Physico-Chemical, Mechanical and Electrical Properties of Polymers
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Lecture - 38
Physical and Chemical Aging

Hello, let’s begin another lecture in this continuing discussion related to the properties of polymeric materials. In this course, we are looking at sustainability aspects in addition to looking at properties, looking at the uses, and also the concepts which are involved in macromolecular materials. And in this lecture we will look at aging. Aging is an important set of processes which occur in polymeric systems and from a point of view of performance many times aging is something which we want to control and minimize. However, from a disposal and eventual sustainability point of view aging is a process that we want to encourage, so, that the polymers become part of a, cyclic processes. So, with this first lecture, while we look at aging from the point of view of application of these materials, we will also discuss them in the within the context of sustainability.

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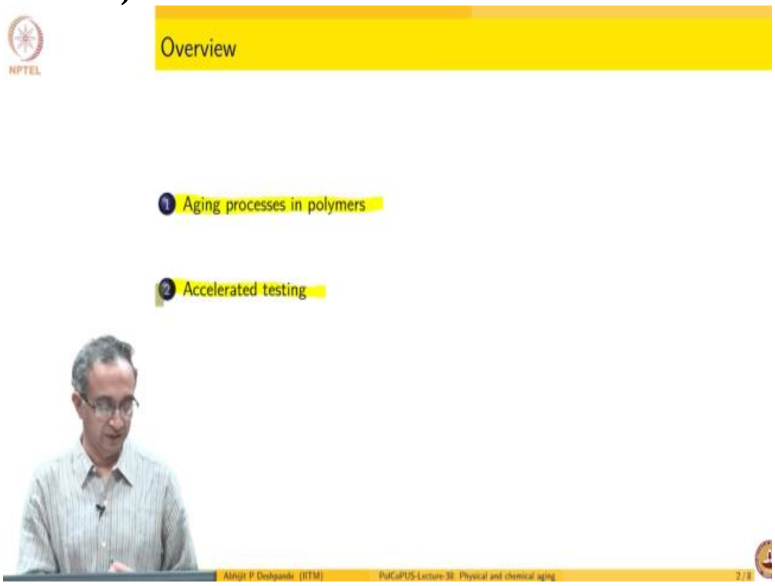

Overview

1. Aging processes in polymers
2. Accelerated testing

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And so, we will do a quick review of what may be different types of aging processes that happen in polymer. And given that we don’t have time to observe the long term performance, what we do is accelerated testing to assess the aging of polymeric materials. So, we will have discussion on accelerated testing as well.

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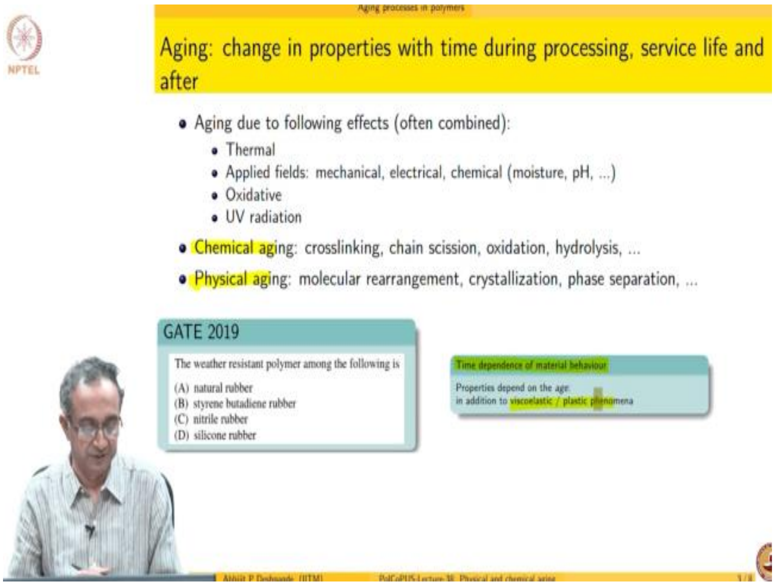

Aging processes in polymers

Aging: change in properties with time during processing, service life and after

- Aging due to following effects (often combined):
    - Thermal
    - Applied fields: mechanical, electrical, chemical (moisture, pH, ...)
    - Oxidative
    - UV radiation
- Chemical aging: crosslinking, chain scission, oxidation, hydrolysis, ...
- Physical aging: molecular rearrangement, crystallization, phase separation, ...

