# Nanomaterials and their Properties

**Prof. Krishanu Biswas**
**Department of Materials Science and Engineering**
**Indian Institute of Technology, Kanpur**

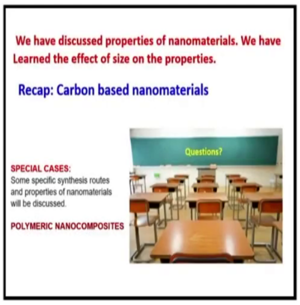
## Lecture - 29
## Special Cases: Polymer-Based Nanomaterials

Welcome to lecture 29, and this is the last lecture; I was supposed to do 30 lectures. But then I understood because it is an online course, I could finish with even one less idea was not that; basically, in online teaching, your level of space is very high. There is no question-answer session going on at the same time. So, we are always trying to teach more in every lecture than what is expected to be taught in an offline course.

So, hence the this is the last lecture, and I only can hope you have enjoyed the course you enjoyed the content of the course, I am very open for discussions or questions or anything which you have failed I may have made mistakes or I may not have covered, or I have made given some reasons, which are not maybe proper according to you.

So, please do use this forum to tell me to provide me the feedback so that I can improve in my future courses on this NPTEL forum. So, in this lecture, we are going to talk about polymer nanocomposites that we discussed about it right.

(Refer Slide Time: 01:42)

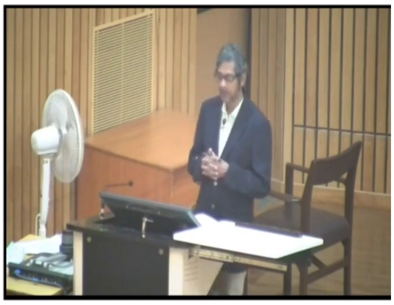


We have discussed properties of nanomaterials. We have Learned the effect of size on the properties.

Recap: Carbon based nanomaterials

SPECIAL CASES:
Some specific synthesis routes and properties of nanomaterials will be discussed.

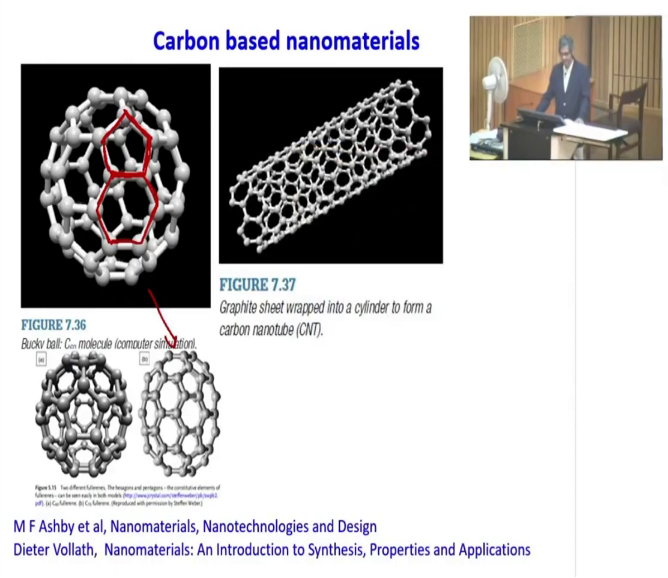
POLYMERIC NANOCOMPOSITES



So, we have discussed over these 28 lectures, various aspects of nanomaterials. We learned the effect of size for on the various properties and we have also tried to understand the structure, nanostructure issues of the nanostructure, how they are correlated with the properties of the nanomaterials. So, other than size many other aspects of size comes into picture right like arrangements at the nanoscale and also how you put things together.

So, that is the one of the important consensus issues in nanocomponents. So, the last lecture we did some discussions about the carbon based nanomaterials in the following, I am going to just give small recap and then I will talk about you know some of the important aspects of polymeric nanocomposites. Because this is something which is coming up very sharply and probably it will this composites will find use in the real time in times to come.

(Refer Slide Time: 03:54)



Carbon based nanomaterials

FIGURE 7.36
Buckv ball: $C_{60}$ molecule (computer simulation).

FIGURE 7.37
Graphite sheet wrapped into a cylinder to form a carbon nanotube (CNT).

Figure 5.15 Two different fullerenes. The hexagons and pentagons – the constitutive elements of fullerenes – can be seen easily in both models (http://www.jcrystal.com/steffenweber/pb/swpb2.pdf). (a) $C_{60}$ fullerene. (b) $C_{70}$ fullerene. (Reproduced with permission by Steffen Weber.)

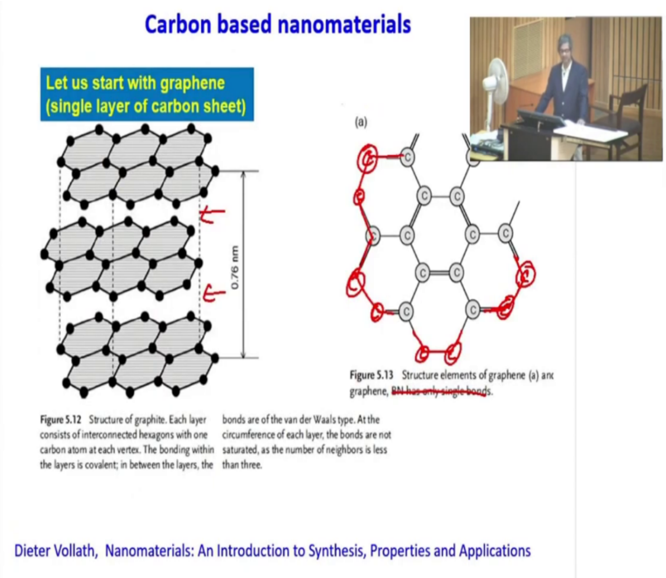
M F Ashby et al, Nanomaterials, Nanotechnologies and Design
Dieter Vollath, Nanomaterials: An Introduction to Synthesis, Properties and Applications

So, what we discussed about the carbon base nanomaterials. We talked about how the carbon can you know cell plus symbol to produce different kind of nanostructures we started with 360 Buckyballs and we showed that by putting arrangements of hexagonal and pentagons of the carbon atoms. Basically we can generate this kind of Bucky balls.

And we also understood or rather we also tried to you know show you that the carbon nanotubes can be produced by using a single layer graphene by simply wrapping around a cylinder and graphene is the recent nanostructure carbon materials although, I did not talk about nanodiamonds they are also very useful materials in the carbon family.

Since nanodiamonds are used in other purposes like coatings, high hardness is can be easily obtained using nanodiamonds and diamonds can also act as lubricants in various applications. So, therefore, the varieties of nanostructures can be produce using carbon based nanomaterials.

(Refer Slide Time: 04:11)



Carbon based nanomaterials

Let us start with graphene (single layer of carbon sheet)

Figure 5.12 Structure of graphite. Each layer consists of interconnected hexagons with one carbon atom at each vertex. The bonding within the layers is covalent; in between the layers, the bonds are of the van der Waals type. At the circumference of each layer, the bonds are not saturated, as the number of neighbors is less than three.

Figure 5.13 Structure elements of graphene (a) anc graphene, ~~BN has only single bonds~~.

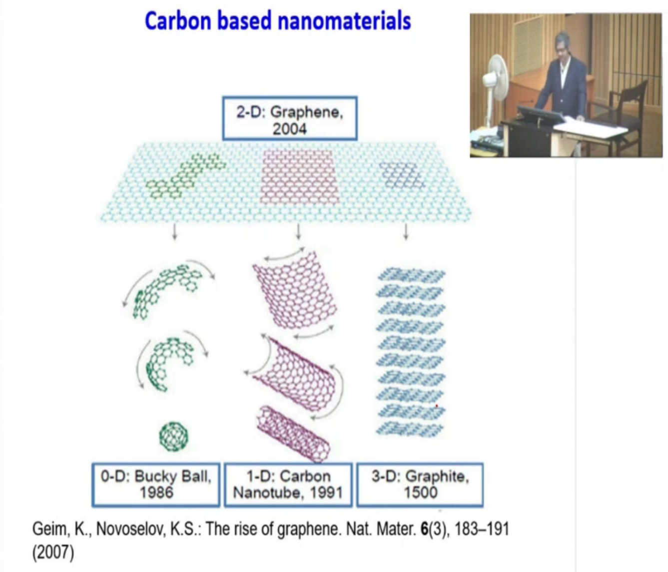
Dieter Vollath, Nanomaterials: An Introduction to Synthesis, Properties and Applications

But the basic thing is this graphite you know graphitic network is the underlying structure for all most all the nanostructures except for a diamond. So, you know that graphite is basically layer structure, it has hexagonal network in each layer and within the layer you have Van der Waal bonds between the sheets of carbon atoms.

So, we can always devise ways and means to cut off these Van der Waal bonds and produce single layer of the hexagonal network, which is very you know easy to say, but not easy to do in real experiments and that is why it took so, much time even though graphite was discovered 1500 years 1500 BC so, AD sorry.

So, there but the discovery of this nanostructures. So, very late maybe 20 to 30 years, not more than that. So, that is the difference of the time scale when you want to produce a new material. So, you can use this sheet of graphene to produce different kind of nonstructures.

