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Lecture - 41 Polymer Additives (Contd.), Blends, Concluding Remarks

Welcome back to this course on Polymer Chemistry, and this will be the last lecture for this course.

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What we will do in this lecture, we will cover, basically complete our discussion, which we are having on chemistry on polymer additives and we will talk about fire retardants, surface-active additives and reinforcing fillers today. And then briefly talk about polymer blends and then go to the concluding remarks about this course.

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Let us talk about fire retardant and we had earlier about 2, 3 lectures, earlier we discussed the fire retardant and the evaluation techniques, and how do we measure the fire retardant properties of a polymer samples. For example, that limited oxygen index, we talked about one of the ways to measure the fire retardants properties. The other or a method, we talked about that method, where we burn the sample from a particular distance, under particular condition and in presences of some ignitable materials like cotton.

And then we range or rank those polymers species, depending upon how long they burn and how they burn, and whether they ignite that cotton, which is present below the sample. One of the also important thing that about fire retardants is that, whether the polymer during the burning, whether they are generating smoke and toxic gases. So basically, a good fire retardant polymer should not generate lots of smoke and obiviously they should not produce toxic gases.

So, fire retardants have chemicals, which are used to retard the ignition and burning of plastics, by interfering with the chemistry and or the physics of the combustion process. Fire retardants additives enable plastics to meet various fire safety and performance standards imposed upon them, you know the application of plastics in various common public purpose like say in Aeroplane or in building materials.

Now, in those applications this fire retardants is a is a very important important criteria

for regularity criteria for the polymers, to be used in those applications. Because for example, if you talk about a building construction material, where the polymer used must be a fire retardants should not catch or ignite fire easily or if in case unfortunately, it is giving ignitable, it should not produced toxic gas or a smoke. So, basically this properties required for the applications, where it is essential for the polymer to be fire retardant.

Now, to design a fire retardant additives, we need to consider the polymer ignitability rate of flame spreading, rate of heat release and formation of smoke and toxic gases, as we mention before. One thing one must note that, there is no uniform FR additives, it is not that, one FR additive is best for all the polymers. So, is basically the choice of fire additives will depend upon the prior of the polymer and the additives, basically one additive may be very good for one polymer, but the same additive may not be as good as for the other polymers.

So, it is it is essential that, the combination is chosen rightly so, no universal FR additives, performance varies with the final form of product. And generally, highly aromatic polymers and halogen containing polymers are inherently better fire retardant.

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Out of fire retardants work and they basically, prevent this ignition or combustion process, by whatever means or some means. For example, they can reduce the or they can absorb the heat release during the combustion process, by releasing water from them. They can form a insulating char on the combustion substrate and thus, by stopping or preventing supply of further fuel to the fire.

So, it basically stops the fire and the fire comes down, it can also interfere, it can design additives, which interfere with the chemical reactions that maintain the fire. To maintain the fire, they are they resume that some chemical reaction happening, which are basically radical processes, which maintain the phase fire. Now, if we can stop those chemicals reaction then basically, we can stop the spreading of the flame.

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Examples of FR additives	
 Absorbing heat by the release of water Alumina Trihydrate, Al₂O₃·3H₂0 – release which inhibits combustion 	es water at around 200 C
Forming an insulating char on the sub	strate
 Phosphorous flame retardants Phosphate esters (RO)₃PO PVC, Polyurethanes, PPO 	
Interfering with the chemical reactions that maintain the fire and promote the spread of flame	
 Brominated aromatics – emits HBr during Halogenated compounds Nylons, polyesters, styrenics, polyolefins 	decomposition
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Example, this was the basis of choosing or designing fire retardants now, we talk about few additives, which work by one of these mechanisms. For example, titania alumina trihydrate, they when in a in a fire situation, it releases water around 200 degree centigrade, which basically inhibits the combustion process. So, that is one example of FR additive, which basically act as a fire retardant additives by absorbing heat, by releasing water.

Second mechanism by which, some of the additives may function is by forming insulating char on the substrate, as we just discuss in a minute. And some examples are phosphorous flame retardant, phosphate ester, PVC and these are used mainly for PVC polyurethane polypropylene oxide type polymer. Look at these are mainly inorganic material because inorganic material, they do not basically burn in those temperature.

