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Lecture – 30 Polymers

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Hello everyone, welcome to the course on bio materials. We will continue on the topic of polymers, we were looking at many properties and thermal properties of polymers are also very very important because polymers, the amorphous region of polymers sometimes exhibit glassy state and then sometimes they exhibit rubbery state. The amorphous is at certain temperatures that are at lower temperature the molecular; molecules of polymer vibrate, but not move significantly. So, they almost look like glass that is why it is called glassy state; that means, they became brittle hard and rigid when the temperature is raised the polymer the amorphous region of the polymer becomes a rubbery state; that means, they become soft and flexible name implies right like rubber.

So, the change wiggles; so, they become like soft and flexible like rubber. So, the glassy state rubbery state that is very very important point and that is known as the glass transition temperature T g; T g is the glass transition temperature and above which it

becomes a rubbery state and below which it will be a glassy state as in mentioned its valid only for the amorphous region it depends on the molecular weight of the polymer rate of heating or cooling what type of measurement method are used and so on.

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So, then melting point the crystalline portion of the polymer at some temperature starts melting that is also very important to know. So, just like T g the glass transition temperature the melting temperature may be 200 degrees or 300 degrees of course, in bio material inside the body you are not going to face such very high temperature, but still it is good to know what is the melting temperature of the polymer that is a property of a crystalline region. So, the polymer is very very crystalline you will see very sharp melting temperature if it is very amorphous you will not see. So, long time back I have introduced this instrument called differential scanning calorimeter or calorimetry DSC it can be used to measure all these properties.

So, what; so important about these temperature the temperature determines the volume of the polymer and dynamic mechanical properties of the polymer and. So, on for example, if you look at crystalline solid the temperature has increased and occupies more volume semi crystalline solid you will see this, this is called the T g. Similarly for glassy solids we will have like this is the T g the dynamic mechanical properties also start going down

you can see this. So, semi crystalline cross linked. So, as the temperature is increased the e modulus can start decreasing. So, that is why temperature is very very important. So, that is why we need to understand this T g and T m, T M is the melting temperature.

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So, the T g when the polymer is cooled below this temperature it becomes hard like glass when it is heated above this temperature it becomes rubbery like rubber and generally the heat flow was plotted against temperature when you use a DSC. So, it looks like this. So, there is a big I mean this is called the phase change and this temperature that is in the middle of this is called the T g. So, hard plastics like polystyrene polymethyl methacrylate are generally used below their T g. So, that it looks like a; that is T g greater than hundred where T g is greater than hundred. So, it is used below their T g. So, that it looks like a glassy material where as if you look at rubber elastomers like poly isoprene poly isobutylene we need to use them above their T g; that means, they will look like a rubber soft and flexible.

So, if I have using rubbers I would like to use it above their T g and if I am using polystyrene PMMA I will use below their T g so that they look hard.

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Acrylonitrie Installene styrene (ABS)	105	
Esb(cedenate) (PC)	145	
Poly(methyl methacrylate) (PMMA stactic)	105	
Poly(viny) acetate) (PVAc)	30	
Poly(viny) alcohol) (PVA)	85	
Poly(viny) shloride) (PVC)	80	
Poly 3-fostcardostarate (PHR)	15	
Polyenside (PA)	67-60	
Pshychlorotrifluoroethylene (PCTFE)	45	
Polyethylene terephthalate (PET)	70	
Polylectic actil (PLA)	60-65	
Bahnackomene	215	
Ephypopylepe (PP atactic)	+20	
Eshperapolene (PP instactic)	0	
Polyotycene (PS)	95	
Debastions	185	
Pulytetrafluoroethilene (PTFE)	115	
Palaximi Evende (PVP)	-10	
Polyvinylidene Ruoride (PVDP)	-25	
The output	-70	https://en.wikipedia.org/wiki/Glass_transition