(Refer Slide Time: 05:20)



Carbon based nanomaterials

2-D: Graphene, 2004

0-D: Bucky Ball, 1986

1-D: Carbon Nanotube, 1991

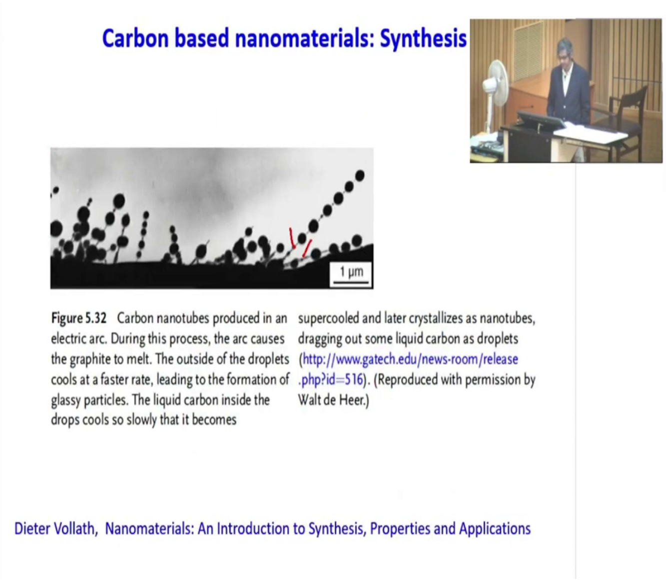
3-D: Graphite, 1500

Geim, K., Novoselov, K.S.: The rise of graphene. Nat. Mater. **6**(3), 183–191 (2007)

Like you can wrap around a ball and create zero dimensional nanostructure like Bucky Ball which came in 1986 and you can also wrap around the cylinder produce nanotubes if you rub several cylinders you can put multiple nanotubes or you can even cut off each of the sheets you can produce 2D graphene or 2D materials like graphene ok. So, this different kind of nanostructures can be easily produced by one single thing that is called graphite when you stack them together you will produce this graphite.

So, that is the connecting link for all these beast ok. I call it beast because they are very powerful materials they can be widely used in different kinds of applications that is what I call them as a beast. So, that means, what? The basic underlying structure although we know is basically single layer of graphene, but it took lot of time to understand that aspects. Now, is the question of how we can apply it and all those things?

(Refer Slide Time: 06:19)



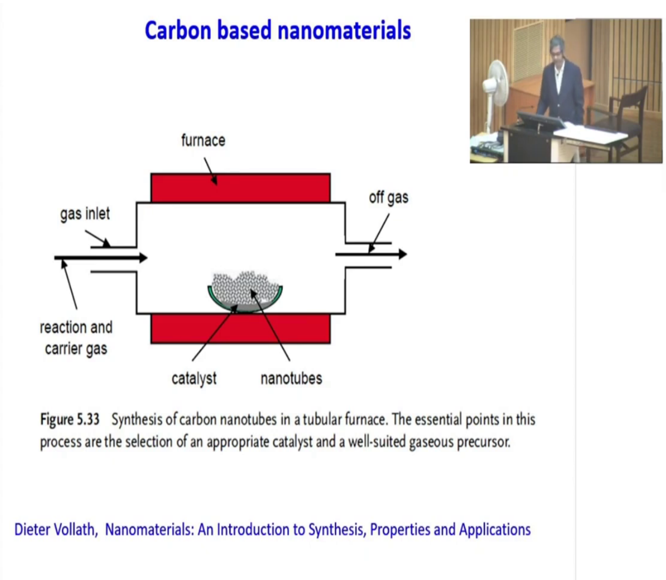
Carbon based nanomaterials: Synthesis

**Figure 5.32** Carbon nanotubes produced in an electric arc. During this process, the arc causes the graphite to melt. The outside of the droplets cools at a faster rate, leading to the formation of glassy particles. The liquid carbon inside the drops cools so slowly that it becomes supercooled and later crystallizes as nanotubes, dragging out some liquid carbon as droplets (http://www.gatech.edu/news-room/release.php?id=516). (Reproduced with permission by Walt de Heer.)

Dieter Vollath, Nanomaterials: An Introduction to Synthesis, Properties and Applications

So, this can be produced mostly by arc discharge method and you know in case of arc discharge of graphite. Graphites tend to melt and during melting most of the graphite will solidify as a glassy particles, but some of them will undergo undercooled heavily and then reproduce this kind of nano based structure materials like nano rods or nano sorry nanotubes actually.

(Refer Slide Time: 06:47)



Carbon based nanomaterials

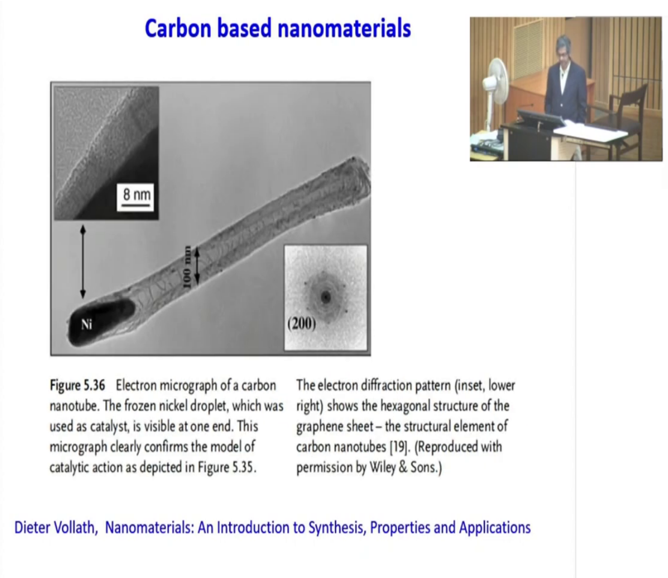
**Figure 5.33** Synthesis of carbon nanotubes in a tubular furnace. The essential points in this process are the selection of an appropriate catalyst and a well-suited gaseous precursor.

Dieter Vollath, Nanomaterials: An Introduction to Synthesis, Properties and Applications

Or you can use a run catalyst in a technique, which is very popular, you can put this graphitic material in a tabular furnace and you can always apply catalyst like iron or nickel and then you can start producing graphene at a much lower temperature. Sorry nanotube is not much lower temperature that is something about 1100 degree Celsius temperature can be used to produce this kind of nanotubes ok.

So, here in this case actually a gaseous mixture of methane and nitrogen or carbon or the argon is used and passed through this catalyst, then you can produce nanotubes and the temperature is much lower its almost 1200 degree Celsius temperature can be used.

(Refer Slide Time: 07:47)



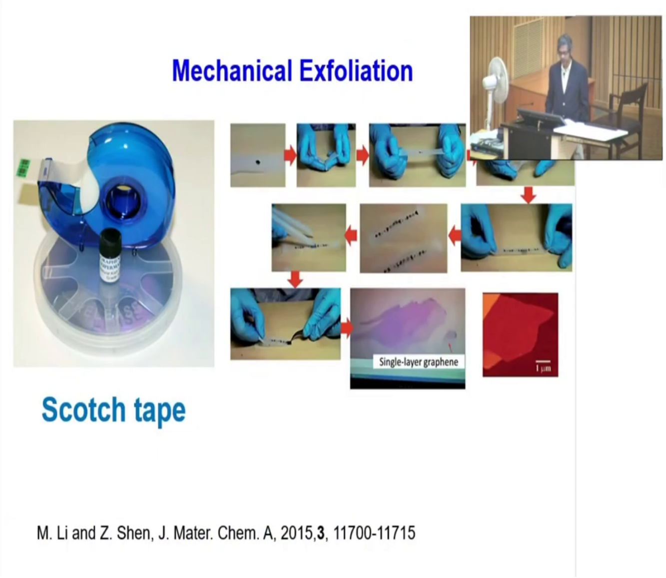
Carbon based nanomaterials

Figure 5.36 Electron micrograph of a carbon nanotube. The frozen nickel droplet, which was used as catalyst, is visible at one end. This micrograph clearly confirms the model of catalytic action as depicted in Figure 5.35. The electron diffraction pattern (inset, lower right) shows the hexagonal structure of the graphene sheet – the structural element of carbon nanotubes [19]. (Reproduced with permission by Wiley & Sons.)

Dieter Vollath, Nanomaterials: An Introduction to Synthesis, Properties and Applications

Well, this is one such picture you can see this nickel catalyst is used to produce this nanotubes and you know nickel is visible at the end of the nanotube and this micrograph clearly confirms that this catalyst can be easily used to produce this kind of Cnts.

(Refer Slide Time: 07:55)



Mechanical Exfoliation

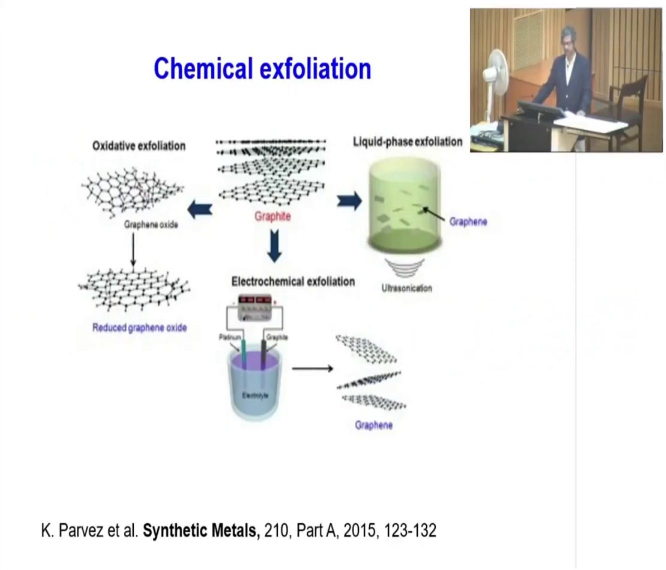
Scotch tape

M. Li and Z. Shen, J. Mater. Chem. A, 2015,**3**, 11700-11715

Well, graphene can be produced in different routes one of the ways basically mechanical exfoliations. In mechanical exfoliations you can have you can take a graphite and take a it will put it within the double sided tape and then you can remove open this peel off the tape. So, once you peel off the tape, the thin layer of graphite can come off and it can produce graphene.

This is how the graphene was discovered and you know you can see these thin layers under optical microscope and then you will find that layers which are dead thin they will be having almost 99 percent transmission of light that is how the Geim and Novoselov discover graphene and award a Nobel Prize for this.

