Toughened hydrogels for biomedical application

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Declaration

'I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.'

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To my family for always being there for me.

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- PAA: Poly (acrylic acid)
- HB: Hyperbranched polymer
- MBA: N, N′-Methylenebis (acrylamide)]
- APS: Ammonium persulfate
- PVA: poly (vinyl alcohol)
- SR: swelling ratio
- U(L): the area under the curve of the load and extension
- m_t: weight of sample in swollen state
- m_i: weight of sample in dry state
- FTIR: Fourier transform infrared spectroscopy)
- SEM: Scanning electron microscope
- a_0, b_0: width and thickness of sample respectively
- µm: micro meter
- N: Newton
- MPA: Megapascal
- mm: millimetre
- J: Joules

ABSTRACT

Hydrogels are the three-dimensional polymer structure. The keen interest in the hydrogel is due to their properties like good water swelling, porous structure, biocompatibility and many more. For these reasons hydrogel has a huge scope in biomedical field. At present, the hydrogel used does not fullfil the demand up to its capabilities. The reason behind that is its poor mechanical properties. As the commonly used hydrogel (Poly (acrylic acid)), PAA has very weak mechanical properties. Therefore, there is great need to provide toughness to the conventional hydrogel so that its range of applications can be extended. The toughness is provided by the hyperbranched polymer (HB) to the conventional hydrogel.

In this thesis, the toughness is provided to the conventional hydrogel and then the mechanical testing is performed to verify this and to see the difference between both the hydrogels. Apart from the mechanical behaviour, other properties were also studied in the thesis.

In this thesis, various experiments were performed such tensile testing, double peeling, water swelling test, FTIR and SEM. The properties of the hydrogel have improved by providing the enhancement to the conventional hydrogel in form of the hyperbranched polymer (HB). According to the experiments the PAA-HB hydrogel or the toughened hydrogel has the fracture toughness of 38.7 J as compared to the 8.25 J fracture toughness of the PAA i.e. conventional hydrogel.

Keywords: Hydrogel, toughness, mechanical properties, PAA and hyperbranched polymer (HB).

Chapter 1 Introduction

Hydrogels are composed of the three-dimensional polymer network. The hydrogels are the wet and soft material made from the hydrophilic polymer chain with physical or chemical cross-linking (Sun, et al. 2012). The hydrogel does not get dissolved into water due to its hydrophilic properties. The hydrogel has the property to absorb huge quantity of water in it, it can absorb up to 50 to 90% of water in it (Haque, et al., 2012). The water absorption quality of the hydrogel gives the hydrogel opportunity to be used in many fields. The properties of the hydrogel change with the change in the quantity of water in it. The properties of the hydrogel can be changed by various factors such as temperature, electric field and pH value. Therefore, the hydrogel can be modified by changing the water content in it, to be able to use in different fields and for different applications (Yang, et al., 2012). By absorbing the water, the hydrogel shows different properties. Therefore, the properties of hydrogel changes with the change in water content in it.

1.1 Biomedical Applications

As the basic aim of this thesis is to increase the range of applications by enhancing hydrogel properties (especially mechanical properties). Application such as Artificial cartilage, scaffold in tissue engineering requires toughened hydrogel. As discussed in thesis the main reason for the less applications of the hydrogel in many fields is due to its weak mechanical properties. Some applications required good mechanical stability of hydrogels (Caló, E. and Khutoryanskiy, 2015). Apart from its weak mechanical stability the hydrogel possesses several other properties that are being used in many fields, properties like capacity to absorb huge amount water, biocompatibility, they are permeable materials etc. (Peak, et al.,2013). Since, this thesis focusses on enhancing the biomedical application of the hydrogel, there are some of the examples where the hydrogel is widely used in various biomedical fields such as:

1.1.1 Drug delivery

Hydrogel are being used as a controlled drug delivery system. This is based on the erosion or the diffusion mechanism. When the hydrogel containing drug is placed in the aqueous solution, the aqueous solution permeates into gel and the drug starts to diffuse into the surrounding environment as shown in figure 1 (Utech, et al.,2016).

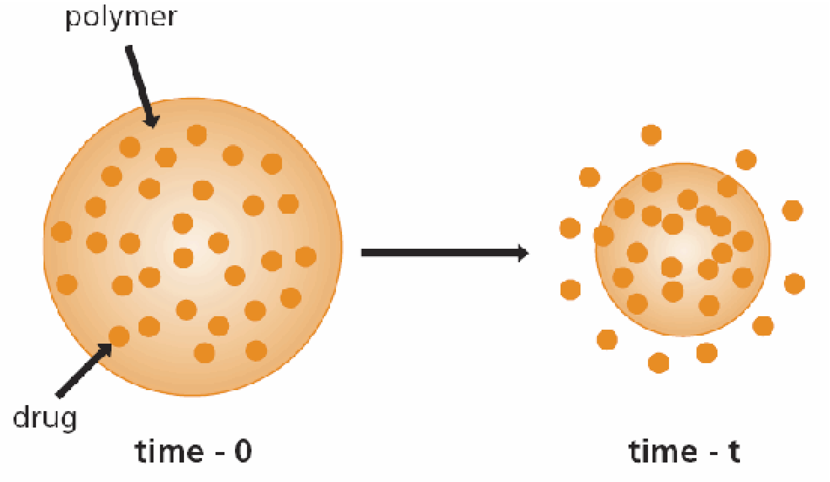


Figure 1 Drug delivery. (Sigma-Aldrich C, 2016)

The hydrogel shows good response towards temperature and the pH. The various sites in the human body where the hydrogel is successfully used as a drug carrier are small intestine, lungs, stomach, oral cavity, colon, nasal cavity and ocular sack.

1.1.2 Tissue engineering

In the tissue engineering, the hydrogel is used as a polymer scaffold. It is used for the replacement of the failed or the damaged organ, for regeneration of new organ or tissue. In the tissue engineering, human cell is used to integrate polymer scaffold and then transfer the cells to the desired locations. At the desired location or site, the cell structure and cell formation can be controlled (Hoffman, et al., 2012). The schematic diagram below Figure 2 shows the working of hydrogel in the field of tissue engineering.

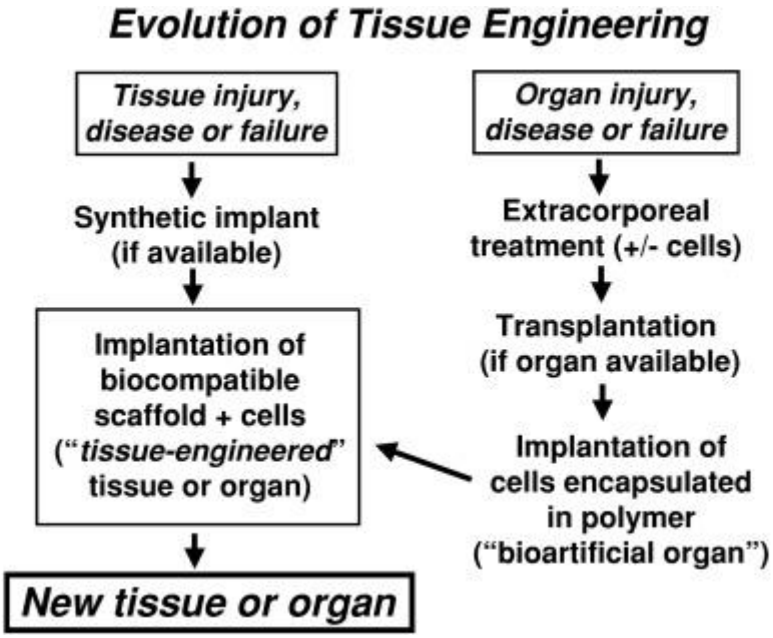


Figure 2 Schematic diagram showing treatment method of injured tissue or organ (Hoffman, et al..*, 2012)*

The hydrogel is used as polymer scaffold in tissue engineering because of it certain properties such as it can transport nutrients to cell as hydrogel allows permeability, easy modification and it is biocompatible.

1.1.3 Sensors

Hydrogels with stimuli sensitivity and showing measurable or detectable changes (shape or volume change) under chemical or physical changes.

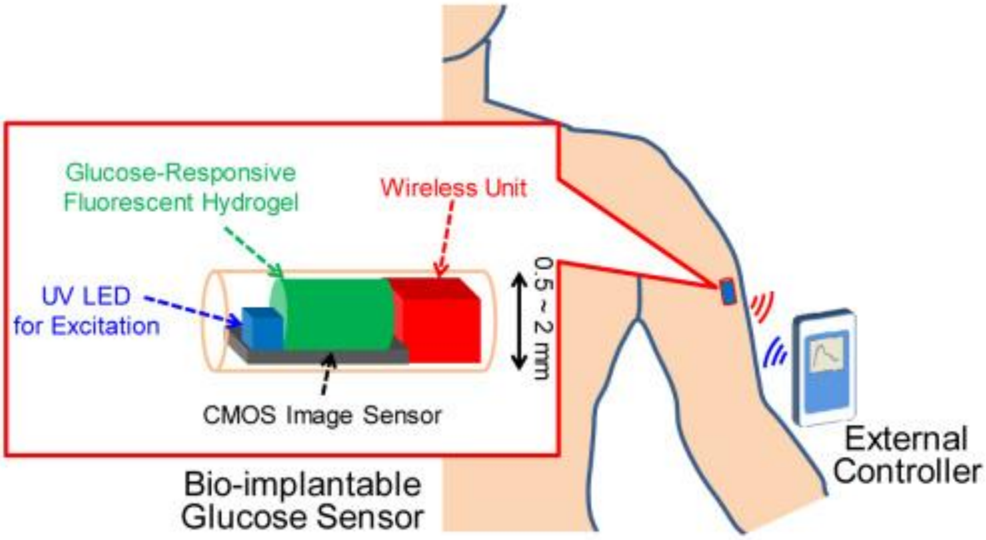


Figure 3 Glucose hydrogel sensor (Tokuda, T., et al. *2014)*

For example, in glucose sensor, the glucose molecules induce swelling in the hydrogel: which leads to the change in the resonant frequency (Peak et al., 2013). This resonant frequency can be detected remotely. One example of this type of hydrogel is shown in figure 3.

1.1.4 Artificial muscle

The hydrogels are used as an artificial muscle as they have similar structure to the living tissue. The other properties that suggest hydrogel as a good artificial muscle are: the shape of the hydrogel can be adjusted, they are not biodegradable and most importantly, they are biocompatible (Hoffman, et al., 2012).

1.2 Problem statement

As from the above listed applications the significance or the important of the hydrogel can be estimated but despite of its unique qualities the hydrogel is not fully utilised because of its poor mechanical properties. Poor mechanical properties mean that the hydrogel cannot able to bear enough load that is needed in some of its applications. The conventional hydrogel has low fracture toughness, it is brittle and has low extension under the applied force. Because of these reasons, the application of the hydrogel is limited in every sector.

In this thesis, the main concerns will be to enhance the mechanical properties of the hydrogel so that it can be used in the wider range of applications. By enhancing mechanical properties, it means that the toughened hydrogel should have high fracture toughness and improved tensile strength as compared to the conventional hydrogel.

1.3 Scope of the study

This thesis starts with the preparing of the conventional hydrogel and the toughened hydrogel (the toughened hydrogel is prepared by providing toughness to the conventional hydrogel). Then the various tests are performed on both the hydrogel to see the significant changes in the toughened hydrogel over the conventional hydrogel. The scope of the study is also illustrated by the flow chart (1) in the objective of thesis section. At the end, the data or the results obtained from various test are to be analysed and conclusion is made accordingly.

1.4 Significant of research

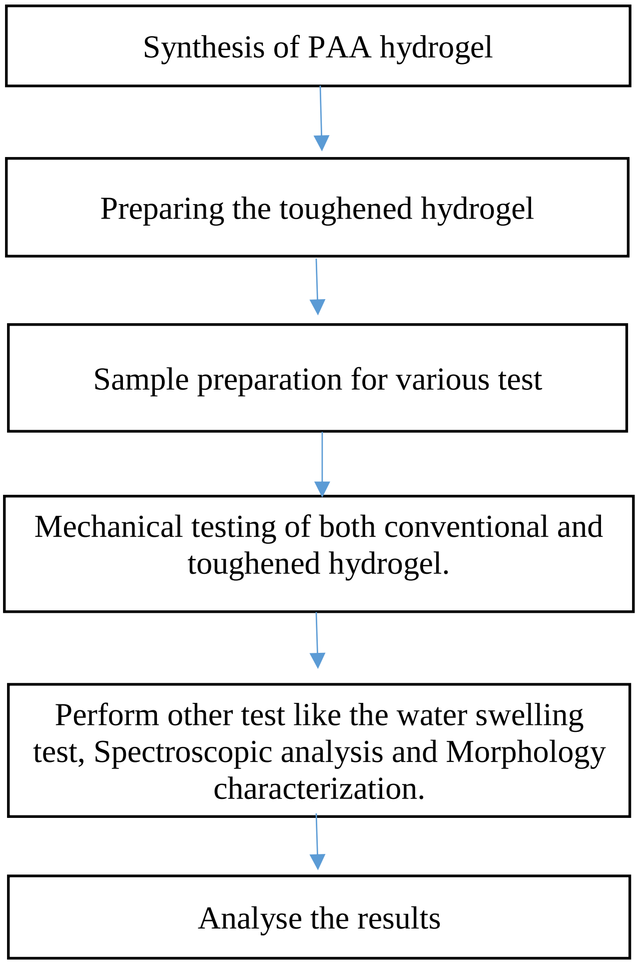
This project is expected to show the significant result in the mechanical properties of the toughened hydrogel over the conventional hydrogel. This is to be achieved by performing the mechanical and other test in between the conventional and the toughened hydrogel. It should be noted that the toughened hydrogel should possess conventional properties of the hydrogel such as water swelling, porous structure, biocompatibility etcetera. The focus in this thesis is to test the mechanical properties of toughened hydrogel in comparison to the conventional hydrogel: which is PAA in this thesis.

1.5 Objectives

The objective of this thesis is to enhance the mechanical properties of the hydrogel by adding known material to it. As by adding known material to the hydrogel will increase the mechanical properties and effect the other properties of the hydrogel such as the water swelling. Then the testing will be conducted on the hydrogel containing the material to note the difference and how much is the improvement in the mechanical properties of the hydrogel.

As the objective of this thesis is to enhance the properties of the hydrogel so that it can widely be used in the biomedical field. The properties, that this thesis is mainly focused on are the mechanical properties such as fracture toughness, tensile strength and some other properties that are very crucial in the biomedical field. The other very important aspect of my thesis is to make sure that the toughened hydrogel should possess the conventional properties of the hydrogel such as the water absorbing capacity. It can be done be preparing the sample of the toughened hydrogel and test it against the conventional hydrogel.

For the toughening of the hydrogel, the layer of the enhancement will be provided the hydrogel the molecular level and then at the sub molecular level of enhancement would be provided to the conventional hydrogel. In the molecular level of the enhancement the enhancement is provided by the hyperbranched polymer and for the sub micro level of enhancement it would be done by the PVA [poly (vinyl alcohol)] nanofibers. The overall objective of my thesis is shown in the flow chart below:



Flow Chart 1 Objective of my thesis (hierarchical level of toughness provided)

After the preparation of the toughened sample of the hydrogel the testing would be done. The mechanical testing includes the tensile testing, double peeling testing and the dynamic testing. The other properties of the hydrogel sample would also be compared such as by the water swelling behaviour. The structure of the both hydrogel i.e. the toughened hydrogel and the conventional hydrogel will also be investigated in order to understand the bonding of the conventional hydrogel with the toughening polymer like the hyperbranched polymer (HB).

