Science and Technology of Polymers
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Lecture - 14
Structure and Properties of Polymers (Contd.)

Shall we see there is a profound influence of this hydrogen bonding in polymer molecules on this solubility, on the melting behaviour, on the mechanical properties, on the processability. So, in case of nylons, in case of cellulose, in case of polyacrylonitrile; that means a polymer if it contains some polar atoms like oxygen, nitrogen, fluorine, chlorine, halogen etcetera. So, that enter into hydrogen bonding and that influences the properties.

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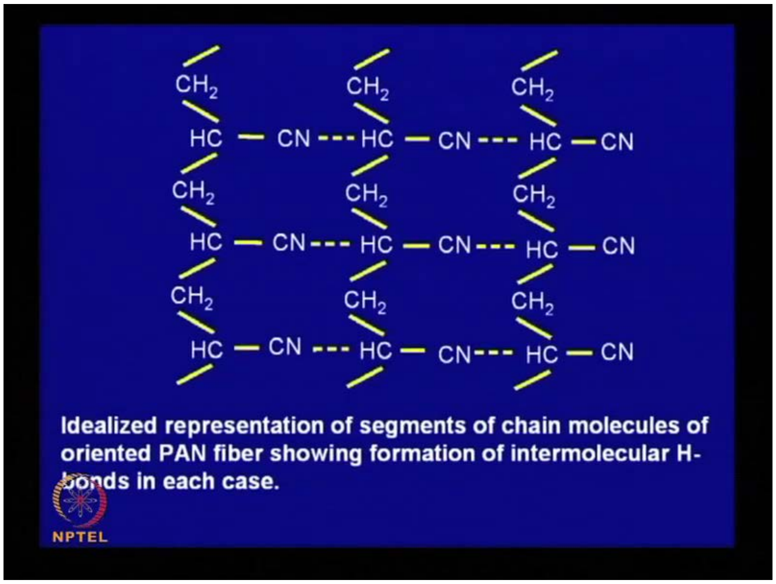

Idealized representation of segments of chain molecules of oriented PAN fiber showing formation of intermolecular H-bonds in each case.

So, you go through these structures and for new polymers, new other unknown polymers whether there is hydrogen bonding or not you can judge yourself looking at the structure.

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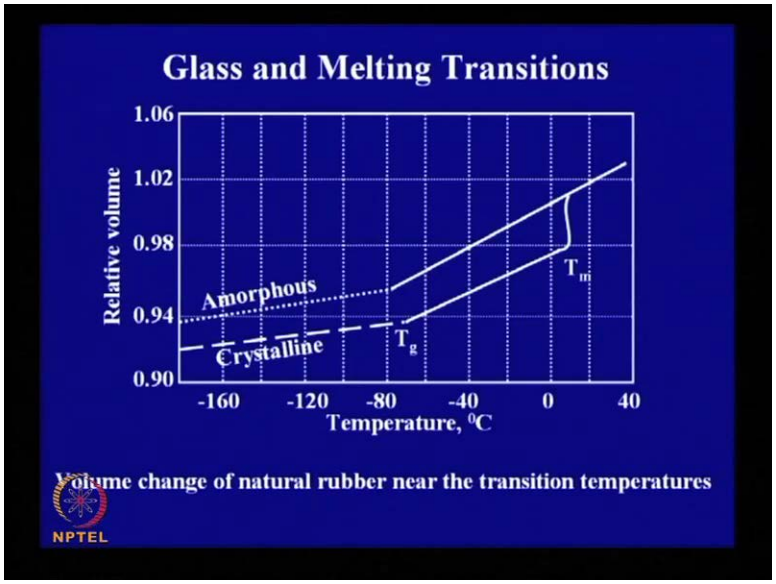

Glass and Melting Transitions

Volume change of natural rubber near the transition temperatures

And this diagram shows the shows the change in properties say volume, specific volume or relative volume with temperature, and if there is a discontinuity from the point of discontinuity you can assess the assess the transition temperature which is known as glass transitions which makes a transition from solid brittle glassy state to amorphous flexible rubbery state. This occurs due to moment of soft segments of polymer chains or segmental moment. This occurs due to onset of segmental moment of polymer chains.

For purely amorphous polymers we get only one transition which is known as glass transition. For a semi crystalline polymer since it contains some crystallides dispersed in amorphous matrix. So, one can visualize two types of transitions one is glass transitions and the other is melting transition. In the glass transition as I said this glass transition occurs due to segmental mobility whereas melting transitions occurs due to mobility of the molecule as a whole. In between these slowly and slowly the mobility of the segments increases and at melting the entire molecule becomes mobile, and so it behaves like a fluid beyond this melting transition temperature.

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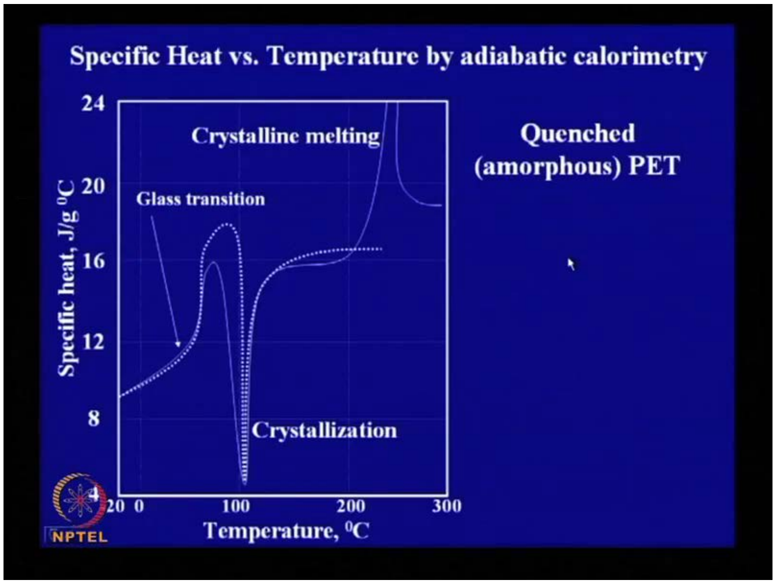
Specific Heat vs. Temperature by adiabatic calorimetry

Quenched (amorphous) PET

This is another diagram which shows a change of specific heat values of polymers with the increase in temperature decrease in temperature. You know what is specific heat of a material of a substance from that definition we can understand and it shows a change in the slope of this curve although it is not suck change, a gradual change is there. So, in order to get the transition we have to draw transient at the two points then at the cross over point of the transient that points gives you the glass transition temperature. Then gradually it undergoes a segmental moment and which helps the crystallization or molecular ornery in the, within the system. So, it shows the crystallization temperature also and beyond the crystallization temperature if this temperature is further increased then it melts showing the melting transition. And beyond melting again all can have certain inflection due to degradation.

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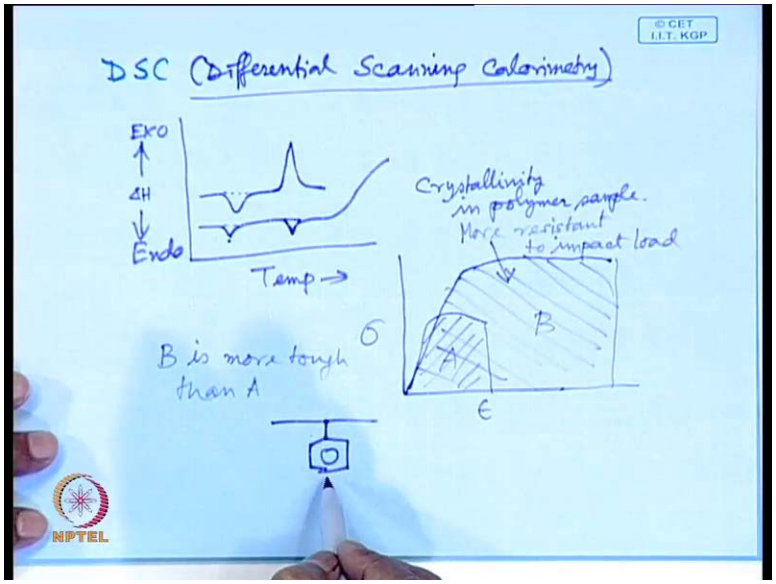

DSC (Differential Scanning Calorimetry)

Crystallinity in polymer sample.

More resistant to impact load

B is more tough than A

And those things can be very clear if one analyze a polymer sample through DSC differential scanning calorimetry, DSC experiment. Basically, measures say enthalpy or energy change may be exothermic and endothermic, this is a temperature axis and you can get curve like this or you can get curve like this, like this. Now, these are actually transitions. Again, change of enthalpy during that transition either endothermic transitions in these cases or exothermic transition. Now, these transitions can be as assigned to glass transition and at what temperature that can be a characteristic of one particular polymer and beyond that again the other transition can be a melting transition where the polymer melts and beyond that it actually shows degradation, energy change again shows the degradation.