(Refer Slide Time: 08:40)



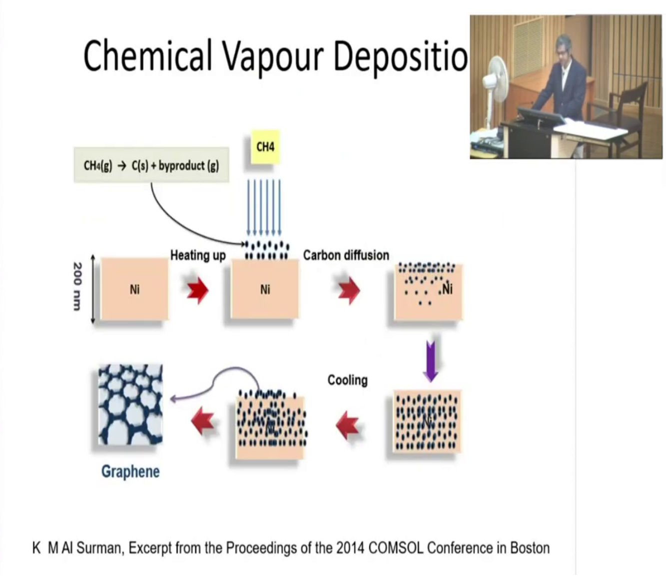
Chemical exfoliation

K. Parvez et al. **Synthetic Metals,** 210, Part A, 2015, 123-132

You can also use chemical exfoliations, oxidative exfoliations electrochemical exfoliations or liquid phase exfoliations there are three different techniques possible, oxidative exfoliations basically use oxidations of the graphite and it can exfoliate and produce different layers of the graphene graphite oxides.

And then you can reduce this graphite graphitic oxide to graphene oxide or reduce what you call a reduced graphene oxide or RGO. You can always produce using electrochemical exfoliations simply by discharging between the two electrodes you can also produce graphene by liquid phase exfoliation also. So, there are many ways you can do that.

(Refer Slide Time: 09:15)



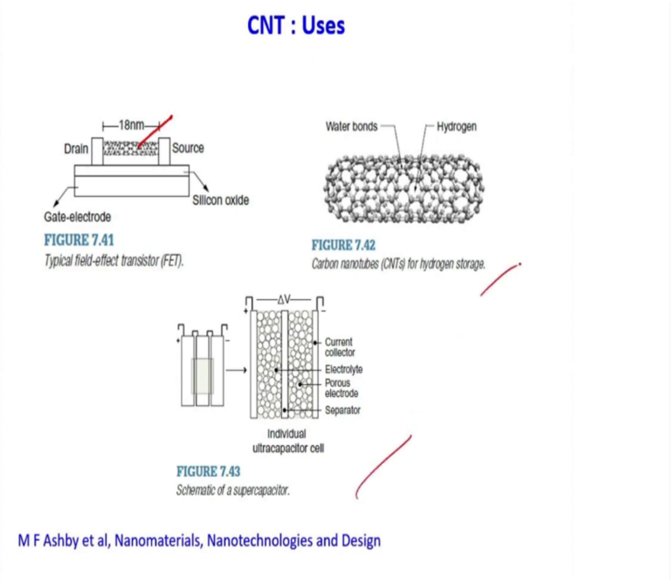
Chemical Vapour Depositio

K M Al Surman, Excerpt from the Proceedings of the 2014 COMSOL Conference in Boston

And third technique is spacing which CVD or Chemical Vapor Depositions we discussed about it you can use methane gas passed on the nickel catalyst or the nickel plate which is kept at 1100, 1200 Celsius temperature. And this methane will decompose into carbon and gaseous hydrogen or basically moisture, it can react with atmospheric moisture and produce moisture.

And it means oxygen produces hydrogen moisture, it can produce such a kind of carbon can dissolve into nickel at the temperature when the super saturation will be reached for the nickel then this carbon will come out and form like a graphene. So, this is how it is used.

(Refer Slide Time: 10:02)



## CNT : Uses

FIGURE 7.41
*Typical field-effect transistor (FET).*

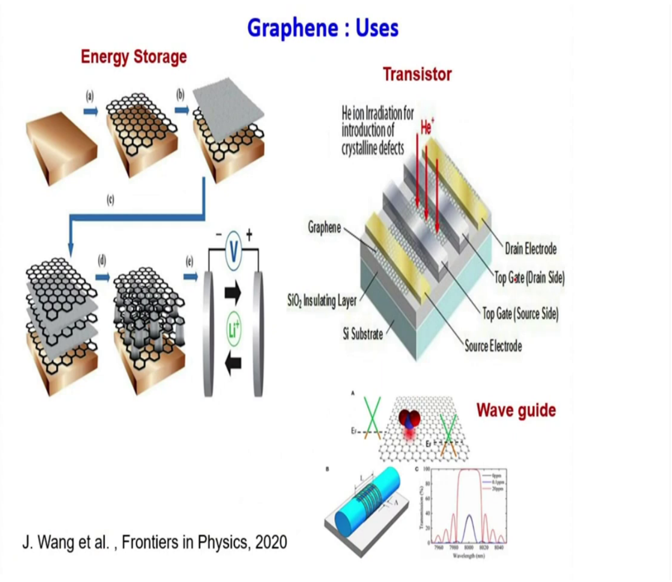
FIGURE 7.42
*Carbon nanotubes (CNTs) for hydrogen storage.*

FIGURE 7.43
*Schematic of a supercapacitor.*

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

You can use this CNT and nanotubes CNT’s and graphene properties which is our purposes like field effect transistors or hydrogen storage or super capacitor ok this is super capacitor this is hydrogen storage.

(Refer Slide Time: 10:14)

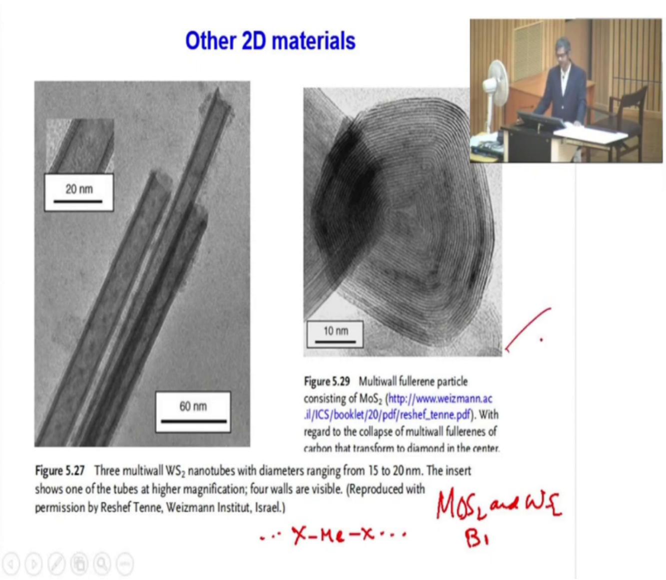


## Graphene : Uses

J. Wang et al. , Frontiers in Physics, 2020

Graphene can be used for energy storage transistor or even wave guides this is what we have seen in the last lecture.

(Refer Slide Time: 10:21)



Other 2D materials

Figure 5.27 Three multiwall $WS_2$ nanotubes with diameters ranging from 15 to 20 nm. The insert shows one of the tubes at higher magnification; four walls are visible. (Reproduced with permission by Reshef Tenne, Weizmann Institut, Israel.)

Figure 5.29 Multiwall fullerene particle consisting of $MoS_2$ (http://www.weizmann.ac.il/ICS/booklet/20/pdf/reshef_tenne.pdf). With regard to the collapse of multiwall fullerenes of carbon that transform to diamond in the center.

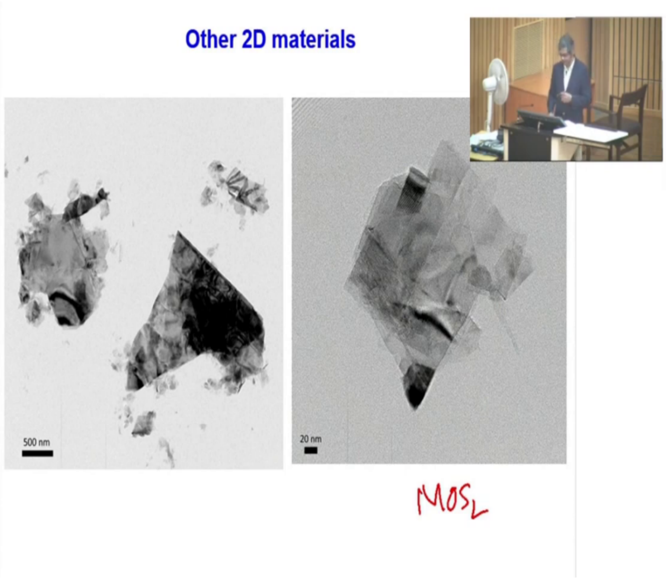
$MoS_2$ and $WS_2$

Bi

$\cdots X-Me-X \cdots$

And there are many other 2D materials most important are the $MoS_2$ and $WS_2$ and they are also produced in a similar way. You can see this is the $WS_2$ multi wall nanotubes or on the right side you can see here the multi wall fluorine obtained from the $MoS_2$ ok. So, you can do that.

