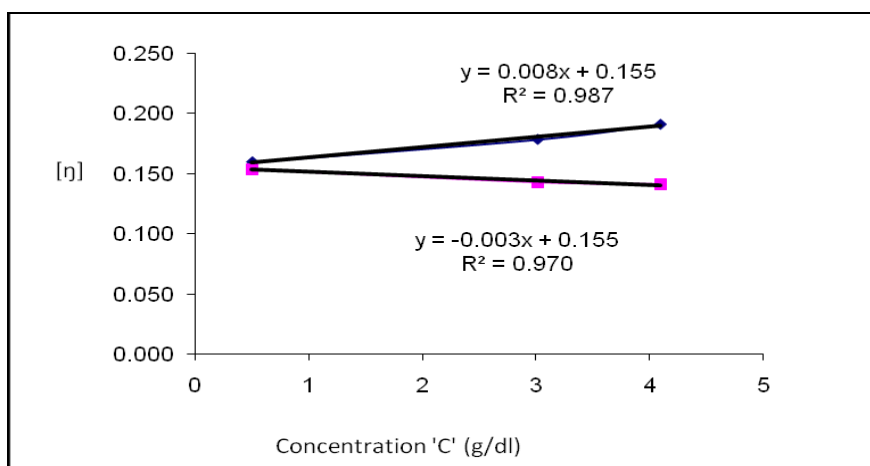


Fig 3.7:  $[\eta]$  vs Concentration plot of HTPB in Toluene

Table 3.13: Viscosity data of HTPB-Cyclohexane solution, Solvent flow time ( $t_s$ ): 366.2 s

Conc. C (g/dl)	Flow time, t, (s)	Relative Vis. $\eta_r = t/t_s$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
1.01424	409.80	1.119	0.119	0.117	0.1126	0.111
1.8204	465.4	1.271	0.271	0.149	0.2398	0.1317
2.5356	505.3	1.380	0.380	0.150	0.3221	0.1270
3.04272	557.3	1.522	0.522	0.172	0.4199	0.1380
3.54984	593.6	1.621	0.621	0.175	0.4831	0.1361
4.5614	669.1	1.827266	0.827	0.181	0.6028	0.1322

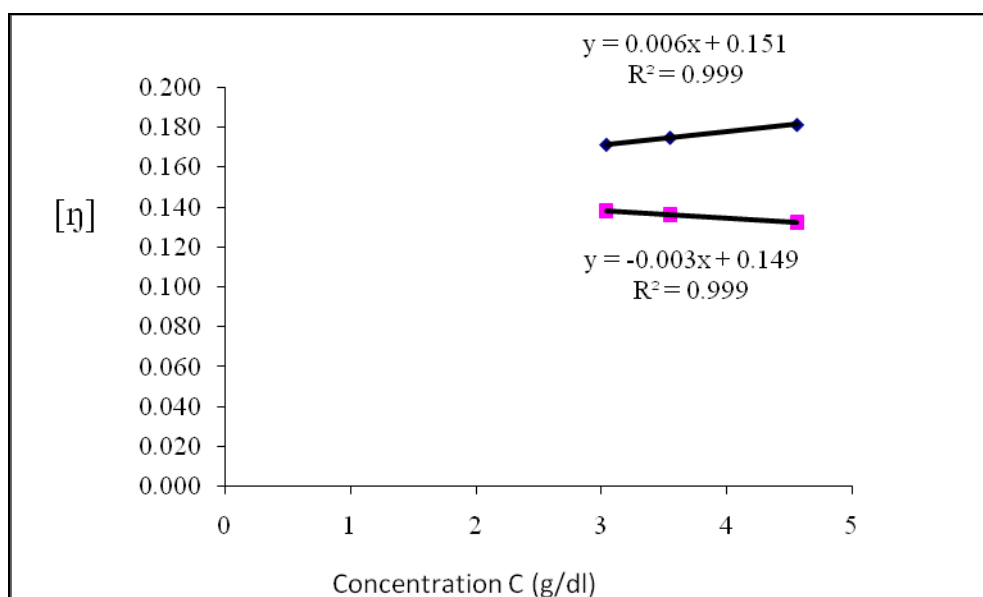


Fig 3.8:  $[\eta]$  vs Concentration plot of HTPB in Cyclohexane

Table 3.14: Viscosity data of HTPB-n-Heptane solution, Solvent flow time ( $t_s$ ): 177.6 s