So, whenever you will be reading the structure for calculation of materials there you will know the detailed principal of differential scanning calorimetric analysis, there you can know the detail, but this can help knowing the glass transition, knowing that melting transition temperatures as well as the crystallinity in polymer sample because the area under this curve, under this peak is professional to the crystallite or if it is crystalline melting, crystalline melting temperature then crystallinity can be measured from this area under this curve or if it is T G then you can get this initial final temperature and the peak temperature. So, you can report these three temperatures or only the peak temperature as T g.

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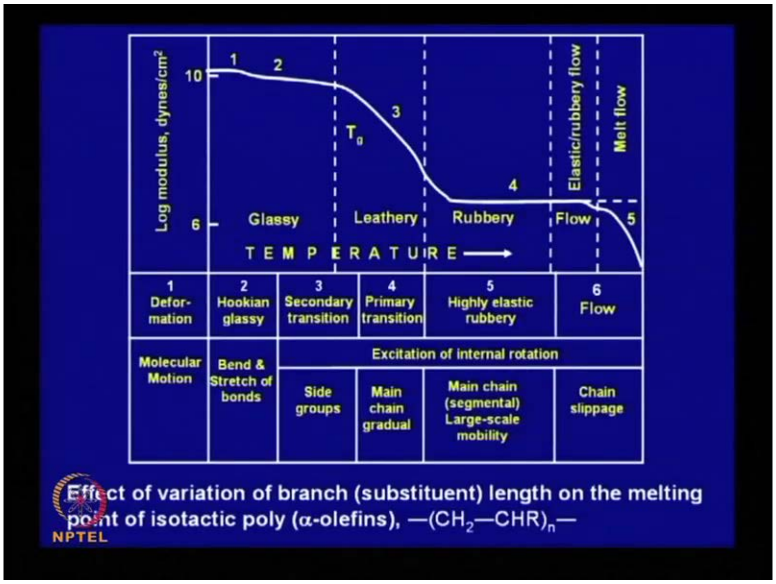

1 Defor-mation	2 Hookian glassy	3 Secondary transition	4 Primary transition	5 Highly elastic rubbery	6 Flow
Molecular Motion	Bend & Stretch of bonds	Excitation of internal rotation			
		Side groups	Main chain gradual	Main chain (segmental) Large-scale mobility	Chain slippage

Effect of variation of branch (substituent) length on the melting point of isotactic poly (α-olefins), —$(CH_2—CHR)_n$—

This diagram shows effect of variation of branch length on the melting characteristics of isotactic poly alpha olefins say polypropylene suppose and it shows the properties versus temperature. So, you can explain such behaviour of change of mechanical properties within freezing temperatures from glassy, solid, brittle state to leathery characteristics to rubbery characteristics to fluid like characteristics. As you can explain with the help of molecular configurations also what is the, what kind of molecular or change in molecular configuration occurs from where you can understand. First of all on application of stress and mechanical stress as well as heat, what happens?

There will be stressing on the bond, chemical bond as well as that means energy is applied in two different forms that helps in the formation of the material and that will be further augmented or accelerated by increasing the temperature. And this range of temperature between these phases is a glassy range, then beyond that it becomes flexible, then so it is leathery range and this transition is the T g from where it passes from glassy to leathery range then from leathery to rubbery which becomes little fluid, more fluid than leathery. So, and look at the modulus. Looking at these values one can know the stress requirement for polymer compounding, for polymer processing say moulding, extrusion all this how much stress is required, how much energy will be consumed for such processing those things can be understood from this behaviours.

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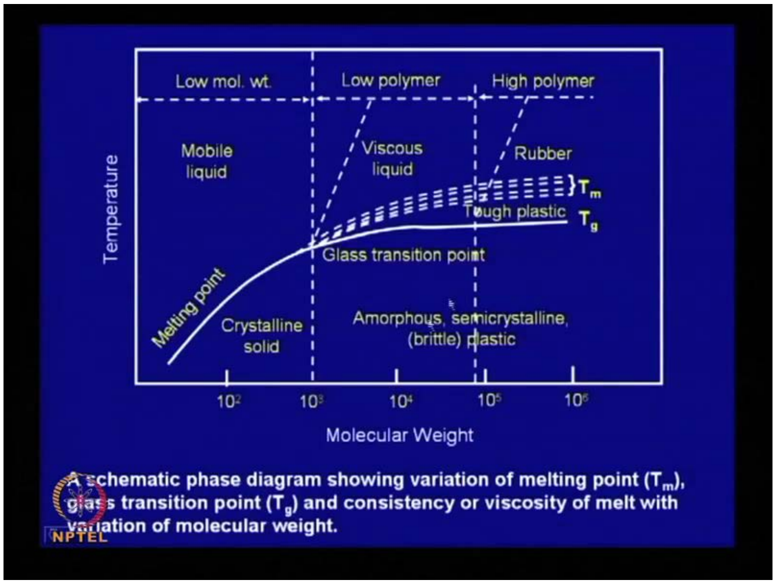

A schematic phase diagram showing variation of melting point (T_m), glass transition point (T_g) and consistency or viscosity of melt with variation of molecular weight.

This is a kind of phase diagram of these polymer materials which changes with molecular weight. That means there is a temperature line above which it remains in one phase below which it remains in another phase. So, this either it will remain liquid phase or solid phase, amorphous solid phase or crystalline solid phase, that depends on the molecular weight and the temperature. So, up to this molecular weight say 1000 molecular weight, molecular mass below this temperature line it is crystalline solid above it is mobile liquid. If you cross this molecular weight, beyond this molecular weight it becomes viscous liquid. So, viscosity of this fluid is lower than the fluid within this region.

And you see it is due to molecular size. Higher molecular size bigger molecular size becomes viscous in liquid phase, more viscous in liquid phase than the liquid phase, the mobility of the liquid phase or discreet molecules. Now, this is the, for amorphous materials this is the line of last transition, the interline is a glass transitions. For crystalline material, you see this may be considered as the melting transition line. For glass transition it can be considered from this initial point to the final point. For crystalline polymers again the transition line changes. That means it goes up, it occurs at high temperature because after this, beyond this line it should be, it becomes liquid, and so this is the region of tough plastic.

Why, it is called tough? Now, toughness if you want to understand the toughness, stress and if you look at the stress and the curve the toughness depends upon this stress level as well as the deformation level. So, if you compare this material with another material like this shows say A and this is B. So, B is more tough than A. What does it indicate? That means it can withstand more stress and absorbs energy before failure. So, this will be more, this material will be more resistant to impact impact load whereas this will be less resistant to impact load.

So, this is tougher than this one. So, this toughness depends on the stress level as well as the deformation level while some impact energy imposed on the material, suppose if you give a blow. If it can absorb that energy then it is tough. So, you have seen the dock finders. Dock finders, those who have gone through ferry service in Kolkata in the dock there are some tyres attached to the dock, when the, your vessel touches it, touches the tyres. So, it absorbs the energy otherwise if there is no such tyres which cannot absorb energy vessel may be damaged that means that material is tough, you understand. So, toughness depends on the mobility of the segments, deformation of the segments, deformation of the polymer chains.

So, here we see here this is a T g beyond T g that means below T g it is brittle for amorphous material, above T g it is little flexible. So, it can absorb the shock. So, it can absorb the impact load and this will continue till there melting transition. Beyond melting transition that can be mobile liquid, may be viscous liquid. So, again that is to molecular weight on the polymer also. So, this shows a picture or behaviour of polymers with temperature and there molecular weight. As you go on increasing the molecular weight that can withstand higher temperature, that can remain dimensionally stable, that can be tougher, tough material, that can behave like a plastic, that can behave like a elastomer. So, you can predict looking at this type of phase diagram.