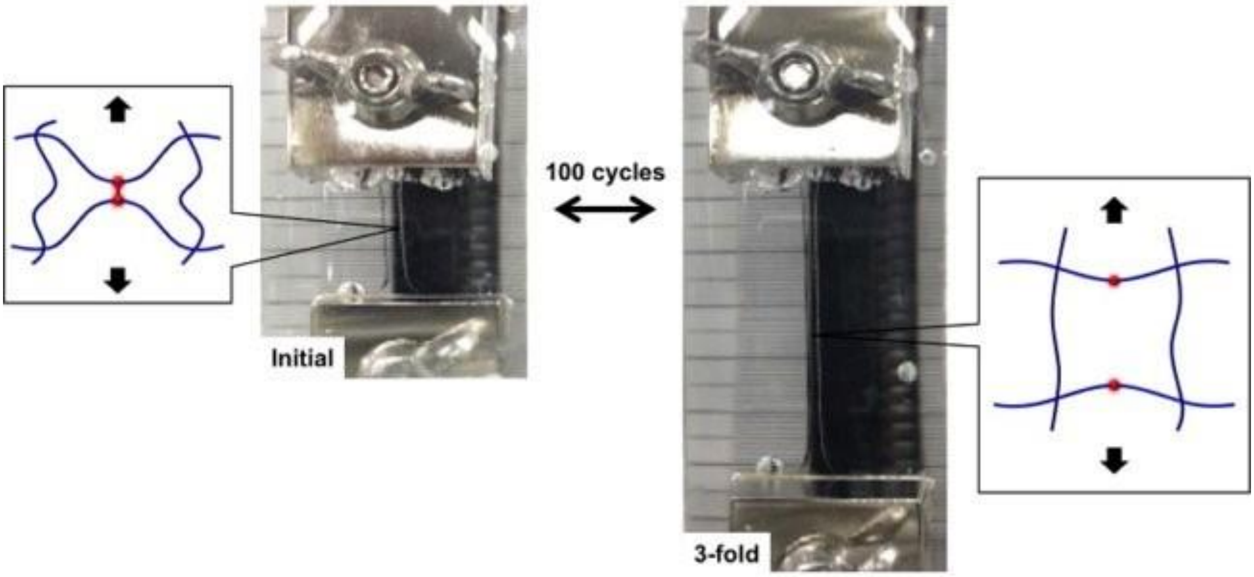
Chapter 2 Literature review

This thesis is based on the toughening of the hydrogel, in order to enhance its application in the biomedical field. In this section of the report, the need for the toughening of the hydrogel is discussed along the other important properties of the hydrogel.

The toughness of the hydrogel is measured by performing various tests and then analysing the output data against the conventional hydrogel.

2.1 Need to toughen hydrogel

Hydrogel is a soft material that is not well known for its various unique properties. In many of the application in which the hydrogel is being used there is not much need for the toughened hydrogel but hydrogel has huge amount of application where it can be used or has a great potential to be used in, the only problem with the hydrogel to be not able to use, is its weak mechanical properties such as fracture toughness. The toughness of the hydrogel is needed to hold its own weight, which is required in many of the applications but the conventional hydrogel fails to provide it. To enhance the applications of the hydrogel it needs to be toughened. As shown in the figure 4, that how the hydrogel fails in mechanical testing.



Figure

4 Hydrogel failing in mechanical testing (Webber, et al.*, 2007)*

2.2 Tough hydrogel for biomedical applications

As discussed in the above section, the applications of the hydrogel are limited by its weak mechanical properties. It is the same case in the biomedical field, the full potential of the hydrogel is limited due to its weak mechanical properties. As some of the biomedical applications, require tough hydrogel. In some case, where the hydrogel is currently used but with the usage of toughened hydrogel, the results can improve drastically.

For example, the hydrogel is used as a polymer scaffold in tissue engineering. There are some limitations of using the hydrogel as polymer scaffold. Those limitations are mainly because of its weak mechanical properties (Drury, et al., 2003). Since, many of the human organs or tissues are always working in high load mechanical environment. Tissue like muscles, bone and even blood vessels that are working in the high load mechanical environment.

For the assessment of the mechanical properties of the hydrogel various mechanical test need to be conducted to assess the mechanical properties of the hydrogel. The hydrogel possesses different mechanical properties depending on particular conditions i.e. the properties of the hydrogel changes when it is swollen (absorbed water), it is without water content in it, temperature and PH value and many of other factors. In the swollen state, most of the hydrogel possesses the properties of the rubber elasticity (Anseth, et al.,1996). In the swollen state, the mechanical behaviour of the hydrogel is mainly dependant on the architecture of the polymer network. Which means in the swollen state, the hydrogel responses instantaneous to the applied stress and fully reversible deformation this is due to the free volume that allows them to respond to the applied stress. The hydrogel losses their rubber elastic properties if the temperature drops down. At the low temperature, the hydrogels show the viscoelastic behaviour.

2.3 Tough hydrogel

As discussed above that hydrogel are the soft material that are well known and widely used for their water absorbing capacities. By modify the hydrogel or by increasing its capabilities it can be used in more and more application such are by providing the adhesive strength to the hydrogel it can be used in the Biomedical filed where adhesive strength is required in some cases (Caló, E. and Khutoryanskiy, 2015). For many of the application the toughness of the hydrogel is required in order to improve its mechanical properties and increase its range to many more fields. For example, the tough hydrogel can be used for the sensors, electrochemical devices, microfluidics devices and many more. However, due to the poor mechanical strength like the fracture toughness or the tensile strength the hydrogel applications are limited (Peak, et al.,2013). By providing the required toughness to the hydrogel according to the requirement of the application, the applications of the hydrogel can be increased in each field. The requirement of the properties of the hydrogel changes according to the field or according to the requirement of the current job. For example, in the biomedical field, the basic requirement of the hydrogel is to be biocompatible where it is not the necessary in every field. Similarly, the toughness is required some areas of application so that it can be used in more fields.

For the toughness of the hydrogel, different layers (polymer layer such as HB) can be added to enhance the toughness of the hydrogel and each layer server its own purpose. The number of the layers enhances the toughness of the hydrogel. The toughness of the hydrogel is increased according to the specific requirement. In case of my thesis, the hyper-branched polymer provides the first level of enhancement. This first level of enhancement is provided at the molecular level. For the molecular level of enhancement, the hyperbranched polymer is chosen because of its structure. As the hyperbranched polymer has a tree like structure with many end groups which can easily interact with the functional group matrix (which in this case in the Acrylic acid). To provide more toughness to the hydrogel the second level of enhancement can be provided to the hydrogel. The second level enhancement is at sub micro level. The PVA poly (vinyl alcohol) polymer provides the secondary level enhancement. The PVA polymer is prepared by the process of electrospinning. The selection of the polymer for any level of the enhancement depends on the requirements. The primary purpose of adding another polymer is to enhance the toughness of the polymer but along with enhancing the toughness of the polymer, it also serves several secondary purposes. For example, the PVA polymer enhances the toughness of the hydrogel as its primary function but as its secondary function it also enhances several other properties such as flexibility, porosity, thermal stability and provide homogeneous structure (Xin, H., 2014). To provide toughness to the hydrogel, there are various methods, which are discussed as below.

As mentioned above, the first level of enhancement is provided by the hyperbranched polymer and this enhancement is at the molecular level (Gaharwar, et al.,2011). On the other side, the second level of enhancement is provided by the PVA [poly (vinyl alcohol)] polymer and this level of enhancement is provided at the sub-micro level. (Deng, et al.2013)

2.4 Ways of toughening of hydrogel

2.4.1 Double network hydrogels

The double network hydrogel is known for its excellent mechanical properties. The double network hydrogel has an interpreting network where the first network is infiltrated by the second network i.e. The first network is allowed to pass through the second network. In this type of these hydrogel, the first network chosen is the poly (2-acrylamido-2- methylpropane sulfonic acid) and the second network is the polyacrylamide (Nakayama, A., Kakugo 2004). The double network hydrogel has high fracture strength and due to low coefficient of friction, they have good wear resistance. The double network hydrogel has good mechanical properties as compared to the conventional hydrogel as they have their fracture toughness around 500 to 1000 J/m^2 ((Xin, et al., 2014) and the fracture toughness of conventional hydrogel is only 10^-1 to 10 J/m^2.(Gong, el al, 2010)

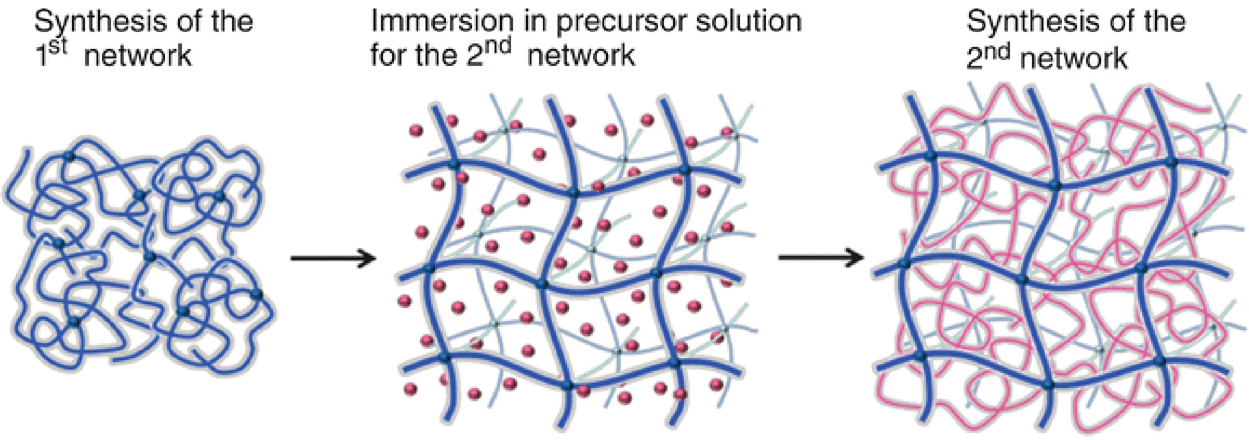


Figure 5 Double network hydrogel (Nakajima, T. and Gong, J.P., 2015)

As seen in the above figure 5, the double network hydrogel is synthesised in such a way that the first network is densely cross-linked and the second network are loosely cross – linked. Also in the double network hydrogel system, the second network is the major component of the overall system. The high toughness of the double network hydrogel as compared to the conventional hydrogel is due to the different network system. In the double network system, the network is complex and has inter polymer bonding whereas; in the conventional hydrogel system, it has simple addition of both the fracture energies.

The double network hydrogel bears high load without the failure due to the complex function of the two-network system. The first network wears most of the stress applied and due to this, there are multiple damage zones formed on it. The second network stabilises these multiple damage zones and prevents them from propagating.

2.4.2 Nanocomposite hydrogels

As the name suggest, these hydrogels are synthesised in the presence of the nanoparticles. The nanocomposite hydrogels are the cross- linked polymer hydrogels. The nanoparticles used in the formation of the nanocomposite hydrogels are of many types. The selection of the nanoparticle for the formation of the hydrogel depends on the application where the hydrogel is going to be used. Some of the nanoparticles that are being used are magnetic particles, silicate and metal particles (Xin, et al. 2014). The basic purpose of using the nanoparticles is to enhance the mechanical properties of the hydrogel and to add other new properties to the conventional hydrogel. The nanocomposites are of various types as seen in the figure 6 below:

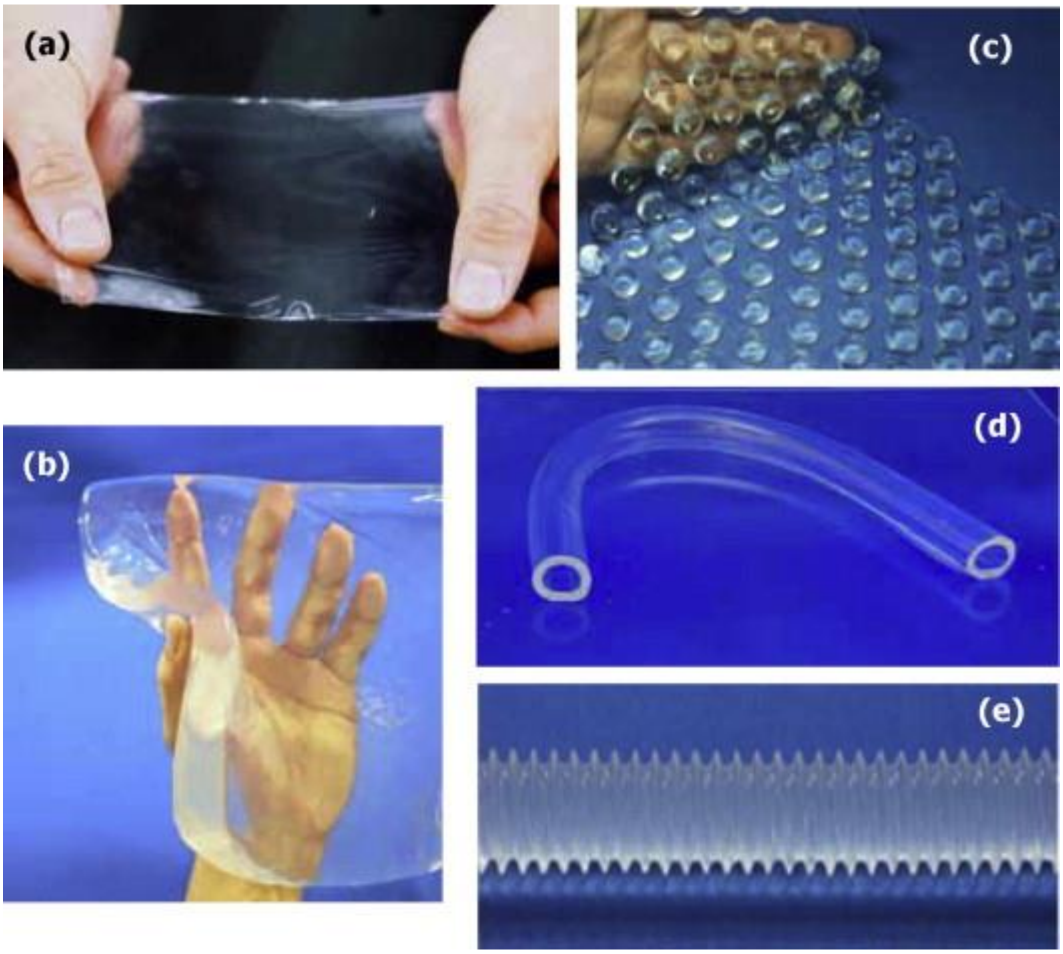


Figure 6 NC gels with various shapes: (a) thin film, (b) sheet, (c) uneven sheet, (d) hollow tube and (e) bellows (Haraguchi, K., 2007)

One such example of the nanocomposite hydrogel which is prepared by the poly (N- isopropyl acrylamide) (PNIPA) and it uses the clay particles as it Nano particles. In this type of hydrogel, the clay particles act as the inorganic cross – link (Haraguchi, K., 2007). These clay particles connect the PNIPA polymer and helps to form the complete gel network. This type of NC hydrogel has provided enhancement from the conventional hydrogel in various aspects such as ability to withstand large amount of deformation, improved strength, improved tensile modulus etc. (Peak, C.W. 2013)

The mechanical properties of the nanocomposite hydrogel depend on the homogeneity of the network. The mechanical properties of the NC hydrogel can be enhanced or controlled by the density of the Nano particles.

The nanocomposite hydrogel prepared by the Takehisa and Haraguchi was made from N-isopropylacrylamide, acrylamide polymers or N, N – dimethyl acrylamide and silicate nanoplatelets. These types of hydrogel provide with the elongation of 1000%. The nanocomposite hydrogels provide the fracture stress about 1 MPa. The conventional hydrogel can have the fracture toughness from 10^-1 to 10 J/m^2 (Haraguchi, et al., 2002)

2.4.3 Slide ring hydrogels

In the slide ring hydrogel shown in figure 7, the linear backbone polymer forms into the cyclic molecules. These cyclic molecules are trapped into the heavy end groups. To prepare the slide ring hydrogel, cyclic α-cyclodextrin (α –CD) molecules and the plyrogtaxane are used ((Xin, H., 2014). The slide ring hydrogel is prepared by crosslinking the two α-cyclodextrin groups with the reactive hydrogel group to form the entire gel network. The slide ring hydrogel have certain properties like high elongation, increase in the water absorbing capacities that is approx. 500 times the dry weight.