Conc. C (g/dl)	Flow time, $t_r$ (s)	Relative Vis. $\eta_r = t/t_s$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
0.5	189.1	1.065	0.065	0.130	0.0629	0.1258
1	200.3	1.128	0.128	0.128	0.1207	0.1207
1.5	213.9	1.205	0.205	0.137	0.1864	0.1243
2	1.276	1.522	0.276	0.138	0.2441	0.1221
5.9914	379.2	2.136	1.136	0.190	0.7587	0.1266

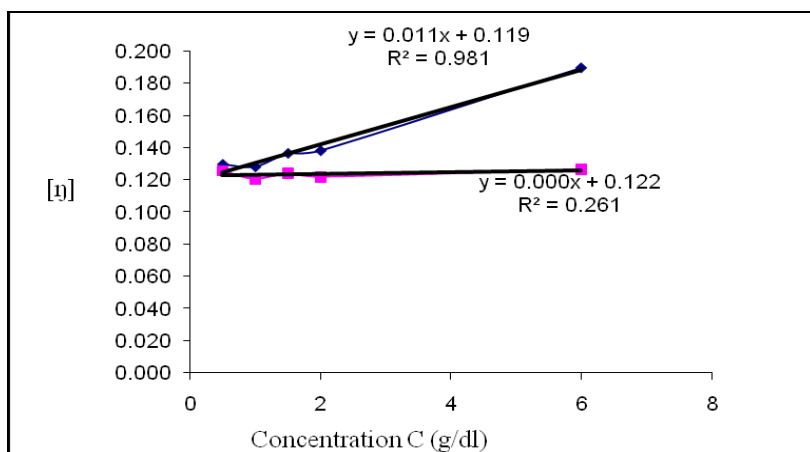


Fig. 3.9:  $[\eta]$  vs Concentration plot of HTPB in Heptane

Table 3.15: Viscosity data of HTPB-Chlorobenzene solution, Solvent flow time ( $t_s$ ): 215.8s

Conc. C (g/dl)	Flow time, t, (s)	Relative Vis. $\eta_r = t/t_s$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
0.9694	247.41	1.146	0.146	0.151	0.137	0.141
1.9388	285.3	1.322	0.322	0.166	0.279	0.144
2.9081	328.8	1.524	0.524	0.180	0.421	0.145
3.8775	380.0	1.761	0.761	0.196	0.566	0.146
4.8469	434.8	2.014	1.014	0.209	0.700	0.144
6.0586	504.8	2.339	1.339	0.221	0.850	0.140

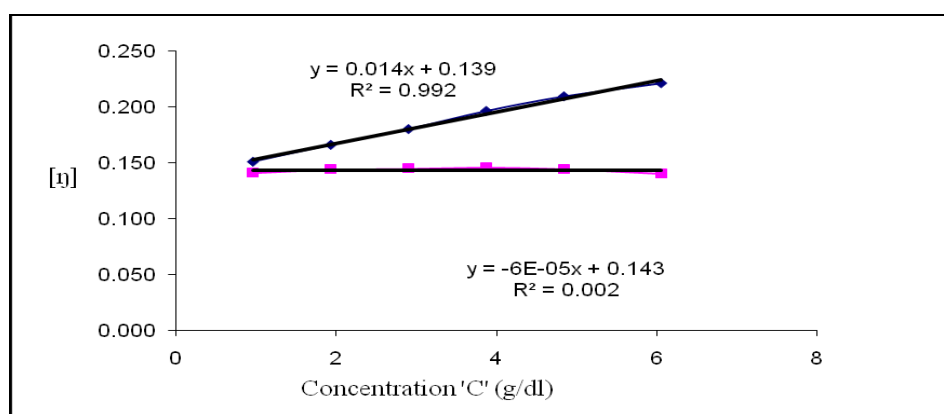


Fig 3.10:  $[\eta]$  vs Concentration plot of HTPB in Chlorobenzene

Table 3.16 Viscosity data of HTPB-1,4- Dioxane solution, Solvent flow time ( $t_s$ ): 378.6s