(Refer Slide Time: 10:40)

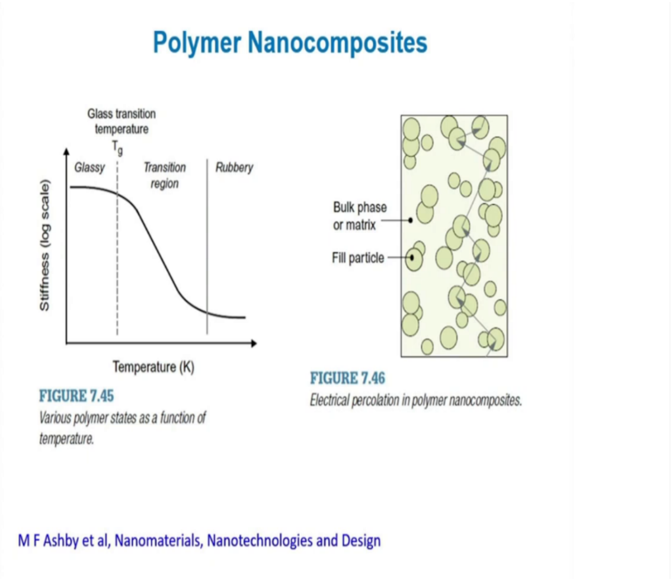


Other 2D materials

$MoS_2$

You can always produce steel sheets of $MoS_2$ by using by the sonic chemical route which we have discussed in earlier part of this course. So, as you can see, there are various 2D materials can be easily produced during this purpose.

(Refer Slide Time: 10:53)



Polymer Nanocomposites

FIGURE 7.45
*Various polymer states as a function of temperature.*

FIGURE 7.46
*Electrical percolation in polymer nanocomposites.*

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

So, now let us come back to our discussion today this is polymer nanocomposites ok. You know what are the nanocomposites we have already discussed about it. They are actually class of materials in which one or more phases are in nanoscale dimensions, it can be 0 D 1 D, or 3, 2 D and this nanomaterial is embedded in a matrix called metallic ceramics or polymer.

General idea is that addition of the nanoscale second phase will create synergy between the various constitutions and novel properties can be achieved. The properties of nanocomposites rely on a range of variables particularly the matrix materials, which can exhibit nanoscale dimensions loading even degree of task dispersion size shape; obviously, and I mean in additional orientations of these second phase.

So, among the various nanocomposite types the polymer matrix composites have been the widely studied one because you can have different kinds of variations possible in polymer matrix composites. So, much like any traditional composite system polymer matrix and composite consist of a matrix, which is made of a polymeric material and the second phase can be anything like nanotubes also graphene also or even ceramics metallic particles can be put up.

So, this secondary matrix is what which is it is a nanoscale dimensions. So, that is what is shown in the picture, you can see this is a polymer matrix and then you have put this particle inside the matrix, which is nanoscale. So, they are in spherical shapes.

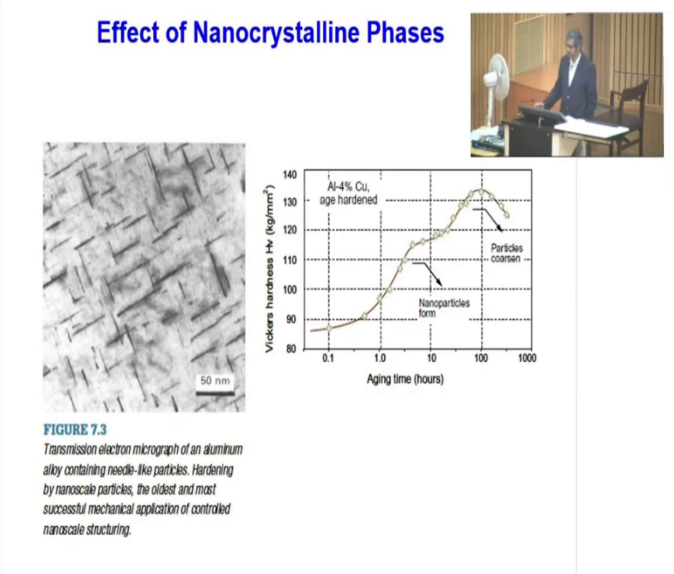
So, we will talk about the left side picture little later as you know polymers undergo glass transitions most of the polymers actually are amorphous or semi amorphous type. So, this amorphous phase will undergo glass transition and then if you keep on heating further it will become rubbery at high temperature.

So, that is why the application of these composites are limited to temperature below T g at the glass transition temperature and this is very common you know plot for the glassy materials, which are widely used as an if any every glassy materials amorphous material you have a glass transitions temperature.

About the glass transition temperature material will become rubbery and liquid like. So, therefore, it cannot be used at the temperature. So, major limitations of the polymer nanocomposites is the temperature issue, we cannot use it at high temperature compared to the ceramic and the metallic nanocomposites that is one of the major limitations ok.

So, you know the in addition to that due to these nanoparticles present in the reinforcement phase, the interface to volume ratio is significantly higher than in combinational composite. As a result volume fraction of second phase can be reduced without regression degradation of the desired properties. Polymeric nanocomposite systems can be; obviously, different types thermoplastic thermoset or elastomer.

(Refer Slide Time: 13:47)



Effect of Nanocrystalline Phases

**FIGURE 7.3**

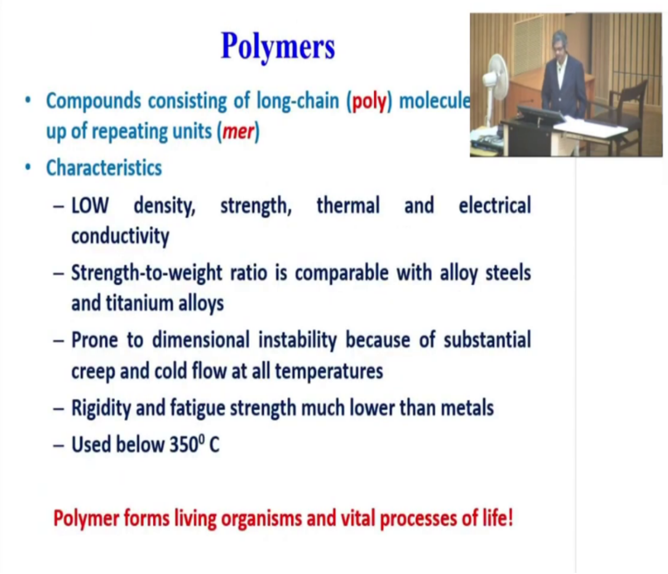
*Transmission electron micrograph of an aluminum alloy containing needle-like particles. Hardening by nanoscale particles, the oldest and most successful mechanical application of controlled nanoscale structuring.*

So, let me talk about little bit about that, before that let me tell you this is also nanocomposites you know this is basically aluminium copper alloy you can see needle separate nanoscale precipitates in aluminium matrix and these particles are actually growing in this various orientations.

And this is routinely used in the real material synthesis you know aluminum four percent copper alloys which is called duralumin is used as a material for the aerospace industries and this is the microstructure. And we this was discovered long long back before even the concept of nanostructure material came up into actual use or actual practice.

So, hence the this picture is taken from the again from the book of Michael Ashby and others. Let me acknowledge their them for this purpose other than that this picture can be available in various published paper from 1950s 19 late 50's to 1970s. You can find it as a kind of microstructure split nicely prepared from hr level aluminum copper alloys. So, that is basically the idea of nanocomposites as you can see.

(Refer Slide Time: 14:58)



## Polymers

- Compounds consisting of long-chain (poly) molecule
  up of repeating units (*mer*)
- Characteristics
  - LOW density, strength, thermal and electrical conductivity
  - Strength-to-weight ratio is comparable with alloy steels and titanium alloys
  - Prone to dimensional instability because of substantial creep and cold flow at all temperatures
  - Rigidity and fatigue strength much lower than metals
  - Used below $350^0$ C

Polymer forms living organisms and vital processes of life!

So, hence the basic idea is the compounds or the polymers. Compound consisting of long chain molecules made up of repetitive units are basically called polymers right. So, we will have a small discussions about polymer, then we will go for the composites and discuss because some of you may have forgotten about polymers let us have a recap of that.

The polymers are basically low density high normal strength and they have reasonably good thermal and electrical conductivity. A strength to weight ratio is comparable with many alloy steels because they have a very low density and they are very prone to instability.

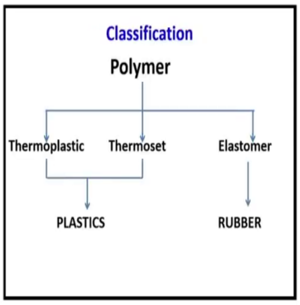
Because of substantial creep and you know cold flow at all temperature rigidity and fatigue strength much lower than the metals and they are normally used below 350 degree Celsius temperature not more that. Most importantly polymers forms living organisms and their vital processes of life.

(Refer Slide Time: 15:50)


Polymer ==Bowl of Spaghetti!

We always compare polymer like a bowl of spaghetti, we all know spaghetti you know you can always see this is the network of different polymeric chains in a real material.

(Refer Slide Time: 16:05)


Classification

Polymer

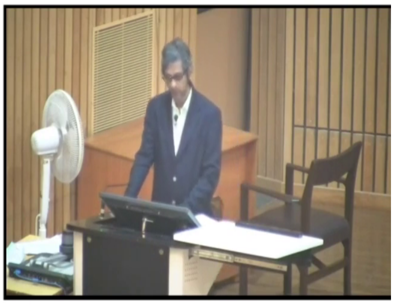
Thermoplastic

Thermoset

Elastomer

PLASTICS

RUBBER

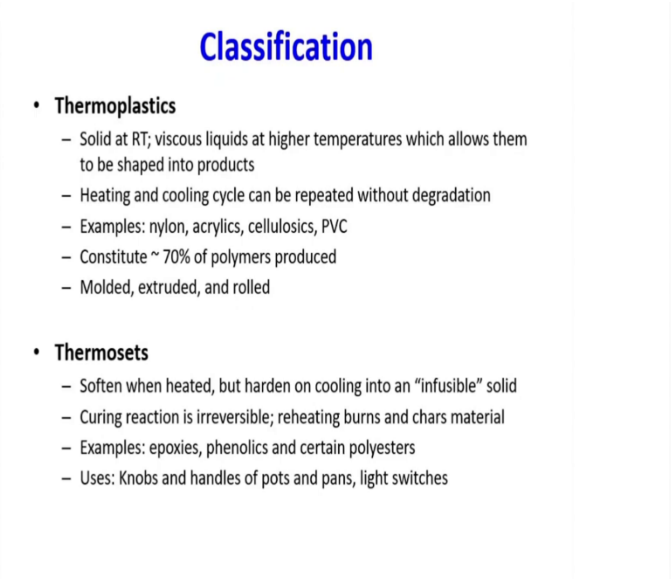


Well, you know polymers as I said they can be classified into three parts three different types thermoplastics, thermoset and elastomer. Thermoplastics are ones thermoplastic and thermosets one which consists of plastics which you see in the real life and elastomers are basically rubbery material right.