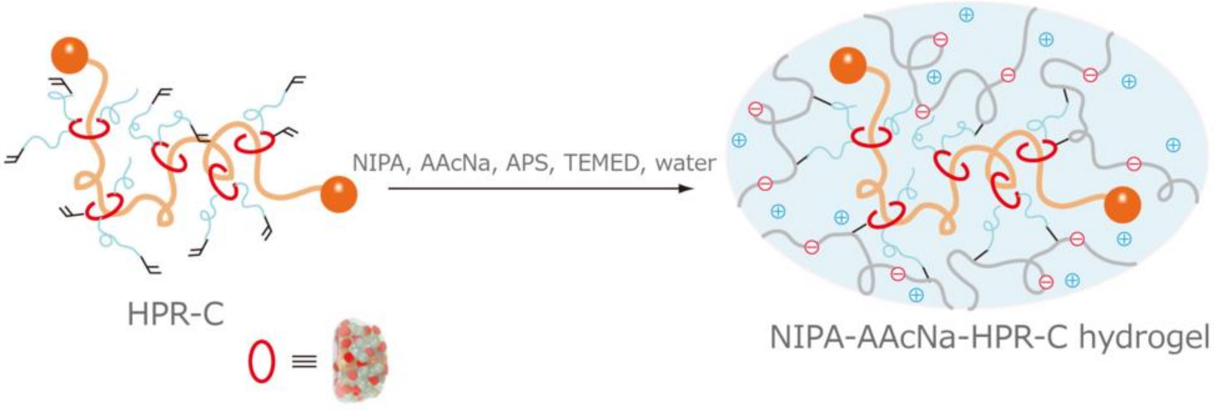


Figure 7 Slide ring hydrogel (Qiu, Y. and Park, K., 2001)

The slide ring hydrogel also shows the pulley effect, which means that it allows the PEG (polyethylene glycol) chain to freely pass through the crosslink (Zhao, et al. 2005). This pulley effect helps the slide rind ring hydrogel to withstand more extension as the pulley effect equalizes the external tension when it is being deformed (when external stress is applied to the hydrogel).

2.5 Advantages / Disadvantages of synthesised methods for toughened hydrogel

As in the above section various methods of hydrogel toughening were mentioned. These methods have many advantages such as these methods provides high fracture resistance to the hydrogel. These methods also enhance several other properties of the hydrogel such as the water swelling properties. These methods for example, the double network method or the nanocomposite methods also provides the option of modifying the properties of the hydrogel according to the specific requirement. As in the double network system the enhancement properties can be varied by changing the polymer.

Apart from these advantages there are several disadvantages of these methods that pushes the researchers to investigate new ways of providing toughness to the conventional hydrogel. As in the above-mentioned methods, the toughness is provided by the chemical processes. These processes are expensive therefore there is need of the new method to provide the toughness to conventional hydrogel.

2.6 Properties of hydrogel

2.6.1 Viscoelastic properties of hydrogel

In case of the hydrogels, the viscoelasticity exhibits the relations between the molecular motions. The viscoelasticity response depends on the magnitude of the mechanical motion (Ahearne, M., Yang 2005). In general, it can be said that most of the hydrogels shows not only elastic behaviour instead they show viscoelastic behaviours. The hydrogels can have the several viscoelastic behaviours such as if the recovery of the hydrogel is complete after a long time and after the applied stress is removed then that behaviour is termed as the viscoelastic behaviour.

2.6.2 Creep behaviour

In creep behaviour, the shear stress of constant magnitude is applied to a viscoelastic material. The effect of the constant shear stress is observed against the time for the time dependence behaviour of the viscoelastic material. From the creep behaviour of the viscoelastic material, the creep compliance is measured; creep compliance is the ratio of the applied stress to the time dependent sheer stress (Anseth, et al., 1996). The below figure 8 shows the graphical representation of creep behaviour of hydrogel.

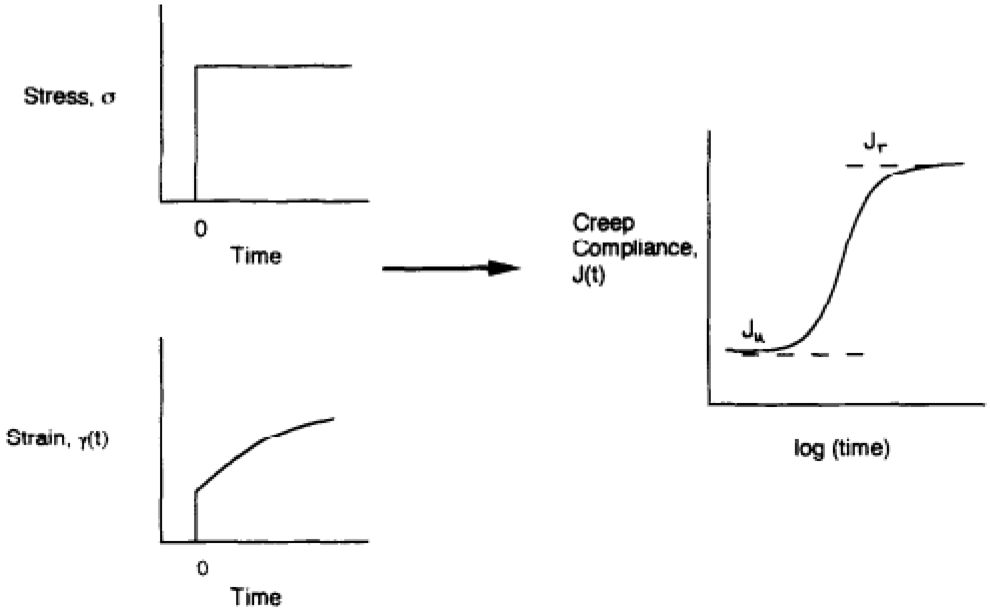


Figure 8 Creep test (Anseth, K.S., Bowman, 1996)

The creep compliance shows the little time dependence at a very long and short times. During the short times, the time scale of the applied stress is very less than the time scale of the molecular motion in the hydrogel. On the other hand, in the long time, the time for the complete molecular rearrangement is less than the experiment time scale. In case of the very short time the system remains in the unrelaxed state whereas in the very long times the system remains in the relaxed state.

2.6.3 Stress relaxation

In the stress relaxation test of the hydrogel, the time dependence of stress required to maintain that strain is measured when it is subjected under a constant shear strain (Anseth, et al., 1996) as shown in the figure 9.

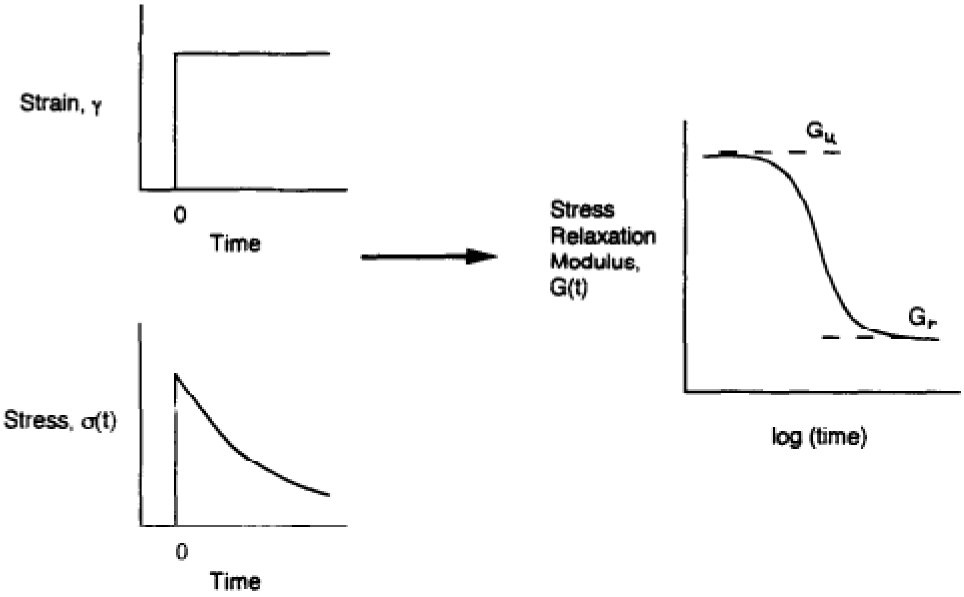


Figure 9 Stress relaxation (Anseth, et al. 1996)

As in the case of stress relaxation, the plotted graph is nonlinear unlike the creep, which means the range of linear stress relaxation cannot be determined. The graphical representation of stress relaxation of hydrogel is shown in figure 9.

2.6.2 Water swelling properties of the hydrogel

The water swelling properties of the hydrogel is a very important and distinctive property of the hydrogel. Due to its water swelling properties the hydrogel has huge demands in various fields. The main advantage of the hydrogel is that it swells but does not dissolve in solvent or in other words, it does not allow the solvent to enter in to the hydrogel (Chen, J., Park, H. and Park, K., 1999). The water swelling property of the hydrogel is due to the crosslinked polymers in the hydrogel. The degree of swelling of hydrogel is dependent on many factors which are nature of solvent, network density interaction parameters of solvent and polymer. (Yang, T., 2012)

The swelling process in the hydrogel can be described as the rubbery state as hydrogel is a hydrophilic network and in the hydrophilic network, the water acts as the plasticizer.

The swelling process in the hydrogel can be described by the free energy of mixing represented as ΔG mix from the polymer and the free elastic energy (ΔG elastic) from the crosslinked network. The swelling equation (1) can be written as below:

$$\Delta G\ \text{system} = \Delta G\ \text{mix} + \Delta G\ \text{elastic} \quad \text{(Yang, T., 2012)} \tag{1}$$

The above given equation changes as the swelling condition or the swelling process inside the hydrogel changes. As at the beginning of the swelling process, the free energy of mixing is very less than zero (ΔG mix << 0), the elastic energy is greater than zero (ΔG elastic > 0) and the combination of the mixing energy and the elastic energy is less than zero (ΔG mix + ΔG elastic < 0). The above-mentioned conditions are favourable for the swelling; therefore, the swelling starts i.e. the solvents starts to diffuse in to the hydrogel network. Now during the swelling process, the mixing energy and the elastic energy both keep on increases until they both are equal i.e. $|\Delta G\ \text{mix}| = |\Delta G\ \text{elastic}|$ and also the system energy is equal to the sum of the both mixing energy and the elastic energy and also the sum of these both energies be equal to zero which is represented by the equation (2) as follows:

$$\Delta G\ \text{system} = \Delta G\ \text{mix} + \Delta G\ \text{elastic} = 0 \quad \text{(Yang, T., 2012)} \tag{2}$$

By these conditions, the swelling stops because the driving force for the swelling is gone and the equilibrium condition of the swelling is achieved.

2.6.3 Adhesive properties of hydrogel

The adhesive properties of the hydrogel describe about the bonding of the hydrogel with the other material or to the other surface. For the bonding of the hydrogel to the other surface or the material requires both cohesive bonding with in the bulk material as well as the adhesive interaction between the both surfaces (Peak, C.W., Wilker, J.J. and Schmidt, G., 2013). The adhesive properties of the hydrogel play a very crucial role in the many fields for example in the tissue engineering and in the biomedical field.

The adhesive interaction is the interaction of the hydrogel with another surface for example with glass, plastic etc. whereas, the cohesive interaction is the inner bonding within the materials i.e. the cohesive properties relate to the inner strength of the hydrogel (Sun, J.Y.,Zhao, X 2012).

In various fields, the application of the hydrogel is limited due to its poor adhesive properties i.e. in various application the sticky nature of the hydrogel is much required along with its other properties. To have glue like properties in the hydrogel, it is very important to balance the adhesive properties and the cohesive properties because the glue functions well when there is perfect balance between the cohesion and adhesion.

When synthesising the adhesive hydrogel for the biomedical field, swelling plays a very crucial role in the successful application of the adhesive hydrogel in the biomedical field. As the fluid from the surrounding can start the swelling of the hydrogel and can thereby restrict the flow with in the repaired body part (for example vessel).

Figure 10 Electrode (Sasaki, M., Karikkineth 2012)

As discussed above that the adhesive nature of the hydrogel plays a very important role in many of its applications mainly in the biomedical field. The adhesive hydrogel can be applicable as the sealant for corneal wounds, arteries or cartilage. It can be used in the adhesive drug delivery depots; it can also be used as haemostasis, sealant for bleeding wounds. The adhesive hydrogel is also used as the tissue integration matrices and surgical sealants. One application of hydrogel is shown in the figure 10 as an electrode.

The major problem with the adhesive hydrogel is that with the increase in the adhesive nature of the hydrogel there are more chances of the decrease in the toughness of the hydrogel (Caló, E. and Khutoryanskiy, V.V., 2015).

The other problem arises when it comes to the measurement of the adhesiveness of the hydrogel, as it is very difficult to measure the strength of the adhesive hydrogel. The complication in measuring the strength of the adhesive nature of the hydrogel is due to the several parameters discussed below, which has huge impact on the adhesive nature of the hydrogel. Parameters such as the difference in the type of material for example metal, glass, rubber etc., due to treatment of the material (dry, wet or moist) and the testing systems such as bust pressure test, lap shear test and peel test.

There are various adhesive hydrogels synthesized from which some are discussed below:

2.6.3.1 Dendritic polymer hydrogel:

In this method, the adhesive hydrogel is formed from dendritic polymers. The dendritic polymer hydrogels are mainly used in the biomedical field such as sealing corneal wounds and repairing wounds. The chemical ligation and the photo chemistry are the cross-linking techniques that are used for generating these hydrogels (Peak, C.W., Wilker, J.J. and Schmidt, G., 2013). This type of the hydrogels has the adhesive strength between 13 to 700KPa and have 10% to 50% polymer composition.

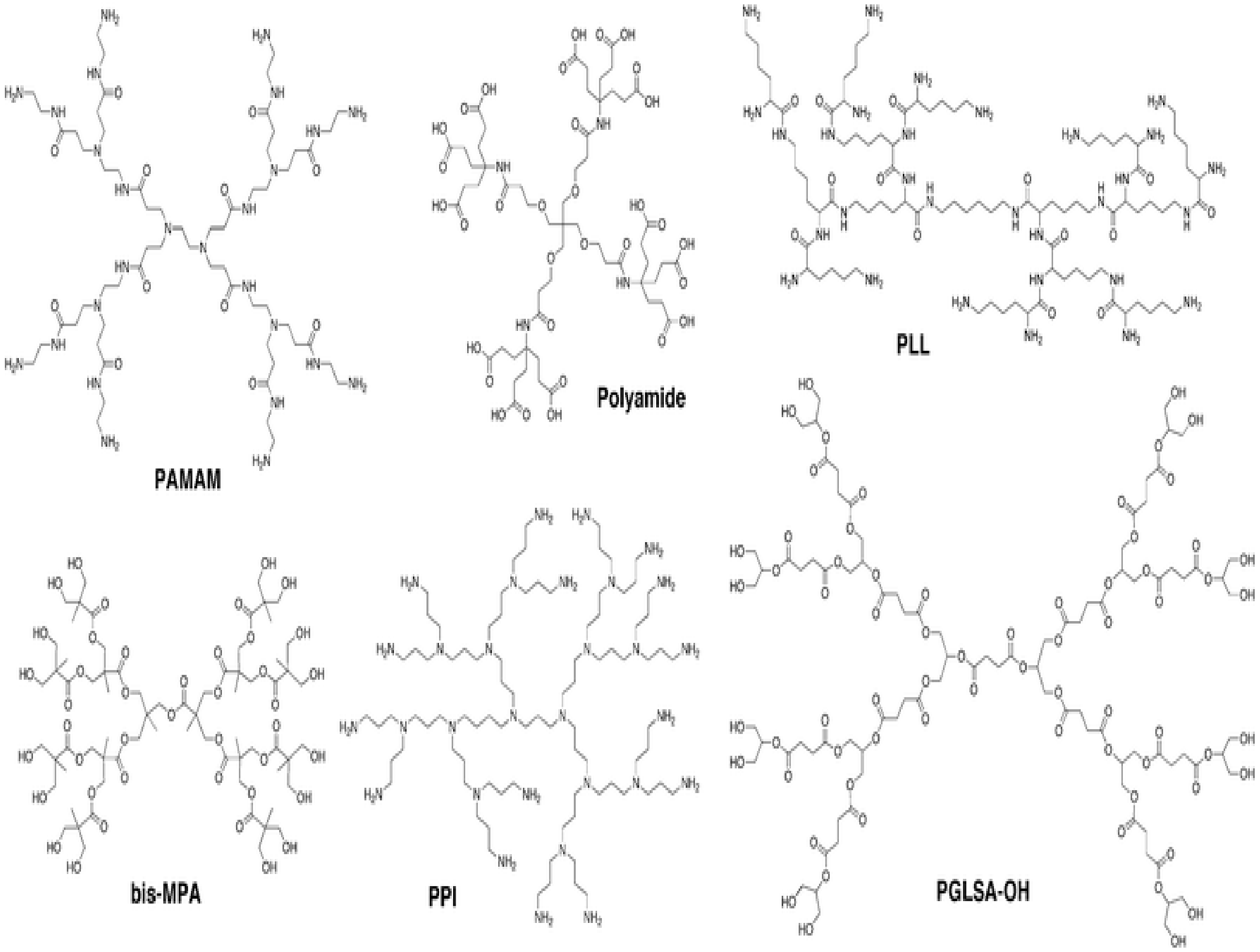


Figure 11 Chemical structures of several commonly used dendritic polymer (Mintzer, M.A. and Grinstaff, M.W., 2011)

2.6.3.2 Hydrogels based on the DOPA chemistry

Theses hydrogels are moist adhesive and wet. These hydrogels have adhesive properties due to the presence of the 3, 4-dihydroxyphenylalanine (DOPA) amino acids. With this DOPA or from the derivatives of the DOPA the irreversible cross linking is possible (Sun, J.Y.,Zhao, X 2012). The irreversible crosslinking is done by the help of metal chelation mechanism and oxidation process.