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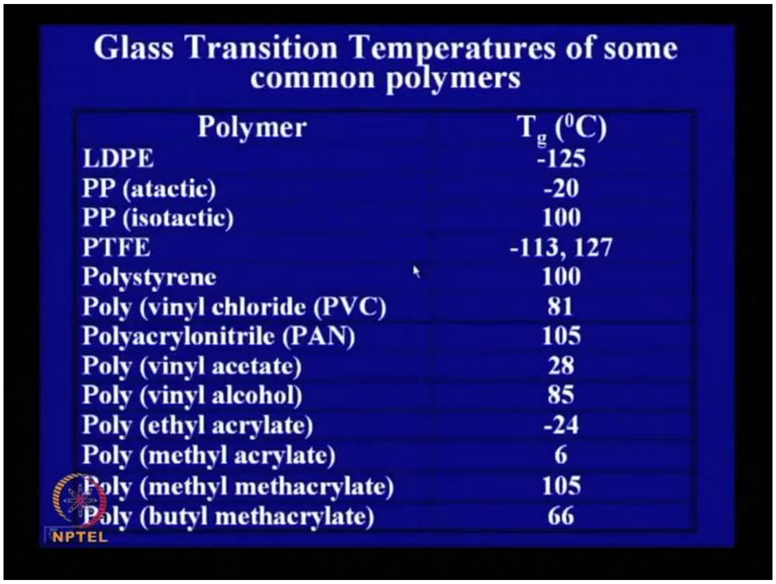

Glass Transition Temperatures of some common polymers

Polymer	T_g (^0C)
LDPE	-125
PP (atactic)	-20
PP (isotactic)	100
PTFE	-113, 127
Polystyrene	100
Poly (vinyl chloride (PVC)	81
Polyacrylonitrile (PAN)	105
Poly (vinyl acetate)	28
Poly (vinyl alcohol)	85
Poly (ethyl acrylate)	-24
Poly (methyl acrylate)	6
Poly (methyl methacrylate)	105
Poly (butyl methacrylate)	66

Now, there are certain glass transition values are shown if you try to correlate these values. LDPE, I explained before also. Its T g is quite low; it may be again minus 120 degree minus 115 degree like that. Now, T g these values are not fixed actually because it can vary from one batch of polymer to the other batch of polymer because not all the batches of polymers which are manufactured in industry will contain same molecular weight level and molecular weight distribution that is why it can vary. So, it is not fixed.

If you see some value in some report, in some paper, in some journal, in some book, it may be written minus 115 degree. It is not wrong particularly value reported over there from one experiment which shows it is this value is minus 115 degrees, but you have seen in a book it is minus 125 degrees. Both are right, it gives you some general idea that the T g vales of this polymer, different polymers as such. So, if you compare say T g value of polystyrene you see it is 100 degrees with this LDPE minus 125 degrees why why because polystyrene contains one pendant phenyl ring. So, that makes the polymer this phenyl ring bulky phenyl ring makes the polymer rigid.

This is for hydrocarbon plastics. Now, if you look into other polymers say like PVC, polyacrylonitrile compared these polymers, that means these substituent substituent at the carbon atom chlorine, nitrile group, C N group, acetate group, alcohol group, acrylate group, ester group again another substitution methacrylate, methyl and acrylate group, methyl and methacrylate group, butyl methacrylate group. You see the variation; you can easily correlate. That means the substitution on the polymer chain.

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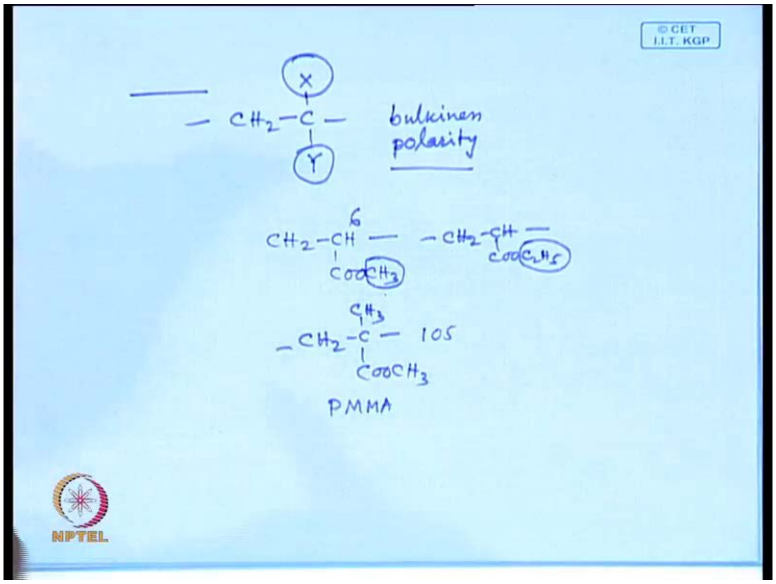

These substitutions alter the glass transition values depending on their bulkiness, on their polarity etc. That means if you correlate these things with cohesive energy density along with this bulkiness then you can correlate their T g properties. How the T g properties are varying? See, look at this methyl acrylate and ethyl acrylate. Methyl acrylate, this is methylacrylate and this is ethylacrylate. You see this is methyl group here, this is the difference between these two polymers, ethyl and methyl and for that the length of this alkali group has drastically changed, this T g values from minus 24 to 6 degree. Further, if you compare another polymers this is PMMA, compare this polymer with this polymer, this T g value is minus 24 6 degree, 6 degree its T g is 105 degree. So, that change has come from this methyl group.

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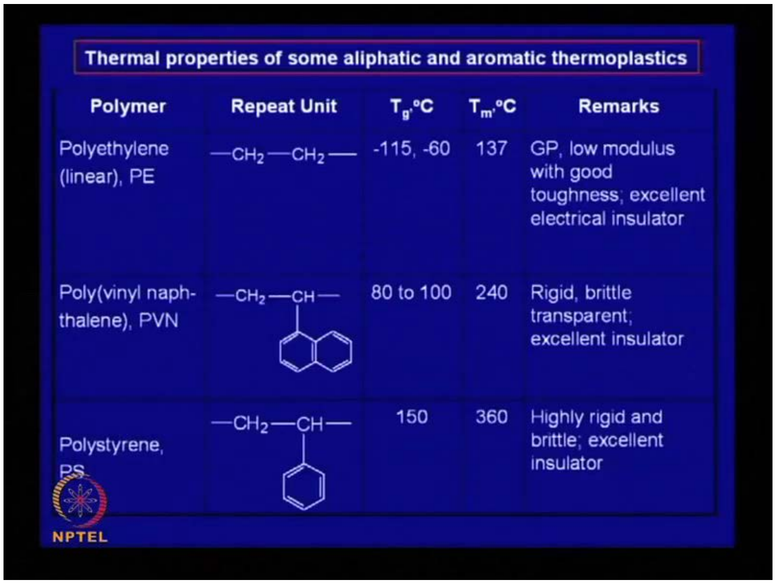

Thermal properties of some aliphatic and aromatic thermoplastics

Polymer	Repeat Unit	T_g,°C	T_m,°C	Remarks
Polyethylene (linear), PE	$-CH_2-CH_2-$	-115, -60	137	GP, low modulus with good toughness; excellent electrical insulator
Poly(vinyl naph-thalene), PVN	$-CH_2-CH-$	80 to 100	240	Rigid, brittle transparent; excellent insulator
Polystyrene, PS	$-CH_2-CH-$	150	360	Highly rigid and brittle; excellent insulator

Now, this shows further examples of other polymers that T g and T m melting transition both say you go through these. These are available in the book. You look at the structure. Try to understand why there T g values are differing from each other, why there T m values is differing from each other.

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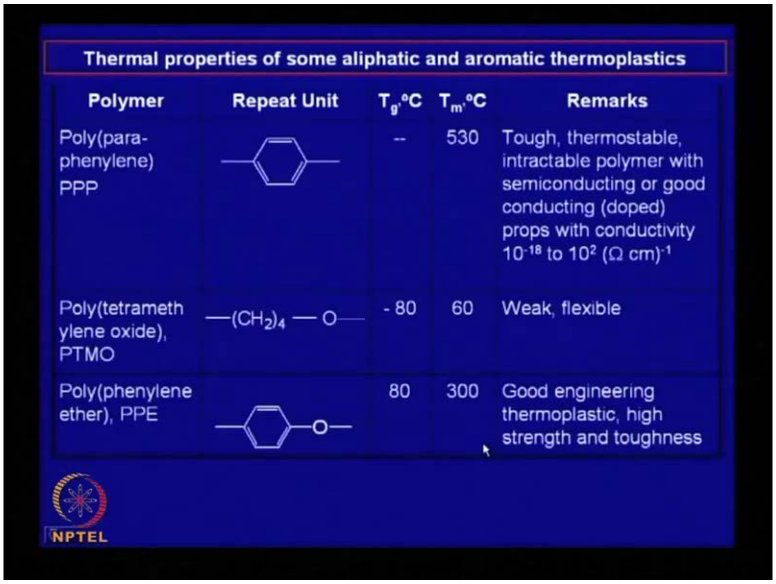

Thermal properties of some aliphatic and aromatic thermoplastics

Polymer	Repeat Unit	T_g,°C	T_m,°C	Remarks
Poly(para-phenylene) PPP		--	530	Tough, thermostable, intractable polymer with semiconducting or good conducting (doped) props with conductivity 10^{-18} to 10^{2} $(\Omega\ cm)^{-1}$
Poly(tetramethylene oxide), PTMO	$-(CH_2)_4-O-$	- 80	60	Weak, flexible
Poly(phenylene ether), PPE	$-O-$	80	300	Good engineering thermoplastic, high strength and toughness

Examples of polymers, poly para phenylene, poly tetramethylene oxide, poly phenyleneether, if you compare each of them only phenylene ring, there is no aromatic ring, only alkyl chain. Methylene groups oxygen is there, again if you compare this polymer with this polymer oxygen is there which is flexible, ethylene linkage is flexible in a polymer chain. So, here you see although because of the presence of the methyl ring, I mean methylene group its T g is minus 80 degrees when this 4 carbon atoms of this 4 methylene units are replaced phenylene ring keeping this ethylene linkage same. Its T g has been changed to 80 degree, plus 80 degree. So, this way you compare these polymers with their structures and their glass transitions and melting transitions. There are many examples here.