Conc. C (g/dl)	Flow time, t, (s)	Relative Vis. $\eta_r = t/t_s$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
1.1120	442.78	1.170	0.170	0.152	0.1566	0.1409
2.2239	505.6	1.335	0.335	0.151	0.2893	0.1301
3.3359	569.8	1.505	0.505	0.151	0.4089	0.1226
4.4478	639.5	1.689	0.689	0.155	0.5243	0.1179
5.4116	712.0	1.881	0.881	0.163	0.6316	0.1167

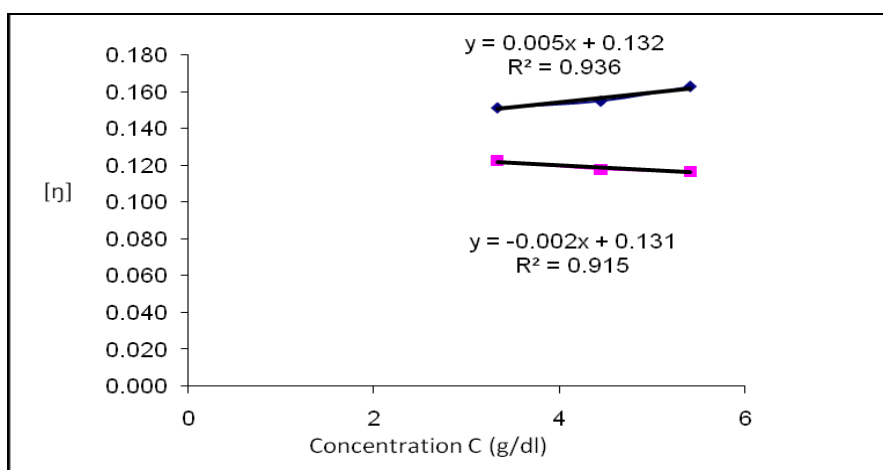


Fig 3.11:  $[\eta]$  vs Concentration plot of HTPB in 1,4- dioxane

Table 3.17: Intrinsic Viscosity of HTPB in Different Solvents

Solvents	Solubility parameter $(J/cm^3)^{1/2}$	$[\eta]$ (dl/g)	$[\eta]^{-1} \ln([\eta_{max}]/[\eta])$
n-heptane	15.1	0.119	1.4903
Cyclohexane	16.77	0.152	0.3586
Toluene	18.2	0.155	0
Chlorobenzene	19.4	0.139	-0.8853
1,4- dioxane	20.5	0.1327	-1.0819

Table 3.17 shows intrinsic viscosity values of HTPB in different solvents. Maximum viscosity is found in toluene, it reveals that polymer chain size is maximum due to uncoiled structure.

### Intrinsic Viscosity studies on SPG-255

The flow time, relative viscosity, specific viscosity and intrinsic viscosity values for SPG-255 in various solvents are shown in Table 3.18-3.22 and the Intrinsic viscosity versus concentration plots are shown in Fig. 3.12 – 3.16.

Table 3.18 : Viscosity data of SPG 255-Toluene Solution (Flow time of Toluene:214.5s in Ostwald viscometer, Size: A)

Conc. C (g/dl)	Flow time, t, (s)	Relative Vis. $\eta_r = t/t_s$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
1.0328	248.93	1.16	0.16	0.155	0.1486	0.144
2.0332	298.5	1.391	0.391	0.192	0.3301	0.1624
3.016	361	1.683	0.683	0.226	0.5208	0.1725
4.0612	427.2	1.991	0.991	0.244	0.688	0.1696
5.0036	496.1	2.313	0.313	0.262	0.6888	0.1675