Typically, organic you cannot use organic material for char form, for making a cement

char because organic material themselves burn off. Similarly, phosphorous containing flame retardant act as a flame retardant by forming insulating char, the other flame mechanism by which, fire retardants works is by interfering with the chemical reactions, that maintain the fire and promotes the state of the fire. And for example, this halogenated or brominated aromatics, they emits hydrogen bromide during decomposition.

And the other halogenated compounds work that way, they basically a trap the radicals, which it is basically assumed or resumed that the radicals, which basically spread the fire. So, this HBR or HX halogenated hydrogen halides basically, trap those radicals and prevent those chemical reactions, which spread fire and they are mainly used for polymers like nylon, polyesters, styrenics and polyolefins.

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A combination of halogenated FR and antimony trioxides also used some cases and it is a the way, it is worked that on combustion with the temperature at 600 degree Fahrenheit. This halogens form hydrochloride or hydrobromic acids, that reacts with the antimony oxides to form antimony halides or antimony oxyhalides, which basically traps those free radicals.

And prevent that chemicals reaction, which basically produces, basically it stops or prevents this thermo oxidation process is, which we generates this volatile or flammable, volatile flammable volatile organic compounds. And it prevents formation of those flammable organic compounds volatile flammable organic compounds, they basically prevent the burning process. So, this is the mechanism by which, halogenated FR along with antimony trioxides synergy works.

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We are now will talk about next type of additives, which are surface-active agents or surface-active additives now, this additives actual work on different interfaces. For example, polymer air interface or polymer mold interface or interface between two polymeric phases in a blend, for example. Now, there are plenty of example of such surface active additives, what I am going to do in this next few minutes is, give examples of or give generic examples of this additives, how they work and give few examples of such additives.

Now, let us first talk about polymer additives, which work in polymer air interface, first let us talk about additives, anti-fog or anti-fogging agents. Now, if you think about the polymer wrap, a transparent polymer wrap which are used in a grocery stores, which we use for wrapping this fruits or food materials, and they are kept in a refrigerator and a freezer. Now, if in a normal situation what will happen, the water droplet with condense in that flame and it will hinder your visibility, somebody is visibility through that flame.

Because of, fog formation and customer will not be able to look at the food material, which is inside the wrapper. So, he or she may not buy that material so, anti-fogging agents basically, a surface-active agent with migrate to this polymer surface. And being

hydrophilic, it measure it makes the polymer surface white hydrophilic and in a hydrophilic surface, the water droplets cannot condense into beads.

When the come in the water vapour come in contact with this surface, they actual form a thin flame of water, which does not interfere with the light, such a way, that it basically gives any reduction in the visibility through this plastic material or it does not decrease the transparency of this plastic material. Similar types of additives is anti-stat additive or anti-static additive where, additives, which migrate to the surface and being water absorbing.

It can absorb water from the atmosphere and form a layer of water molecules, which form path ways for dissipating the static charges. So, if there are anti-stat additives were not used during the normal usage of the plastic material, the static can static charge can generate on the surface, which might give lot of hazard to the user. But if anti-static additives surface-active anti-static additives are used then what happened the agent surface-active agent migrate to the surface.

And they absorb water, which form channels through which, the static charge can dissipated so, there is no formation of static charge. Easy clean or self-cleaning type additives, which are basically very hydrophobic additives, which on migrating to the surface make the polymer surface very hydrophobic, such a way such a extreme that, when the water droplet condense on it, it cannot hold on to the surface, it basically rolls off.

Because, the contact angle between the water and the polymeric surface is very high so, it basically rolls off and giving the strolling of process, it can take away that, they are the impurities, which are present in the surface. So, basically this type of may this additives make the surface self-cleanic so or easy cleanic, the cleanic of the surface is done easily. Next step of additives are basically use to make the polymer surface useful for biological applications, there are lots some applications, where polymers or parts of parts made of polymeric polymeric polymers are used in biological application.

In those cases, the polymer surface comes in contact with biological fluid now, the surface of the polymer should be such that, it should not interfere the normal biological processes or it should not basically introduce, or start the coagulation process in the biological fluids. For example, when a patient goes through a open heart surgery, the

blood of the patient's body is taken out and by help of external machine called oxygenator, which act basically as lungs and heart. So, it basically purify the blood and also pump into the body.