The best thing about the hydrogels prepared from the DOPA is that, the hydrogels have properties like toughness, good adhesiveness and works in wet environment. Most of the hydrogels are not able to work well around the wet environment which was a huge drawback considering in the biomedical field. For example, Brubaker synthesised the hydrogel which was made from the branched PEG and then modified by the DOPA. These hydrogels were wet adhesive and can be used for sealing the human feral membrane defects. These can also be used for attaching the transplanted islets to tissue surface for surgical wound closer and for reverse diabetes. The adhesive shear strength of this hydrogel was around 30KPa.

2.6.3.3 Hydrogels based on the interpenetrating networks.

The adhesive nature of the hydrogel opens a wide range of the application where the hydrogels can be used, for example in tissue engineering. The most important concern when anything is used in the vivo is the biocompatibility of that material. The desired hydrogel to be used in the vivo should have the perfect balance of adhesiveness and toughness and should be biocompatible. For the vivo purpose, a hydrogel was prepared from a PEG-dextran aldehyde, this hydrogel possesses good adhesiveness due to the presence of the excess aldehyde group but due to the presence of these functional groups, the hydrogel has induced inflammation in vivo. (Sun, J.Y.,Zhao, X 2012).

To overcome the inflammation in the vivo attempts were made to balance the adhesive strength with the biocompatibility of the hydrogel. For this purpose, the hydrogel was synthesised by the Artzi, which was made from the animated eight – arm star PEG and dextra aldehyde. In this type of hydrogel, the biocompatibility of the hydrogel can be controlled by adjusting the density and the number of the aldehyde groups (Peak, C.W., Wilker, J.J. and

Schmidt, G., 2013). For enhancing the adhesive strength of the hydrogel, aldehydes can be coupled with the amine groups to enhance the adhesive strength of hydrogel.

2.6.3.4 Adhesive nanocomposite hydrogels

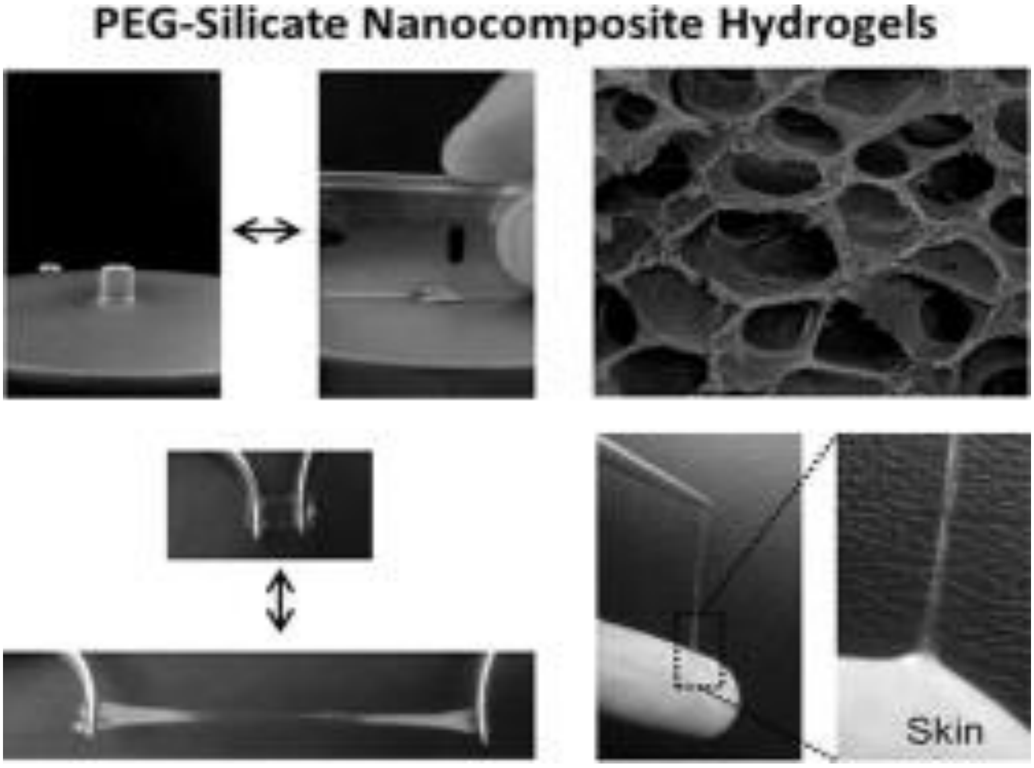


Figure 12 PEG-Silicate Nanocomposite Hydrogel (Gaharwar, A.K., Rivera, 2011)

The nanocomposite polymers can have the properties like the softness and toughness but these materials are not adhesive. The nanocomposite hydrogels can be made adhesive such as the adhesive hydrogel was prepared from the photopolymerized PEG-DA in the presence of the silicate nanoparticles. The resulting hydrogel produces the adhesive strength around 13KPa. The adhesive properties in this type of hydrogel are due to the presence of the hydrogen bonding, dipole and covalently cross-linked PEG-DA chains (Sun, J.Y.,Zhao, X 2012). These types of hydrogel have one more additional advantage that is the adhesion is reversible in these types of hydrogels which means that material can be removed if it is no longer needed.

2.7 Evaluation of mechanical properties of hydrogel.

Evaluating the mechanical properties is an important aspect of my thesis work. The evaluation of the mechanical properties of the hydrogel is done considering the biomedical application of hydrogel. As discussed in the above sections, that for the biomedical application the hydrogels need to be toughened. To determine the toughness of the hydrogel, the fracture toughness is determined. Along the fracture toughness of the hydrogel there are some other important mechanical properties that need to be evaluated such as fatigue behaviour of hydrogel as in some cases in the biomedical field, there is need for the hydrogel; to withstand in the cyclic loading.

2.7.1 Dynamic loading behaviour

The fatigue behaviour is determined by putting the hydrogel in the cyclic loading. By putting the hydrogel in the cyclic loading, it will show loading curve and unloading curve as shown in figure 13. From the loading and unloading curve, the energy dissipated can be calculated, as the energy dissipated is the area under the loading and the unloading curve. This will provide very crucial information about the properties of hydrogel, when the hydrogel is under the same extension (due to the applied force) for the number of cycles. The behaviour of hydrogel might also vary if dynamic test is performed at different time intervals.

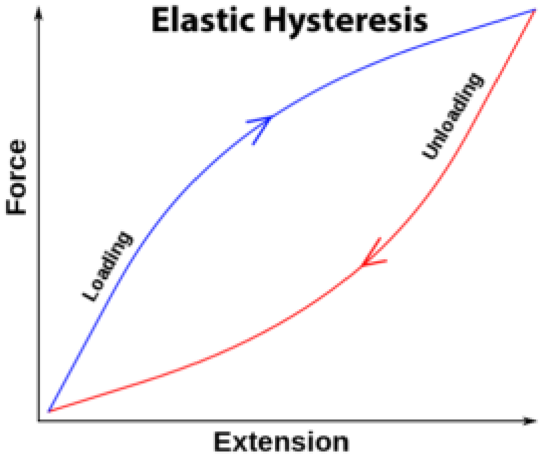


Figure 13 Loading and unloading curve (Liptak, B.G., 1993)

Chapter 3 Methodology

3.1 Material preparation

After reading the literature, the next step was to synthesise the hydrogel. As the objective of my thesis is to show the toughness of hydrogel as compared to the conventional hydrogel. Therefore, samples were prepared for both the conventional and toughened hydrogel and then their properties were compared mechanical testing and look for significant result. The hydrogels were synthesised according to the previous work done in Dr. Youhong Tang laboratory (Yu and Tang 2015).

As the comparison between the various samples of the hydrogel are to be made therefore, it was very important to make the all types of sample in similar condition. So, as to eliminate any kind of variation in between the different samples, it was very important to prepare every sample in the exact same environment to minimize any variations.

The most crucial thing that was in the material preparation was to minimize the thickness difference between the hydrogel samples. As preparing the different types of hydrogel and then to perform the mechanical testing on them. The thickness of the sample would have a huge impact on the results on the mechanical properties of the hydrogel sample. In other words, my aim was to keep the thickness of the material uniform. To achieve this, the samples was prepared many times to get the right amount of thickness and make sure that the thickness of the materials was same for the entire sample of the material.

For the synthesis of the hydrogel and its hybrids various materials were used. The materials that were used in the hybrids of the hydrogel were intended to enhance the toughness of the hydrogel (to enhance mechanical properties). For the conventional hydrogel sample, the material used was the Acrylic Acid, water and sodium hydroxide (Noah). The catalyst was also used to speed up the process of chemical reaction. Apart from the catalyst, one cross linker was also introduced into the solution to increase the bonding between the solution. The cross linker that was used was MBA [N, N′-Methylenebis (acrylamide)] and the catalyst used was APS [ammonium persulfate]. For the synthesise of the hybrids of the hydrogel, the same materials were used but a toughening polymer was added to enhance their toughness. In case of the PAA-HB, the hyperbranched polymer was used along with other materials used in the conventional hydrogel. In the PAA-PVA hydrogel, the PVA [poly (vinyl alcohol)] polymer was used with the other materials used in the synthesis of the conventional or the PAA hydrogel.

3.1.1 Synthesis of PAA hydrogel

The first hydrogel that was synthesised, was the PAA or the conventional hydrogel. For the synthesis of the PAA hydrogel, firstly the solution of acrylic solution was prepared by using 37g of acrylic acid and then dissolving into 35cm^3 of water. The solution of acrylic acid and water were mixed thoroughly. On the other hand, the sodium hydroxide solution was prepared, the solution was prepared by dissolving 16.3g of sodium hydroxide (Noah) into 36.2 cm^3 of water. After that the solution was thoroughly mixed using the vortex shaker. It is very important to make sure that there are no undissolved particles left in the solution i.e. the solution should be homogeneous. Then both solutions i.e. the acrylic solution and the sodium hydroxide solution were placed into the water bath to decrease their temperature. While both the solutions were placed in to the ice bath, at the same time both the solution containers were placed on the magnetic shaker. Magnets were put down into both the solutions before placing them on the magnetic shaker. The reason of putting the solution on the magnetic shaker was that, the shaker would not allow the solution to settle down as the magnetic shaker will keep on rotating the small magnets inside both the solutions and both the magnets keep on mixing the solution and does not allow the solution to settle down. As both the solutions were kept in the ice bath and they were kept at the magnetic shaker at the same time both the solutions i.e. the acrylic solution and the sodium hydroxide solution were mixed. The mixing process of these solution were as; the sodium hydroxide solution was poured into the acrylic solution drop by drop wise by using the dropper. The solution of sodium hydroxide was poured into the solution of acrylic for approximately 20 minutes (Yu and Tang 2015).

The next step was to add the catalyst and the cross linker into the solution to speed up the chemical reaction process and to increases the bonding of the solution. The MBA was used as cross linker and for catalyst APS was used. Both the MBA [N, N′-Methylenebis (acrylamide)] and the APS were added into the solution. 0.25 g of MBA and 0.8 g of APS were mixed into the prepared solution of acrylic acid and sodium hydroxide. The mixing of the catalyst and the cross linker into the solution was done by the vortex shaker. As the MBA is in the power form and the APS is in the crystal from therefore, it takes some time to completely dissolve both the catalysts and the cross linker into the solution. It is very important that the cross linker and catalysts are completely dissolved because it if these are not completely mixed, then the particles of these would explode in some areas of the sample and this will destroy the sample. After this the complete solution is placed in the container. It is very important that all the containers used for the synthesised of hydrogel much be cleaned by the methanol (or other cleaning agent) so as to avoid any kinds impurities into the sample. As the solution is poured in the container then the container is placed in the oven for 30 minutes. When the container containing the solution was placed in the oven then temperature of the oven was set at 60 degree Celsius. As the sample has to be kept in the oven for 30 minutes so, the temperature of the oven was increased from 60 degree Celsius to 80 degree Celsius. It is important to note that the temperature of the oven was increased by 1 degree at a single time to reach 80 degrees Celsius in 30 minutes.

After taking the sample out of the oven, the sample is placed in the open environment to cool the sample as the sample is very hot therefore, it is very difficult to hold the sample. When the sample recaches at room temperature the sample is peeled from the container. The process of peeling the sample out of the container was done very precisely otherwise it would damage the sample.

It should be noted that the period of time for which the sample was kept at room temperature is very crucial. As when the sample was taken out of the oven and then kept at room temperature for long period (approx. 15 hours), it was very difficult to peel the sample from the container. The bonding of the hydrogel sample was very strong with the glass by that time and it was adhesive. The sample was braking instead of separating from the container. On the other hand, when the sample was immediately tried to be peeled after taking out of the oven. Then the sample was very sensitive and very sticky (it was not sticky with the container rather it was sticky with itself). It was very difficult to peel the sample off the container as it was very sensitive, it was breaking with a very little force applied to peel it off. Therefore, placing the sample in the room temperature should not be too long or it should not be very short. Otherwise, these things will damage the sample.

3.1.2 Synthesis of PAA-HB hydrogel

After the synthesises of the PAA hydrogel then the next step was to provide the toughness to the conventional hydrogel. For the synthesised of the toughened hydrogel, the same process was followed as for the PAA hydrogel. The only the difference in the PAA-HB was that, hyperbranched polymer was added in the solution to enhance the toughness of the hydrogel. The hyperbranched polymer was added in the acrylic acid solution and the same process of PAA hydrogel synthesised was followed. The hyperbranched polymer provides toughness to the hydrogel at the molecular level. The hyperbranched polymer has tree like structure with many ends groups and because of this, the properties of the hyperbranched polymer can be modified easily and the hyperbranched polymer can make a bond easily, which will enhance the toughness of the hydrogel. In case of the PAA-HB the PAA acts as the matrix upon which the hyperbranched polymer is bonded (Yu and Tang 2015).

In the synthesises of the PAA-HB hydrogel, the Acrylic acid used was 9.25 g, 8.75 cm^3 of water was used, 1.5 g of hyperbranched polymer, 4.075 g of Noah and water in the Noah was 9.05 was used. The amount of cross-linker and catalyst that was used in the PAA-HB hydrogel was 0.0625 g of MBA and 0.2 g of APS respectively were used.

It is very important to synthesise the hydrogel under the same conditions because the different environment conditions like temperature can affect the properties of the hydrogel. After the preparation of the PAA-HB hydrogel it was kept in the freezer along with the PAA hydrogel in order to provide the same atmosphere to both the hydrogel samples.

3.1.3 Synthesise of the PAA-PVA and PAA-HB-PVA hydrogel

After the first level of enhancement that is at the molecular level, the secondary level of enhancement was provided by the PVA [poly (vinyl alcohol)] polymer. The enhancement provided by the PVA polymer is at the sub micro level. This level of enhancement is also considered as the enhancement by the Nano particles.