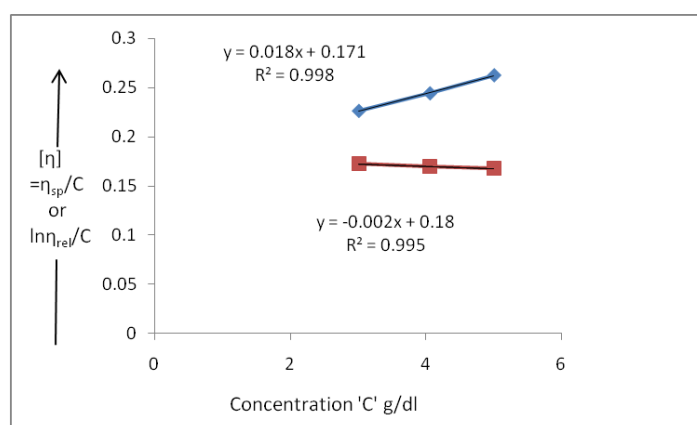


Fig 3.12: Intrinsic Viscosity of SPG-255,  $[\eta]$  vs Concentration in toluene



Table 3.19: Viscosity data of SPG-255-Chlorobenzene (Flow time of Chlorobenzene: 217.5s in Ostwald viscometer, Size: A)

Conc. C (g/dl)	Flow time, t, (s)	Relative Vis. $\eta_r = t_s/t$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
1.0292	269.77	1.24	0.24	0.233	0.215	0.2092
2.0036	330.8	1.521	0.521	0.260	0.419	0.2093
3.0196	401	1.843	0.843	0.279	0.611	0.2025
3.962	478.9	2.202	1.202	0.303	0.789	0.1992

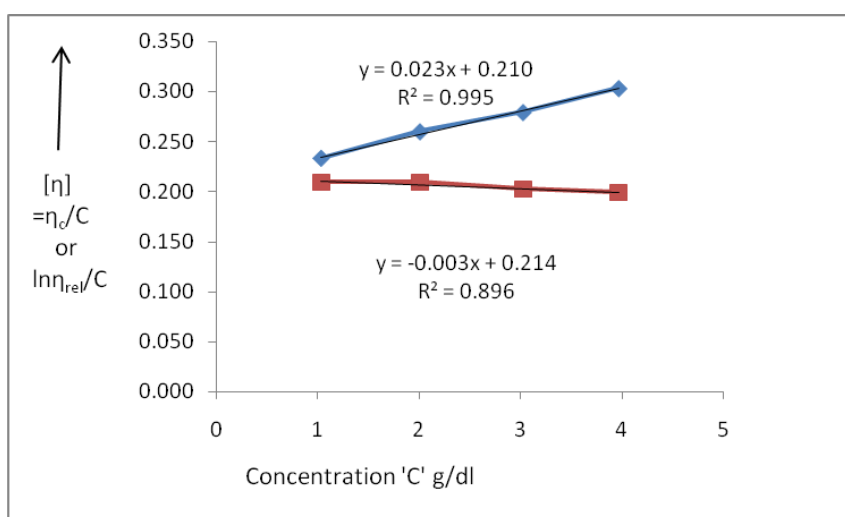


Fig 3.13: Intrinsic Viscosity of SPG-255,  $[\eta]$  vs Concentration in chlorobenzene

From Fig 3.13, Intrinsic viscosity of SPG-255 in chlorobenzene is 0.210 dl/g.

Flow time of 1,4-dioxane in viscometer of size A was very high, Size B was selected to evaluate the intrinsic viscosity of SPG-255.