So, this oxygenator is mostly made up of polymeric materials and the membranes by which, this purification is done is also made up of polymeric material. Now, there are so many other example I can give where, polymers are used for medical application where, they are in contact with the biological fluids, may be blood or serum or or tissues and so on. So, the polymers must be biocompatible and hemocompatible if it is contact with real blood, anti-thrombogenic because it should not start the coagulation process.

Now, if you look at the steps or the process of what happened when a polymeric surface, or any for the matter fact, any other external surface come in come in contact with biological fluid, the first step what happen, proteins present in the bio fluid, they get absorbed on the external surface. And subsequently, they have lots of others steps which happens following the absorption process.

Now, if we can make the polymer surface such that, this absorption of protein can be prevented or minimized. Then we can make this polymer surface hemocompatible or anti-thrombogenity, whatever we called that of anti-fogging to protein, whatever name we can give. And that is done typically, by using by making the polymer very hydrophilic or drafting or modifying the surface using surface-active additives, surface-active additives make the surface reach with the hydrophilic polymer.

So, that the protein coming proteins is prevented from absorbing on the surface theoritically and one of the examples of the polymers used for surface polyurethanes, polyethylene glycol, very often. So, they are the some examples, where surface active additives are used for medical application, modifying polymer surface is, that are utilized for medical applications.

One other example is anti microbial, where basically there is some devices, which are used by many people like a computer mouse of the (()) using, may have been used by somebody else. So, if this is a this mouse is made up of anti, this surface is anti-microbial additives, made up by anti-microbial additives then it prevents formation of microbes on the surface of the polymers and that actually prevent spreading of microbes between among people.

And typically, surface active agents are used for this purpose, surface active agents are used basically to improve the mechanical property of the polymer surfaces like scratch scratch resistances, improved wear performances and so on. And then some other specific examples like anti-glare, anti-piracy, these are the some examples, where surface-active agents are used. Now, to be successful as a surface-active additives, the additives must have some attributes for example, it must be partially comfortable.

If it is completely comfortable with the polymer matrix then it will soluble in the polymer matrix so, it will not come out to the surface and if it is completely in comfortable then it will bloom out of the surface.. So, the additives in this case, must be partially comfortable so, that it may get the surface but be in the polymer matrix.

Second, it should have low surface energy components so that, it migrates during processing technique during processing technique or molding processor, it migrates to the surface, to minimize the surface energy. At least part of the surface, part of the additives must have a low surface energy component, it must be thermally stable. So, that, it can survive the processing condition and it should be chemically unreactive to the base polymer, it is being used. So, basically, these are the attributes, surface active additives must have to be successful in any application.

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In some other application, which work other type of surface like polymer mold surfaces, to improve the mold release property of the polymer polymer material polymer material mole release are added. Mold release basically, the a polymeric surface-active agent, which have long hydrophobic tail and because of, presence of this high surface low surface energy long hydrophobic tail, they migrate to the surface. And as a result, they form a lubricating layer on the molds on the polymer surface.

So, they can be easily released from the polymer mold, the other examples of surfaceactive agents, which are used for this parsing a solid filler in polymer matrices. So that, the if you use external fillers, particular fillers to disperse them well in a polymer matrices. Some surface-active agents are used, which are basically cover our seat in the interface between the filler and the polymer matrices and thus, help the depression of the particular fillers.

Compatibilizers, they are like a lock copolymer type surface-active agents, which which go and occupy the interfaces between two polymer phases, to reduce the interfacial energy between that two polymer phases and act as a compatibilizer.



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Some example or few example of surface-active additives now, like this this additives or the other additives we talked about, they could be a small organic molecules or inorganic molecules. So, they would be polymeric or polymeric additives as well for example, this PTFE polytetraflurideethylene are added to the polymer to improve the wear resistances or coefficient of friction. Because of, the low surface energy, it migrates to the surface during processing and the coefficient of the friction of (()) polymers are very low.

So, they form a lubricating layer on the base polymer surface and improve the wear resistances, these are the examples of few mold release agent. As I said there have long tail, hydrophobic tail and because of this, they migrate to the surface and and form a lubricating layer. And which is release of the article, polymer article form the mold, examples of improving hemocompatibility or biocompatibility of polymeric surface is a tegomer, which is (()) and PDMS.