GATE 2019

The weather resistant polymer among the following is

(A) natural rubber
(B) styrene butadiene rubber
(C) nitrile rubber
(D) silicone rubber

Time dependence of material behaviour

Properties depend on the age
in addition to viscoelastic / plastic phenomena

So, maybe just to begin with an exam question, you can look at and think about, which one of these is a weather resistant polymer and while you think about the this topic of stability or aging processes, you will have to think of you know, what are the set of aging processes possible? And given the macromolecular structure and what are the functional groups which are present here? What are the elements which make up the macro molecule? What type of bonds are there and whether they can be resistant to the aging processes?

And so, what does the aging imply? So, it could be basically in the presence of thermal energy breakup or reaction so, it could be chain scission or chain cross linking due to thermal energy available, it could be also aging which is induced because of very high amount of load that's present in the material mechanical, it could also be a chemical load in terms of maybe a solvent, which can react with the macromolecule, it could also be the ionic environment. So, acidic and basic conditions will change the reactivity of functional groups along macromolecule and so, any of these could influence the aging. It could also be given that oxygen is a very reactive species and it can oxidize many of the functional groups which are present in macromolecule, what is the role of oxygen? And of course; energy in the form of UV radiation as well.

So, aging could be due to all of these and in most application there will be some combination. In some cases, you may have to worry more about UV resistance in some other case, you may have to worry about thermal resistance more, but generally you will have a combination of all of these aging processes. And when we think of aging in the form of a chemical aging, we are looking at basically bond formation or breakage and so, you could have reactions like cross linking, chain scission, oxygen or hydrolysis, because of water or other chemolysis due to other chemicals, solvolysis because of solvent. So, lysis is basically breaking of bond and which could be due to several mechanisms. Thermolysis would imply temperature breakage and so on. On the other hand, we can also have physical aging, in which case we have processes like rearrangement of macromolecules, some of them may start interacting with each other and form let’s say hydrogen bonding networks, because the macromolecules get a chance to come closer together due to aging, because of molecular rearrangement. It could also be crystallization. So, because the small molecules which present can plasticize and therefore, can lead to crystallization and segmental motion. With time and with aging processes, we could have inducement of phase separation also.

So, many of these are physical processes, many of them are chemical processes and so, this leads to an important time dependency in terms of material behavior. So, given all these aging processes that happening in the material naturally, there is a time dependence of material behavior, we need to distinguish the effect of aging, which is due to the chemical and physical changes that are happening in the material to the other time dependent processes which are related to macromolecular relaxations.

So, whether it’s plasticity associated or viscoelasticity associated phenomena. So, real material behavior will have contributions from both of these and sometimes it is challenging to try to especially for the long term performance, to try to make a hypothesis of how much contribution is there from each of these performances.

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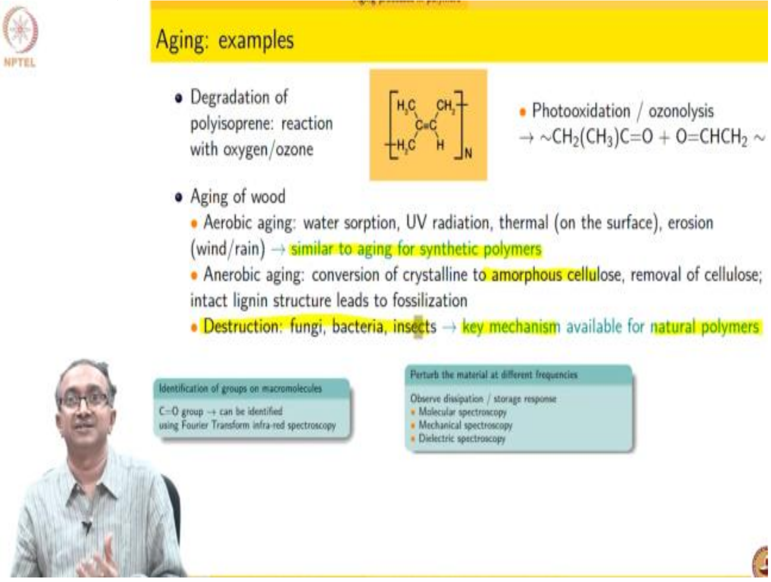