Table 3.20: Viscosity data of SPG 255-1,4-Dioxane Solution (Flow time of 1,4-Dioxane :101.2s in Ostwald viscometer, Size: B)

Conc. C (g/dl)	Flow time, t, (s)	Relative Vis. $\eta_r = t_s/t$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
1.008	124.94	1.235	0.235	0.233	0.211031	0.2094
2.0204	152.8	1.511	0.511	0.253	0.412589	0.2042
3.0188	183.2	1.811	0.811	0.269	0.593667	0.1996
4.2884	228.1	2.255	1.255	0.293	0.813157	0.1896

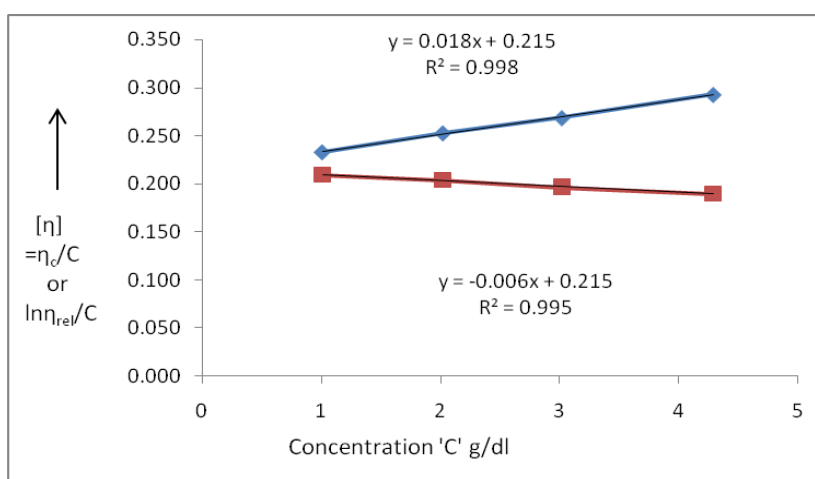


Fig 3.14: Intrinsic Viscosity of SPG-255,  $[\eta]$  vs Concentration in 1,4-Dioxane

Intrinsic viscosity of SPG-255 evaluated in 1,4-Dioxane and it's value is 0.215 dl/g.

Table 3.21: Viscosity data of SPG 255-Aniline Solution (Flow time of Aniline: 309.5 s in Ostwald viscometer, Size: A)

Conc. C (g/dl)	Flow time, t, (s)	Relative Vis. $\eta_r = t_s/t$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
0.964	383.05	1.237	0.237	0.246	0.2131	0.221
1.928	471	1.522	0.522	0.271	0.4199	0.2177
2.892	569.1	1.839	0.839	0.29	0.6090	0.2106
3.856	683	2.206	1.206	0.313	0.7914	0.2052

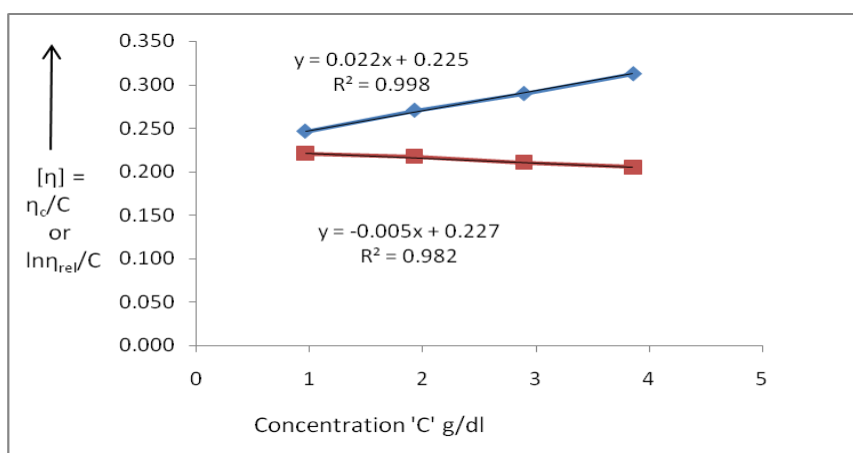


Fig 3.15: Intrinsic Viscosity of SPG-255,  $[\eta]$  vs Concentration in Aniline

Table 3.22: Viscosity data of SPG 255-Acetonitrile (Flow time of Acetonitrile :141.7s in Ostwald viscometer, Size: A)