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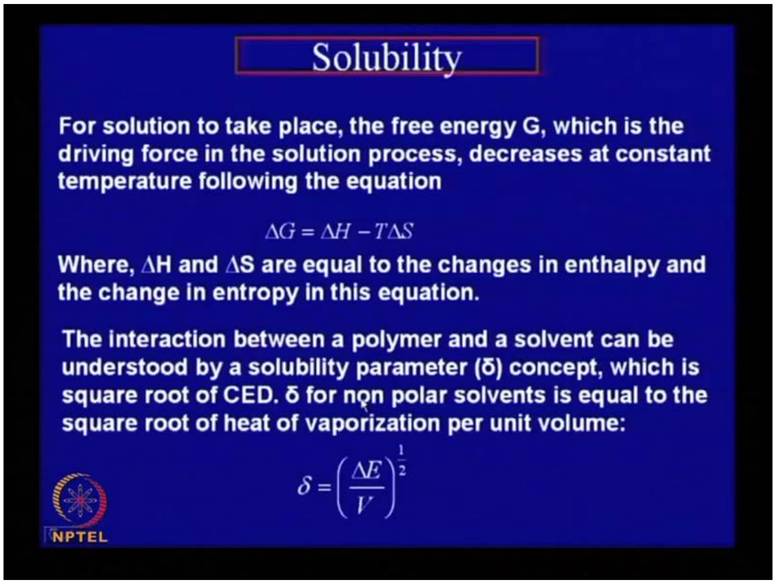

Solubility

For solution to take place, the free energy G, which is the driving force in the solution process, decreases at constant temperature following the equation

$$\Delta G = \Delta H - T\Delta S$$

Where, ΔH and ΔS are equal to the changes in enthalpy and the change in entropy in this equation.

The interaction between a polymer and a solvent can be understood by a solubility parameter (δ) concept, which is square root of CED. δ for non polar solvents is equal to the square root of heat of vaporization per unit volume:

$$\delta = \left(\frac{\Delta E}{V}\right)^{\frac{1}{2}}$$

Now, let us come to the solubility behaviour, dissolution behaviour of polymers. Already, I have devoted some time to explain before you what do you mean by solubility. Now, for solution to take place the free energy is the driving force in the solution process which decreases at constant temperature following the equation. That means a solution can take place or miscibility of two components can take place. Solubility, what do you mean by solubility?

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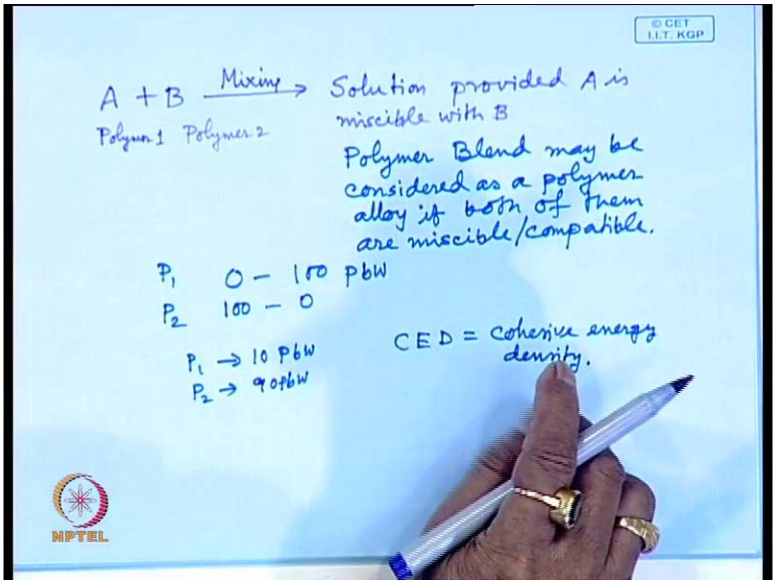

$A + B \xrightarrow{\text{Mixing}}$ Solution provided A is miscible with B

Polymer 1 Polymer 2

Polymer Blend may be considered as a polymer alloy if both of them are miscible/compatible.

P_1 0 – 100 pbW

P_2 100 – 0

$P_1 \rightarrow$ 10 pbW

$P_2 \rightarrow$ 90 pbW

CED = Cohesive energy density.

If you mix a component A with a component B, we can get a solution provided A is miscible with B. In this two components, out of these two components one may be considered as a solvent and other may be considered as a solute. You can take the example of simple case of a solution sugar in water. Suppose, A is sugar B is water. It forms a homogeneous solution because sugar is misroute with water. Now, if you take A as polymer 1, B as polymer 2 then you can get a polymer blend of polymer 1 and polymer 2 provided they are miscible. That means you can say this polymer blend may be considered as a polymer alloy if both of them are miscible or compatible. So, we can get a new product from two component polymers by mixing one polymer with another polymer provided they are miscible.

We can say that these two components polymers are miscible at entire range of compositions between 0 to 100 parts by weight, means this is a pure polymer 1 say P 1 P 2 0 to 100 and 100 to 0. These are the two P O and in between you can have 90 10, 80 20, 70 30, 40 60, 50 50 like this. So, in this entire range of compositions if we see that these component polymers are fully miscible we can say it is a miscible polymer blend, but it can so happen that one polymer can be miscible with another polymer up to certain specified composition. Say, suppose P 1 up to 10 parts by weight can be miscible with P 2 with 90 parts by weight. Beyond 10 parts of P 1 it will separate into phases.

That will be too persistent. That means there will be some new phase boundaries will be created. One phase of polymer 1 and the another phase of polymer 2, that is we cannot say that beyond this 10 percent of this P 1, it is not miscible so we can say it is an immiscible blend. So, this is the concept. How to know that one polymer will be miscible with another polymer or one polymer can be dissolved in a solvent or one solvent can be a good solvent for one polymer and the vice versa. So, the end that depends on the interaction between a polymer and a solvent and that can be understood by a solubility parameter delta concept which is the square root of cohesive energy density CED cohesive energy density.

Delta for non polar solvents is equals to the square root of heat of vaporization per unit volume. Heat of vaporization per unit volume under square root and this delta or solubility parameter can be calculated if we know the formula, repeating need formula of a polymer if we know the chemical formula of a solvent. So, we can calculate the solubility parameter value of a solvent as well as a polymer.

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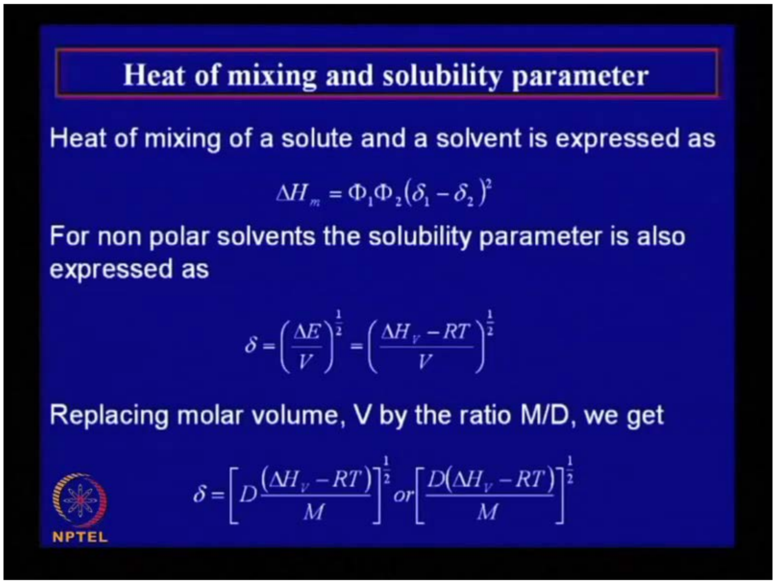

Heat of mixing and solubility parameter

Heat of mixing of a solute and a solvent is expressed as

$$\Delta H_m = \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2$$

For non polar solvents the solubility parameter is also expressed as

$$\delta = \left(\frac{\Delta E}{V}\right)^{\frac{1}{2}} = \left(\frac{\Delta H_V - RT}{V}\right)^{\frac{1}{2}}$$

Replacing molar volume, V by the ratio M/D, we get

$$\delta = \left[D\frac{(\Delta H_V - RT)}{M}\right]^{\frac{1}{2}} or \left[\frac{D(\Delta H_V - RT)}{M}\right]^{\frac{1}{2}}$$

Now, you see heat of mixing of a solute and solvent is expressed by delta H m, delta H m equal to phi 1 and phi 2 where phi 1 and phi 2 are the volume fractions of polymer 1 and polymer 2 or solute and the solvent, if you consider 1 as the solute and 2 as the solvent. These are the value fractions and delta 1 and delta 2 are the solubility parameters of the two components solute and the solvent. This can be two polymers also, polymer 1 and polymer 2. Now, for non polar solvents the solubility parameter is also expressed as you have seen earlier it is the heat of vaporization per unit volume, then delta is equal to delta H V minus delta R T by V. Replacing this molar volume, replacing this molar volume V by the ratio M by D we get this relation.