Because of, presences of PDMS, it migrate to the surface and because of, hydrophilic nature of polycapton electron, it basically form a domains of hydrophilic and hydrophobic regions. So, which actually have in, being the surface biocompatible or hemocompatible.

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Let us move to the next set of additives, which are fillers, which are mainly use to reinforce the polymer performances mainly, benefitting the mechanical properties of the base polymers. And many types of fillers mainly inorganic or added to polymers for different purposes and some of them are listed here. And inorganic fillers, they themselves has high modulus so, these by adding these inorganic fillers, at least increases the modulus of the base polymer.

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And some of the mover fillers, which are now a days used in polymer matrices, polymer formulation are nano-fillers. And when they are added this nano-fillers are added to the polymer formulation, the resulting formulation or resulting polymers are called nanocomposites. Some nanomaterials, which are used as a filler or nanoparticles, they are the particles having diameters between 1 nanometer to 100 nanometer range. It would be silica particle titaniumdioxide and conducting particles and so on, there are many examples of such nano particles.

Nanowires or nanofibers, where it is basically whiskers or filaments with diameters in the range of 100 to 10 to 100 nanometer, having high aspect ratio. Nanotrubes specially, carbon nanotubes because of, they are very highly potential, this single one carbon nanotube or multi one carbon nanotubes are now a days, used for different polymeric nanocomposites.

Nanoclays, they are layered two dimensional structure, having thickness in nano dimension, they also used for in nanocomposites. And other fuller in spherical fullerenes and others also used as a nano-fillers.

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Now, what it does to the base polymer, the nano-fillers actually improve the some of the properties of the base polymers like strength, modulus, toughness, heat distortion temperature, UV resistances, barrier properties, we get the example of nanoclay during the discussion of barrier properties. It basically increases the tortuosity or increase the path to be covered by a gas to to come out of the polymer thickness. It also increases thermal and electrical conductivity, if they are used in proper amount and their dispersion is proper.

Obviously, they also being some challenges for example, with this inorganic fillers the transparency of the base polymers is basically come down. And that is because as we discussed earlier, differences in the refractive index between this fillers and the polymer matrix, and if the size is large then it can cause lot of scattering. The ductility also come down along with increasing in the modulus, by this nano-fillers and thermal stability may be sometime also questionable because this might being some impurities along with this fillers.

So, that might cause some questions about the thermal stability of this polymers specially, at the high temperature or during the processing condition, one example is shown here.

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This is a montmorillonite clays, which is very commonly used nanoclay and they have enlayered two dimensional structure and so, ideally to get the best property from the clay as a filler, they has to be dispersed quit well. So, their as the layer has to be dismandled and dispersed like, what is shown here and we call this as exfoliated nanocomposite. And that happens there, is if there is the very good interruption between the polymer matrices and the surface of these clay.

There could be intermediate scenario between these two, where the layers are separated to some extent with polymer chains in between and we call this as a intercalated nanocomposite. Obviously, to improve property one, this type of exfoliated nanocomposite with nanoclays always preferred. So, with with a use of this nanoclay, the base polymer it has improvement in modulus, tensile strength barrier and fire retardant property.

But, obviously, with this the transparency come down and ductility of the matrices is comes down, with this let us basically come to our discussion on polymer additives. And there are other additives can be discussed but due to lake of time, we cannot discuss the entire list of additives used for polymeric material, what I did I did discussed the important additives, which are very commonly used in polymer industries. Now, briefly talk about polymer blends, polymer blends is basically mixture of more than one homo polymers or copolymers.

Now, to be why there why do we require to bring or mix to polymers, sometimes what happen one polymer is not sufficient enough to meet all the strange and requirement of properties for a product. So, sometimes by using another polymer mixed with other polymer, the properties is met so, we discuss, let us define few terms related to polymer blends, polymer blends as we know, it is a mixture of at least 2 polymers or copolymers. And miscible polymer blend is a mixture of polymers, which are homogeneous at molecular level.

