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Module – 01 Polymer materials Lecture – 03 Topic – Characteristics of Polymers and Advanced Polymeric Materials

Welcome back; so let us start the third lecture of the module titled Polymeric Polymer Materials and today I will discuss the characteristics of the polymer and we will introduce three different advanced polymer materials. The normal polymer materials when we will solve the problems I will introduce, but three different advanced polymer we will describe in this class.

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So, first we will start with the normal stress strain behavior of polymeric material then I will introduce the concept of the so called viscoelastic deformation, fracture of the polymers they are important. And we will just have a look at it then mechanical properties of the polymer in terms of its impact strength, fatigue then tear strength and hardness of the polymer that will be sequentially described, And finally, application of polymers in terms of advanced polymeric material we will introduce.

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So, to start with the mechanical behavior here you can see that for three different polymeric material you have the stress strain curve. The first one denoted by a it is basically a straight line with having very high slope of stress and strain and this suddenly fails here as you can see marked with cross. So, this is brittle polymer one example of brittle polymer. Then curve V you can see its having a yield strength region.

And the elastic region which is a straight part is followed by this region. So, this is a plastic polymer and the tensile strength is somewhere here for this polymer. And third one you see that this straight line is having very low slope and it is going like this and then suddenly lot of deformation. You can get very high deformation and this is rubberlike behaviour. Large recovery strain produces at very low stress level and this is displayed by so called elastomer which are rubbery.

So, modulus for highly elastic polymer which is brittle here maybe as low as 7 mega Pascal to 4 giga Pascal. So, there is a range and if you compare it with typical metal it is 48 to 410 GPS. So, this is no way nearer to metal. So, these are weak material of course.

And the tensile strength that is usually 100 mega Pascal and certain metal alloys will give you about 4100 MPa. So, this is also not a high strength material, but you see the elongation for elastomer is as high as 1000 percent for a rubbery material and typical metal is having the elongation only 100 percent.

So, in that way that is quite good this table shows the material characteristics in terms of the prominent mechanical properties. The specific gravity for two different types of polyethylene

that has been compared along with their tensile modulus certainly for high density polymer the modulus is higher.

Then tensile strength is compared, yield strength this elastic to plastic region that is compared and elongation at break which is much higher in high density polymer as you can see it starts from 10 to 1200 which is reasonably higher from this range of low density polyethylene.

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So, the mechanism for this kind of elastic deformation as you can see that you have a near crystalline region. Remember that in the last class we showed the spherulitic regions, which is having a crystalline region separated by amorphous region.

So, this the first stage the elastic deformation that results from the chain molecules in amorphous region. So, this chain molecules they are elongated in the direction of the applied tensile load. So, this is shown here and in stage 2 this amorphous chain they continues to align along with this tensile load.

In addition there are bending and stretching of the strong chain covalent bonds within the lamellar crystallite which are crystalline in nature. So, this in fact, leads to a slight reversible increase of the lamellar crystallite thickness which is denoted here as del t, but as soon as you just remove the stress then it comes back to its original position.

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So, when this elastic region is going to plastic region then this elastic to plastic deformation occurs when this adjacent chain in the lamellae slide past one another. So, there is a difference between this one and this one stage 3 and stage 4 in this region you can see that this slide past to each other.

And finally, this block segments of this region this is broken. The segment attached to each other is by this tie chains of the amorphous regions and in the final stage as you can see this tie chains are oriented in the direction of the tensile axis.

So, now, it is properly oriented along with the direction of this tensile load and this elastic to plastic change corresponding to this yield strength that curve which I showed. So, there is elastic to plastic deformation takes place.

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Now, it is temperature dependence; this phenomena is temperature dependent. So, a typical example is shown for PMMA kind of polymer you see at four degree Celsius it is brittle it is having a elastic modulus which is much larger as compared to when it is heated at 60 degree Celsius. So, this much temperature change the elastic modulus progressively decreasing tensile strength is also reduced, but the ductility improves you see that slowly the ductility is coming into picture.

So, 4 degree Celsius it is totally brittle, but progressively it is becoming ductile at higher temperature and if you decrease the strain rate during the deformation this has the same influence of increasing the temperature. So, the elastic modulus will progressively reduce. So, in that respect it is having similar kind of effect.