Simple derivation to get this relation, D is the density, M is the molecular weight and delta H V is the heat of vaporization, R is the gas constant, T is the temperature in Kelvin and M is the molecular weight of the repeat unit of the polymer. Now, since this delta solubility parameter relates with this heat of vaporization, heat of vaporization, if you correlate this with the intermolecular interactions or interactions between the solvent and the solute or using the solvent during evaporation or during the boiling of solvent what happens? If the energy supplied to the solvent is crosses beyond the, crosses beyond the intermolecular forces of interaction then only it starts vaporization, start boiling, vapour formation. So, it is very much related to the heat of vaporization which is related to the cohesive energy density and I told you what is cohesive energy density, earlier.

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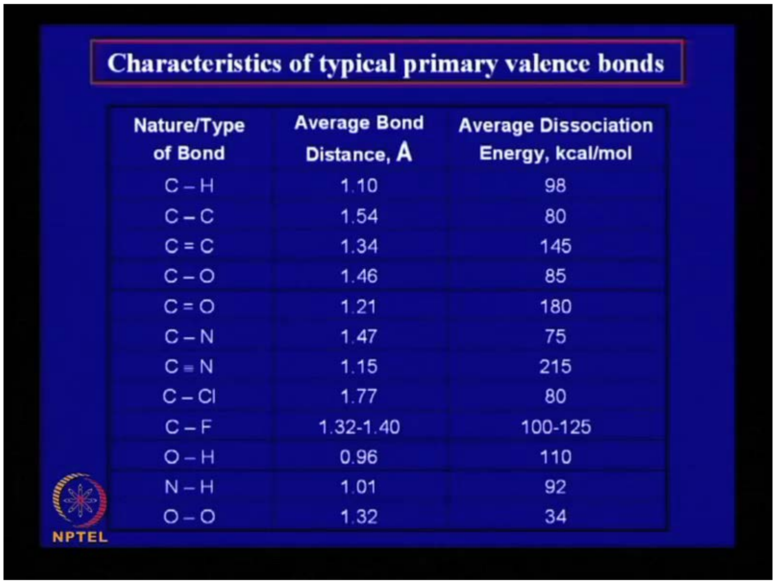

Characteristics of typical primary valence bonds

Nature/Type of Bond	Average Bond Distance, A	Average Dissociation Energy, kcal/mol
C – H	1.10	98
C – C	1.54	80
C = C	1.34	145
C – O	1.46	85
C = O	1.21	180
C – N	1.47	75
C ≡ N	1.15	215
C – Cl	1.77	80
C – F	1.32-1.40	100-125
O – H	0.96	110
N – H	1.01	92
O – O	1.32	34

Look at these values, characteristics of typical primary valence bonds, bond length, bond distance and bond dissociation energies. Of course, these bond dissociation energies has nothing to do with the vaporization of the molecules in which these bonds are present. What I mean to say, if you think of the energy for Van Dorens bonds or hydrogen bonds which is around 2 to below 5 kilo calories per mole. If the salvation energy goes beyond 5 kilo calories per mole then only it can break those hydrogen bonds.

Do you understand? Take the example of cellulose. Last day I told cellulose contains extensive hydrogen bonding. Almost, all the hydroxide groups in ring are involved in intermolecular hydrogen bonding. It is a thermoplastic polymer, when it is put in butter it is supposed to go into solution, but the salvation energy of water at room temperature is not sufficient enough to break that hydrogen bonds, but if you add other chemicals then that chemical energy would cross that hydrogen bond energy and that breaks and then only cellulose goes into solution.

Exploiting this phenomenon technologies have been developed to manufacture processed cotton, mercerized cotton, cellophane, (( )) or other regenerated cellulose fibres. So, this is done by breaking of hydrogen bonds only with the help of chemical energy, so but actually these strong bonds again that depends on the position of the atoms in the periodic table. If there is a more distance between the atoms in the periodic table the energy becomes more, polarity integers energy becomes more. So, bond distance average becomes more. So, this way you can correlate looking at these values.

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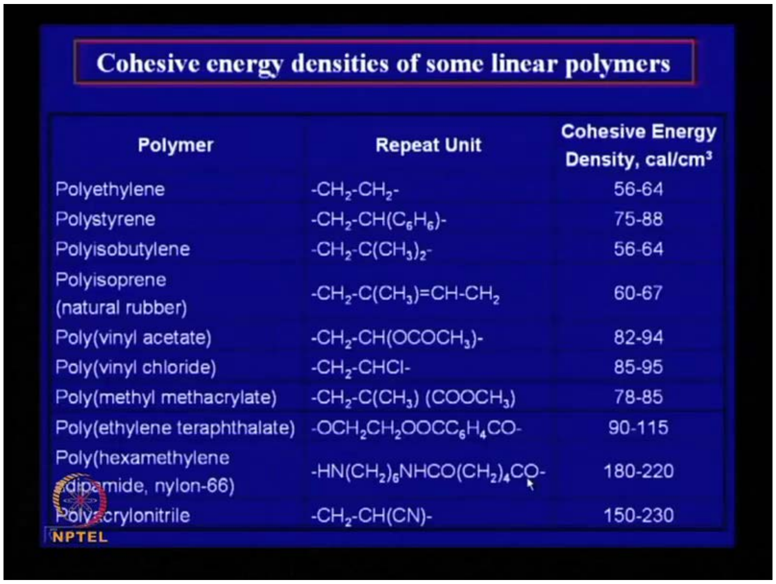

Cohesive energy densities of some linear polymers

Polymer	Repeat Unit	Cohesive Energy Density, cal/cm^3
Polyethylene	$-CH_2-CH_2-$	56-64
Polystyrene	$-CH_2-CH(C_6H_6)-$	75-88
Polyisobutylene	$-CH_2-C(CH_3)_2-$	56-64
Polyisoprene (natural rubber)	$-CH_2-C(CH_3)=CH-CH_2$	60-67
Poly(vinyl acetate)	$-CH_2-CH(OCOCH_3)-$	82-94
Poly(vinyl chloride)	$-CH_2-CHCl-$	85-95
Poly(methyl methacrylate)	$-CH_2-C(CH_3)\ (COOCH_3)$	78-85
Poly(ethylene teraphthalate)	$-OCH_2CH_2OOCC_6H_4CO-$	90-115
Poly(hexamethylene adipamide, nylon-66)	$-HN(CH_2)_6NHCO(CH_2)_4CO-$	180-220
Polyacrylonitrile	$-CH_2-CH(CN)-$	150-230

So, look at this data cohesive energy density which was calculated, which was calculated or sometimes experimentally determined for these different polymers. You see for polyethylene cohesive energy density is 56 to 64, for polystyrene it is higher. Again for poly isobutylene it is lower than this value, natural rubber is almost comparable, poly vinyl acetate it is little higher, poly vinyl chloride little higher, poly methyl methacrylate still higher, poly ethylene terphthalate still higher, this way if you go on move from polyethylene to different other polymers.

And if you look into the structures and the configurations and the atoms present over there then you can correlate their cohesive energy density. Cohesive energy density is the sum total of secondary valence force, sum total of secondary valence force or secondary valence energy, valence force energy related to, that energy related to secondary valence force total quantity per mole of course, per mole, per gram mole or per mole. Here, it is shown per CC calories per CC, energy consumed or required to break those secondary bond forces are like this 56 to 64 calories per cc. You can calculate in terms of mole, mole basis.