Aging: examples

- Degradation of polyisoprene: reaction with oxygen/ozone
- Photooxidation / ozonolysis $\rightarrow \sim CH_2(CH_3)C{=}O + O{=}CHCH_2 \sim$
- Aging of wood
  - Aerobic aging: water sorption, UV radiation, thermal (on the surface), erosion (wind/rain) → similar to aging for synthetic polymers
  - Anerobic aging: conversion of crystalline to amorphous cellulose, removal of cellulose; intact lignin structure leads to fossilization
  - Destruction: fungi, bacteria, insects → key mechanism available for natural polymers

Identification of groups on macromolecules

C=O group → can be identified using Fourier Transform infra-red spectroscopy

Perturb the material at different frequencies

Observe dissipation / storage response
- Molecular spectroscopy
- Mechanical spectroscopy
- Dielectric spectroscopy

So, let's look at aging in rubber as one example, and so, polyisoprene the natural rubber, there is a reaction with oxygen and ozone, which leads to basically what's happening, is there is an oxygen attack, so, that you form the carbonyl bonds and you also have the chain scission, so the chain breaks it into two and so, this can lead to strong changes in terms of the performance of the material because there is macromolecular molar mass distribution is getting affected significantly. And if you look at another example of aging, let's say in case of wood, we can have aging in the presence of oxygen or air and its absence and whenever we have aerobic aging important components, there are given that it will also be subjected to water sorption, there is UV radiation which it will be subjected to, temperatures may vary because whenever it is exposed and also there may be mechanical erosion in terms of water running off from the material or wind and dust particles impinging on the surface. So, all these variety of processes can influence the aging of wood. Anaerobic aging, on the other hand would be physical aging, where there may be transformations from amorphous to crystalline and so on. There may be slow removal of cellulose based on the breakdown of hydrogen bonding structures. And of course, eventually the lignin structure leads to fossil and that is how we know fossils are formed and fossil fuel that we get are due to this anaerobic aging processes that happened in geological timescales.

One important aging mechanism, which is also there is in terms of breakdown of the macromolecular structures, which is based on fungus, bacteria and several other species that contribute to this breakdown. So, in the end, the biological processes of enzymes baking inducing first a set of reactions, which makes sure that the macromolecules undergo reactions and change their functional groups and eventually lead to chain scission or breakdown of macromolecules. So, therefore, one important way in which we can track especially the chemical aging processes in which the bonds change in the material, for example, here, we saw that instead of a double bond, which was there in isoprene, it leads to formation of carbonyl bonds. So, we can use what's called Fourier transform infrared spectroscopy. By using spectroscopic tools, we can try to impinge the material using different wavelength radiation. And whenever the radiation energy is suitable for a bond formation, bond vibration and bond stretching and so on, then we get a resonance and therefore, we will get absorption. So, based on the energy absorption or transmission, when we are impinging infrared radiation on a polymer, we can then find out what are the set of bonds which are present. And so, in this case, for example, you can easily identify the CO group which is a result of aging in the process. So, you can use FTIR to track aging chemical aging in rubber. And of course, FTIR therefore, can be used for any process in which reacting groups form or reacting groups disappear and therefore, the bonds which are there in the material change. And in general spectroscopy is not just confined to molecular spectroscopy, which is what we saw right now, this is molecular spectroscopy is FTIR is an example. But in this course, we will also look at dielectric spectroscopy when we subject the material to different frequencies of electrical input. So, that's dielectric spectroscopy. We will also discuss, we will subject the material to different frequencies of mechanical input. So in each of these cases, the stimulus whether in the form of radiation or a load, or a current is in a form of sinusoidal variation. And the frequency determines what's the timescale? And then depending on the timescales of the material, we will obtain different responses. So that's the idea of spectroscopy, vary the frequency analyze the material response.

