

# **Advances in Additive Manufacturing of Materials: Current status and emerging opportunities**

**Prof. Bikramjit Basu**

**Materials Research Center, Indian Institute of Science, Bangalore**

## **Lec51**

Welcome back to this lecture on challenges and opportunities in additive manufacturing. As I have explained in the previous lecture that I will be covering a few topics under this series of lectures. In this particular lecture, I will be mostly focusing on the 3D printing related challenges. Not only extrusion, but also other 3D printing related approaches and challenges. In the subsequent lectures essentially I will be showing you my thoughts along with some of the literature studies on the exploiting AI-ML approaches or additive manufacturing of structurally complex implants and so on so forth. The tissue engineering as a subject was introduced to you much earlier in this particular course and also 3D bioprinting has been mentioned very very clearly with lot of examples. Essentially if you recall 3D bioprinting essentially means that it is a layer by layer manufacturing of materials containing biological cells or biological macromolecules in a manner that one can essentially maintain the viability of the biological cells or do not compromise on the biological expression of those macromolecules along with the materials when you are going to print it.

the essentially the printing process do not compromise the viability or biological expression of those either biological cells or macromolecules. This is one such examples of the urological treatments for replacement tissues. You have urinary bladder graft for example, one is to use either urinary bladder graft or urethral graft and so on. Urological system has a specific tissue structures which are lined up of the organizations, architecture of the cells and tissues locally.

what are the challenges in this thing? The challenges in the whole urological tissue engineering like inhomogeneous distribution of cells, it is not patient specific and poor control of the scaffold microarchitecture. And advantages, it should be easy control over scaffold microarchitecture and porosity. Your conventional manufacturing can be either electrospinning based techniques for fabrication of nanofibre scaffold or it is like a 3D bioprinting strategy. Essentially you give it is an input on the design, then you have a pressure control, then you have a bio ink as I said biomacromolecules, biomolecules or polymeric hydrogels plus polymeric hydrogel and then you can print the urological graft.

this is that kind of approach that has been mentioned very-very extensively in one of the review papers published by Sulob from our group in Journal of Materials Research more than 3 years ago. If you see apart from some of the techniques which I have covered during the earlier lectures, there are also other techniques which has essentially gained lot of interest in the community. One of them is stereolithography, another is digital light processing DLP and then third one is a multiphoton lithography. Now this is the essentially

stereolithography, this is the DLP and this is the multiphoton lithography. what you see in the stereolithography, you have a UV laser system.

These optics are being guided in the mirror scanner and these are polymerized structure which is getting built in a layer by layer manner in this way. this is the building platform. This building platform essentially is immersed in a polymerized structure. In the DLP technique certainly is much less explored than the extrusion printing. You utilize a photoreactive regime and then you have a UV projections, this is a digital mirror device.

And this digital mirror device, this UV projection, UV things is being guided and there again you have a layer by layer way of making the structures and then you make these total structures. This is a multi-photon lithography technique, you have a XY movable stage and you have objective here. here you use not the UV projector or not the UV laser but it is a femtosecond laser. Now, femtosecond laser goes through optics and scanning system, then it can be focused and there you can make a much complex structures in these things. All these techniques has its own specific advantages but at the same time they have specific challenges in terms of the large buildability of the structure and also their ability to make complex structures with very very different shapes functions and so on.

this is another way, this is the extrusion based bioprinting technique. Now, extrusion based bioprinting techniques, you know, it can be used for the direct writing. So, you essentially make a filament, then directly write. Then printing in coagulation bath, this is also another technique. Printing in support bath and this support bath can be granular or colloidal and coaxial extrusion.

Coaxial extrusion means this is one type of in the you use the cross-linking agent here and the coaxial extrusion means essentially both the strands they are mixed and then they are extruded in this extrusion based bioprinting techniques. Now in all these techniques, there are 2 things that are important. One is the sizes of the structures, resolution and sizes. Resolution can go down to very very low like 100 nanometer and so on but at the same time volume of the structures that can be essentially built by these techniques that also needs to be considered. What you see in these 3 techniques they have almost like it goes kind of this kind of arrow like your resolution is increases.

as well as the total build size also increases. laser bioextrusion printing or extrusion bioprinting, inkjet printing and LDM essentially liquid deposition modelling. liquid deposition modelling, this is also another technique which allows you to build large structures. And, this large structures is like 1 centimeter cube, 200 decimeter cube, this kind of large structures can be built. this essentially ensures very good buildability of the structures.