The PVA polymer used in the sub micro level enhancement was prepared by the process of electrospinning. From the process of electrospinning, the PVA polymer was collected on the aluminium sheet. Then the PVA polymer was peeled from the aluminium sheet. For the synthesised for the PAA-HB-PVA hydrogel all the process was the same, the only difference between this was the addition of the PVA polymer. As the PVA polymer was peeled from the aluminium sheet, then the layers or the sheets of the PVA polymer were placed on the solution of the PAA-HB and the PAA. It is important to make sure that these pieces or the sheets of the PVA polymer are completely dispersed in the solution. After this, the solution was placed in the oven as like the process followed for the synthesised of PAA and PAA-HB hydrogel.

For the synthesis of PAA-HB-PVA hydrogel, 14.8 g of Acrylic acid used, 14 cm^3 of water for the Acrylic acid solution, 21 g solution of hydroxide was prepared from the 6.52 g of sodium hydroxide and 14.48 cm^3 of water. 0.66 g of PVA polymer was used in the PAA-HB hydrogel and 0.63 g of PVA polymer was used in PAA solution.

The synthesised PAA-HB-PVA hydrogel was not considered for the mechanical testing because of various reasons which are discussed at the end of this thesis.

3.2 Sample preparation

After the synthesises of the hydrogel and its hybrids, the next step was to prepare the sample for the mechanical testing. The samples need to be prepared to conduct mechanical testing on them as the mechanical testing cannot be performed on the entire synthesised sample because the size of the entire sample is too large to be tested. The mechanical testing was performed on the Instron testing machine and for this the sample size cannot be large.

Moreover, there are various tests that are to be conducted on the hydrogel sample. For different test, the requirement of the sample was different. In order to meet the requirement of the test, the samples were laser cut by the laser cutting machine as per as the requirement of the particular test. As under the mechanical testing of the hydrogel three tests were performed i.e. the tensile test, the double peeling test and dynamic loading. Each of this test have their own requirement of samples i.e. for each test the dimension of the sample are specific. So, in order to prepare the samples for each test, the samples are laser cut according to the specific requirement of the test. Also in some testing techniques, the samples are also needed with some notches. For tensile and double peeling test, the sample with different sizes notches were needed and for those notches the samples were made to laser cut, to get the precise size of the notch. The precise size is also important to get the exact dimension of the sample according to the test that is why the samples were made laser cut.

As the entire size of the sample was 160 mm ×100mm. Out of this the various sample was laser cut and then various notches were made on the different sample and of different sizes. As listed below the size of the sample and the size of the notches, more than one sample was used for each type of sample for example 4 samples were made for the notch sizes of 5mm.

This was due to the reason that, during the testing many things can go wrong which can damage the sample and as a result will produce incorrect information. To avoid this, number of samples were used of same type. So, as to make sure that the output results are accurate and are reliable.

For the tensile test, the dimension of the sample was 30mm ×10mm i.e. the length of the sample is 30mm and the breath of the sample is 10mm. For the tensile test, both the samples were used i.e. with notch and without notch. For the notches, five different types of notches were made which were 1mm, 3mm, 5mm and 7mm. For each notch, there were 4 samples each. For the unnotched sample again 4 samples were prepared. For the tensile testing the total of 20 samples were made through the laser cutting machine. The 20 number of samples were of each material which means that 20 sample of PAA and 20 samples of PAA-HB were tested in the tensile testing. So, in total 40 samples were tested in the tensile test.

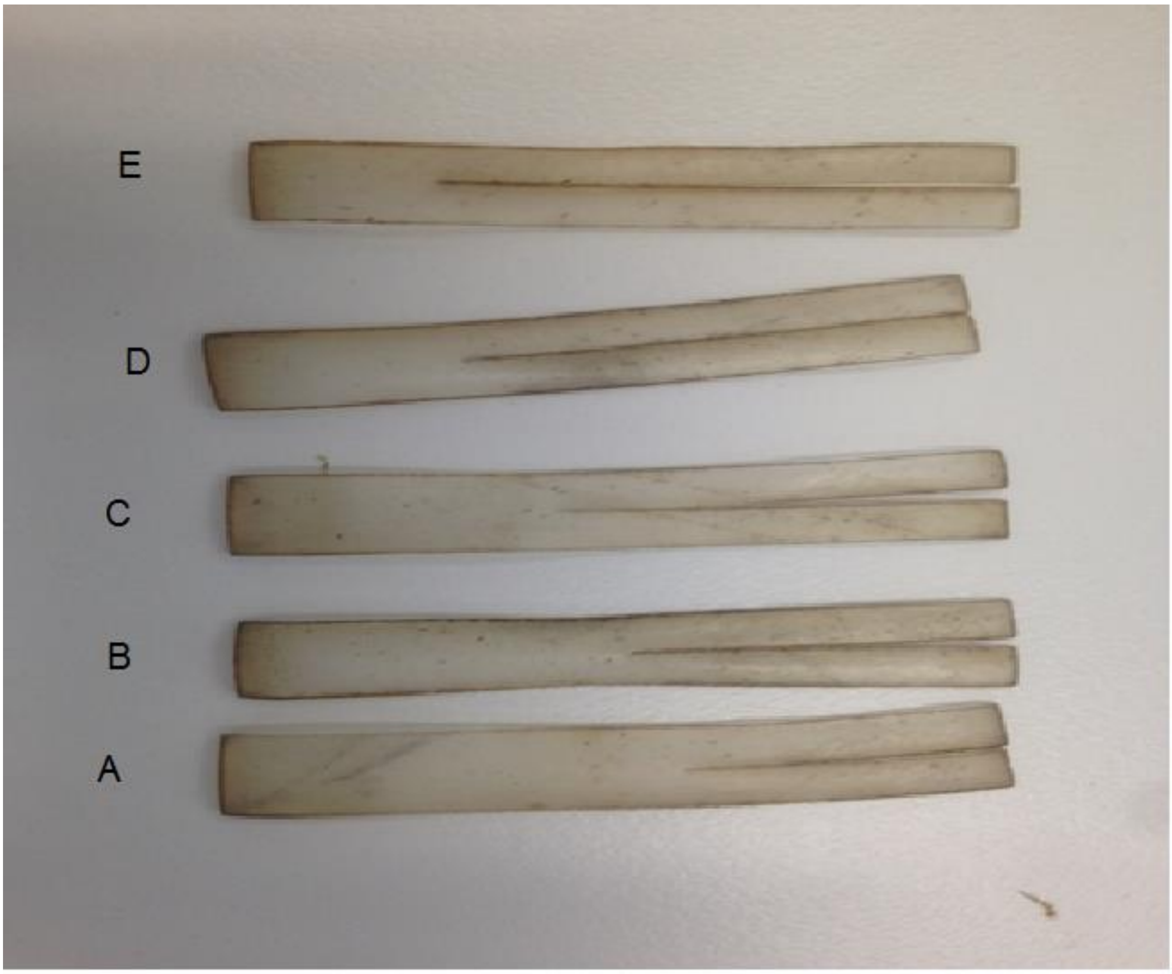


Figure 14 Notches of different sizes for double peeling test (A, B, C ,D &E as 25,30,35,40,45 mm respectively)

For the double peeling test, the samples were laser cut from the entire sample which had the dimension 160 mm ×100 mm. From this, the samples were laser cut form the laser cutting machine. For the double peeling test, the dimension of the samples was 60mm×10mm i.e. the length of the sample was 60 mm and the breath of the sample was 10mm. Again, like the tensile test different size of notches were made on the sample. For the double peeling test only the notched samples were used. For the notched samples, the size of notches was 25 mm, 30 mm, 35 mm, 40 mm and 45 mm as shown in the figure 14. For the each notch the 4 sample were made i.e. 20 samples were made with notches for each material. The different size of the notched used in the double peeling test are shown in the figure 14. As shown in the figure, the size of notches varies from 25 mm to 45 mm.

3.3 Mechanical testing

After preparing the samples from the laser cutting machine, the mechanical testing was performed on them. Mechanical testing was performed on both unnotched and notched samples. The mechanical testing was performed on the Instron machine. Three types of tests were performed under the mechanical testing of hydrogel namely tensile test, the double peeling test and the dynamic loading. The setup was same for all the tests that were performed on the Instron machine. The rate of the Instron machine was set at 5mm per minute. As the hydrogel is a very sensitive material that is why only 500 N load cell was used on the Instron machine for all the tests. The clamps which were used to hold the sample in place were operated pneumatically. All data for the different tests that were performed on the Instron machine, the results were recorded on the blue hill software which was linked to the Instron machine.

There are no (ISO or ASTM) standards for the testing of hydrogel. The testing speed was set as 5 mm per meter (Peak, et al.,2013). The load cell used was of 500 N because the hydrogel is very sensitive material therefore it cannot withstand large load.

3.3.1 Tensile testing

The first test that was performed on the Instron machine was the tensile test. In the tensile test, the sample were placed in the Instron machine and then the tensile force was applied on the sample i.e. the sample was pulled apart by applying the force. Before placing the sample in the Instron machine the dimension of the samples were uploaded on the system software because the system has to generate the raw data about the sample in the excel: information like the stress, strain, load and extension. For the information like the stress and strain, the system need specific data like the original length of the sample (original length of the sample is the length of the sample in between the two clamps on the Instron machine), width of sample and thickness of sample. As for the calculation of the strain, the area of the sample is needed and for the calculation of the area of the sample, the dimensions of the sample are needed. Similarly, for the calculation of the stress, it need the original length of the sample along with the final length of the sample (final length is the length of the sample after the extension of the length of the sample). As shown in the figure 15 the sample is holded by the clamps from both side and the tensile force was applied on the sample.

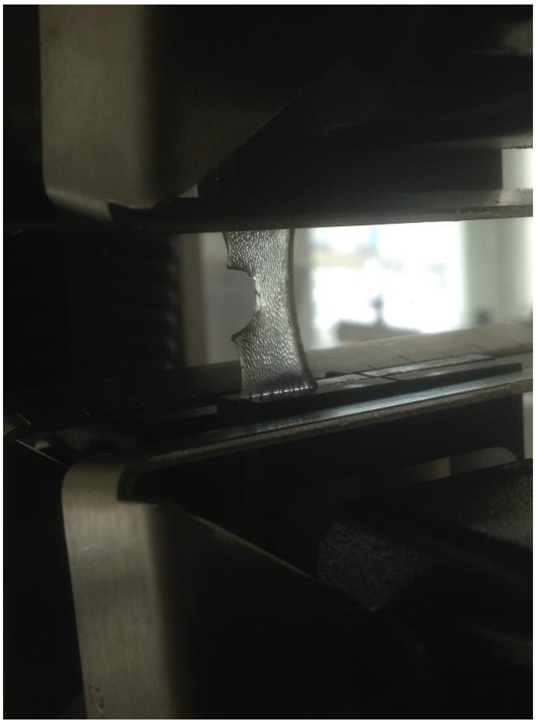


Figure 15 Sample placed in for tensile testing

By performing the tensile test, two types of data can be calculated. The first one is the stress and strain data, from the stress and strain data various material properties of the material can be detected. Material properties such as ductility, brittle properties, maximum fracture energy of material. All this mention data can be evaluated from the curve of stress and strain graph: as the stress and strain graph shows the information like the elastic linear region, yield point, toe region of material, elastic failure region, plastic region and the modulus of the material can also be calculated from the strain and strain curve. The other advantage of stress and strain curve is that the comparison of the properties for two or more different materials can be made by this. As the modulus of the materials can be compared with other material for example the modulus od steel can be compared with modulus of iron which is very beneficial for the selection of material.

The second thing that was produced by performing the tensile test is load and extension data. From the load and extension data, the load versus extension graph can be plotted. Form the load and extension data, the fracture energy was calculated. The fracture energy was calculated using the equation (3):

$$Fracture\ energy = \frac{\mathrm{U(L)}}{a_0 b_0} \quad \text{(Sun, J.Y., Zhao, 2012)} \tag{3}$$

Where $\mathrm{U(L)}$ is the area under the curve of the load and extension.

a_0 is the length of the sample between the clamps.

b_0 is the width of the sample.

3.3.2 Double peeling test

After the tensile test, the double peeling test was performed. The basic idea to perform the double peeling test was to make sure that the results obtained from the tensile test are appropriate. The double peeling test was difficult to perform as there are no standards for this test. In this test, the sample was placed between the clamps as shown in the figure 16 and then the tensile force is applied on the sample. In the double peeling test only the notched samples were tested. From the double peeling test, the same data was calculated which was, the stress and stain data and the load and extension data. Like the tensile test, the fracture energy was calculated from the load and extension graphs. Also in the double peeling test, the dimensions of the samples were uploaded on the blue hill software so as to produce the raw data.

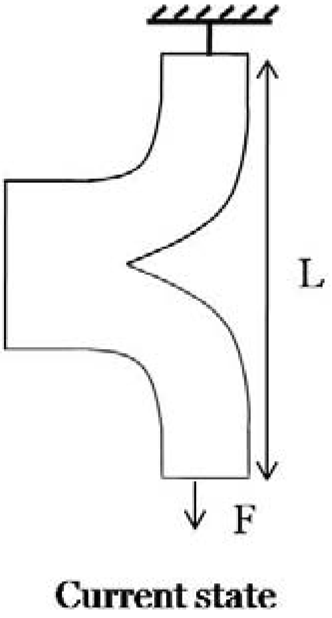


Figure 16 Double peeling test (Rivlin &Thomas1953)

In the double peeling test, the length of the sample was taken as the length in between the clamps but in case of this test, the length of the sample in between the camps would change for each sample. In case of the tensile test, the length of the sample was similar for all the sample.

3.4 Fracture toughness

Determining the fracture toughness of the hydrogel is an important aspect of my thesis. As after determining the fracture toughness of different samples, (PAA and PAA-HB) comparison can be made about the enhancement in the mechanical properties of the hydrogel after toughening the hydrogel.

For determining the fracture energy of hydrogel, Rivlin and Thomas method is used (Rivlin,et al,2012). This helps to determine the fracture energy of the extremely stretchable gel. To determine the fracture energy two samples are made from each material. Out of these two samples, one sample is kept unnotched while the notch is made on the other sample. After the samples are ready the proper dimensions of the samples are taken which includes width, thickness of the sample and the distance between the two clamps of the INSTON testing machine is also necessary to measure.

The unnotched samples are stretched to get the force – length curve. For the determining the fracture energy, it is not necessary to completely rapture the sample. The work done is given by the area between the force and length curve when the two clamps are at some given distance. For the notched samples, the notched samples are similarly pulled apart and when the notch starts to turn into a running crack then the fracture energy can be calculated. The formula for calculating the fracture energy can be represented as below equation (4):

$$\dagger = \frac{\mathrm{U}(L_C)}{a_0 b_0} \tag{4}$$

where:

$\dagger$ = fracture energy

U (L) = applied force

(L_C) = distance between the clamps

$a_0 b_0$ = width and thickness of sample respectively

The verification of this test can be done by two other methods, which are also introduced by Rivlin and Thomas. The tests include testing the sample with double peeling test and by varying the crack length (with different notch size). The fracture energy obtained from all three methods should match (approx.) (Rivlin, R. S. & Thomas1953). These tests are discussed as below:

3.4.1 Tensile test with varying sample length.

In this test, various sample with varying crack length are tested in the tensile test to obtain the fracture energy. The area under the curve of the force- extension gives the total energy stored. The energy stored is measured at a certain deformation length (Liu, R., Liang, S., Tang2012). From this method, the fracture energy is given by equation (5):

$$\dagger = \frac{1}{b_0}\left(\frac{\delta \mathrm{U}}{\delta \mathrm{C}}\right)_L \tag{5}$$

where:

b_0 = width of sample

$\left(\frac{\delta \mathrm{U}}{\delta \mathrm{C}}\right)_L$ = calculated from the slope of crack length and total energy

L = change in the length of the clamps

3.4.2 Double peeling test

The double peeling test was also introduced by Rivlin and Thomas. In the double peeling test, the crack sides are stretched for determining the fracture energy as shown in the figure 17.

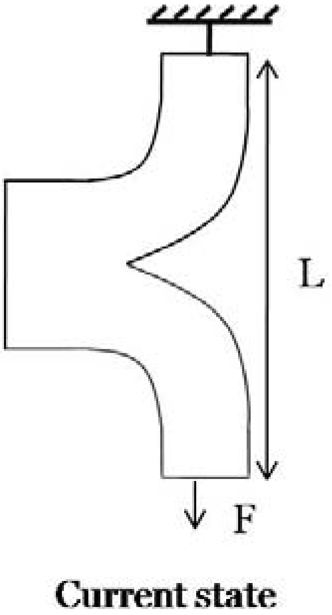


Figure 17 Double peeling test (Rivlin &Thomas1953)

From the double peeling test, all the properties could be determined as from the tensile test. Therefore, the purpose of having the double peeling test is that the results obtained from the tensile test can be verified. In the double peeling test, only the notched sample are required for determining the various properties of the material.