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And if you look at the macroscopic deformation whatever is taking part I mean taking place. So, this is a typical tensile sample of the polymeric material. In the elastic region it comes back once the load is removed and then there is elastic to plastic transformation and whenever it takes place you can see that there is a small kind of neck formation is there and then the strain is increased and this is increased this region is progressively increased.

So, here both upper and lower yield points are evident and then it is followed by a nearly horizontal region. So, the neck forms at upper yield point as you can see it from here and the chain becomes oriented which leads to localized strengthening. So, to some extent it is just like strain hardening whatever you have in case of metal and elongation proceeds with the propagation of this neck. So, macroscopically you can understand this like this.

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Mechanical behaviors of polymers Viscoelastic deformation An amorphous polymer behave like a glass at low temperatures, a rubbery solid above glass transition temperature (intermediate temperature), and viscous liquid at higher temperature. Above Tgr polymer exhibits viscoelastic behavior Elastic deformation is instantaneous, deformation occurs when the stress is applied. Upon release of the stress the Elastic deformation is totally recovered. In viscous behaviour, strain is dependent on time and not completely recovered as the stress is Viscoelastic released Viscous In viscoelastic behaviour, instantons elastic strain is followed by time dependent strain. As the load is released, elastic strain is recovered. (Silly Putty is one of the examples.

Now, an amorphous polymer they basically behaves like a glass at low temperature and a rubbery solid above the glass transition temperature. So, which I will explain later on what is exactly the glass transition temperature and then it is a viscous liquid at relatively high temperature. So, the above this glass transition temperature polymer actually exhibits a viscoelastic behavior.

So, as you can understand the elastic deformation is instantaneous, you are applying the load and sudden suddenly I mean in favoring this load you have instantaneous deformation whenever the stress is applied and upon release the strain stress when you release it again it comes back . So, the deformation is totally recovered, but in the viscous behaviour strain is independent of time sorry strain is dependent on time and it is not completely recovered as the stress is released.

So, viscoelastic behaviour is some way in between the elastic and the viscous behaviour. So, there is a instantaneous elastic strain followed by a time dependent strain and then as the load is removed the elastic strain is recovered, but this is recovered as a function of time.

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So, the silly putty is one of the example of this viscoelastic behaviour. So, we can define a viscoelastic relaxation modulus and this decreases with time because it is a time dependent phenomena and it decreases also with temperature, this view graph shows it.

So, it depends on this viscoelastic behavior depends on both time and temperature. So, the stress relaxation quantifies this behavior and the example the experiment that usually is done is initially the specimen is strained at a predetermined low level rapid tension and stress necessary to maintain this strain is measured as a function of time.

So, temperature is kept constant. So, it is found that the stress decreases with time due to the molecular relaxation and the time dependent elastic modulus for this viscoelastic viscoelastic polymer. This is defined as E r as a function of t as you can see and here the stress is varying as a function of time and strain is predetermined the strain is constant. So, this is defined as E r as a function of t, the elastic modulus and it is dependent on the time dependent stress divided by predefined strain.

So, here you can see that T 1 to T 7, T 7 is the highest temperature and T 1 is the lowest temperature. So, progressively the value of E r as a function of t that reduces and this also decreases with temperature. So, both the stress if you increase the stress then this decreases with time and decrease also with increase in temperature.

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Now, you can have a predefined time here you can take a time value t. So, that remains constant say time you take 10 second and then log of this viscoelastic modulus is plotted with temperature. So, this is for a atactic polystyrene polymer we have shown it. So, at the lowest temperature as you can see it is called a glassy region the material is rigid and brittle. The strain time characteristics is like; elastic material same like elastic material and the molecular chains are essentially frozen in that particular temperature.

Now, when the temperature is further increased there is a sudden drop sudden drop of the relaxation modulus and this is the glass transition temperature where this inflection point is there. So, it forms a leathery kind of region and this is a time dependent deformation and it is not completely recoverable with the release of the applied load.

And the plateau region followed by this; after this leathery region there is a plateau region and this plateau region the material deforms like a rubbery fashion and temperature is also increased here as you can see.

At still higher temperature the modulus is dramatically dropped and this rubber material start to flow initially and the region is totally viscous and here both vibrational and rotational motion is operative of the polymer chain and finally, the polymer completely melts at T m.

So, this inflection point corresponds to glass transition temperature and this is the melting temperature of the polymer that we are talking about. In this case it is the graph from a polystyrene polymer.