Remember, we talked about while discussing with Tg, glass condition temperature, we discussed that this miscible polymer blend has single Tg. Basically, they are molecularly soluble with each other so, they are homogeneous at molecular level and (()) of mixing for this type of blends is negative. So, they are thermodynamically miscible, immiscible polymers blends were the individual polymers components are phase separated. So, they are thermodynamically immiscible the (()) mixing is positive.

Now, for application point of view, immiscible polymer blends is is not useful because then what happen during processing, they delaminate from each other. Because they are not miscible at all, they come out and you have the delamination problem, one layer comes out. Whereas, miscible polymers blend is also not desirable from, in practical point of view because if it is miscible then you get the property, which is average of those 2 homopolymers.

So, you do not get best of the two polymers, which are mixed for making the blends so, it is always preferred to make blends, which are partially miscible or comfortable we say, we use the term comfortable, where the individual phases of those polymers are maintain. But the interfaces are somehow, compatibilized using compatibiliser like block copolymers made up of two different homopolymers. So, basically interface between those two phases are stitched so that, they are not immiscible to that extent, that they delaminate, but they are not also miscible so, you can get the base properties of those two polymers as well. (Refer Slide Time: 37:53)



So, we talked about compatible polymer blend and polymer alloy are basically immiscible polymer blends with modified interface. Now, if you look at the thermodynamics of mixing, we discuss that Flory-Huggins Flory-Huggins theory of polymer solubility.

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Where we have seen that, entropy of mixing is given by k t N one 1 N 5 1 N 2 1 N 5 2 remember, we did this expression and (()) of polymer solution where, N 1 is the number of molecules of component 1, N 2 his for component 2 and 5 1 and 5 2 are the volume

fraction of first component and second component. Now, if we increase the molecular weight if we increase the molecular weight of the polymer what happen, this number of molecules comes down.

So, the entropy of mixing contributes less and less to the mixing (()) energy so, if you have very high molecular weight then the entropy of mixing is basically negligible. So, the high molecular weights blends or the polymer mixing is not entropy is given so, it is basically the entropy of mixing what determines, either two polymer will be misicible or not. So, if entropy of mixing entropy of mixing is negative enough then the polymers will make miscible blend and if there even 0 then aslo because of, slight entropy contribution, they may form misicible polymer blend.

What if this is positive then obviously this will form immiscible polymer blend now, to have a negative value of entropy of mixing, there should be some specific interaction between the polymers. And those specific interaction are shown here, some of them are this hydrogen bonding, ionic interactions or electron donor acceptor complex types. So, basically, what am what we need to know that because of, the high molecular weight of the polymers, the entropy of mixing is not contributing significantly to the (()) energy of mixing. So, it is basically the entropy of mixing, which entropy of mixing which determines whether a polymer will blend, will form miscible blend or not.



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We shall be clear with few example, let us talk about two molecules decane and

substitute methyl substitute decane like 2 4 6 8 10 pentamethyldodecane. Now, if you mix this two molecules, they will mix it easily no problem but similar polymers like polyethylene, if we increase this chain long enough, it will make polyethyl. And if we increase the chain both sides long enough, it will make polypropylene but they do not mix mix, they do not make miscible blend.

Because, this this no specific interaction between this two polymer, their entropy of mixing is not negative and because of their high polymer their high molecular weight then tropy of mixing is not contributing enough to the (()) energy of mixing so, they form immiscible blends. Another example we can talk about say, Bisphenol A polycarbonate and polymethylmethacrylate, if the length or the molecular weight of the polymethylmethacrylate is high then they do not form miscible blend whereas, this two form miscible blend as long as the molecular weight of PMA is small like polymer.

So, as we increase the molecular weight, the solubility are miscibility between two polymers come down unless, there is a specific interaction, which makes the entropy of mixing negative, which happens here like polyphenyleneoxide and polystyrene. Because of, rings of aromatic rings they can do (()) interaction between them and because of this specific interaction, they form their entropy of mixing is negative and as a result, they form as result they form miscible blend.

So, basically to form miscible blend, the molecular weight has to be low, which is not a practical so, polymers which having high molecular weight, mixing is always governed by entropy of mixing. And that has to become that negative, there must be a specific interaction like hydrogen bonding are pi pi (()) or ionic interaction between the two polymer molecules.