3.4.3 Dynamic loading test

The dynamic loading test was performed in order to understand the effect of cyclic loading on the both hydrogels materials. As the toughened hydrogel has huge potential in various fields, for example in the tissue engineering field, where it might have to go through the cyclic loading. Therefore, it would be interesting to know the cyclic loading effect for the PAA-HB vs the conventional hydrogel (PAA).

In the dynamic loading, the sample are subject under the extension and relaxation. The extension length was fixed for 10mm. therefore, the sample has to experience a cycle which starts with extension load up to 10mm and then brought back to its initial position. By performing this test, it will provide the load and extension data and from that data the stress and strain graphs were plotted.

As from the stress and strain graph, the loading cyclic can be drawn for the sample. The difference between the loading and unloading curve give is the energy absorbed by the sample. To get the better understanding about the properties of the hydrogel, the dynamic test was performed at different time intervals for the same sample. The dynamic test was performed at 0 seconds, 10 seconds, 10 minutes, 1 hour and 24 hours. The reason for performing the dynamic test at different time intervals is that, this will give the information about the redevelopment properties of the hydrogel: means how the hydrogel recovers from the previous loads, what effect the previous load cycle can put on the next loading cycle.

3.5 Water swelling test

As the objective of my thesis is to enhance the mechanical properties of the hydrogel and also to make sure that the toughened hydrogel does not losses it's conventional hydrogel properties. One of the main and unique property of hydrogel is that, it can absorb huge quantity of water. As mentioned above, the hydrogel can have up to 90 % of water in them. The huge water absorbing quality of hydrogel is used in many of its applications. Therefore, it is very important to make sure that the toughened hydrogel (PAA-HB) has good water absorbing properties. By providing the good water absorption properties to the toughened hydrogel, it further enhances the qualities of hydrogel and therefore, it can be used in many other applications and it can be more effective in its previous applications.

The swelling behaviour of PAA and PAA-HB was compared in the water swelling test. In this test, firstly the dry weight of the both hydrogel samples were measured. After this, the samples were dispersed into water and their behaviour is observed. The weight of these samples was taken many times during this testing. The test was performed on the three different samples of each material i.e. for PAA and PAA-HB. The swelling ratio was calculated from both the materials and then the comparison was made. The swelling ration was calculated by using the equation (6):

$$SR = \frac{m_t - m_i}{m_i} \times 100 \tag{6}$$

where SR is the swelling ratio.

$m_t \; and \; m_i$ are the weight of sample in swollen state and weight of sample in dry state respectively.

3.6 Other tests

Apart from the mechanical test and the water swelling test there were couple of other tests that were performed in order to investigate the difference in the structure of the conventional hydrogel and the toughened hydrogel. The aim of these test performed is to understand the interaction of the hyperbranched polymer into the PAA matrix and also to see the distribution of the hyperbranched polymer in the PAA. To investigate this, two tests were performed namely; Spectroscopic analysis and Morphology characterization (Dehbari, et al., 2016).

3.6.1 Spectroscopic analysis

This test was performed in order to understand the possible interaction between the hyperbranched polymer and the PAA. The FTIR (Fourier transform infrared spectroscopy) was used to describe the functional groups of the PAA and the PAA-HB. In the FTIR, each sample was placed on the central crystal of the ATR plate. The air was used as the reference for each scan for both the samples. The recording for the FTIR was done with the resolution of 4 cm^{-1}. 64 scans were used for the recording of the FTIR spectra.

3.6.2 Morphology characterization

The morphology characterization of the PAA and PAA-HB sample was done by scanning electron microscope (SEM). The model of SEM used was the MX2500. Before placing the sample in the electron microscope, the samples were coated with the platinum of 2mm thickness. The voltage used by the electron microscope was 10 KV. The scanning distance for all the samples were kept constant. The aim of performing this experiment is to investigate the distribution of the hyperbranched polymer in the PAA. For this experiment only the dry samples were used.

The Morphology characterization help us to understand the distribution of the HB particles in the PAA hydrogel. As with the Morphology the HB particles can easily be detected in the PAA hydrogel. The Scanning of the both hydrogel was done at different level; 50,100 and 200 µm. the reason for choosing the different scanning magnification is to see the spread of HB particles at the highest level of magnification and to observe better, the interaction of the HB particles in the PAA hydrogel.

Chapter 4 Result and discussion

After performing the mechanical testing of hydrogel on both the materials, the results were analysed. The data derived from the mechanical testing was used to generate several graphs and values: the graphs of stress -strain and the graphs of load -extension and the calculated values of the fracture energy. After generating all the results, then the results were analysed to get a conclusion out of it. The reason for this analysis was to see results of the toughness of PAA-HB hydrogels over the conventional hydrogel that is the PAA hydrogel.

The graphs were plotted for both the hydrogels after getting the raw data in excel sheet. The graphs were plotted for all three tests i.e. tensile test, double peeling and dynamic loading. The results of the tests are analysed below:

4.1 Tensile test

In the tensile test, both samples were tested i.e. notched and unnotched samples. From the tensile test, both stress- strain and load- extension graphs were plotted.

4.1.1 For PAA

The stress and strain graph shows the significant different between the notched and un notched curves. It is clearly seen from the stress and strain graph of PAA that the various curves are plotted for the stress and strain. The maximum curve is for the sample with no notch (unnotched). As the notch size for the hydrogel sample increases, the stress and strain curve decreases. From the graph, it should be noted that, there is a significant difference between the curves of unnotched sample and sample with 1mm notch. The difference between the curves decreases as the size of the sample notch increase from 1mm to 7mm. The reason behind this is that, for the unnotched sample, lot of stress is required to fracture the hydrogel but in case of the notched sample, the resistance to the fracture decreases. The resistance to the fracture decreases as the notch size of the sample increases.

It can also be seen from the graph, that the linear elastic region is maximum for the unnotched sample but it decreases with increases notch size. The toe region for the sample decreases with increase in the notch size. Th stress is maximum for the unnotched sample, it is around

0.23 MPa and the corresponding strain is 2.5 mm/mm. For the notched samples, the corresponding stress and strain decreases as the size of the notch increases from 1m to 7mm.

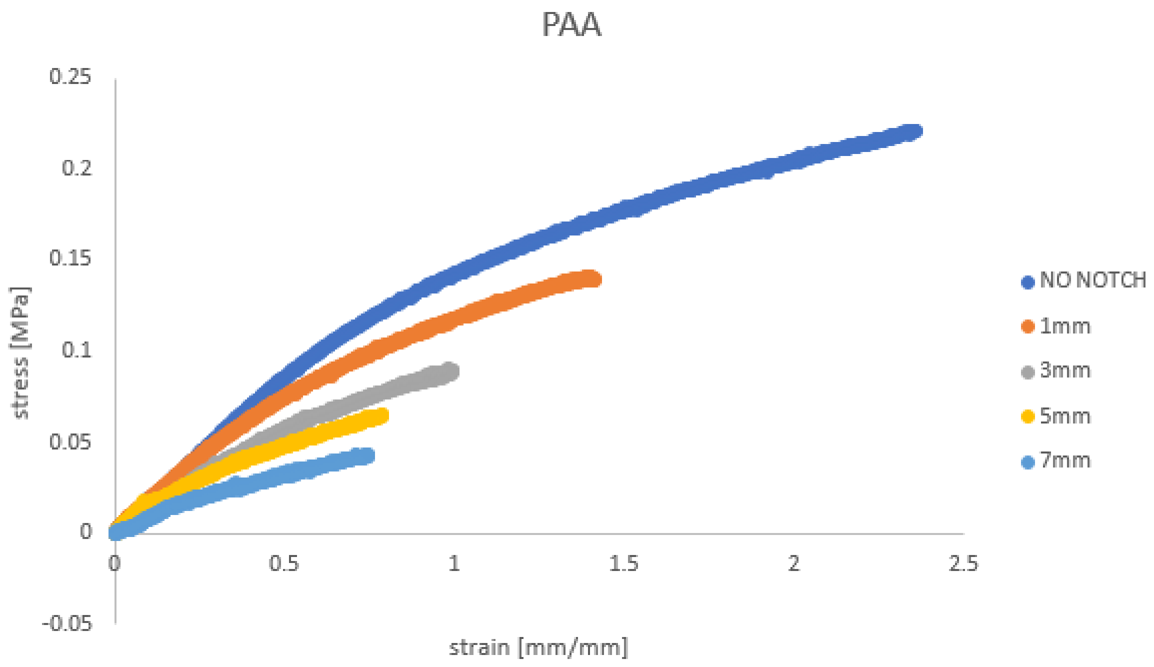


Figure 18 Stress vs strain graph for PAA

4.1.1.1 Load and extension graph

For the PAA hydrogel, the load versus graph was plotted as shown below. As seen from the stress and strain graph, the curve decreases as the notch size increases. The maximum load is 4.5 N and the corresponding extension is 14 mm, this result is obtained for the unnotched sample. After this, as the size of the notch increases, the load and corresponding extension decreases.

The work done for the applied force is also the maximum for the unnotched sample and the work done for the applied force decreases as the notch size increases. The work done is calculated by the area under the load and extension curve. As it is evident from the graph, that the area under the graph is maximum for the unnotched sample. As the notch size increases, the length of the load and extension curve decreases hence, decreases the area under the curve. Which means the least work done is for the sample of notch size 7mm because the curve of load and extension is smallest therefore has the least area under the curve.

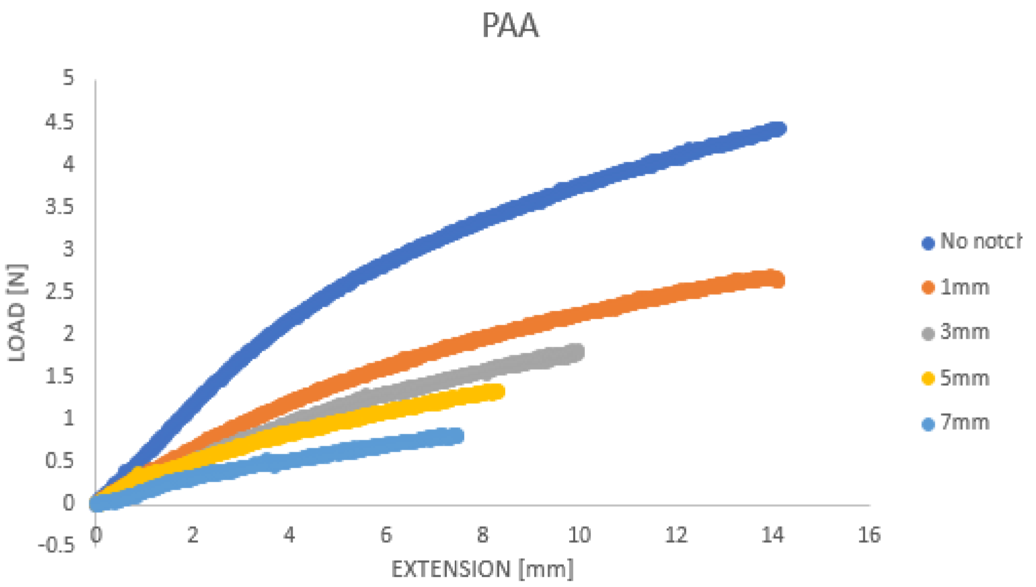


Figure 19 Load vs extension graph for PAA

From the graph of load and extension, the fracture energy for the sample is calculated. The fracture energy is calculated by using the area under the graph and using the dimensions of the sample: dimensions of the sample such as thickness and length of sample. Following

4.1.1.2 Fracture energy for PAA

The fracture energy was calculated from the tensile test with different notches as shown in the table below:

No.	Notch size (mm)	Area under the curve mm^2
1	0	39.9
2	1	23.4
3	3	7.5
4	5	4
5	7	2.4

Table 1 Area under the curve for PAA

No.	X1 (mm)	X2 (mm)	Y1 (Joules)	Y2 (Joules)	Slope (Joules/mm)	Fracture (J)
1	0	1	39.9	23.4	16.5	8.25
2	1	3	23.4	7.5	7.95	3.975
3	3	5	7.5	4	1.75	0.875
4	5	7	4	2.4	0.8	0.4

Table 2 Fracture energy for PAA

For the calculation of the Fracture energy, firstly the area under the curves of different notches were calculated as shown in the table 1. After this the area under the curve of various notches is used to calculate the slope as shown in equation (7):

$$\text{Slope}=\frac{(Y2-Y1)}{(X2-X1)} \tag{7}$$

Then the slope value is used to calculate fracture energy by using the formula:

Fracture energy=$\frac{1}{,b_0}\left(\frac{\partial U}{\partial C}\right)$

Where , b_0 is the thickness of the sample and $\left(\frac{\partial U}{\partial C}\right)$ is the value of the calculated slope.

It can be depicted from the graph that as the size of the notch increases, the fracture energy for the PAA hydrogel sample decreases. The maximum fracture energy is 8.25J, this fracture energy was calculated for the sample with no notch. On the other hand, the least fracture energy i.e. 0.4 J was calculated for the sample with maximum size notch and the size of sample notch was 7mm. From the calculated data, it can also be noted that the difference between the decrease in the fracture energy of sample, decreases with the increasing notch size. For example, the difference between the fracture energy from unnotched sample and the 1mm notch sample is very significant but of the sample of notch size mm and 7mm, the difference in the fracture energies decreases. In the tensile testing, the width of the sample remains same but the thickness of the sample changes.

4.1.2 For PAA-HB

In case of the tensile testing of the PAA-HB sample, the similar pattern of the stress and strain curves is observed. As seen from the graph that the stress and strain curve of unnotched sample is much more than that of the notched samples. As the notch size increases the stress and strain curve decreases. As mention, the stress and strain curve is maximum for the unnotched curve, the value for the stress is 0.55 MPa and the value for the corresponding strain is 4 mm/mm.

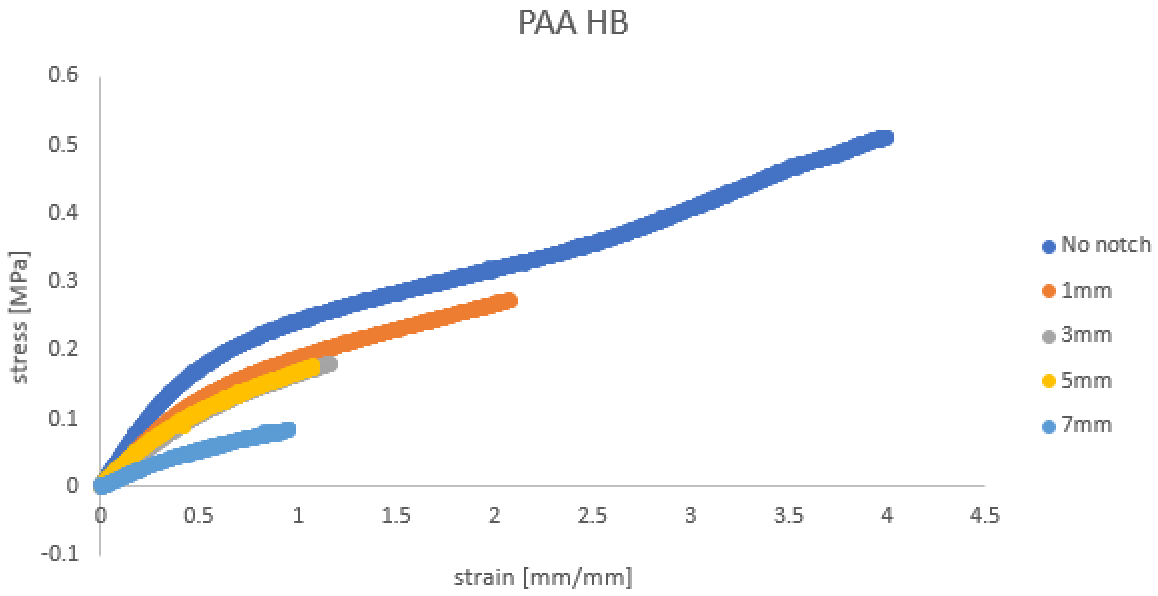


Figure 20 Stress vs strain for PAA-HB

It is very important to note, that for the PAA -HB sample the value of maximum stress and corresponding strain is much greater than the conventional hydrogel i.e. PAA hydrogel. The graph for the PAA -HB follows the similar pattern as for the PAA i.e. with increasing the notch size the stress and strain curve decreases but in the value, there is significant different. Which means that, the value of strain for each sample is grater then that of the PAA to the corresponding strain. The difference between the curves decrease as the size of the notch increases but it always stays more than that of the results of tensile test for PAA hydrogel.