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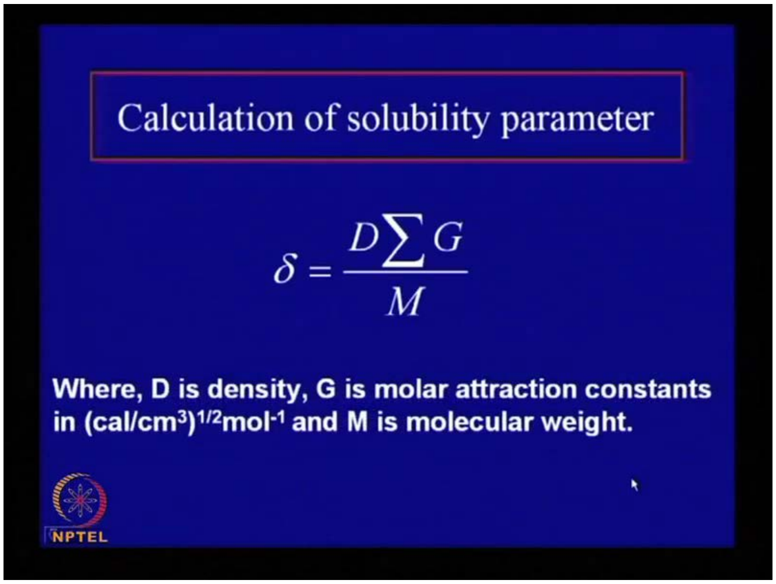

Calculation of solubility parameter

$$\delta = \frac{D\sum G}{M}$$

Where, D is density, G is molar attraction constants in $(cal/cm^3)^{1/2}mol^{-1}$ and M is molecular weight.

As I was telling solubility parameter can be calculated from this relation delta is equal to D into sum of molar attraction constants and these molar attraction constants are nothing but these are used as measure of the cohesive energy density G value calories per CC square root per mole and M is the molecular weight and this G can be calculated, this G can be calculated…

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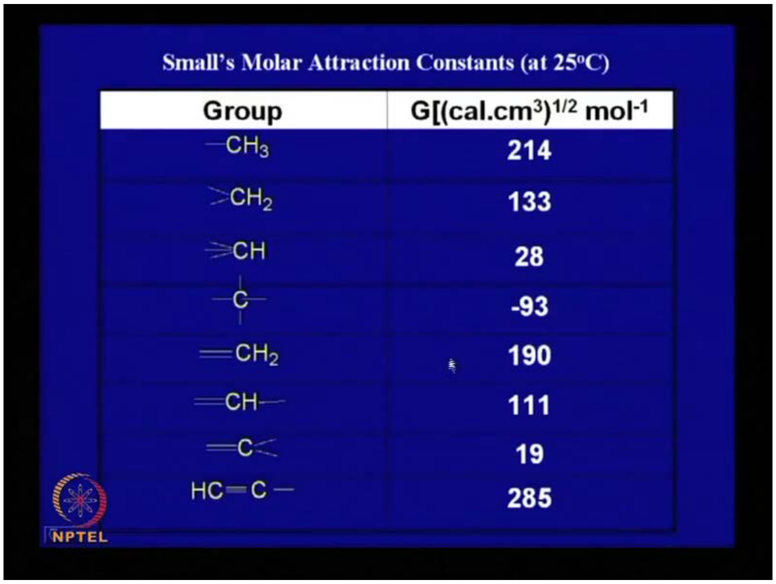

Small's Molar Attraction Constants (at 25ºC)

Group	G[(cal.cm^3)$^{1/2}$ mol^{-1}
$-CH_3$	214
$>CH_2$	133
$>CH-$	28
$>C<$	-93
$=CH_2$	190
$=CH-$	111
$=C<$	19
$HC=C-$	285

Because it has been evaluated that this G values molar attraction constants known as Smalls molar attraction constants measured by some experiments by 25 degree Celsius for if there is a methyl group, its contribution is 214, for methylene group it is 133, for C H is connected to other three bonds it is 28, for carbon attached to four different atoms it is minus 93, for C H 2 attached to a double bond it is 190. So, even correlate these thing with the bond energies that means these values if these values are available.

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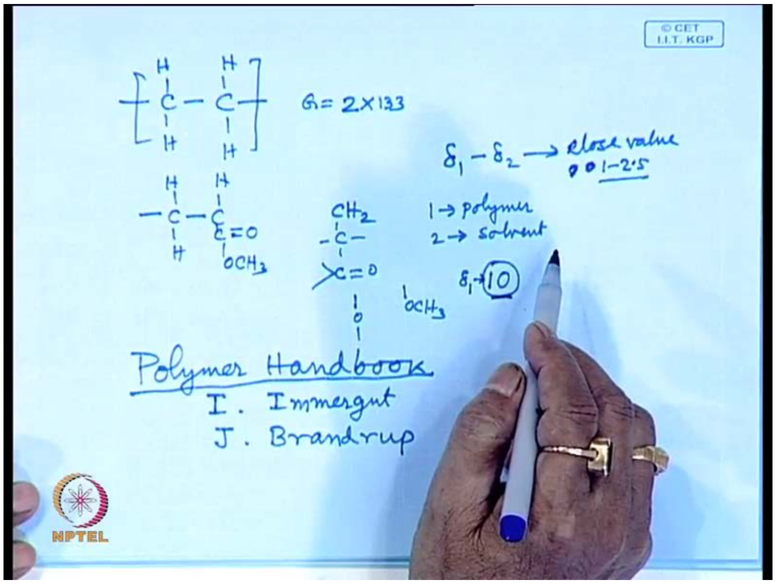

Suppose, if you take a polymer say this polymer and you are asked to calculate this G values. So, contribution due to this C H 2 group is there, so here in this polymer in per repeat unit, there are two C H 2 groups. So, you can have this total value for this repeated 2 into 1 33. In the previous formula you see sum of G values here you write this 2 into 1 33 for G. G is equal to 2 into 1 33. You can have a molecule of or repeat unit formula like this have, you have to the contributions from C H 2, you have to have the contribution from C H that means like this.

You have to have the contribution from this, you have to have the contributions from oxygen or you have to have the contribution from O C H 3. All these contributions for different groups present in a molecule, in the repeat unit formula and if this data are available for different, you see only few examples are given, shown over here. In the data book say there is a data book, it is a huge data book available in the library known as Polymer Handbook and the book editors are I Immergut and J Brandrup from what I remember.

You look at that (( )) you will get several physical constants for polymers. This molar attraction constants, that T g values of different polymers, T m values of different polymers, many physical data you can get from those books. There you can get the Small's molar attraction constants exhausted list of molar attraction contribution to molar attraction constants in chemical compounds, that may be a simple solvent, that may be a polymer molecule. So, with the help of those data available in data book you can calculate the solubility parameter either for a solvent or for a polymer.

Now, you will ask sir what is the necessity of calculating the solubility parameter, is there any necessity? Yes, there is a necessity. If you deal with polymer, if you deal with polymer, suppose you want to do some work on application of polymers, you want to make a biomedical device say for drug delivery device made of polymer, you want to make a conducting polymer film for sensing purpose. You want to make a surface coating using a polymer. So, for all these you have to go through some processing steps involving solvents, say solution processing or (( )) processing.

If you go for solution processing then you have to go for selection of a suitable solvent. It is unknown to you, but being a polymer scientist if you know that this is this polymer. If you know the repeat unit formula of that polymer then you can easily calculate the solubility parameters of the particular polymer from this equation, from this relation. We calculate the solubility parameter for the polymers, then you see what solvent should be suitable for dissolution of this polymer or what will be good solvent for this polymer. How to charge then?

Now, if the solubility parameters of a polymer and a solvent are very close say the difference is say 0 to sorry 1 to 2.5 the difference in solubility parameters is 1 to 2.5 then that can be miscible. If the solubility parameter is almost identical then that solvent may be a good solvent for that polymer. So, if you know the solubility parameter value suppose it is 10 solubility parameter, delta value for your polymer it is 10 then find out a solvent whose solubility parameter is close to 10 or 10 say it is 10.5 or 11 or 11.5 or even 12.

So, if you find a solvent whose solubility parameter close to this 10 then you can select that solvent. It is again not always true that that solvent can dissolve or the solubility of that polymer cannot be very may not be very high in that solvent, but it can be used as a solvent. Say, you can easily dissolve 1 gram of polymer in 100 gram of solvent, but you may not be able to dissolve 5 gram of the same polymer in the same solvent, 100 gram of the same solvent, you understand. So, 1 gram is soluble, but 5 gram is not soluble. So, that depends on the solubility limit, what is the solubility value. Look at the data.