So, this table gives you T g of many polymers this is taken from this reference as you can see some of them has T g below their room temperature, if you take 30 as our room temperature polyvinyl acetate PHB, this is a polymer produced by bacteria polypropylene, polyvinyl chloride, polyvinylidenen fluoride rubber they have very low T gs, as you can see below their room temperature where as if you look at other like acrylonitrile butadiene poly carbonate polymethyl methacrylate polyvinyl alcohol polyvinyl chloride polyamides PET polyesters polyethylene terephthalate polystyrene polysulfone, PTFE: polytetrafluoroethylene, they have T g above room temperature above 30 degree centigrade. So, there is lot of difference between the T g, it will becomes hard brittle like your glass. So, you can measure T g using a DSE the face change it can be nicely seen in the DSE.

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Polymer blends the beauty of polymer is we can blend different polymers to achieve the required mechanical properties required softening required T gs and so on actually. So, physical mixture of 2 or more polymers without with or without any chemical bonding; so, if I am going to have 2 or more polymers and I put a chemical bonding that can be called cross linked we use cross linked linking agent we use cross linking agents like butyraldehyde where as if I have just physical mixture I will not any reaction in cross linking. So, they are called homogeneous or they are called heterogeneous; heterogeneous will be immiscible homogeneous will be miscible on molecular level.

So, when we blend it nicely interfacial tension between the polymers faces approaches 0 large interfacial tension; that means, they can have a phase separation low critical solution temperature; that means, low critical solution temperature. So, the phase separation of a miscible blend during heating upper critical solution temperature, phase separation of a miscible blend during cooling so this is during heating as you can see here and this is during cooling. So, this region you will have a single phase where as above in this region and this region you will have 2 phases. So, ideally if I want to have 2 polymers well blended miscible mixed very well then I would like to have them in a single phase. So, I need to operate in this region of temperature. So, we can get this type of a graph where you have the y axis as temperature x axis as composition. So, I mix

them together and n this region of temperature they will be in single phase where as if it goes here or here this is the low critical solution temperature during the heating phase and this is during cooling phase where we will have the 2 phase separation taking place. So, I would like to work in this region.

So, suppose if my room temperature is 30 degrees here I need to select the concentration. So, that I am in the single face region. So, we need to understand, what is the mixing behaviour of 2 polymers? So, that do they form single phase or do they form 2 phases.

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So, advantages of this type of blend easy to prepare cost effective properties can be manipulated that is the beauty of it we can blend nylon and urethane. So, for example, urethane is like rubber nylon is very strong. So, we can achieve both by mixing and generally blend properties will be superior to the individual property. So, we can achieve advantages of both the polymers in to this blend.

Palymer	Disaburringes	Polymer blend	Property enhancement	Application
Polyvryl chloride	Poor impact resistance, brittle	Polyvoryl chionide/ethylene- vinyl scetare copolymer	Improved toughness and impact	Medical films, blood bags, coloctomy bags, tubing
Polyesters (PET, PBT)	High skrinkage, dimensional stability	Polyester/polycarts onate	Improved dimensional stability, reduced ubviolage	Bood therapy, drug delivery IV kits and components, flexible medical tubing, surgical instruments
Acrytonitrile butadiene styrene (ABS)	Low heat distortion temperature	ABS/polycarbonal e	improved thermal resistance	Housings, surgical Instruments, diagnostic devices, drug delivery, IV

Property enhancement using polymer blend

Some examples PVC it has got poor impact resistance brittle it can break. So, what do they do they add ethylene vinyl acetate copolymer. So, improved toughness and impact so it will not be brittle some flexibility is there that is it is used in medical films blood bags. So, PVC alone if you use its very brittle it is not flexible. So, they add ethylene vinyl acetate copolymer of this. So, it can be used for bed bags or films or tubings and so on.

Polyesters shrinks they have problems with dimensions maintaining the dimensions. So, when you add poly carbonate it gives you good stability it reduces shrinkage again its used in blood therapy drug delivery intravenous kits components flexible medical tubing surgical instruments because poly carbonate is very tough it is called an engineering plastic. So, it can be used for strong application surgical acrylonitrile butadiene styrene this is like a rubber its low heat distortion temperature. So, they add poly carbonate poly carbonate has very good temperature resistance of course then we can use it for housing of material surgical instruments diagnostic devices drug delivery and so on actually.