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Now, reasons for blending, as we quickly, as we have just mention this improvement with, for the base polymer develop in broad property range of material, dilute or high cost engineering resins and so on. So, let us, we have discussed enough earlier, we can blend by just mechanical mixing, we can do solution mixing as well we can dissolve those two polymers in a cosolvent and then form a film. After that, we can make a interpenetrating network by dissolving one polymer in another monomer and then polymerizing the monomer to make a polymer, which will make this as a interpenetrating network.

Let us come to the last very end of this course, I just want to make few concluding remark. But this is the polymer tree where, basically we make polymers from monomers and monomers has to be characterized very well by all other techniques, to make sure that they are free of impurities.

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Because, if there are impurities in the monomer, they will be carried over to the polymers and they are very detrimental for the use of the polymers. Once you make the polymer, we have we basically understood what the different polymerization mechanism like step growth mechanism, chain growth mechanism and define specific technique polymerization technique. We started them in detail and once a polymerization is formed, we have learned how to characterise those polymer, both from a chemical point of view, chemical characterization.

And determines their molecular weight, their solution behavior, their morphology, their thermal behavior, whether they are crystalline or amorphous so that, all we we discused how to characterise polymer completely. Once the polymer characterize is over, we go to the processing step and finally, make the product, for the processing step we need to know few information about the polymers.

And we have not studied the processing part in detail but what I have done, I gave you the basic processing technique, which you must know to be understand the polymer completely. And then we last few lectures we discussed the applications of polymer, in the sense that, the different polymers properties and how they are evaluated like mechanical properties (()) and so on.

So, we discussed in so as a polymer chemist, you we very efficient in first two step monomer characterization, monomer synthesis and then polymerization process and characterisation of the polymers for synthesis. As a polymer chemist, you probably what have to do, the processing part or the characterisation part but then you must know the techniques by which, the processing is done or the techniques or the different properties, and importantly the structure properties relationship between the property and the chemical structure. Unless, you do not know the structure property relationship between the property, which enable the polymer to be at the final application, you cannot design the new polymers.

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Last we just go back and look go back and look at the big picture a bird's-eye view of the polymers, polymers applied when they met their are may be solution are in bulk They are synthesized in solution polymerization, they can be synthesized in bulk like a milk condensation polymerization. Polymers are also can be procute though, very very less quantity from natural resources. And these polymers are formed from monomers by polymerization different polymerization techniques.

What are the sources of this raw materials monomers, mainly they are from petroleum sources so, current end one of the important trend or requirement for polymer chemist at present is to find out natural sources. Because petroleum sources will be over soon or sooner or later, not only the petroleum sources, the polymers made up of petroleum sources actually causes lots of environmental problem like green house gas emission and. so on.

So, as a polymer chemist the challenge, the current challenge is to make polymers, the good which have good properties for application to be able to find application how they are how they can be made form monomers, which are sourced from natural sources. We talked about additives, which will be added during compounding or processing, and we get either the intermediate products, which are sold in market or we can get the simple shaped final product like sheets, film etc. And some of the and some will take these resins in plates or granular form and then make the other additives to make the final part.

"The Big Picture":
Final Product
Application
Treuse / recycle
Vaste
Waste

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Now, after making the polymer product, what is the fate of the polymer, this is again another very contemporary topic of polymer waste. In a lots of governments are banning plastics, plastic bags mainly because the waste it generates are not degradeable and so, basically, they creates lots of environmental hazards. So, waste management of polymeric materials is a very important step and like the one, where polymers are need to be synthesized or produced from natural sources.

Again this is another contemporary, very important topic for a polymer researcher that, what happened after. So, new researcher a researcher should focus on to make efficient base management of the polymers, which are used for different application. If they can make biodegradable that is, fine. If they are not able they are not biodegradable then if base whether they can be recycleable again to meaningful product or if they are not biodegradable or recyclable then how they the waste can be managed.

So, that is one of the very important question for polymer chemist at this movement and obviously now a days, polymers are finding newer and newer applications, not polymers or not only applies for the commodity applications. The polymers are now getting and finding applications is very, very high in products specially, also in health care related products. So, with this, I come to the conclusion of this course and thank you, for being with me with this course and good luck to you. And I leave my email address, in case you need to contact, with a need for any reason.

Thank you.