And so perturbing the material at different frequencies and analyzing the response is what we will do not just in molecular domain, but mechanical and electrical domain as well. One of the key things from the point of view of sustainability is to contrast these two aging materials, natural rubber on one side and wood on the other side. And what's key difference is that aerobic aging, where you have thermal UV radiation induced chain scission or cross linking reactions, that's available in neoprene also. Similarly, processes which are changing from crystalline to amorphous, some of these processes are also available. But what's the key mechanism which is different for natural polymers is this macromolecular break down due to biological processes, and so, one key idea related to sustainable polymers is can we not induce these functional groups, sometimes they can be induced during the initial polymerization stage itself o that polymer once it is through with its service life can then get integrated with this mechanism once disposed. The other idea is can these functional groups be not induced once it is ready for disposal. So, scientists are working on both of these ideas to make polymeric materials as sustainable as possible.

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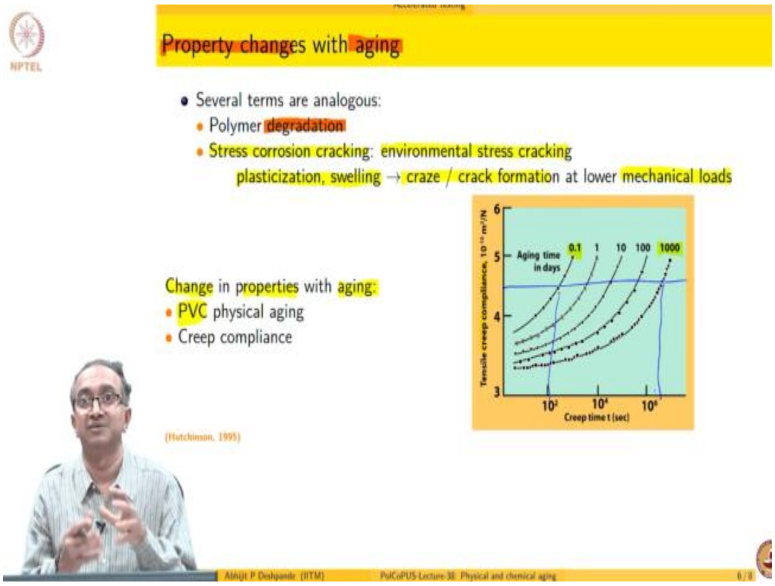

Property changes with aging

- Several terms are analogous:
  - Polymer degradation
  - Stress corrosion cracking: environmental stress cracking
    plasticization, swelling → craze / crack formation at lower mechanical loads

Change in properties with aging:
- PVC physical aging
- Creep compliance

(Hutchinson, 1995)

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So, one other important feature of aging is as we have said is, properties get affected because the underlying microstructure gets affected. And generally, when we discuss the property change with aging, there are several different terms we use, for example, we will say there is degradation of properties in the material, so polymers is degrading. So for example, modulus of the material may increase or decrease and can you rationalize as to why a modulus increase may also be negative or modulus decrease may also be negative and it completely depends on what type of application one is looking at. And I hope you can quickly see that gasket, which is a sealant application, if modulus increases; then that's a negative. On the other hand, if it's a structural component and modulus decreases, then its load carrying capacity would go down and that may be a negative. So, therefore, any mechanical property change is something to be considered and something to be understood clearly when we have these polymers being used in their applications.

There are also other mechanisms which may also operate for example, stress, given that you have environmental stress, which is due to the physico-chemical environment as well as the loading condition of the sample, you may have what's called environmental stress cracking, which is nothing but plasticization and swelling and formation of crazing. Cazing is something we discuss during plasticity discussion. You can go back and again, try to think of what is meant by craze? And also we discussed damage in these materials, which is basically crack formation, but what is crucial about environmental stress cracking or stress corrosion cracking is it much lower mechanical loads, these phenomena can happen because of the surface is being exposed to different physico-chemical environments. So, this is something where it will start from surface and then penetrate, but in the end, it will influence the overall properties of the part.