But, if you look at the resolution, it is 200 micron. Here, you can go to laser bio extrusion based printing, you can go up to 5 micron. if you want to have very very fine structures, but then buildability will be compromised. If you have relatively coarser resolution like 200 micron so, then buildability is up to 1 centimeter cube to 100 decimeter cube that you can do. Now, one of the techniques that I have not covered at all in the previous lectures

and I thought that this is the relatively less explored 3D printing techniques is the melt electro-writing.

electrospinning for example, as a technique which is used for ultra-fine diameter fibers in a chaotic. it is a dynamic manufacturing technique electrospinning that produces ultra-fine diameter fibers in a chaotic deposition technique. Now, what if the placement of every single electrospin fiber could be predetermined and what if manufactured construct could reach millimeter volume while maintaining accurate fibre placement, these are the two questions. Now while addressing these questions, people have developed melt electro-writing MEW as a technique and you can achieve this with a solvent-free manufacturing approach. what are the different environmental variables that is humidity and temperature and what is the solution variables? Solution variables is concentration, conductivity, molecular weight of the gel, viscosity, molecular structure, solvent volatility and molecular weight.

Now, this is the electrospinning technique and what are the variables of the electrospinning technique. Here, what is the distance between the collector and electrospinner? What is the accelerating voltage that you are applying? What is the flow rate of this particular unit and what is the collector that you are using? And typically, this is the scanning electron microscope image what you can see. These fibers, they are oriented in different manner. you can have fibres oriented in a specific in a particular orientation or in most cases you get randomly oriented fibres in this particular cases. Now, if you see that fused deposition modelling.

in the fused deposition modeling, you can also get that aligned fiber deposition. But in all these cases, fused deposition modeling, melt electrowriting and electrospinning, essentially we use polymer melt. either precursor or polymer melt or polymer solution. And in case of melt electro-writing, we use essentially spinner it like high voltage is applied and then charges are generated and then collector plate this thin fibres are kind of generated. In the electrospinning, you get much coarser fibres and random fibre deposition.

Now, if the question that should arise that you know then what is the difference between electrospinning and melt electro-writing in case of MEW, it is much finer sized fibres are deposited compared to ES. compared to electrospinning. this is very important that you get much coarser fibres here in electrospinning and melt-electro-writing is much finer fibres that are being generated. Now, if you look at this particular video taken from nanoscience instruments, this is without voltage and with voltage you can see very clearly that filaments are being generated. definition wise melt electrowriting is an additive manufacturing technique that integrates electrospinning and 3D printing to create high resolution polymer fibres.

It uses electrostatic forces to stabilize a molten polymer jet to precise layer by layer deposition onto a collector resulting in scaffolds with customized microstructures. right and high voltage electrode you know and this polymeric melt. This polymeric melt if it is pushed through and you can see that polymer fibres are being generated and this polymer fibres are being generated and this is the electric field that is being created and then

according to the collector movement this polymer fibres will be deposited on the collectors. Now, if you look at the process little bit more finer way, now you can see that in the electrospinning chamber, you can essentially control both temperature and humidity. This polymer solution is being injected through a nozzle here and these fibres are going there.

So, this is E1 electric field, this is E2 electric field, the difference between that it is essentially this voltage, this E1 electrode 1, electrode E2 electrode 2 and there is one of the things that is very important is the Taylor cone that is being formed in this particular case and the Taylor cone near field electrospinning that is 0.05 to 1 millimeter that is being generated that is x value distance between the 2 electrodes. and then fibres are being deposited. There should be a movie now. This is actual operation of the melt electro-writing machine and this movie was taken in our collaborative work between my research group and Professor Michael Gelinsky's research group at Technical University at Dresden.