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So poly carbonate; I was talking about, so this is the structure of poly carbonate, this is the repeating unit of poly carbonate how is it made diphenyl carbonate that is here diphenyl carbonate and this phenol a that is how we make diphenyl carbonate and this phenol, it gives you poly carbonate and it gives you phenol, it is called an engineer cross plastic temperature resistance impact resistance and transparent can undergo large deformation without cracking or breaking its used in heart lung assist devices coating of contact lenses. So, poly carbonate is it is almost like glass you can see through. So, it is used in some of those applications coating on contact lenses and so on actually.

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It is also used for high impact strong medical devices another polymer which I mentioned just now, poly urethane this is like a rubber this is the poly urethane it is a condensation of di or poly isocyanide with the polyol polyol is a alcohol when I say polyol its an alcohol here this portion is polyol this is the isocyanide here see this is isocyanide bond this is the poly alcohol bond. So, it is a soft elastomaric applications used for foams encapsulating hollow fibre devices dip moulded gloves balloons asymmetric membrane functional coatings then extrusions for catheters artificial heart pacemaker lead even urethral stents and so on. So, poly urethane this is very soft elastomer poly carbonate very hard engineer plastics. So, let us look at a problem.

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UHMWPE is used in knee or hip joint prosthesis. Its molecular weight =
2x10<sup>6</sup> gm/mol. Monomer repeat unit = -(CH<sub>2</sub>-CH<sub>2</sub>-).
a) Calculate the number of repeat units
Weight of one repeat unit = 2*12+4*1 = 28
Number of repeat units = 2x10<sup>6</sup> / 28 = 71428
b) Calculate M<sub>n</sub> if polydispersity = 1.5
Polydispersity = M<sub>n</sub>/M<sub>n</sub>
M<sub>n</sub> = 2x10<sup>6</sup> / 1.5 = 1.33 10<sup>6</sup>
c) Calculate the length of a stretched chain. Since the tetrahedral
structure of the carbon leads to a C-C-C bond length of =0.126 nm
Number of -(CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>)- repeat units = 2x10<sup>6</sup> / (3*12+6*1) = 47619
= 47619 * 0.126 = 6000 nm = 6.0 μm
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Ultra high molecular weight polyethylene is used in knee or hip joint prosthesis its molecular weight is 2 into 10 power 6 gram per mole and because its polyethylene it has got only CH 2, CH 2 as repeating. So, it has got say CH 2, CH 2 as repeating. Now calculate the number of these repeat units, how do we do that its quite simple weight of one repeat unit. So, it is got 2 carbons into 12, 12 is the atomic weight and then it has got 4 hydrogen 4. So, 2 into 12 is 24 plus 4 is 28. So, how do we calculate number of repeat units its molecular weight is 2 into 10 power 6 divided by twenty eight that will give you 71,428, this repeat units.

Now, calculate M n that is the number average molecular weight poly dispersity is 1.5. So, the weight average is this I mentioned before that weight by a number average is equal to the poly despersity 1.5. So, it is quite straight forward. So, poly despersity is 2 into 10 power 6 divided by 1.5 that is 1.33 into 10 power 6.

Third part; calculate the length of a stretched chain. So, this poly ethylene ultra high molecular weight polyethylene it occupies the tetrahedral structure. So, the C-C-C bond length of 0.126, we have 3 carbons as the repeat unit. So, we need to calculate the mass of that which is 3 into 12 plus 1 into 6. So, we have the molecular weight as 2 10 power 6 and divided by 42. So, that leads to 47619 as repeat units and if you multiply that with

the 0.126 we get 6,000 nano meters which is 6 microns.

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So, look at it, polyethylene; it forms tetrahedral where as you look at polytetrafluoroethylene which is there are no hydrogen, only fluorine, fluorine, fluorine. So, you have C-C-C F 2 C F 2 connected together it forms a rhombohedral where as polyethylene which has got CH 2; CH 2 it forms a tetrahedral. So, these are fluorine atoms.