So, in general, we have to worry about the change in properties with aging and in this data here, this is related to aging in PVC and only physical aging. So, therefore, there is only molecular rearrangements taking place, but you can see that depending on the aging in days, where from 1000 days to .1 days, and we measured something which is called creep compliance, and this we will discuss when we look at the viscoelasticity. Compliance is basically one over modulus. So, it's inverse of modulus and creep is an experiment in which we just subject the material to a constant loads. It's like hanging a weight and so, we subject the material to a constant load and then we look at the strain as a function of time. So, the more compliant a material is which means it is straining, the strain is much more in that material. So, we can see that the compliance of this material changes quite significantly with aging and if let's say I take one particular constant value of compliance, let's say 4.5, what happens to this 4.5 reaching at what time? So if I age the material at 0.1, it looks like in 100 seconds itself, I reach this compliance, which means the strain becomes high, which is indicative of let's say this 4.5 compliance is in 100 seconds itself. But if I age the material for 1000 days, then I can go up to 10 to the power 6 seconds and beyond before I see the same amount of compliance. So you can see how significantly there is an orders of magnitude in response of the material due to physical aging alone. And this is because molecular rearrangements take place, glass transition changes, free volume changes, molecular interactions change and due to that the property of the material, which is creep compliance here, gets modified significantly. So that's the importance of aging, it modifies the material properties in a very significant way.

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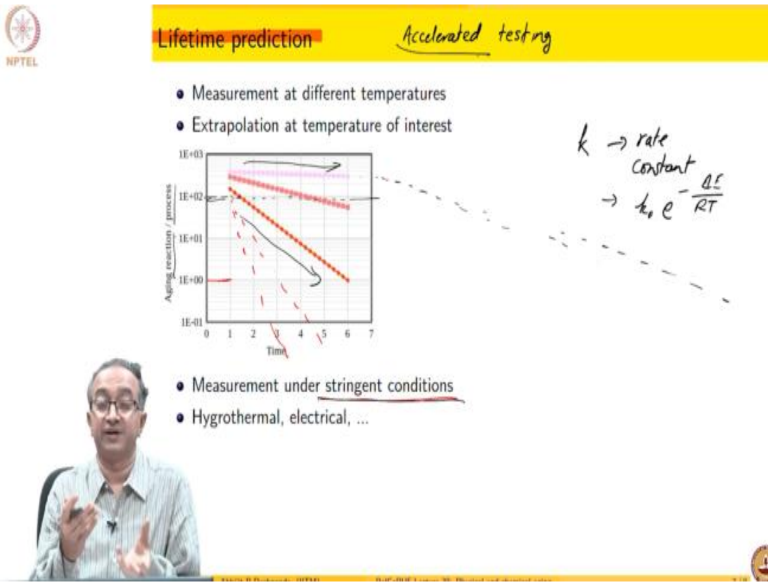

Lifetime prediction Accelerated testing

- Measurement at different temperatures
- Extrapolation at temperature of interest

$k \rightarrow$ rate constant

$\rightarrow k_0 e^{-\frac{\Delta E}{RT}}$

- Measurement under stringent conditions
- Hygrothermal, electrical, ...

And so, one other thing is that we need to do this for years. So I don't know if you can do a quick calculation and see what is 10 to the power 6 seconds in terms of years. And if let's say service life is 25 years, that's how many seconds, so and of course, we have not the luxury of doing tests over the years. So we necessarily need to do tests, and in maybe hours, maybe days, maybe in some cases, because of the validity required maybe for a few weeks and that is about it. So based on this data set, which is over seconds, hours, days and weeks, we need to extrapolate and find what could be the performance over years, 25, 30 years. And what becomes, very useful in this case, is the tools of lifetime prediction, and which are all based on what's called accelerated testing. So accelerated testing, is the key idea by which we extrapolate performance at lower times to higher times. Now, how do we do that? We subject the material to much stronger condition. So let's say if acid resistance is one idea, and generally acids which are stored in a container, maybe have a pH of 3 or 4, then what we can do is subject it to much stronger pH for a shorter amount of time and see how it ages, how it degrades. And then if we are able to make a correspondence between stronger conditions, and lower time to degradation with respect to less stringent condition, but longer time, so then we can assess.

And this is just highlighted here in this graphical hypothetical data, where let's say we have some reaction which takes place in the material, which is a consequence of aging. And so this reaction or process, it's taking place and of course, when time goes on, there is a certain change. And let's say this is being done at different temperatures. So these 3 curves are at 3 different temperatures then what we can see is, let us say this 100 happens at different times. And let's say this could be modulus decrease due to aging. In that case, you can clearly see that red must be the hotter condition, if it’s temperature induced degradation, or red must be higher pH, if it’s pH induced degradation in the material, or it could be higher amount of UV radiation, if it’s UV radiation induced damage in the material. So, red is the highest because at very short time it decreases very rapidly, while the pink curve leads to a very gradual change, so, the rate of reaction under pink condition is very low.