And this melt electro-writing facility is available in the TU Dresden which we have been collaborating with. this is that polycaprolactone based scaffolds and this polycaprolactone based scaffolds are essentially have been used for milk electro-writing for a number of years in recent past. And, you can see this particular machine can draw this fibres very thin fibres continuously without fibre breakage and they can change the orientation and they can start essentially depositing fibres in a specific angle to this particular case. in this and you can see this is the case for the multilaterally written PCL based scaffolds. You can see nice grid structures.

You can change the orientation of the grid structure and see for the orientational dependence on the mechanical properties for example, in this particular case. little bit more on the melt electro-writing like as I mentioned that is a voltage is required, temperature humidity is controlled and you have a distance between distance with the collector and then what are the things that are important in the melt in the scaffolds or the precursor solution, surface tension. concentration of the second phase or other structures and then viscosity. And in the spinneret you can see there is a straight jet and there is a rapid whipping and swinging that takes place during this on this path to the collector here. Now parameter, effect and fiber morphology, solution parameters, polymer concentration, polymer molecular weight and viscosity.

the diameter of the fiber increases with increasing polymer concentration and increasing the molecular weight of the polymer decreases the number of beads and droplets. higher the molecular weight of the polymer that will decrease the number of beads. If the polymer molecular weight is lower then those beads like you know these knots and beads like in individual these knots and beads will be more. Increase the viscosity of the solution has been shown to increase the fibre diameter and avoid bead formation. Again, higher the viscosity of the solution that more is the lesser is the chances for the bead formation.

And what are the processing parameters? Applied voltage, flow rate, tip to collector distance and then diameter of the fiber decreases with increasing applied voltage, too high a flow rate results in the appearance of bits, decrease in the flow rate and no significant effects on the fiber morphology. Temperature and humidity, that higher temperature results

in fibers with small diameters and circular pores on the fibers are observed in the higher humidity. Now, there are also other things that which are important in the melt electric writing that how the jet is formulated and that depends on the polymer characteristics, also the heating system like either conduction, convection, radiation, what is the back pressure and what is the spinner rate, whether custom made nozzle or the platinum tipped meter size. And this is the melted temperature and polymer flow rate that is important. Now, in terms of jet trajectory, applied voltage, distance, environmental condition, voltage system is very important.

And how fibres are collected? Is it collector dynamics and collector material that is spinning and collector distance. But out of this, I would say this particular set of parameters are very important for the success of the melt electrowriting of any new system. I repeat voltage that decreases the voltage or very high voltage they can consider the arcing. Then pressure like if your pressure decrease then thinner fibres, if your pressure increase then it is a thicker fibres. Collector speed there is a small lag and there is a large lag in the collector speed.

And these are like different parameters that has been mentioned to you and it is a summary of all the different parameters like whether solution concentration or orifice diameter. Orifice diameter essentially dictates that what is the fibre size . Then temperature, then humidity, flow rate, tip collector distance, applied electric field and so on. Now in terms of the materials aspect which are the materials which are useful that is the low melting polymers like PVA, PEO, PCL. Out of that I will put a double star to this particular material PCL.

Why PCL I put a double star, when the melt electro-writing started and then Paul Dalton who was that time at University of Würzburg, Germany now he moved to United States. Paul Dalton actually has done lot of experiments with one of the first machine, he invented the first machine of the melt electro-writing and then he used polycaprolactone PCL is one of the materials which has been very widely investigated. Some of the natural polymers like gelatin, collagen, silk fibrin, these are also natural polymers, these are used. And materials not suitable for melt electro- writing that high melting points, low viscosities and poor electrical conductivity, these are materials which are not suitable for melt electro-write. materials properties which affect the melt electro- writing processing, one is the viscosity, melting point, electrical conductivity, mechanical properties, solubility, surface tension, molecular weight.

But out of that, surface tension is important, very, very important. So, I put a star. Viscosity is very important. electrical conductivity is also another important parameters. Now, you can see the such as polymers which are printed using the melt electro writing I have mentioned to you just 2 minutes ago that PCL based materials which are most widely investigated and there is a series of papers which started in 2011 more than 12-13 years ago when This melt electrowriting as a new 3D printing technique was introduced in the scientific community.