Conc. C (g/dl)	Flow time, t, (s)	Relative Vis. $\eta_r = t_s/t$	Spec. Vis. $\eta_c = \eta_r - 1$	$\eta_c/C$	$\ln \eta_r$	$(\ln \eta_r)/C$
0.9865	162.98	1.15	0.15	0.152	0.14012	0.1421
1.9729	184.2	1.5	0.5	0.152	0.262359	0.133
2.959	217	1.532	0.532	0.18	0.4263	0.1441
3.945	249.5	1.761	0.761	0.193	0.565758	0.1434
6.165	341.6	2.412	1.412	0.229	0.880257	0.1428

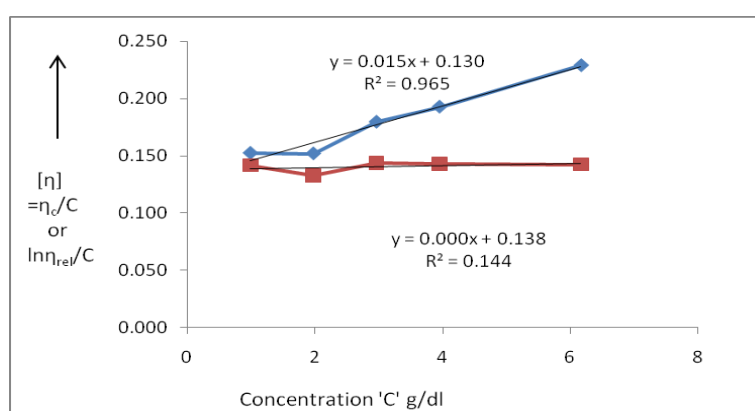


Fig 3.16: Intrinsic Viscosity of SPG-255,  $[\eta]$  vs Concentration in Acetonitrile

Table 3.23 shows the intrinsic viscosity of SPG-255 in different solvents, from the analysis of this data, intrinsic viscosity in aniline is found maximum.

Table 3.23:  $([\eta]^{-1} \ln([\eta]_{\max}/[\eta]))$  vs solubility parameter data of SPG 255

Solvents	Intrinsic Viscosity $[\eta]$ (dl/g)	$\delta$ (J/cm <sup>3</sup> ) <sup>1/2</sup>	$[\eta]^{-1} \ln([\eta]_{\max}/[\eta])$
Toluene	0.18	18.2	1.1134
Chlorobenzene	0.21	19.4	0.5732
Dioxane	0.215	20.5	0.4598
Aniline	0.225	21.1	0
Acetonitrile	0.13	24.1	-2.0542

Solubility parameter by intrinsic viscosity method is similar to the equilibrium swelling methods; however, this can be applied to polymers that are not cross-linked and highly soluble in the solvents. Intrinsic viscosity  $[\eta]$  is a measure of the size of a polymer molecule in solution, a high value of  $[\eta]$  is realized in a good solvent which induces pronounced polymer-solvent interactions and chain extension. When considering group of liquids for solvent power towards polymer, solvent that possess solubility parameter closest to the polymer is the best among the group.

Plot of  $[\eta]$  versus  $\delta_{\text{solvent}}$  for HTPB and SPG255 polymers are shown in Fig. 3.17. Similar to the swelling experiments, Gaussian distribution is achieved with the  $[\eta]_{\max}$  of 0.155dl/g for HTPB and 0.225dl/g for SPG. Best solvent identified to be toluene for HTPB and aniline for SPG255. Further plot of  $\pm([\eta]^{-1} \ln([\eta]_{\max}/[\eta]))^{1/2}$  against  $\delta_{\text{solvent}}$  results in straight line and solubility parameter polymer is determined from the intercept (Fig. 3.18). The obtained  $\delta$  of HTPB and SPG255 are 17.95 and 20.71 (J/cm<sup>3</sup>)<sup>1/2</sup> respectively.