So, what we have to do is we have to figure out you know, when does this go to some from a performance point of view, we will always have some limit. So there may be always a red line below which we cannot go. So there must be always some condition, we will say that it should not go below that. And so, the idea is, when will this reach? When will the condition let’s say which is a room temperature performing material, when will it reach? So can we get that idea, because, this more stringent conditions can be done in lab conditions. So for example, we can even do maybe a higher temperature and it will degrade even faster. And we have basically the way I have drawn graph is time is just arbitrary units, but you get the idea that more stringent the condition quicker will be the aging process.

So, now, by measuring properties under stringent conditions, how can I extrapolate? And one key idea here is the fact that the rate of these processes dependent on temperature. For example, let’s say this aging reaction is an oxidation reaction. So, we know that any oxidation reaction will have a rate of reaction and the rate of reaction will be let’s say given by some rate constant and this rate constant is basically some k_0 e to the power - delta E / RT where delta E is the activation barrier. So, these are all activated processes. So, using this kind of hypothesis of how rates change as a function of temperature, I can do experiments under stringent conditions and evaluate the rate constants and then extrapolate the rate constant to a much lower temperature. So, I can and then that rate constant can be used to assess the real life condition and the aging performance under those conditions.

And what I have done basically, because I have done experiments in the stringent conditions, I can shorten the period. And that’s why it’s called accelerated testing. So, this is quite commonly used. And this basic underlying idea is also what is useful for time temperature superposition in case of viscoelasticity. So, in both in aging processes as well as long term prediction from a viscoelastic point of view, this idea of time temperature equivalence is a very powerful empirical tool available to us.

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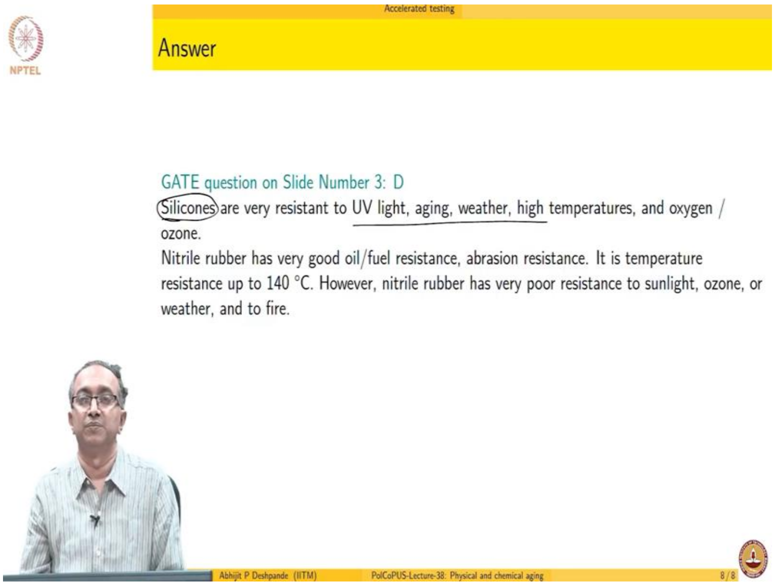

Answer

GATE question on Slide Number 3: D

Silicones are very resistant to UV light, aging, weather, high temperatures, and oxygen / ozone.

Nitrile rubber has very good oil/fuel resistance, abrasion resistance. It is temperature resistance up to 140 °C. However, nitrile rubber has very poor resistance to sunlight, ozone, or weather, and to fire.

So, with that, we will close this lecture. And silicones are actually excellent materials for weather resistance because they are resistant to a variety of conditions in terms of whether it’s UV resistance, or whether it’s resistance to thermal energy, and oxygen, ozone. So, you will see that silicones are used in many applications where weather resistance is a key. On the other hand, all the other rubbers will have pluses and minuses depending on whether it is resistance to oil or resistance to acidic media, or resistance to temperature. So, all of them will have differences in terms of their strengths and weaknesses for all these other conditions. But silicone is one of the best sort of rubber materials for weather resistance. So with this, we will close this lecture and we will continue our discussions related to properties of the materials in many of the lectures to come. Thank you.