So, thermoplastics basically can be molded thermosets cannot be they have once they are produced you cannot remelt and reduce, but thermal plastic can be used again and again that is why they are called thermoplastics. So, as you heat the temperature they will melt and again they can then form the plastics, thermosets are also like the ones like Bakelite, which once you set you cannot get it back.

So, this is basically the problem of polymeric material most of the polymeric materials, hence thermoplastic materials are basically more widely used in thermosets. Elastomers you already know from the literature, elastomers are basically rubber or rubber bands and even tires also elastomers they are widely used in the materials in the community.

(Refer Slide Time: 17:15)



## Classification

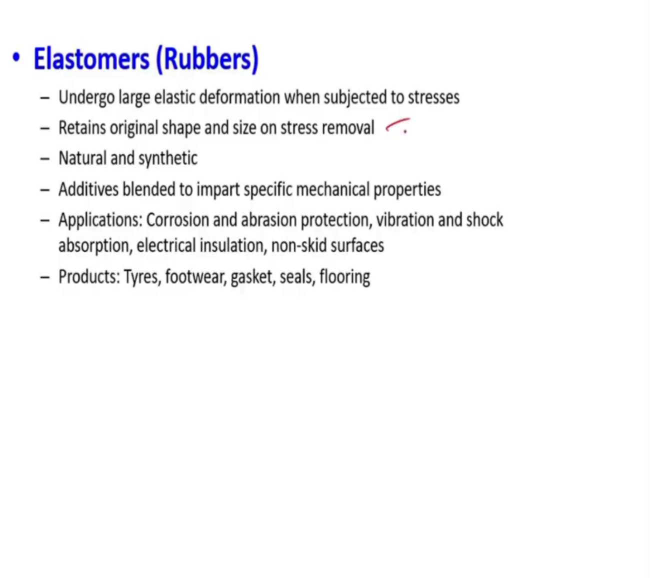
- **Thermoplastics**
  - Solid at RT; viscous liquids at higher temperatures which allows them to be shaped into products
  - Heating and cooling cycle can be repeated without degradation
  - Examples: nylon, acrylics, cellulosics, PVC
  - Constitute ~ 70% of polymers produced
  - Molded, extruded, and rolled

- **Thermosets**
  - Soften when heated, but harden on cooling into an "infusible" solid
  - Curing reaction is irreversible; reheating burns and chars material
  - Examples: epoxies, phenolics and certain polyesters
  - Uses: Knobs and handles of pots and pans, light switches

Well. So, as you said as you said that thermoplastics are basically solid at room temperature, viscous liquid at high temperature which allows the them to be shaped into products, heating and cooling cycle can be repeated without degradations examples of basically nylons, acrylics, cellulose or PC they constitute almost 70 percent of the polymer produced as I said they are the widely used ones and you know they can be molded extruded roll.

On the other hand, thermosets are softened when they heated, but hardened when they cooled into infusible solid you cannot melt it back again they get cured and this curing is basically irreversibles, reheating then burns and chars the material example epoxy phenolics and even certain polyesters they are used as a knobs and handles of the pots and pans and the light switches.

(Refer Slide Time: 18:05)

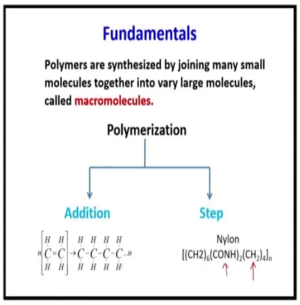


- **Elastomers (Rubbers)**
  - Undergo large elastic deformation when subjected to stresses
  - Retains original shape and size on stress removal
  - Natural and synthetic
  - Additives blended to impart specific mechanical properties
  - Applications: Corrosion and abrasion protection, vibration and shock absorption, electrical insulation, non-skid surfaces
  - Products: Tyres, footwear, gasket, seals, flooring

Rubbers that undergo elastic large elastic deformations when subject to forces or stresses they can retain original shape and size of the stress matrix removal naturally available synthetic it can be produced (Refer Time: 18:20) both and they can be additive blended to produce specific mechanical properties.

They are widely used in various application like corrosion abrasion protections, vibration and shock absorption, electrical insulations and non skid surfaces there are different products like tires, footwear, gaskets most of the gaskets, seals and floorings are used ok.

(Refer Slide Time: 18:39)



Fundamentals

Polymers are synthesized by joining many small molecules together into vary large molecules, called macromolecules.

Polymerization

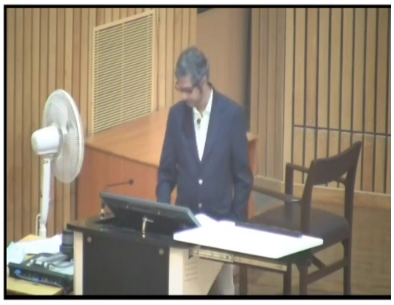
Addition

$$n\begin{bmatrix} H & H \\ C = & C \\ H & H \end{bmatrix} \rightarrow \begin{matrix} H & H & H & H \\ C- & C- & C- & C\ldots n \\ H & H & H & H \end{matrix}$$

Step

Nylon

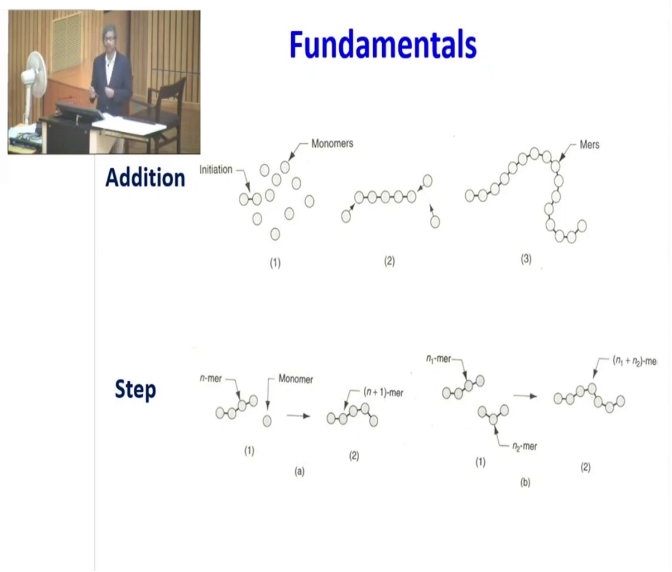
$[(CH2)_6(CONH)_2(CH_2)_4]_n$



So, what are the fundamental things about the polymers, as I said polymers are synthesized by joining many small molecules together into a very large molecule called macromolecules right. So, obviously, the major process which is used to produce polymers is polymerizations right. There can be two types of polymerization addition and you know step polymerization what is addition polymerization?

Well, addition polymerization is basically very simple. Here I am showing you the case of you know polyethylene you know you can take one molecule of ethylene and join the molecules as large many numbers is possible they are called polyethylene. And nylon is produced by step polymerization because it is has different groups like this is a mild groups or urea groups or ethyl groups. So, therefore, they will be produced by other step kind of polymerization techniques ok.

(Refer Slide Time: 19:35)



Fundamentals

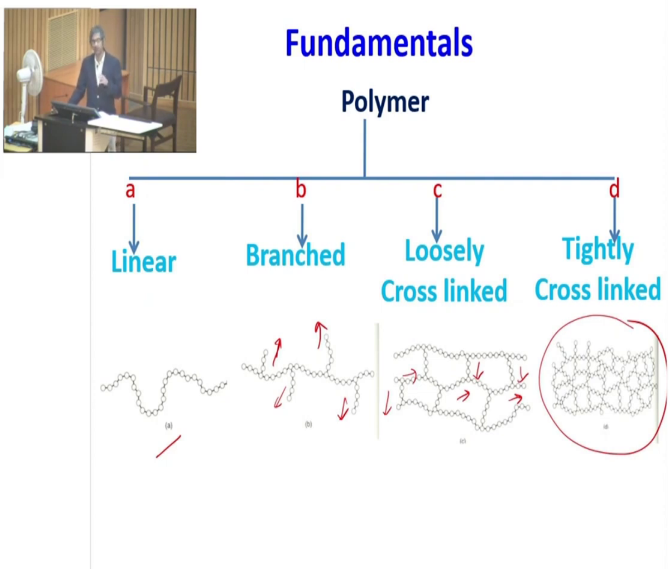
**Addition**

**Step**

Now, you know addition polymerization is like this, you can have monomers, then monomers will join from dimers, dimers will then join and form polymers, ok. So, you can do that. Step polymerization is like that once you have n mer you can add a monomer. You can put this n plus one mer, $n_1$ mer can be added to $n_2$ mer, and then you can join these two is called step polymerizations ok; that means, different types of monomers can be joined and produce a polymer.

That is what happens in step polymerization; you can clearly see that. So, fundamentally the different polymers can be reproduced by both these techniques are the additive addition polymerization or the step polymerizations, and this is very commonly available routinely.