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So, there are several cases that is shown that molecular configuration of polymer is changed from amorphous to lightly cross linked because the earlier case whatever I have shown that is for amorphous polymer. So, curve C is for the amorphous polymer here it is the region for elastic region then it is rubbery region somewhere here and leathery region here and then viscous flow and melting.

So, if you change to slightly cross link B, you can see the rubbery region is extended. So, once slightly cross linked polymer not fully amorphous then it is extended and the polymer does not melt up to this temperature. And if you increase the cross linking remember the value of t, the time is constant. So, it is therefore, since it is a function of time.

So, we have defined as E r as a function of time. So, this value is further increased when increased cross linking takes place and the decrease of this E r is less pronounced. Here you see that the modulus is still at the higher regime and melting temperature of this isotactic polystyrene the same material is far higher as compared to that of the amorphous materials so it is about 240 degree Celsius.

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So, another phenomena which is important is viscoelastic creep. Many polymers they are susceptible to time dependent deformation when stress level is maintained constant such deformation we have termed as viscoelastic creep. So, here the experiment is as follows. A tensile stress is applied instantaneously and maintain at the constant level. So, it is a constant stress measurement while strain is measured now as a function of time.

In earlier case we measured stress as a function of time and this is a isothermal measurement we are keeping temperature constant. So, creep results that are represented as a time dependent creep modulus which is defined as E c t which is stress instantaneous stress sigma 0 which is constant and strain as a function of time.

So, this deformation can be significant at room temperature under modest stress level and this stress level lie below the yield strength of the polymer. The creep modulus is also temperature sensitive and diminishes with increasing temperature like the other modulus and with increase crystallinity of the polymer creep decreases almost concomitantly and increase of E c take place. So, if epsilon is reduces then suddenly the value of this will increase.

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Now, let us consider the fracture of the polymer. So, for thermosetting polymer which are heavily cross linked one, the mode of fracture is brittle. So, at crack tip there are localized stress that is for any brittle material that is quite effective that when you are applying a stress level it is multiplied there. So, the crack starts to propagate and it is amorphous there is no mechanism to stop it.

So, it breaks the covalent bonds in the network cross linked structure. For thermo plastic polymer both ductile and brittle modes are possible even for some thermoplastic this transition people have noticed from ductile to brittle transition. Usually the brittle fracture they will be favored when as I showed temperature is low, increase the strain rate during the measurement.

If there is any sharp notch present inside the polymer, so, the stress concentration will be more. Thickness of the polymer if it is increased then also brittle fracture is favored and if somehow this glass transition temperature is increased then also you have this fracture of the polymer is expedite.

So, an example I have shown the same curve 4 degree Celsius as you can see it is totally brittle whereas, 60 degree Celsius it becomes extremely ductile and some temperature in between there is a ductile to brittle transition takes place.

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So, the phenomena of crazing is important for thermoplastic polymer. What happens that there are localized plastic deformation that leads to the formation of this small kind of interconnected micro voids . So, this micro voids is separated by this fibrillar bridge this regions.

So, when you are applying sufficiently high tensile load this micro voids starts to grow and then they start to coalesce and this results the formation of the crack that is true, but in the process the crack absorbs the fracture energy and eventually it increases the fracture toughness.

So, actually the actual figure has been shown here. So, this is forms a highly stressed region associated with scratches flaws and molecular inhomogeneity. It arises from there, but eventually it is good because this cracking absorbs the fracture energy and effectively increases the fracture toughness. So, crazing is not bad in case of thermoplastic polymer.

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So, impact strength is important because when the force is applied instantaneously polymer may exhibit tactile or brittle fracture that depends certainly on temperature and specimen size and strain rate and the mode of loading that is also important whether its tensile or compressive or a flexure mode of loading and both semi crystalline and amorphous polymer they are usually brittle at low temperature and their impact strength is also low and it is desirable to have the high impact strength under ambient condition.

So, ductile to brittle transition temperature lies below room temperature it is important and impact strength decreases at high temperature as the polymer begins to soften. Fatigue is under cyclic loading we consider fatigue. The stress level is usually kept low than the yield strength and fatigue strengths and fatigue limits for polymeric materials are much lower than for metal that is true because it is not fatigue resistance as good as metal suddenly.