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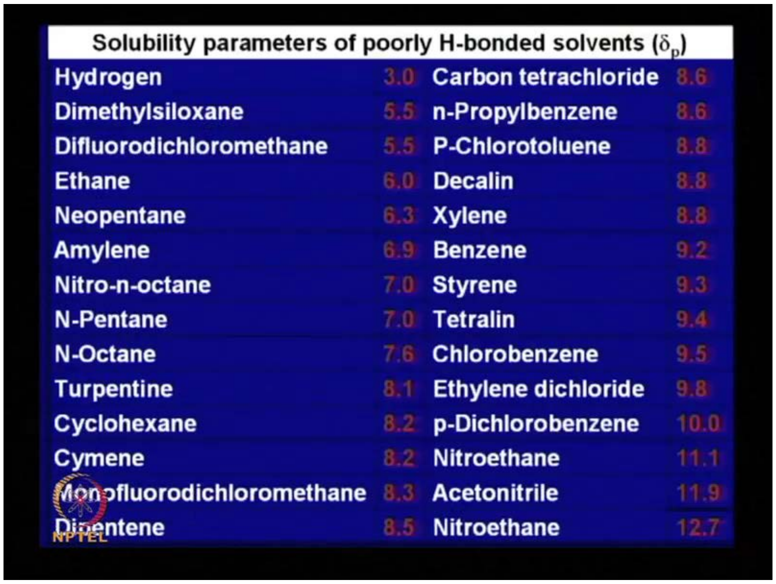

Solubility parameters of poorly H-bonded solvents (δ_p)

Hydrogen	3.0	Carbon tetrachloride	8.6
Dimethylsiloxane	5.5	n-Propylbenzene	8.6
Difluorodichloromethane	5.5	P-Chlorotoluene	8.8
Ethane	6.0	Decalin	8.8
Neopentane	6.3	Xylene	8.8
Amylene	6.9	Benzene	9.2
Nitro-n-octane	7.0	Styrene	9.3
N-Pentane	7.0	Tetralin	9.4
N-Octane	7.6	Chlorobenzene	9.5
Turpentine	8.1	Ethylene dichloride	9.8
Cyclohexane	8.2	p-Dichlorobenzene	10.0
Cymene	8.2	Nitroethane	11.1
Monofluorodichloromethane	8.3	Acetonitrile	11.9
Dipentene	8.5	Nitroethane	12.7

So, from these Small’s molar attraction constants you can calculate the solubility parameter. Look at the solubility parameter values which was calculated or experimentally determined values. For hydrogen it is 3, for dimethylsiloxane it is 5.5, difluorodicholoromethane 5.5, ethane 6.0 these are for purely hydrogen bonded solvents, carbon tetrachloride, propylbenzene, decalin hydrocarbon solvent, xylene aromatic hydrcarbon solvent, benzene aromatic hydrcarbon solvent, styrene structure is different from that of benzene, tetralin, chlorobenzene. So, these solvents are considered as solvents whose hydrogen bonding effect is minimum purely hydrogen bonded solvents. Now, the boiling point of a solvent would be high if the molecules in that solvents have very strong hydrogen bonding.

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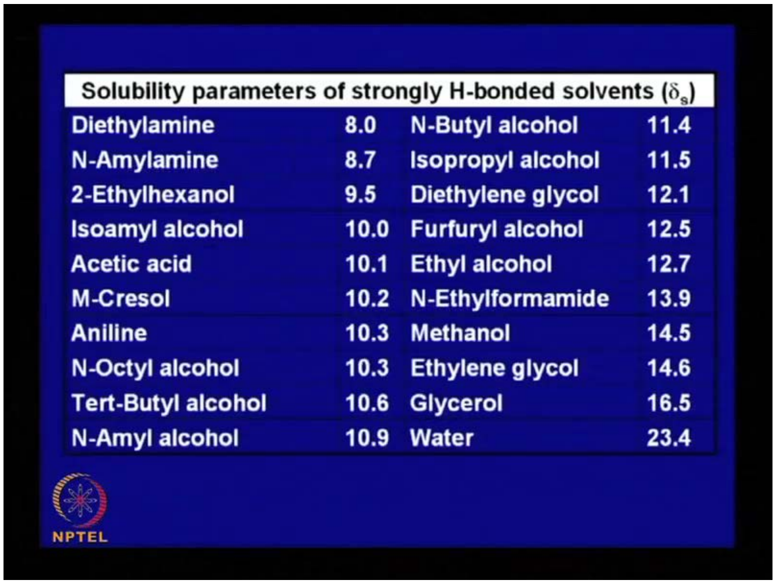

Solubility parameters of strongly H-bonded solvents (δ_s)

Diethylamine	8.0	N-Butyl alcohol	11.4
N-Amylamine	8.7	Isopropyl alcohol	11.5
2-Ethylhexanol	9.5	Diethylene glycol	12.1
Isoamyl alcohol	10.0	Furfuryl alcohol	12.5
Acetic acid	10.1	Ethyl alcohol	12.7
M-Cresol	10.2	N-Ethylformamide	13.9
Aniline	10.3	Methanol	14.5
N-Octyl alcohol	10.3	Ethylene glycol	14.6
Tert-Butyl alcohol	10.6	Glycerol	16.5
N-Amyl alcohol	10.9	Water	23.4

So, you look into these values, solubility parameters of moderately hydrogen bonded solvents solubility parameters values increase, increasing or increasing in the solvents. Then you see the solubility parameters of strongly hydrogen bonded solvents. Earlier, I told you a statement that like dissolves like that is the chemical nature of two solvents are equals or the two components are close chemical nature. It is a solute and the solvent, then they can be miscible and one can act as solvent for the other and that can be calculated or from the molecular point of view, from the chemical nature point of view one can see in terms of cohesive energy density or solubility parameter values.

So, you have seen the solubility parameters values of purely hydrogen bonded solvents, moderately hydrogen bonded solvents and strongly hydrogen bonded solvents. Now, we come to the polymer side, if your polymer contains strong hydrogen bonding, strong intermolecular hydrogen bonding. So, you have to take strongly hydrogen bonding solvents for its dissolution as a solvent.

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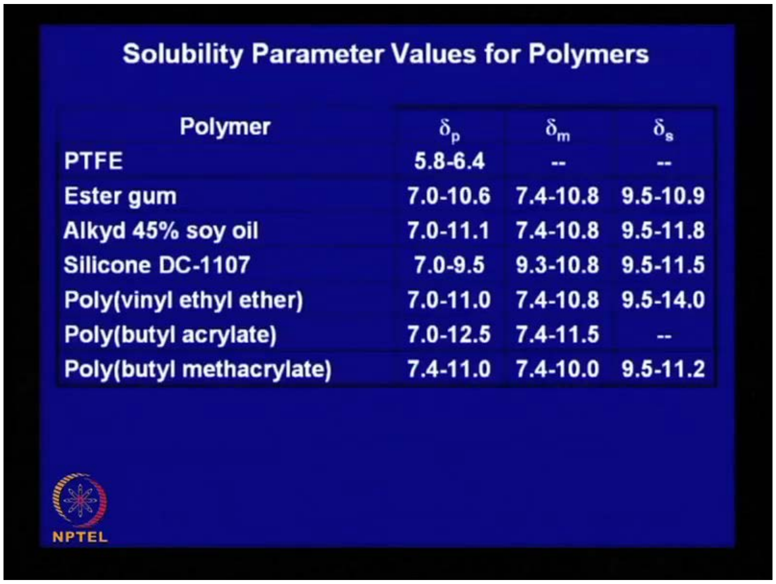

Solubility Parameter Values for Polymers

Polymer	δ_p	δ_m	δ_s
PTFE	5.8-6.4	--	--
Ester gum	7.0-10.6	7.4-10.8	9.5-10.9
Alkyd 45% soy oil	7.0-11.1	7.4-10.8	9.5-11.8
Silicone DC-1107	7.0-9.5	9.3-10.8	9.5-11.5
Poly(vinyl ethyl ether)	7.0-11.0	7.4-10.8	9.5-14.0
Poly(butyl acrylate)	7.0-12.5	7.4-11.5	--
Poly(butyl methacrylate)	7.4-11.0	7.4-10.0	9.5-11.2

So, look into the polymer. Solubility parameters values for polymers poly terphthalate ethylene 5 point, again you see it shows different values for purely hydrogen bonded, moderately hydrogen bonded and strongly hydrogen bonded solvents. Ester gum is a polymer. What is the ester gum? Ester gum is a regime made from a (( )) acid and (( )) sorry (( )) or (( )) acid or and some glycol, using some oils also in combination with oil. So, ester gum because those are ester like polymers. So, ester gums and alkyd regimes with soya bean oils, silicone polymer, poly vinyl ethyl ether, poly butyl acrylate, poly butyl methacrylate you see that their solubility parameter values are lying in the ranges from 7 to 10 like this for this polymers.