(Refer Slide Time: 20:18)



## Fundamentals

Polymer

a Linear

b Branched

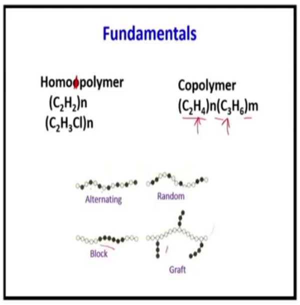
c Loosely Cross linked

d Tightly Cross linked

So, chains in the polymers can be different types based on how you produce there can be an earlier simple linear chain as you see here or they can also be branch like this or this or this or this they can be also cross-links right you can clearly see they can be other cross-links right they can also be tightly cross-linked very very tightly cross-links ok.

You can clearly see how the cross-link is very you know all the directions, which is why the three-dimensional poly structures can be built up. Once you have tightly cross-linked structure, you can build three-dimensional polymers. So, you know this is what normal routinely we find for most of the polymeric products that they are linked differently ok.

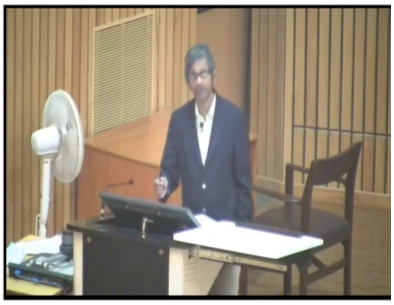
(Refer Slide Time: 21:11)



Fundamentals

Homopolymer
$(C_2H_2)n$
$(C_2H_3Cl)n$

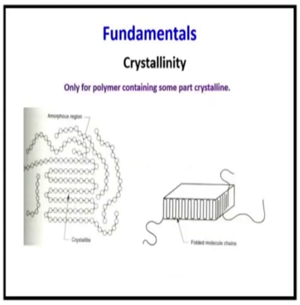
Copolymer
$(C_2H_4)n(C_3H_6)m$



Now, you can also have copolymers or homopolymers ok this is homo; homo means similar type; this is sorry there is a mistake here ok this. So, homopolymers means, you can have one type like ethylene groups or you can see $C_2$ and $C_1$ groups. Copolymer means there are two types ones called ethyl groups, other is called you know poly methyl ethyl poly layer ok.

So, you can have different types of groups and they can have different values of n and m, then you can also have alternative things for the copolymers you can see that or you have a random you can have a block copolymer or you can have a grafted copolymer, you can have a you can do grafting also like here, hair grafting in your head. So, all kinds of situations are possible to produce different kinds of polymeric substances ok.

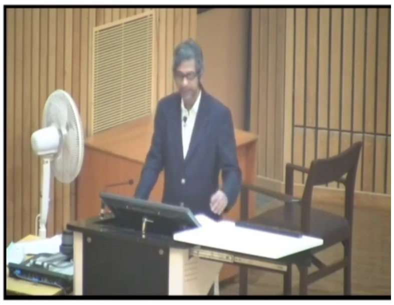
(Refer Slide Time: 22:07)



Fundamentals

Crystallinity

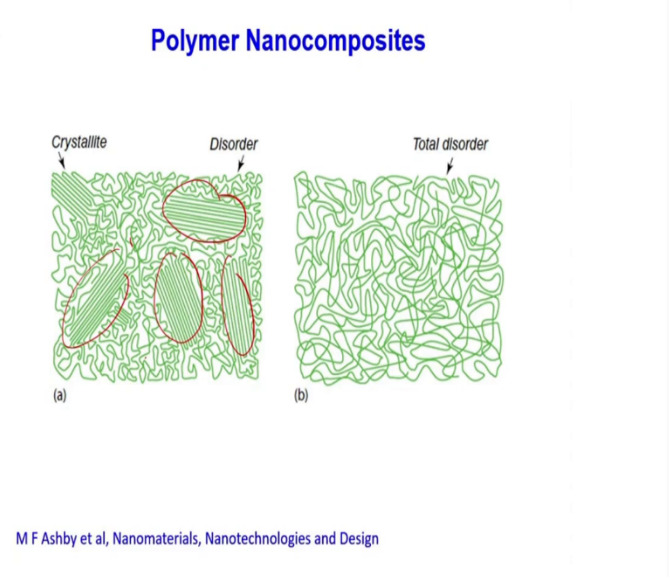
Only for polymer containing some part crystalline.



Now, you can polymers as I said, they are mostly amorphous, but they are not fully amorphous there will always be some crystallinity presence in this ok and these crystalline structures are basically randomly present in the material. As you can see here I am showing this, this is there is a crystalline structure there is an amorphous structure, or you can have such a kind of folded regions also possible.

So, what is the meaning of this? You can have. So, a bit of crystallinity in the polymers and actually affects some properties of the polymers extensively. When you add these nanomaterials like metallic ceramics or you know carbon based into the polymers, these kinds of things can happen actually. The amorphous polymer can get crystallized into some part of as a crystalline polymer.

(Refer Slide Time: 22:59)



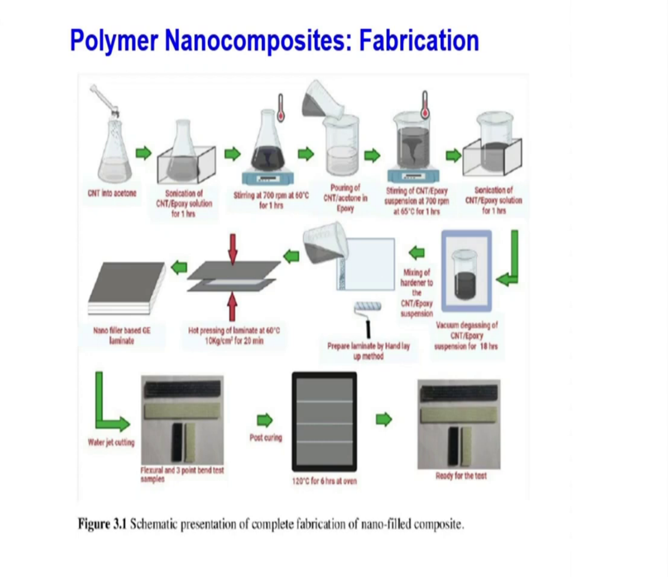
Polymer Nanocomposites

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

This is what something is a very nice picture taken from Michael Ashby’s book; you can clearly see these are the regions of crystalline or order regions which are called crystalline regions ok. And this is the region of the random oriented whenever a completely total disorder. This is called amorphous polymer completely amorphous. You can see is they are, you know, random completely.

So, this is how actually different kinds of polymers can present and you can have in nanocomposites, you can have either of these phases can be either crystalline, or this phase can be the otherwise you know amorphous also. You can always put carbon black into you know an amorphous polymer produces polymer nanocomposites that is also possible.

(Refer Slide Time: 23:46)



Polymer Nanocomposites: Fabrication

**Figure 3.1** Schematic presentation of complete fabrication of nano-filled composite.

Well how polymer nanocomposites are produced, you know some of these things I am showing you they are researched in my lab by my students, ok. So, I will be using that those pictures also as you see this is a polymer nanocomposite preparation using CNT's.

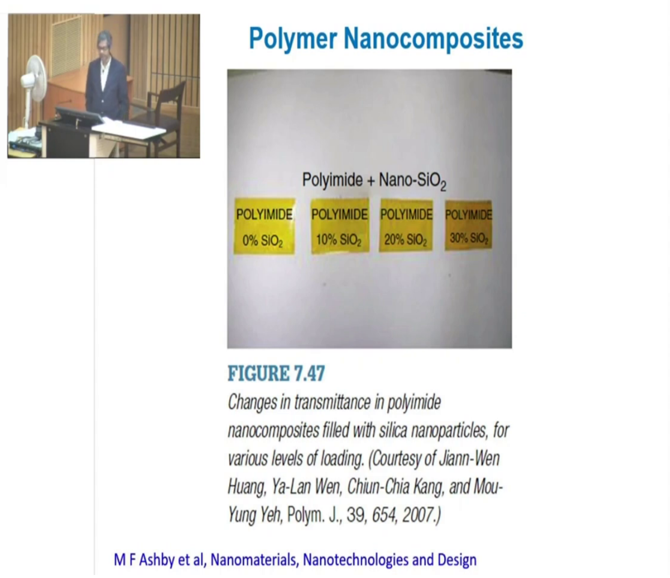
First you do that you put the CNT's into acetone and then sonicate it for long and you do it because you know both the CNT and epoxy solution to the they gets there is not much agglomeration happens in the actual picture, then you can stir at a very high rpm for a 60 degree Celsius about 1 hour. This is the second step you can see here; this will be followed by pouring this, you know, CNT acetone mixture in the epoxy, ok.

And once you do that then you can again stir it at 65 degree centigrate for 1 hour for better mixing and then you can sonicate it again for large watts and after that you can do vacuum degassing. So, that all the water everything goes off. After that you can mix the hardener of the epoxy; actually, epoxy has a hardener also and then it will be hardened and then you can hot press a 60 degree Celsius temperature by application of some pressure for about 20 to 30 minutes. Then you can quickly get nanofiller based laminates.

You can one by one you can produce laminates and after that you can cut the laminates and you can do different kinds of testing. So, basically the important aspect of this preparation fabrication route is that, this is a widely used fabrication route you know that you have to mix them very well. Once you mix them properly then you can pour in a container and degasing or vacuum degasing that is widely used technique ok.

Vacuum degassing this is not a very difficult thing to understand, you can remove of by vacuum degassing all the water and other species, which are easily removable and you can it will leave behind the solid composites ok. So, that is something which is very routinely practiced in the real world or material world, ok.

(Refer Slide Time: 25:52)



Polymer Nanocomposites

**FIGURE 7.47**
*Changes in transmittance in polyimide nanocomposites filled with silica nanoparticles, for various levels of loading. (Courtesy of Jiann-Wen Huang, Ya-Lan Wen, Chiun-Chia Kang, and Mou-Yung Yeh, Polym. J., 39, 654, 2007.)*

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

You know these composites can show different kinds of properties; here you see the polyimide composites with nano silicon dioxide, having different kinds of transmittance 0 percent polyamide 10 percent. Sorry, 0 percent silicon dioxide 10 percent to about 30 percent. So, the transmission levels change by different loading.