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A 15 repeating unit of PTFE has a hexagonal structure with a=5.65 A and c= 19.5 A. Calculate its theoretical density Mass = $15(12+19*2)6.023*10^{23} = 1.25*10^{-21}$ gm/mol Velume = $(\sqrt{3}/2)*5.65^2*19.5 = 5.39*10^{-22}$ cc/mol Density = 2.31 gm/cc

You have 15 repeated units of PTFE has a hexagonal structure with a that is the side of the hexagon 5.65 Armstrong and C; that is the height of the hexagonal structure 19.5, calculate its theoretical density. So, mass 15 into 12 is the carbon F 2 C F 2, fluorine is 19 into 2 divided by 60.3 into 10 power 23 that is the Avogadro number. So, when we do this calculation 1.25 into 10 power minus 25 gram per mol, why do we do this 15 repeat units and each repeat unit as C F 2; C F 2 and so on, C is the carbon 12 F 2 that is why 2 into fluorine divided by the Avogadro number that gives you the mass of the 15 repeat unit in mol per mol now the volume of a hexagon square root of 3 divided by 2 a square CA square is 5.65 square, C is 19.5 so that comes out to be this CC per mol. So, mass by mol density is 2.31 gram per CC.

Composites

- Combination, on a macroscopic scale, of two or more materials different in morphology and general physical properties
- Exhibit properties that the single constituents do not have
- Tailorable to specific applications

So composites; what is this composites? So, we can have a combination of microscopic scale of 2 or more of materials which have a general physical property. So, I can put in glass bees in polymers I can put in carbon fibres into the polymers you must have heard about fibre reinforced plastics you must have heard about carbon reinforced plastics. So, we can have very fine carbon particles put into some polymers we can even put fibres into polymethyl methacrylate. So, that adds to the tensile strength. So, we can tailor depending upon the specific application for example, boat parts are made of fibre reinforced PMMA and they are extremely strong these fibre when they are aligned in certain direction it adds quite a lot to the tensile strength. Similarly we can have glass b or even carbon mixed with polymer to make these composites and that adds quite a lot of strength mechanical properties to the polymer.

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So, polymer ceramic composites for example, collagen hydroxyapatite collagen is a polymer, hydroxyapatite is a inorganic material. So, they add to each other and they give lot of strength they are used in dental and bone applications polymer it will promote cell growth the ceramic is bio active polymer can degrade without living any foreign substance where as the ceramic is not going to be degrading they may be helping in osteoconductive osteoinductive properties. So, by adding this you can see the applications the advantages of both are taken in the ceramic could be bio active may be osteoconductive osteoinductive polymers do not have that property the polymers can promote cell growth they can also degrade without leaving any foreign substance over a long period of time. So, we can nicely use them for tissue engineering purposes grown growth purposes of course, polymers do not have good mechanical properties and they are also not bio active; that means, taken care by these ceramic ceramics are brittle. So, they cannot take load bearing applications where as polymers are more better than these ceramics. So, these are very good example of polymer ceramic complex and lot of dental bone applications have this type of combinations.

So, polymers are reinforced inorganic it could be calcium sulphate alumina hydroxyapatite after all your bone is a polymer ceramic composite ceramic right they can give better self response they will have very good mechanical properties improved tissue integration. So, this type of combination also has some usefulness and advantages.

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Polymer	Commie	Application	
Type I collagen	Hydroxyapatite (INA), Tricalcium phosphate (TCP)	Acute long bone fractures, traumatic osseous defects, bone void fillers	
Type I collagen, chondrottin-6- sulfate	ма	Filling of peridontal defects, preprosthetic osseous reconstruction, maello-facial reconstructive surgery	
Fibrin	Biphasic calcium phosphate	Bone void filler	
Collagen .	TOP	Filling, bridging, reconstruction and hone fusion	
Type Ecologen fibers	Magnesium enriched IKA neniorystałs	Long bone fractures, revision hip arthroplasty to All acetabular defects	

Few examples of polymer ceramics type one collagen combined with hydroxyapatite or tricalcium phosphate they can be used for long bone fractures traumatic osseous defects bone void filler. So, in a bone void sometimes we can fill it up only with the inorganic material, but then they could be brittle. So, we add collagen in to that.