4.1.2.1 Load and extension graph

The load and extension graph is plotted for the PAA-HB. In this, the pattern of the graph remains the same as it should be, that the load and extension curve should decrease with the increase in the size of notch. The maximum load value for the PAA-HB is 4.5 N corresponding to the 40mm strain value. As compare to the PAA graph, it has greater value of load and extension, especially the extension: in case of PAA the value of extension was 14 mm approx. but in case of the PAA -HB the extension is about 40mm. Because of this the area under the load and extension curve for the PAA -HB is greater than the area under the curve for the PAA. Which also means that the work done by the PAA-HB is also greater than that of the PAA as the work done is the area under the load and extension curve. In case of the PAA-HB the work done decrease with the increase in the notch size but as compared to the PAA, the work done by the PAA-HB is always greater than that of PAA.

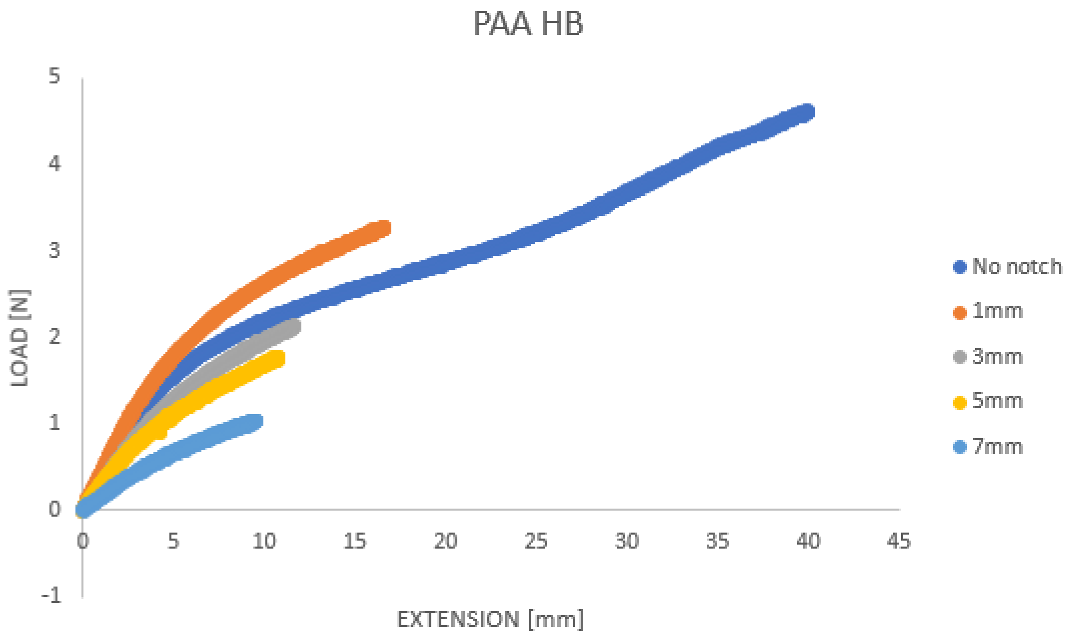


Figure 21 Load vs extension for PAA-HB

4.1.2.2 Fracture energy for PAA HB

The calculations for the fracture energy for the PAA-HB is same as it was for the PAA. The values of the area under the curve for different notch and the fracture energy is shown in the tables below:

No.	Notch size (mm)	*Area under curve (mm^2)*	*Standard deviation*
1	0	113.3	1.13
2	1	35.9	0.14
3	3	17.8	0.42
4	5	10.8	0.28
5	7	4	0.42

Table 3 Area under curve for PAA-HB

NO.	X1(mm)	X2 (mm)	Y1 (mm)	Y2 (mm)	Slope (Joules /mm)	Fracture (J)
1	0	1	113.3	35.9	77.4	38.7
2	1	3	35.9	17.8	9.05	4.525
3	3	5	17.8	10.8	3.5	1.75
4	5	7	10.8	4	3.4	1.7

Table 4 Fracture energy for PAA-HB

From the above table, it can be seen that the maximum fracture energy was calculated for the sample with no notch and then it decreases for the 1mm notched sample. This process continuous, with the increasing notch size the fracture energy for the sample decreases. It can also be noted that there is significant decrease in the fracture energy from unnotched sample to the notched sample. Which means that ones the crack starts to propagate then there is significant decreases in the fracture energy.

It can also be noted that there is a huge difference in the fracture energy of the PAA and PAA-HB hydrogel sample. The maximum fracture energy in case of the PAA-HB is 38.7 J for the unnotched sample but the maximum fracture energy for the PAA hydrogel is 8.25 J. The difference of fracture energy between the PAA and PAA-HB hydrogel sample stays for the all samples but the fracture energy for the PAA-HB hydrogel samples is always greater than that of the PAA hydrogel samples.

4.1.3 Fracture energy vs notch size

To understand the effect of the notch size, the graphs are plotted for the fracture energy versus the notch size, the graphs are plotted for the both PAA and PAA-HB samples. As mention above that as the size of the notch increases there is decrease in the fracture energy. As seen from the graph, the fracture energy is 8.25 J for the sample with no notch and as size of the notch increases the fracture energy decreases. The fracture energy decreases from 8.25 Joule to 0.4 Joules as the notch size increases.

As mentioned above, for the 1mm notch sample there is a huge decrease in the fracture energy from the unnotched sample, this is verified from this graph.

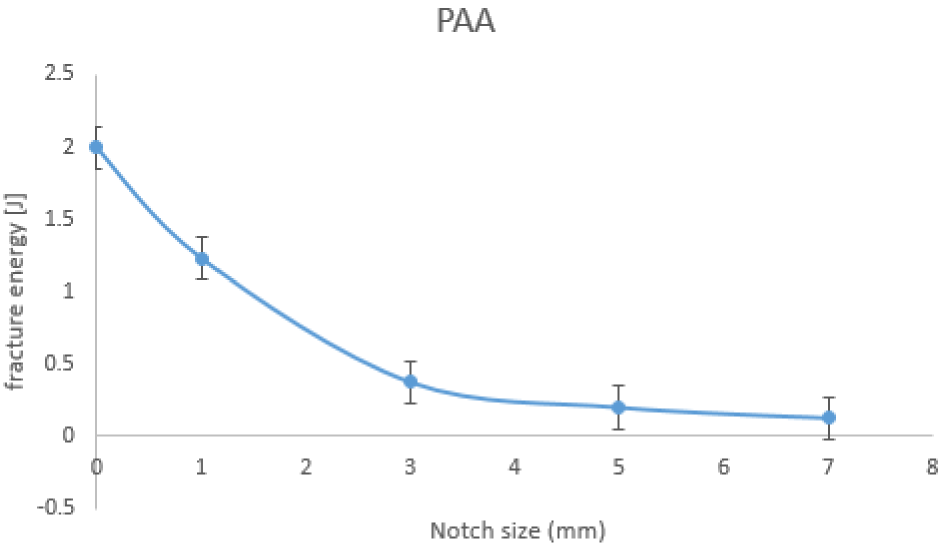


Figure 22 Fracture energy vs notch size for PAA

In case of the PAA-HB, the same thing is observed that the fracture energy decreases with increases notch size. The fracture energy decreases from approx. 38.7 Joules to 1.7 Joules with increasing notch size.

As noticed from both the graphs, there is a significant difference in the fracture energy between the PAA and PAA -HB sample for the same notch size. The fracture energy decreases with increasing notch size still the fracture energy of PAA-HB is ahead of PAA at every notch size.

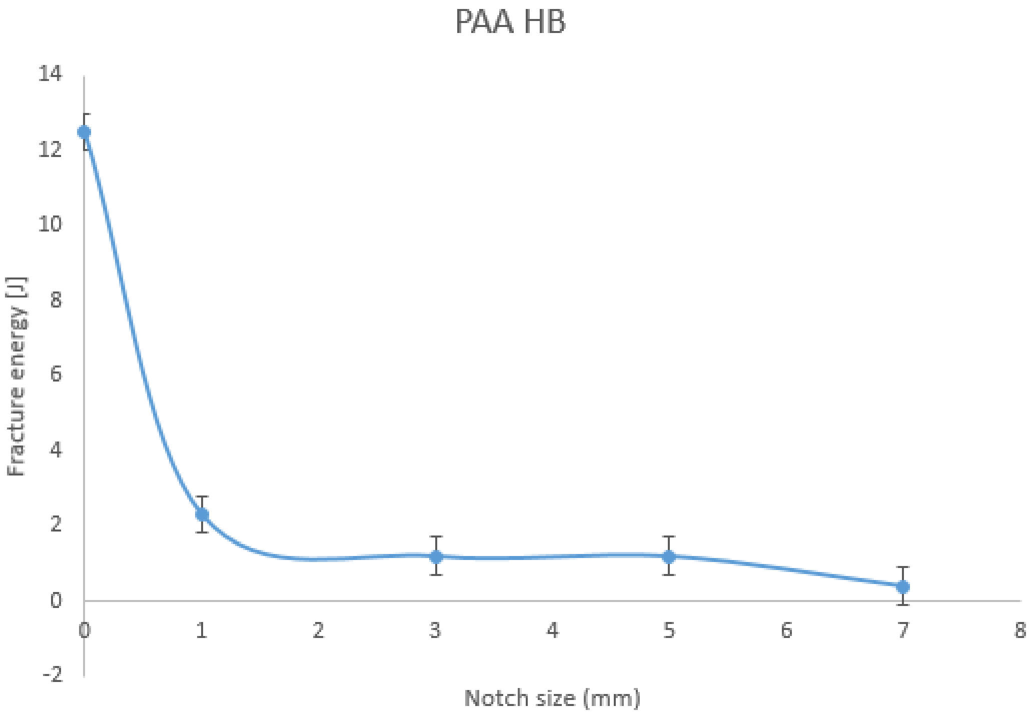


Figure 23 Fracture energy vs notch size for PAA-HB

4.2 Double peeling test

After the tensile test, the second test that was performed on both hydrogel sample was double peeling test. The double peeling is another method to determine the fracture energy of the hydrogel and to check the different mechanical properties form the stress and strain curve. The main reason for performing the double peeling test was to make sure that the results obtained from the tensile test are appropriate. The other advantage of performing the double peeling test is to analyse the data obtained from double peeling test and make sure that the almost similar conclusion can be made for both the hydrogel samples.

The issue or disadvantage of performing the double peeling test it that, there are no standards set for performing this test. Due to this, there are variations in the result obtained. The main limitation or the drawbacks of the double peeling test are listed in the later section. Because of those reasons there were some distortion in the presented results. Still the comparison can be made from the results from the performed test.

4.2.1 For PAA

For the PAA hydrogel sample, the double peeling test was performed on the five different samples. In the double peeling test, all the samples used for the testing were notched samples. The notched samples have the notches of different size. The size of the notches for PAA sample were 25 mm, 30 mm, 35 mm, 40 mm and 45 mm.

The stress and the strain curve for the unnotched sample shows the maximum stress which is 0.045 MPa for the PAA hydrogel sample and the corresponding strain was approx. 2.5 mm/mm. The stress and strain curves are very fluctuating because the propagation of the crack during the testing was uneven (discussed in detail in the later session of thesis) and same is the reason for the longer stress and strain curve for the 30mm notch sample. As the size of the notch increases the stress and strain curve decreases, which means that the modulus also decreases with the increase in notch size. As seen from the graph, the slope of the samples also decreases with the increasing notch size.

Despite of all the factors, the results represented through the stress and strain graph by the double peeling test suggest that the result obtained from the tensile test are appropriate and can be trusted. As both these test result suggests that, the increase in the notch size of the sample decrease the stress and strain curve for the sample and also decrease the modulus for the sample as the slope of the sample decreases with increasing notch size.

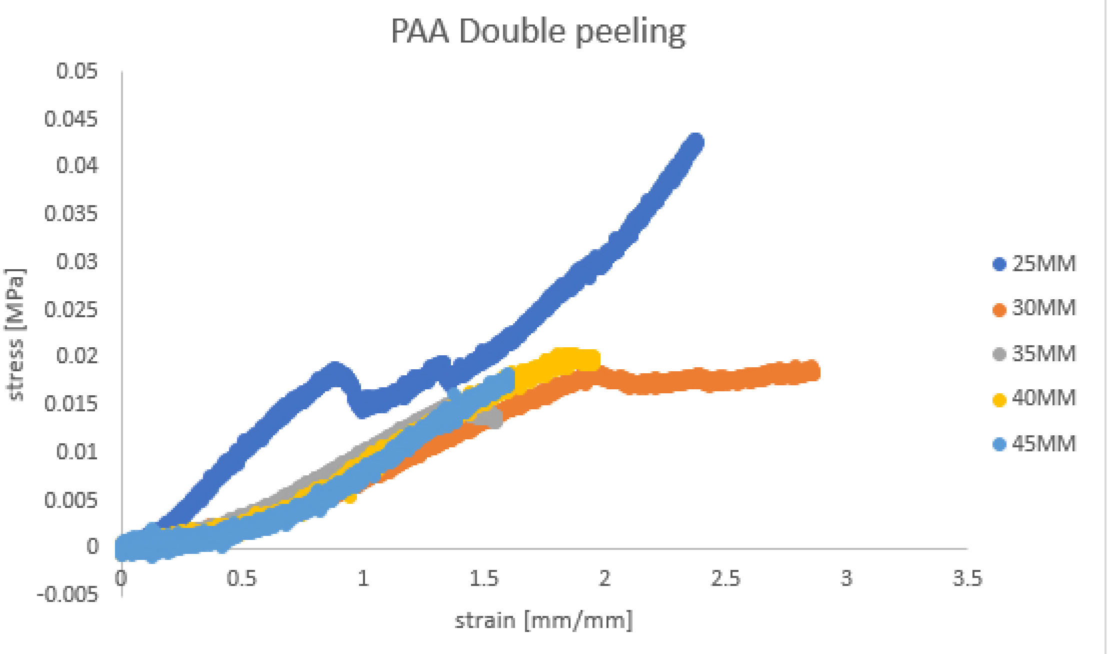


Figure 24 Stress vs strain for PAA (Double peeling)

4.2.2 For PAA-HB

In the double peeling test for the PAA -HB, similar like the PAA double peeling test, it was also performed on five different samples. As excepted, the stress and strain curve decreases with increasing the notch size. The maximum stress is for the unnotched curve which is approx. 0.08 MPa and the corresponding strain is 5mm/mm. This also signifies that the result obtained from double peeling for the PAA-HB sample, have higher values for the stress and corresponding strain as compared to the PAA hydrogel sample. The stress and strain values of the PAA-HB sample is also greater than that of the stress and strain values for the PAA for all the sample. This result signifies the reliability of the tensile test. Therefore, according to double peeling test, the outputs obtained from the tensile test can be trusted and the values obtained can be used for further calculations and analysis.