This is the property which is you know sometimes is required for having you know the different level of transmission to light it can be only normal light or UV. So, that is something can be easily obtained. You know nanoscale reinforcing phase in a material what we discuss here like silicon dioxide or carbon can be grouped into three categories.

They can be nanoparticles like zero dimensions, they can be nanotubes, they can be nanoplates or they can be even nanograin materials. In the case of nanoparticles, particle size and distribution are of great importance. The mechanical, electrical, and electronics optical properties and thermal properties will change depending on the type of nanoparticles added.

In the field of mechanical properties, change in the modulus and strength depends on the strength on the degree of the interaction between the particle and the polymer. In poly vinyl methacrylate or PMMA like polymer nanocomposites reinforced with alumina modulus decreases due to weak interaction between the alumina and the PMMA.

Whereas, if you use polystyrene nanocomposites reinforced with silica, then the modulus increases due to strong bonding. So, bonding between this second phase is the polymer is very vital another advantage of using nanoparticle reinforcement is that their size is smaller than the as critical crack lengths typically found in the polymers.

So, as a result nanoparticle provide improved toughness very high toughness and strength; however, agglomeration of nanoparticles is a big problem in all these things that is why the strong stirring of everything is used. So, hence agglomeration is a big problem; hence several investigations have shown that a small level of agglomeration can decrease the strain to failure by several tens of percent.

And additional mechanism that occurs in for well dispersed nanoparticles which weakly bonded to the matrix is the phenomenon of cavitations ok. In other words, nanoparticle can act as voids actually; they can create voids which will initiate the yielding and increase the volume of material going through the deformations. Nanoparticles can also significantly affect, as is you know discussed already the Tg or the gas transition temperature.

Typically, this occurs because nanoparticles influence the mobility of the polymer chains due to bonding between the particles and the polymer and even the bridging to the polymer ok. So, hence, in some cases depression in the Tg is observed, which is not good news; however, in many cases, the temperature Tg temperature increases a lot.

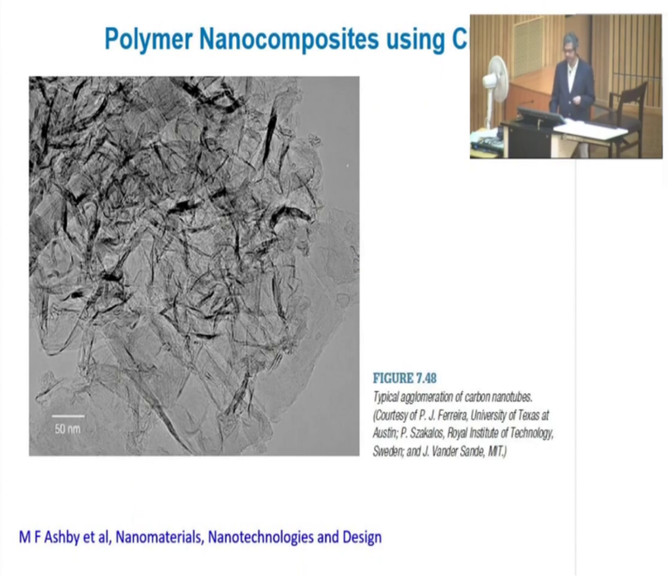
Electrical and optical properties of polymer matrix is can be also improved by addition of nanoparticle with respect to the electrical properties or the you know matrix and this is can be done by various arrangements of the nanoparticles in the matrix and type of nanoparticle.

Low-density polyethylene nanocomposites filled with ZnO nanoparticle shows you know extensive improvement in properties as we as I have shown you here; let me just go back. Yes, this is the one you can see; this is a picture of ZnO nanoparticles in poly low-density polyethylene nanocomposites it can improve electrical properties a lot.

So, in terms of optical properties, there is a large development large interest in the transparent nanocomposites ok. Transparent nanocomposites are very widely used this is what I discussed just a couple of minutes back. With enhanced mechanical and electrical properties to achieve transparency the what is called the scattering must be minimized, which means the nanoparticles should be as small as possible while the index of refraction should remain as similar as small as possible of the matrix.

For example, the addition of nanoparticles of silicon dioxide to you know silicon dioxide to these things can control the transmissions of the nanocomposites; furthermore, the addition of nanoscale alumina to gelatin has improved total transmittance by as much as 100 percent.

(Refer Slide Time: 30:23)



Polymer Nanocomposites using C

FIGURE 7.48
*Typical agglomeration of carbon nanotubes. (Courtesy of P. J. Ferreira, University of Texas at Austin; P. Szakalos, Royal Institute of Technology, Sweden; and J. Vander Sande, MIT.)*

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

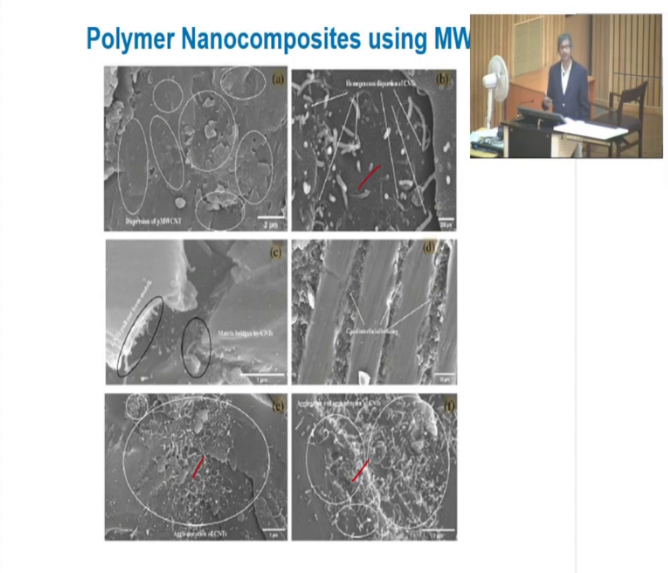
Next you know, let us talk about the little bit of carbon nanotubes. As you know, the one-dimensional nanomaterials in particular CNT's can act can be used as reinforcements for the nanocomposites, a comprehensive discussions on this you know cannot be done because of you know the shortage of the time, but one can read the different books and find out.

The use of CNT’s in the composites has received wide-scale you know, attention due to their external and physical and mechanical properties; however, to take full advantage of the CNT’s nanocomposites applications, several critical issues must be addressed first is the uniform dispersion which is very difficult to achieve. Second is this alignment of CNT’s and in the composites.

This is very challenging to disperse nicely these CNT’s in the matrix, particularly as compared to the polymer; you know that procedure I just discussed just now because CNT exhibits smooth surfaces and intrinsic Van der Waal’s interactions, which can promote clustering when in a polymeric matrix. So, at least this problem many people have basically modified the CNT surfaces ok by putting some, you know, some kind of a layer on the ceiling somehow functionalize them.

So, that can be done or you can have shear mixing in during the mixing process. Or you can have surface and edited assisted processing also, the different kinds of techniques can be used. This is a typical picture of agglomeration of carbon nanotubes; you know this is taken from the work of P J Ferreira et al. from MIT. I am just using this picture from Michael Ashby’s book. So, I acknowledge both of them for using this picture for the class.

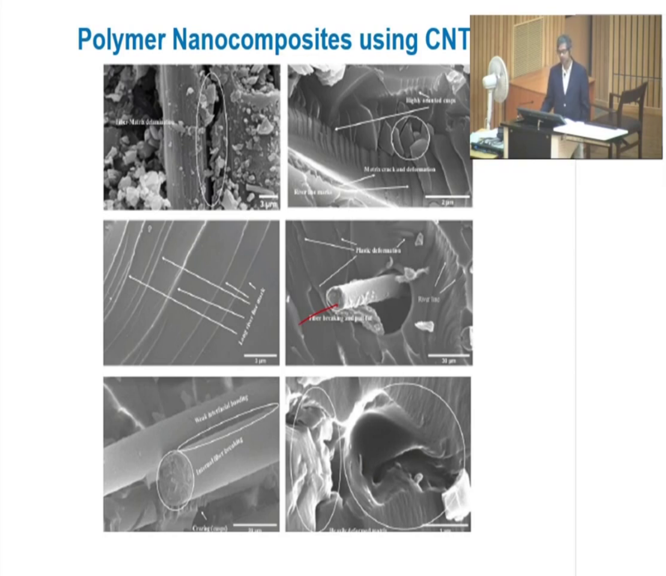
(Refer Slide Time: 32:09)



Polymer Nanocomposites using MW

Well, now, let us see some of the examples of which we can; these are the works done by my students, and this is the polymer nanocomposites epoxy-based basically using multi-wall CNT's. You can clearly see that the CNT's are present here, there, here lot of CNT's are present, and this CNT is basically you know many cases got agglomerated it is very difficult to avoid this agglomeration of the CNTs.

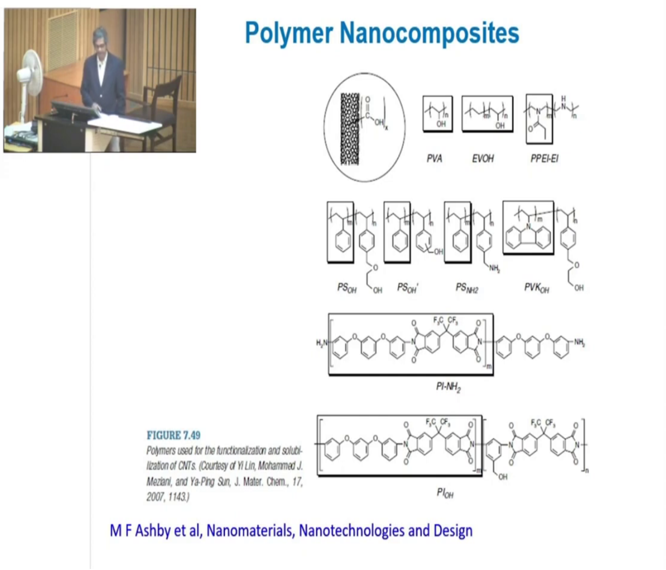
(Refer Slide Time: 32:41)



Polymer Nanocomposites using CNT

But CNT's provide many, many interesting you know many many improved properties of this nanomaterial. This is the one you can see these are actually CNT's; some of the cases you can see they pull out of the CNT's; also, it is possible to observe that ok or you know they are well dispersed many cases. So, this is something which is routinely found.