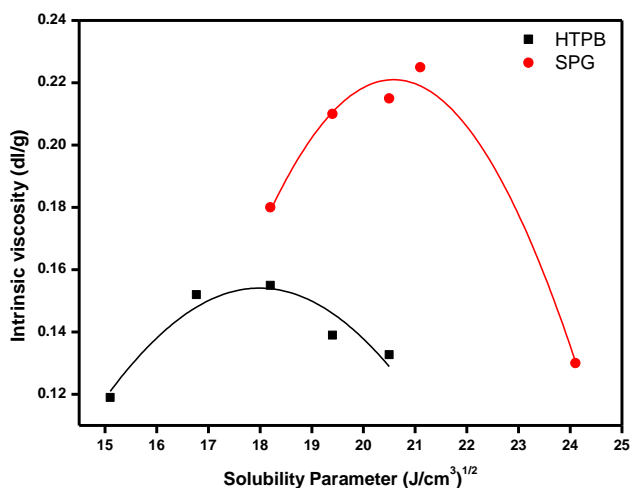


Fig 3.17 . Intrinsic Viscosity Vs solubility parameter of solvents

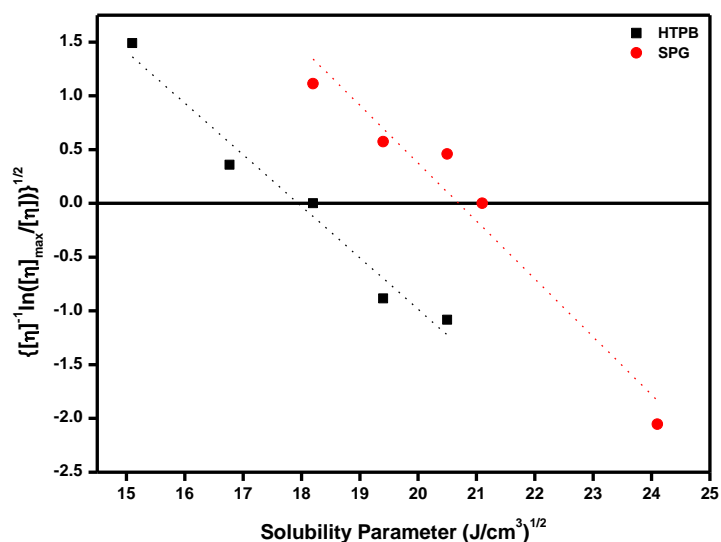


Fig 3.18.  $[\eta]^{-1} \ln([\eta]_{\max}/[\eta])$  Vs solubility parameter of solvents

### 3.4.3 Solubility Parameter evaluation of NBR by Solvent Spectrum

Solubility parameter of Nitrile butadiene rubber was not achieved through swelling and viscosity methods and it was determined through solvent spectrum method. NBR found completely miscible in chlorobenzene, dichloromethane, 1,4-dioxane, aniline, NMP and shows partial miscibility in acetonitrile. In toluene,  $\text{CCl}_4$ , cyclohexane, heptane, the polymer was found completely immiscible. Hence it can be inferred that the solubility parameter of the polymer exists in between  $19.4 - 23.1 (\text{J}/\text{cm}^3)^{1/2}$ . Hence,

midpoint of this miscible range ( $21.25 \text{ (J/cm}^3)^{1/2}$ ) is noted as the solubility parameter of NBR qualitatively.

### 3.5 Comparison of Experimental and Simulation Data

MD simulated solubility parameter of studied systems are compared with reported and our experimental data in Table 3.24. Solubility parameter determined from equilibrium swelling and intrinsic viscosity studies are close to each other which show the applicability of these methods in evaluation of  $\delta$ . Further, it infers that  $\delta$  does not change significantly if the linear polymer is partially cross linked. Solubility parameter determined from our studies is well correlates with reported results. Comparison of experimental and predicted  $\delta$  show minor deviation and the deviation increases as the polarity of the polymer/plasticizer increases. Predicted value of DOA overlaps well with experimental results. Recently, Arenaza et al. reported that MD simulation using COMPASS forcefield underestimates the strength of intermolecular interactions. It is also understood that parameterization of COMPASS force field is done by low molecular weight compounds which may explain some of the observed deviations[Ref]. Further, it important to highlight that comparison with experimental results is difficult because the model systems inherently lack of some details/defects which may be present actual/real polymers. However, predicted properties from simulations are still in good agreement in reproducing the proper trend.