So, cycling the polymer at higher frequency or relatively higher stresses can cause localized heating because you are doing the stress cycling at very high frequency very repetitively we are doing. So, localized heating can soften the polymer and that can also result a typical fatigue process. So, this is interrelated phenomena.

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So, typical fatigue curves looks like this that here the stress amplitude is plotted with number of cycles to failure and you can see that stress amplitude versus number of cycles to polyethylene terephthalate which is PET.

Then nylon then polystyrene then PMMA then polypropylene it is shown and the fracture the testing frequencies typically 30 Hertz was kept and you can see that progressively depending on the type of the polymer the fatigue resistance is varied.

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Tear strength and hardness is important. The ability to resist tearing of the property is important for certain plastic, specially, those used for thin film packaging um. So, you need high strength

. The magnitude of tensile and tear strength are somehow related . The hardness represents a material resistance to scratching penetration.

Polymers are softer than metals and ceramics and most hardness test usually are conducted by penetration technique similar to that we do it for metal. And Rockwell test are frequently used for the polymer. I will describe it when I will talk about the characterization of this polymeric material later in the course. Another indentation technique like Durometer or Barcol is also used to know the fatigue.

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I mean know the hardness of the polymeric material. So, factors that influence the mechanical properties of the polymer is certainly molecular weight is one of them. So, tensile strength if you have a infinite molecular weight then the tensile strength is very large. So, it is basically due to the inter chain increased chain entanglement and rising number average molecular weight. Degree of crystallinity is another factor. So, degree of crystallinity if it is good then your strength will suddenly be larger.

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And this is a typical curve it shows that pre deformation by drawing is some way it is important, the drawing polymer is analogous to strain hardening of the material. So, when you draw pre draw the molecular chain slip past to each other and become highly oriented and when draw in uniaxial tension significantly greater in this direction of deformation than other direction.

For amorphous polymer drawing at high temperature increases basically the tensile strength. So, this is the example of the hard plastic and where percent crystallinity you can see it varies with the molecular weight. So, you have different regions here. Depending on the percent crystallinity and molecular weight you have different state of polymer materials and in this region you can define either it is a hard plastic or soft plastic.

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So, heat treatment improves the percentage crystallinity towards its perfection. So, the following effects are actually identified in case of undrawn polymers, the increase of tensile modulus or increase of yield strength and reduction in ductility. For drawn polymer fibers strain modulus decreases with increasing annealing temperature because mainly the loss of chain orientation with strain induced crystallinity.

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So, there are three advanced polymeric materials that I told that I will be covering in this lecture and these three are this ultra high molecular weight polyethylene it is a linear polyethylene and its having extremely high impact resistance and outstanding resistance to wear and abrasion and friction coefficient is also quite low and this is used for helmets or fishing lines key bottom etcetera.

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Another one is liquid crystal polymer. I will not go into the details about this, but this are some kind of crystallinity is maintained at during the melting temperature as well and when you cool it down then it forms a domain structure. So, LCD display is quite popular.

So, in this polymeric crystals are switched between two conducting glass plate and the voltage is applied in certain region there is a disorientation takes place where you can see the digit or whatever display you want to see. So, that those are darken and remaining part is more or less faded regions where this disorientation is not taking place.

So, it is definitely different from semi crystalline polymer where in the melt and the solid you see the ordered structure is there. In case of amorphous there is no ordered structure between melt and solid, but here in the melt structure also some kind of ordering is there. Three different liquid crystals are there; smectic, nematic and cholesteric. So, LCD display is basically for the cholesteric kind of thing.

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And finally, thermoplastic elastomer is defined as a polymeric material which is having a rubber in between. So, styrene isoprene and styrene, so, this is a block copolymer. So, one is hard phase rigid thermoplastic and another one is soft flexible thermoplastic. So, this hard polymerized segments are located at the chain ends and this anchor, the solid soft elastomer in between.

So, beyond the melting point this can be processed and this M to S this thing is reversible. This is a reversible thermoplastic the S region is totally reversible. So, this basically has replaced the conventional thermoset elastomer. This thermoplastic elastomer are also considered one of the special polymeric material.

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So, in this lecture we have described the stress strain behavior; showed the brittle, plastic and rubber like behavior. We talked about viscoelastic deformation then mechanism of your plastic and elastic deformation. Then we talked about the mechanical behavior impact strength fatigue of the polymer then tear strength and hardness of the polymer and finally, three special polymeric material was introduced.

Thank you for your attention.