(Refer Slide Time: 33:00)



Polymer Nanocomposites

FIGURE 7.49
Polymers used for the functionalization and solubilization of CNTs. (Courtesy of Yi Lin, Mohammed J. Meziani, and Ya-Ping Sun, J. Mater. Chem., 17, 2007, 1143.)

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

And now polymer is also used for functionalization and stabilization of CNT's, and you know you can also stabilize the CNT's to produce different kinds of structures ok. Like here, we can see the different kinds of structures; you can clearly see that these are the different radicals that can be used for this purpose.

So, in order to in fact, in addition to the uniform dispersion of the polymer matrix, a crucial aspect of providing optimum reinforcement polymer is the orientation of the CNT's. Because of the very high aspect ratio, CNT's process highly anisotropic mechanical properties took advantage of their load-carrying efficiency along the axial direction is essential that CNT's are well aligned within the matrix; several methods have been used to do that, ok.

So, polystyrene nanocomposites are basically filled with multi-sized CNT's have been produced compared to the pristine sample modulus of line composites, increase almost by 50 percent ok. So, that is something which is widely used in many purposes. In addition, aligned CNT's or polystyrene nanocomposites were also shown to exhibit increased yield strength and ultimate tense ultimate UTS also for compared to the pristine ones.

Due to the fact that CNT's exhibit high electrical conductions, you know applications of the magnetic field or electric field have also been used to produce CNT alignments. It was observed that elastic modulus measured in the direction parallel to the magnetic field was far greater than the perpendicular to the magnetic field so, in fact, this suggests that alignment of the CNT's contributes significantly to the increase in the mechanical properties of these polymer nanocomposites.

Finally, the interfacial bonding between the CNT's and the polymer is very important. It is believed that the efficiency of the load transfer in nanocomposite depends on the interfacial characteristics of the reinforcement phase and the matrix. So, in the case of polymer matrix nanocomposite reinforced by CNT's, the main mechanism of load transfer is mechanically interlocking between the CNT and the matrix.

So, that is the main mechanism other than that you have a chemical bonding or nano-bonded interaction between the CNT and the matrix, addition it is believed that key factor in forming a strong bond is the polymer matrix, and the CNT lies in polymer morphology, especially the ability to form large-diameter helices around these individual CNT's.

The strength of the interface is then due to molecular level entanglements of the CNT's and the matrix. In the inclusion of CNT's is a polymer matrix nanocomposites can also be used to improve the thermal conductivity of these nanocomposites; the CNT's create a percolation network in you know nanocomposites ok.

To conduct the heat and conductivity up to 3.5 times higher than what is observed in pristine polymers; however, the thermal conductive nanocomposite is still far from lower than the theoretical value.

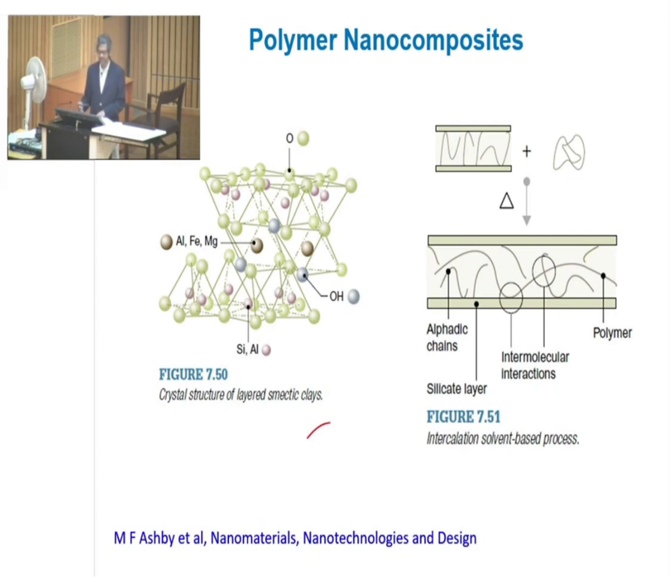
And this is something which is a big concern, the major reason for the discrepancy is the large thermal resistance that exists between the polymer matrix and the CNT surface. Because CNT possesses a high surface-to-volume ratio when CNT's disperse in a polymer matrix large, you know interfacial area creates a significant resistance.

And this effect has been attributed to the difference in the phonon dispersion a phonon frequency between the CNT and the polymer matrix. Some solutions have been suggested in the literature to decrease this thermal resistance. It is proposed to covalently bond the CNT's to the polymer to improve the phonon scattering.

But it has also been suggested that multi wall CNT's use of multi wall CNT's instead of single wall CNT's because former or the multi wall CNT's can you know have smaller aspect ratios therefore, less interfacial area. The use of CNT's in nanocomposites has also improved the thermal stability of the polymeric composites it has been found that CNT's can improve that.

Well, there are many other aspects, which are you know can be discussed about that you know the last one is basically 2 D second phase particles nanocomposites in polymer nanocomposites. There are plate-like layers materials with the thickness of the order of 1 millimeter we got aspect ratio of 25 above can be used most common ones are layered silica structures ok, which is widely used this is the one you can see the thick layered silica structures silica can be used that.

(Refer Slide Time: 37:40)



Polymer Nanocomposites

FIGURE 7.50
Crystal structure of layered smectic clays.

FIGURE 7.51
Intercalation solvent-based process.

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

And once if you use you can improve several properties of polymer nanocomposites ok, which is a layered silicon structure and which can be reproduced, which can be used as one of the reinforcing materials, and it can lead to improving UV resistance, improve strength gas permeability greater dimensional stability many other properties can be improved ok.

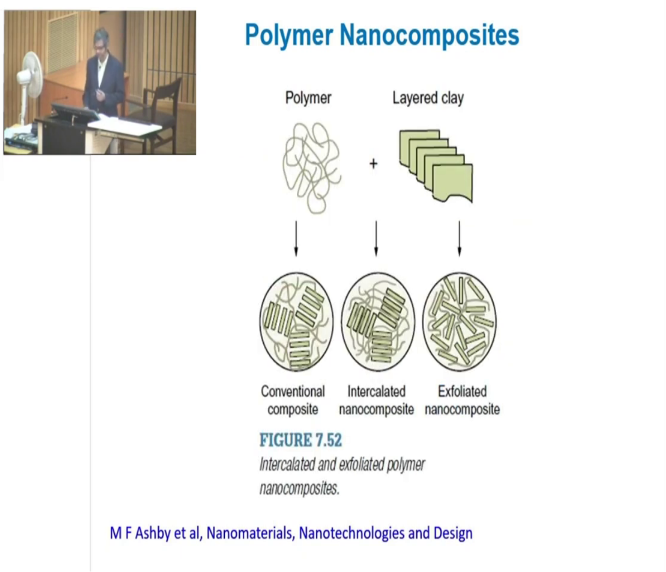
So, among the layered silicas, mica and smectic clay mica and smectic clay can also be used ok mica is readily available and can be you have seen probably they can also be used for this purpose they are layered structures. Mica consists of large sheets of silicate with strong bond among the layers on the other hand, and basically, they can be used for this purpose.

Also on the other hand, contrary smectic clays exhibit weak bonds between the layers; semantic layers consist of a three-layer sandwich structure composed of two outer layers containing silicon and oxygen bonded to the inner aluminum magnesium or any other atoms presence there or the hydroxyl groups.

Due to the substitution of the divalent magnesium to trivalent aluminum a negative charge can be produced and this can lead to. This charge has to be compensated by the absorption of the cations like sodium, potassium, calcium, lithium.

Layer structures are you know ok it is shown here in the 2D; you can see this aluminum iron-manganese is produced to charge for creating this charge imbalance. And which later on can be used for better bonding between the polymer and matrix. So, to overcome this problem, you know, sometimes exchange reactions usually varied or carried out a variety of organic cations openly open the clay structure.

(Refer Slide Time: 39:31)



Polymer Nanocomposites

FIGURE 7.52
*Intercalated and exfoliated polymer nanocomposites.*

M F Ashby et al, Nanomaterials, Nanotechnologies and Design

Well, so, polymers nanocomposite can be it can be used the two types conventional composites, intercalated nanocomposites, exfoliated nanocomposites ok. So, nanoscale layer silicates are proven to be provided much better insight into the properties. So, there are many such ingenuities that can be used; I am just telling you only a few of the ingenuities which are there. So, with this, I will close this class and close this course; I hope you have enjoyed this over the last, you know, three months, this course.

And you have enjoyed various you know parts of the course, and they are always deficiency when you develop a course. It is not possible to cover every subject of the course systematically because of time constant because of the available literature, and this field is basically evolving; this is not a field that is already mature enough.

This field is evolving, so the subject matters are also available in many cases in the published literature, not in books. That is another big challenge we face when you talk about this course.

And so, but most importantly if you should study books and try to understand the basic part of the course so, that you can use such concepts for your own research or technology developments or preparation of different kinds of new materials. So, thank you for your attention, thank you for your, you know, participation in large numbers; I know many of you have joined with a lot of expectations, I hope I have lived up with the expectations and did in justice to the course.

Thank you again for your attention.