Similarly, type one collagen or chondroitin 6 sulphate with hydroxyapatite this is used in dental periodontal effects pre prosthetic osseousary construction maxillo facial reconstructive surgery after a trauma the facial reconstruction we can combine this type of h composites fibrin biphasic calcium phosphate again bone void filler collagen tricalcium phosphate filling bridging reconstruction and bone fusion collagen magnesium enriched hydroxyapatite nano crystals. So, magnesium ha is also bio resolvable. So, we can think about long bone fractures hip arthroplasty to fill acetabular defects. So, you see we can use calcium tricalcium phosphates you can use hydroxyapatite calcium phosphates with collagen generally for bone applications filling up of voids long bone segmental defects and also for dental orthodontic applications because your inorganic material cannot bear loads. So, we need collagen, but the beauty of the inorganic material is they are osteoconductive osseointegrative. So, we can use them. So, this type of

combinations are very very advantageous each helping each another.

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Let us look at on simple problem related to this composites look at this finely ground silica that is the density is used for a filler for poly dimethoxy siloxane which has a density of 0.9, this is a polymer this is the structure of this polymer poly dimethoxy dimethoxy siloxane silica is there, that is why it is called siloxane. It is optically clear inert non toxic good flow properties non flammable it is used quite a lot in cosmetic consumer product industry it is used as filler in breast implants. So, because of its clarity it is. So, used widely in cosmetic that is this.

Now, question is I am mixing silica with PDMs. So, what volume fraction of silica is needed to make this silastic rubber because PDM is very rubbery to achieve a density of 1.25. So, we have silica density 2.65 siloxane that polymer PDMs density 0.9. So, I want to achieve this destiny of 1.25, what should be the volume fraction of silica I need to add.

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Finely ground silica (density = 2.65 gm/cc) is used as a filler for PDMS (poly dimethyl siloxane, density =0.9).

a) What volume fraction of SiO<sub>2</sub> is required to make the silastic rubber with density of 1.25 gm/cc
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\rho = \rho1 V1 + \rho2 V2
1.25 = 2.65 * V_{silies} + 0.9 V_{PDMS} V _{silies} + V _{PDMS} =1 V _{silies} = 0.20
Park and Lakes, Biomaterials, 2007)
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So, same thing what volume fraction of silica is required to make the silastic rubber with density of this, this problem was taken from this reference book. So, what do we do? It is called a mixture of mixture rule that is the density of the composite density of component one the volume fraction of component one density of component 2 volume fraction. So, I want to achieve 1.25 silica is 1.65 siloxane is 0.9, what should be the volume fraction of silica.

Now, this fraction and this fraction is equal to one that everybody knows. So, VPDM s we can put is 1 minus V silica. So, from there we can calculate volume fraction of silica volume fraction of silica is 0.2. So, I need 0.2 volume fraction or 20 percent silica to achieve a density of 1.25 for the composite when I say 20 percent silica, the 80 percent is this polymer PDMs, interesting problem; what is the weight percent of silica? So, this is volume fraction. So, I need to calculate the weight percent that is also very simple weight of on CC of rubber is 1.25 grams.

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And the volume fraction is 0.2; the volume fraction is 0.2 weight is this much. So, we can calculate 0.2 into 2.65 divided by 1.25, 2.65 divided by 1.25, that gives you 0.42. So, I need to add a 42 percent by weight of silica where as I need to add 20 percent by volume of silica, why 42 percent because density of silica is very high that is why weight wise it is very high.