Now, one of the things that you notice that how many layers they have formed, 50 layers,

circular paths, box, 60 layers and so on, 30 layers, 50 layers. these are like different number of layers. buildability was essentially introduced in this melt electrowriting. And what is the diameter? diameter of the fibers you can see is mostly micron size like few microns like few tens of microns either 15 micron or 21 micron or 60 micron. Sometimes people have developed tubes like 60 micrometer diameter tubes and all that they have utilized like 30 layers or 20 layers or single layer of 30 micron fibers.

So, these are like different kind of materials. Researchers have used PLLA, polylactic acid. Then PLLA, polylactic acid, pH copolymer they have used and also many other classes of PCL based techniques that researchers have used. Some of them they have also used the shape memory polymers like TPU. thermoplasty urethane and then polypropylene they have used with some limited success.

melt electrowriting is one of the, perhaps is one of the relatively unexplored 3D printing techniques where people, where researchers can explore more opportunities in terms of utilizing new materials which can be used for melt electro-writing so that This can give you very delicate structures or very soft structures which cannot be used for example otherwise by other 3D printing techniques. Now, these are like different examples of the melt electro writing like you know very researchers predict that electro-writing can be used for the biosensors application, wound healing, drug delivery and also for tissue engineering kind of applications. And these are taken from different snapshots, taken from different research papers which are published using melt electro-writing scaffolds made of PCL. and then you can see the different kind of structures. Here you can see 100 micrometer diameter, here you can see 500 micron diameter.

large structure of melt electro-writing scaffolds can be used. And here you can see that you know how cell culture studies were done and then you can see that cells have proliferated very well on this kind of structures. In some of the cases it is not a straight line kind of fibres but it is more like a wavy type of fibres and this wavy type of fibres are can be manufactured in this melt electro-writing case. in the melt electro-writing there is a concept of critical translation speed. Critical translation speed means what is the speed that the collector essentially will move, will translate and how that will impact on the quality of the melt electro write and fibres.

This has been investigated to some extent and in one such papers which is published in advanced healthcare materials, you can see that is the typical electro write and setup, it is  $T$  is less than 270 degree Celsius. polymer melt polymer which melts at less than 270 degree Celsius which is melted and then you can see this kind of x motion and y motion you can get the fibers essentially it is either going these directions or going this directions. And this is like  $V_0$  is equal to  $V_{jet}$  that is roughly equal to or  $V_c$  is greater than  $V_{jet}$ . with increasing collector speed what you can see there is a straight fibers.

that is kind of formed as 330 millimeter per minute. 330 millimeter per minute if the critical translation speed anything less than that you can see such kind of wavy, you cannot get a straight. And then this is the minimum and here in 320 again you can see there is one kind of fiber, there is a kind of this wavy kind of structures. if you want to have a very very

straight line kind of a fiber structure and then what is the minimum speed that is required and in this particular case they have shown that it is like a 330 meter per second. to sum up, melt melt electro-writing is one of the promising 3D printing technique which has been relatively less explored certainly compared to the 3D extrusion printing or some of the metal printing techniques. And which holds promise like you know to show the capability of one of the variants of the 3D printing as how this 3D printing technique can be used to make the fibre scaffolds of different kind of architecture and also different sizes.

And then how many layers you can print it using the melt electro writing. As I said that Polycaprolactone is perhaps is the most well investigated material whenever people recall about this, whenever researchers mention the melt electro writing But there are plenty of other polymers which may be explored in recent or which should be explored in the near future so that we can expand that capability of this melt electro writing beyond polycaprolactone. And, that is one of the primary challenges, secondary challenges is that every 3D printing technique we develop some kind of process maps and this process maps allows you to put the printability and buildability of the different materials in some parametric space. here in this particular parametric space can be either voltage in along the let us say y-axis or translation speed of the collector may be x-axis or it can be this is kind of a printing related parameter or it can be simply materials related parameter like for example, viscosity, surface tension or electrical conductivity. So, some of these parameters can be plotted along y and x axis and you can put the different melt electrode writable polymers which people have printed in this parametric space and then they can see that you know what are the parameters.

what are the kind of polymers which can undergo melt electro-writing to provide a very-very stable, smooth and clinical application specific structures using this melt electro-writing technique. So, I stop here and then I will continue in the next lecture again on the challenges and opportunities of the additive manufacturing. Thank you.