Table 3.24: Experimental value of solubility parameter for comparison

<b>Polymer/ Plasticizer</b>	<b><math>\delta \text{ (J/cm}^3)^{1/2}</math> Equilibrium Swelling</b>	<b><math>\delta \text{ (J/cm}^3)^{1/2}</math> Intrinsic viscosity</b>	<b><math>\delta \text{ (J/cm}^3)^{1/2}</math> Reported Exp. values</b>	<b><math>\delta_{MD} \text{ (J/cm}^3)^{1/2}</math></b>
HTPB	17.97	17.95	16.6-17.6	16.34
GAP	23.62		22.5	-----
SPG-255	21.327	20.706	21	18.31
NBR	----	21.2 <sup>a</sup>		19.04
HTPB-b-CP	18.97	---		16.8
DEGDN	25.38	----		21.12
DOA	16.158	----	17.6-19	15.92

<sup>a</sup>: solubility parameter of NBR evaluated by solvent spectrum

#### 4. General Summary

Polymeric binder is the vital component in Composite propellants. It makes a cross-linked network to withhold all ingredients inside matrix of composite, play a vital role in maintaining the structural integrity. Efficiency of the binder depends on the right selection of polymer and plasticizer. Recent developments in rocket propellants demand composite propellants to have high energy, sufficient structural integrity and low temperature capability to qualify for application in propulsion system. Polymer-plasticizer contributes to all the above three important characteristic of propellant. But the contribution of each ingredient can be exploited only when these systems are miscible otherwise immiscible system will not be homogeneous, the phase separation will take place. Hence, the screening of plasticizer and polymer need to be done rigorously to get most suitable combination.

The present study addresses the miscibility studies on polymer-plasticizer systems that are employed in composite propellants. Classical mechanics based Molecular dynamics simulations have been attempted to predict the solubility parameter of polymers and plasticizers. The same has also been determined by experimental methods which include Equilibrium swelling studies, intrinsic viscosity studies and solvent spectrum methods.

The solubility parameter of the polymers, HTPB, NBR, SPG-255, HTPB-b-CP copolymer and plasticizers, NG, DOA, DEGDN, BTTN, TEGDN, BuNENA, TMETN have been simulated by molecular dynamics using COMPASS forcefield. Equilibrium swelling method has been employed for partially cross-linked HTPB, GAP, SPG-255 and HTPB-b-CP and the solubility parameter of these polymers are 17.97, 23.62, 21.33 and 18.97  $\text{J}^{1/2}\text{cm}^{-3/2}$  respectively. Alternatively, in order to find out the solubility parameter of linear polymers, HTPB and SPG-255, intrinsic viscosity measurements have been carried out in different solvents. The results from both experimental methods reveals that there is no significant change in solubility parameter value of linear and cross-linked polymer of same backbone. Solubility parameter of NBR is evaluated by solvent spectrum method and value of solubility parameter found to be about 21.2  $\text{J}^{1/2}\text{cm}^{-3/2}$ . Analysis of solubility and interaction parameters reveals that NBR and SPG-255 are miscible in some of energetic plasticizers (BuNENA, DEGDN, and TMETN) while, HTPB is immiscible with most of the energetic plasticizers. It is also inferred that

introduction of CP unit to HTPB improves the solubility parameter in case of HTPB-b-CP and hence, energetic BuNENA may exhibit miscibility with the copolymer system.

MD simulated solubility parameters of polymers/plasticizers are found to be less compared to corresponding experimental values. The deviation in simulated and experimental values increases when polarity of the molecules increases. However, predicted properties from simulations are still in good agreement in reproducing the proper trend.

Overall, this study helps to choose the most suitable plasticizer for a given polymer, which is an initial step for achieving successful propellant formulations. In future, further attempts will be made to copolymerize HTPB with polar co-monomers which can be right approach to make HTPB more energetic and also to miscible with energetic plasticizers.



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