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An isotopic composite which contains spherical silica particles the modulus is 72 Giga Pascal in a polymer which is 1 Giga Pascal. Now I am adding this 33 percent by volume of this into the polymer what is the modulus of the composite. So, there are some equations available in literature one equation is this Gibson and Ashby especially for dilute material spherical material if you add an isotropic composite this is the equation that is given E that is modulus of this composite 1 plus 5 E I that is the inclusion material which you are going to add and this is the M of the polymer V I is the volume fraction divided by 3 plus 2 E I by E M E I is the inclusion material you are adding E M is the polymer material this is taken from this reference.

So, we just have to substitute 572 minus 133 percent, here 3 plus 2 again 72 by 1 that gives you 1.8 Giga Pascal that is the modulus of this particular composite when you have 33 percent of silica and rest is the polymer 30 percent by volume. Now long time back I mentioned about Reuss model, this is the Reuss model where the E that is modulus is given by 1 divided by 1 divided by 1 divided by 0.33 that is the volume fraction divided by 72 plus 0.67 is the volume fraction of the polymer divided by 1 that gives you 1.5 Giga Pascal. So, some difference you can see. So, depending upon the type of the module which we use we can get slightly difference in the number of the composites.

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Average bond energy of C-CI in PVC is 340 kJ/mol. Can visible light (\lambda =4000-7000 Å) have enough energy to break the bond

E= h\delta/\lambda

h=Plank's constant = 6.626 × 10<sup>-34</sup> joules. s

c = 299,792,458 metres per second = 3.0 *10<sup>10</sup> cm/s

\lambda=4000 Å = 4000* 10<sup>-8</sup> cm

Avogadro number = 6.023*10<sup>23</sup>

Energy per mol = 6.023*10<sup>23</sup> x 6.626 × 10<sup>-34</sup> x 3.0 *10<sup>10</sup> / 4000* 10<sup>-8</sup> = 299222 J

= 299 kJ/mol

Park and Lakes. Biomaterials. 2007)
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So, let us look at another problem average bond energy of carbon chlorine in PVC as you know polyvinyl chloride it contains lot of chlorine or the bond energy of the C-Cl is 340 kilo joule per mol. Now can visible light which has got lambda 4,000 to 7,000 Armstrong have enough energy to break the bonds. So, we need to calculate whether the energy is greater than 340. So, it can break the bond this can happen especially when I have bio material and which is made up of PVC and I am trying to sterilize it using u v radiation, will the bonds get broken I need to do that. So, from with respect to that this is a very very important problem.

So, what do we do? You remember this equation E is equal to h c by lambda, h is your planks constant c is the wave wavelength the light the speed of the light lambda is this that is the wavelength. So, c is the speed of light lambda is the wavelength h is the plank constant that gives you energy planks constant is given by 6.626 into 10 power minus 34 joule second c is the speed of light. So, many metre per second that is 3 into 10 power 10 centimetre per second lambda. Let us take this smallest 4,000 Armstrong that is 4,000 10 power minus 8 centimetre, Avogadro number is 6.023 10 power 23. So, energy per mol 6.3 into 10 power 23. 6.626 10 power minus 34 c is 3 into 10 power raised to the power 10 divided by lambda 4,000 minus 8. So, that gives you 299000 joule or 299000 kilo joule, per mol. So, which is not enough average bond energy is 340.

So, I need to achieve 340, but I got only 299. So, if the; if I am using light whose wavelength is 4,000 to 7,000 then I will not break the Cl bond where as the lambda is going to be much less than this 4,000.

For example if another 30 or 40 percent less than this number may go up 30 or 40 percent. So, I may come very close to this and chances are I may be breaking the bond of Cl this is a very interesting problem. So, if I am using visible light wavelength 4,000 then I will not breaking this Cl, but if I am going down say may be 3,000 or less then the bond between C and Cl can break. So, this is also very interesting problem worth pondering about. So, we did quite a lot of in the past 3 lectures on polymers looked at different types of polymers applications of polymers in different areas of bio material and implants then properties of polymers and also we will looked at a few simple problems which gives you some idea about polymers and their application area.

Thank you very much for you time.