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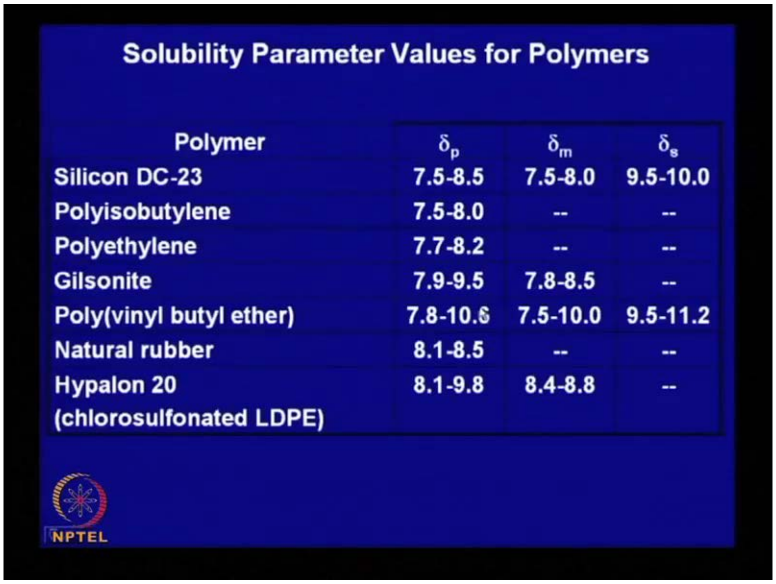

Solubility Parameter Values for Polymers

Polymer	δ_p	δ_m	δ_s
Silicon DC-23	7.5-8.5	7.5-8.0	9.5-10.0
Polyisobutylene	7.5-8.0	--	--
Polyethylene	7.7-8.2	--	--
Gilsonite	7.9-9.5	7.8-8.5	--
Poly(vinyl butyl ether)	7.8-10.6	7.5-10.0	9.5-11.2
Natural rubber	8.1-8.5	--	--
Hypalon 20 (chlorosulfonated LDPE)	8.1-9.8	8.4-8.8	--

I will come to explain later, it should be silicone not silicon, silicone C O N E, silicone.

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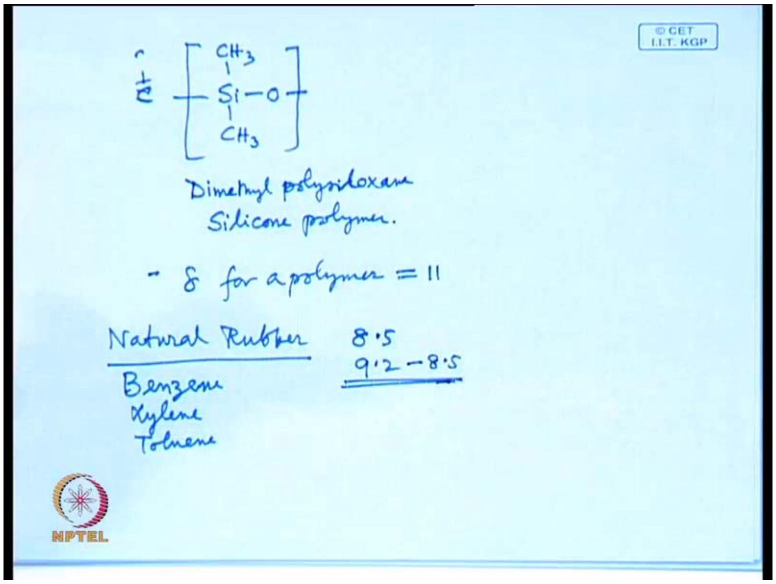

$$\left[-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O- \right]$$

Dimethyl polysiloxane
Silicone polymer.

- δ for a polymer = 11

Natural Rubber 8.5
9.2 − 8.5

Benzene
Xylene
Toluene

Silicone Dimethyl polyoxidoxane silicone polymers; silicone one grade, polyisobutylene, polyethylene is trade name of polymer, poly vinyl butyl ether, natural rubber, hypalon which is chlorosulfonated polyethylene silicone trade name of a polymer natural rubber hypalon which is chlorosulfonated polyethylene, chlorosulfonated polyethylene and then the other polymers ethyl cellulose, chlorinated rubber, dammer gum again versamid trade name, polystyrene, polyvinyl acetate, polyvinyl chloride, phenolic resins, natural rubber, P M M A, carbowax, polyethylene oxide, polycarbonate, cyclised rubber these are the values.

So, solubility parameter values for polymers again mylar in the form of film, Mylar film, poly ethylene terphthalate film, vinyl chloride, vinyl acetate copolymer, polyurethane, styrene acrylonitrile copolymer, shellac, cellulose. You see here from these data if you know the solubility parameter delta for a polymer say suppose it is 11 then you look at the solubility parameter of a solvent. Go to the solvent chart.

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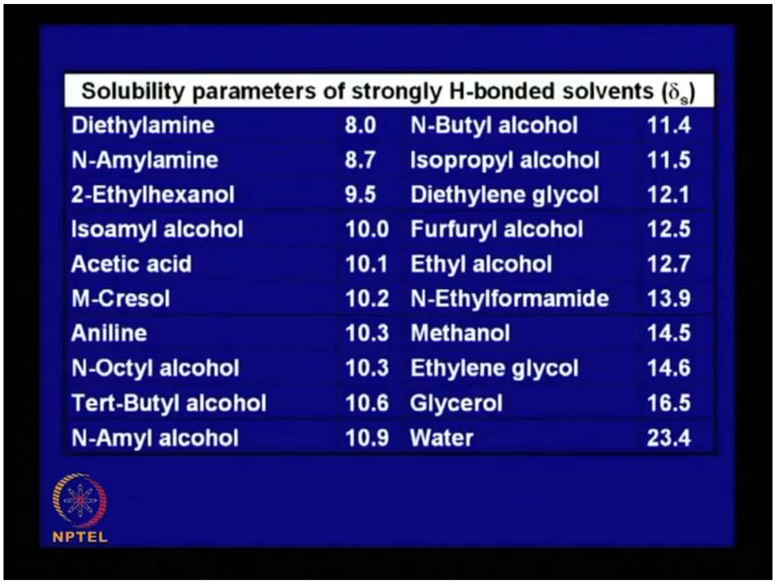

Solubility parameters of strongly H-bonded solvents (δ_s)

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N-Amyl alcohol	10.9	Water	23.4

Here you see there are solvents whose solubility parameters are 11.4, 11.5, 12, 10.9, 10.6, 10.3 and go through the polymer chart you see this polymer, you take a polar polymer say alkyd resin or this ,it will be complicated. You take natural rubber, example of natural rubber. Natural rubber its solubility parameters is around to say 8.5 and its solvent for natural rubber, good solvent for natural rubber is benzene, xylene, tolvene these are the solvents, hydrocarbon solvents, decalin tetralin these are also good solvent for natural rubber.

So, if you put natural rubber in benzene it will go into solution. So, look at the solubility parameters value of benzene and benzene, tolvene, xylene, 9.2, for benzene it is 9.2. So, the difference is 9.2 minus 8.5 is very close. So, if the solubility parameters value of these two polymers are close then we can consider that these polymer, these solvent, these particular solvent can be used as a very good solvent. So, this way you can go for selection of solvent for a suitable polymer. So, if there is any question on this thing you ask me, any doubt, any question? The structure, properties, relations of polymers

Student: (( ))

But bond energy is related to the cohesive energy density.

Student: (( ))

Of course, you take, you take the example of polyethylene and and polyethylene terphthalate and or nylon. In nylon there is a hydrogen bond in addition to Van der Waals forces, say learn the dispersion force and this hydrogen bond is present due to the presence of nitrogen and oxygen Na H C O, amide linkage. So, this polar polar interaction is there. So, due to polar polar interaction these hydrogen bonds coming into picture. In case of polyethylene no polar polar interaction only it is London dispersion force, where from it is coming?

It is coming from the bonding electrons, induced effect of bonding electrons. So, that is the cohesive energy density of polyethylene. In case of nylon cohesive energy density is the contribution from polar bond as well as non polar bonds. That is why the nylon is soluble in acid, it is a strong solvent, it can dissolve, it can be dissolved in say dimethyl formamide or dymethyle acitemic or dymethyl sulphoxide, these are highly polar solvents. So, highly polar solvents can dissolve this polar polymer, even there are some polymers like polyemides.

Sometimes, cresols, meta cresols, para cresols, phenols, concentrated sulphuric acid these are used as solvent for those polymers whereas, these common solvents cannot dissolve them. Tetrahydrofuran is a good solvent for polyvinyl chloride. What is the solvent for polyvinyl alcohol? Water, this is a water solvent polymer, but hydrocarbon solvents cannot dissolve this polyvinyl alcohol. Polyethylene, for polyethylene although this hydrocarbon solvents can be a good solvent, but it does not dissolve at room temperature, you have to break the crystallites.

So, for LDP tolvene it is a good solvent at its boiling temperature, for HDP xylene is a good solvent for HDP, xylene is a good solvent. So, you please go through these slides I have told. You have taken some notes and then read some books, complete the note and try to understand.

Thank you.