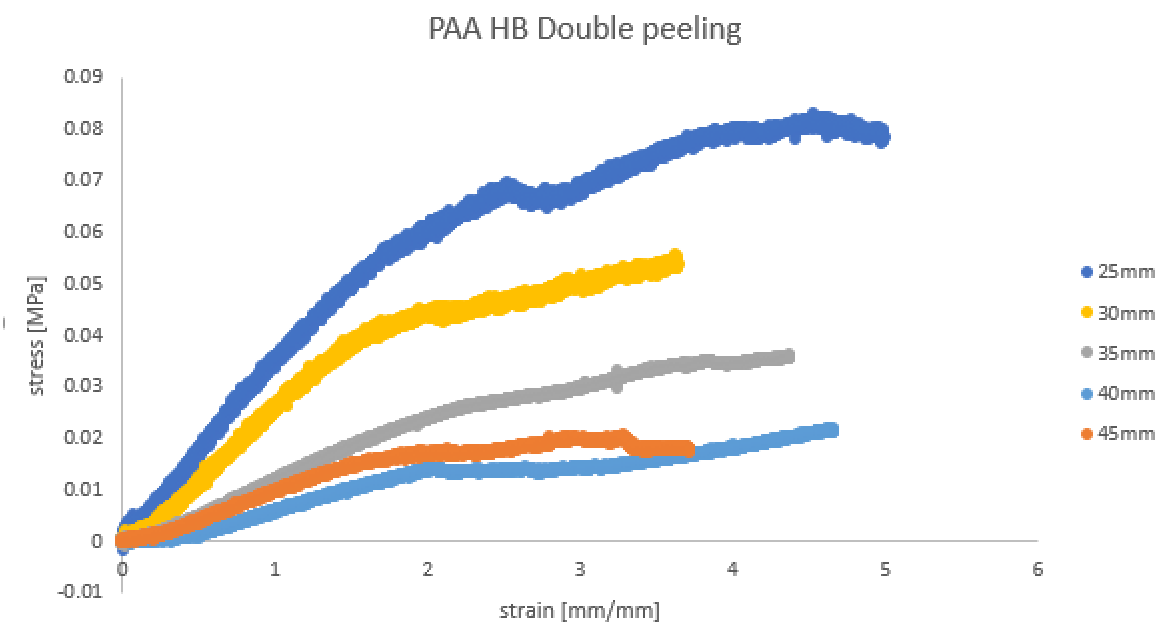


Figure 25 Stress vs strain for PAA-HB (Double peeling)

4.2.3 Fracture energy for double peeling test

As like the tensile test, the fracture energy for the double peeling test was calculated from the load and the extension curves. The load and extension curves for the double peeling test are plotted below:

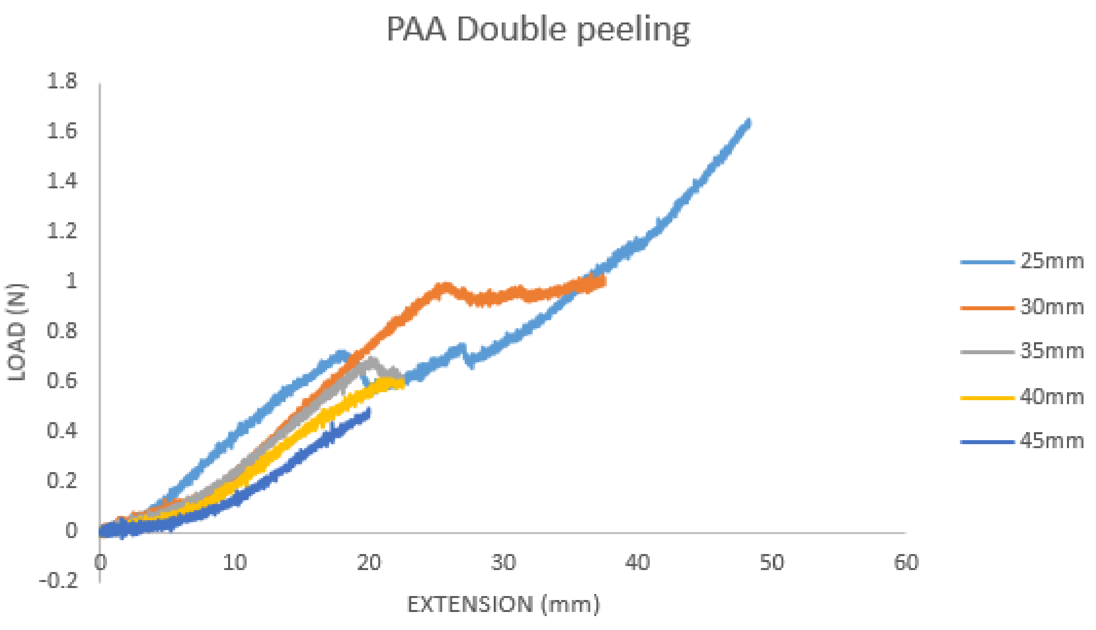


Figure 26 Load vs extension for PAA (double peeling)

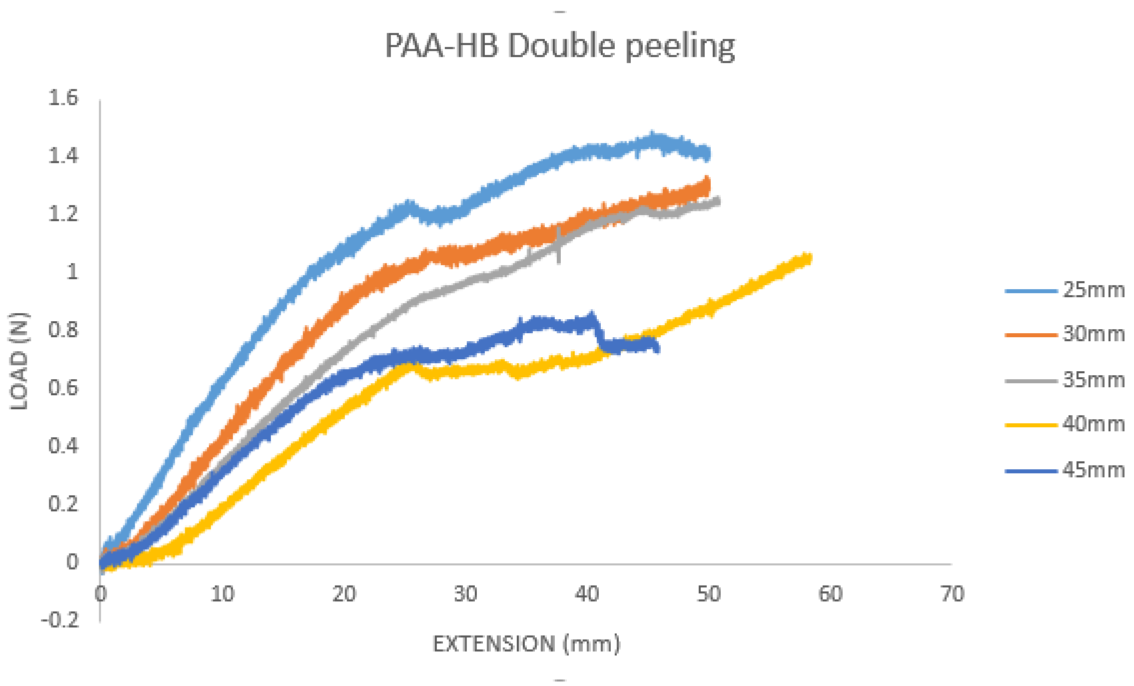


Figure 27 Load vs extension for PAA-HB (double peeling)

For the calculation of the fracture energy form the load and extension curve, it was calculated from the crack length of different sizes (as in the tensile test). As seen from the load and extension graphs, the area under the curve for the PAA-HB is greater than that of PAA for any notch size, which is also shown in the table 5 and table 7. As observed from the graphs or from the tables it is clear that, with increasing notch size the area under the curve decreases for both samples. The area under the load and extension gives the work done. Therefore, the work done for the PAA-HB sample is greater PAA samples. The fracture energy graphs for both the tests are plotted below:

For PAA

No.	Notch size (mm)	*Area under curve (mm^2)*	*Standard deviation*
1	25	35.05	0.36
2	30	22.16	1.27
3	35	7.19	0.14
4	40	6.06	1.41
5	45	3.51	0.35

Table 5 Area under curve for PAA

NO.	X1(mm)	X2 (mm)	Y1 (mm)	Y2 (mm)	Slope (Joules /mm)	Fracture (J)
1	25	30	35.056	22.167	2.5778	12.889
2	30	35	22.167	7.198	2.9938	14.939
3	35	40	7.198	6.062	0.2272	1.136
4	40	45	6.062	3.511	0.5102	2.551

Table 6 Fracture energy for PAA-HB

For PAA-HB

No.	Notch size (mm)	*Area under curve (mm^2)*	*Standard deviation*
1	25	51.34	1.89
2	30	42.28	3.22
3	35	39.16	0.12
4	40	33.36	1.92
5	45	25.70	0.99

Table 7Area under curve for PAA

NO.	X1(mm)	X2 (mm)	Y1 (mm)	Y2 (mm)	Slope (Joules /mm)	Fracture (J)
1	25	30	51.3433	42.287	1.81126	9.0563
2	30	35	42.287	39.164	0.6246	3.123
3	35	40	39.164	33.368	1.1592	5.796
4	40	45	33.368	25.703	1.533	7.665

Table 8 Fracture energy for PAA-HB

The tables 6 and table 8 shows the calculated fracture energy for PAA and PAA-HB respectively. Process followed for the calculation of fracture energy is similar to calculations performed in the tensile testing. Overall, the fracture energy decreases with increasing notch size for both the sample. There are few unexpected result as well for example for some notches the fracture energy of the PAA hydrogel sample is greater than PAA-HB, the reason behind this may the experimental errors (discussed in the 4.7.2 section of this thesis).

4.3 Dynamic loading

4.3.1 For PAA

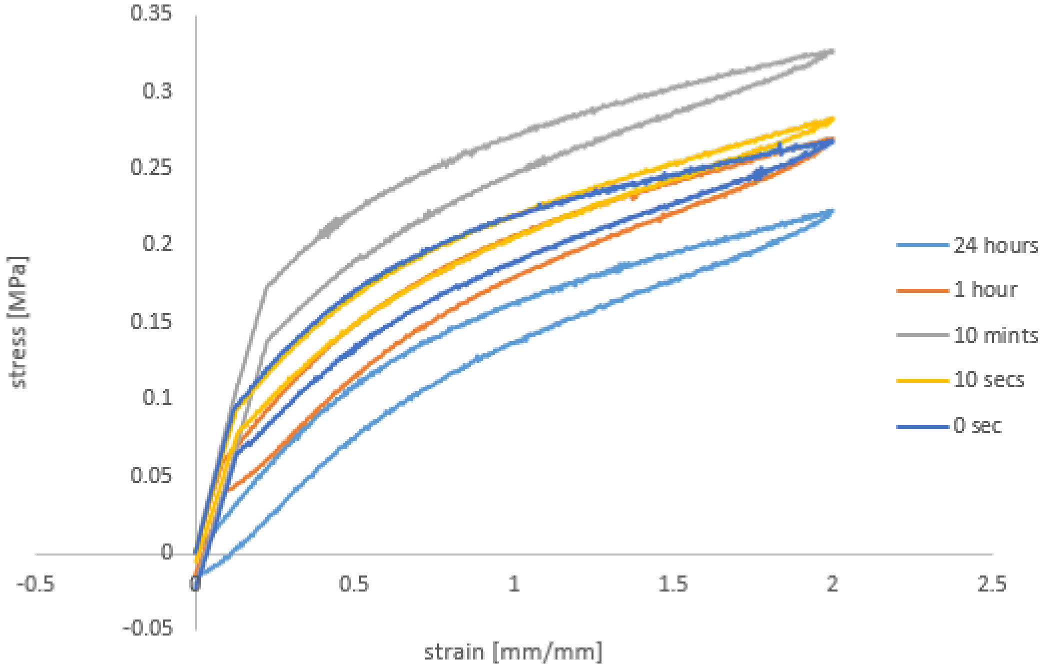


Figure 28 Dynamic loading for PAA

The dynamic test was conducted on both the PAA and PAA-HB hydrogel samples. For each materials 3 samples were used in order to make sure that the obtained results are correct. During the dynamic testing of the PAA hydrogel sample, one sample fractured during the 10 minutes loading test, it shows that the PAA is not great in case of the dynamic loading test as compred to the PAA-HB.

It can be seen form the test that during the first loading cycle, there is significant difference between the loading and unloading curve. The difference in the loading and unloading curve is because the smaple was in the rest state before and when the loading force was applied on it, the sample took some time to allign itself according to the axis of forces. The area between the loading and unloading curve is the energy absorbed by the sample. As in the second loading cyclic , the area between the loading and unloading cyclic decreases which means that the energy absorbed by the sample during the second loading cyclic after 10 second was low as compared to the first cycle. This is due to the reason that during the second loading, the sample was alredy alligned in the direction of the forces therefore, there was less energy absorbed during the second loading cycle.

In the third loading cycle, there was increase in the stress but the energy absorbption was quite the similar. In the next loading cycles, the stress of the stress and starin curve of the loading cycles decreses for the 1 hour and 24 hour cycle. In the last loading cycle, the area between the curve has incresed i.e. more energy is absorbed during this cycle, this was due to the reason that during this time period (24 hours) the PAA sample may have redeveloped its structure and this is why it absorb more energy.

4.3.2 For PAA-HB

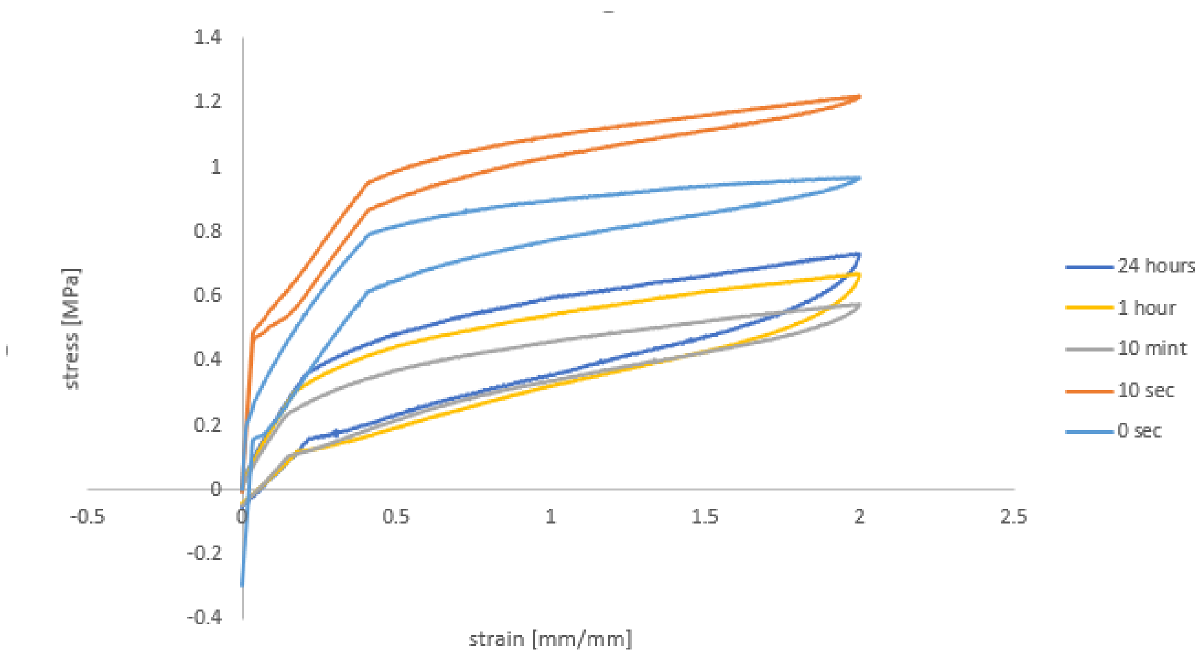


Figure 29 Dynamic loading for PAA-HB

In the dynamic loading of the PAA-HB, the first thing that is observed is that, the stress for the stress and strain curve is far more than the PAA loading cycles.

As seen from the graph, the maximum energy was absorbed in the first and the last cycle of the dynamic loading cycle. This is because in these cycles the sample was at stable state and there was no internal damage due to the force applied by the previous loading cycles. In the second loading cycles (10 seconds) there was decrease in the energy absorbed because of the same reason that the sample was under the same load before and the sample has not fully recovered to its initial state.

For the 10 minutes loading graph, the stress decreases, the decrease in the stress is due to the reason that the sample has gone through the same amount of loading cycle couple of times which means that the sample has already gone through same amount extension and because of that the sample absorbs less energy to go through same amount of extension.

For the last two loading cycles, the sample redevelop from the previous loading cycle therefore, the stress value for theses loading cycles is more and hence the energy absorbed by the sample also increases.

4.4 PAA vs PAA-HB

This section provides the comparison between the PAA and PAA-HB.

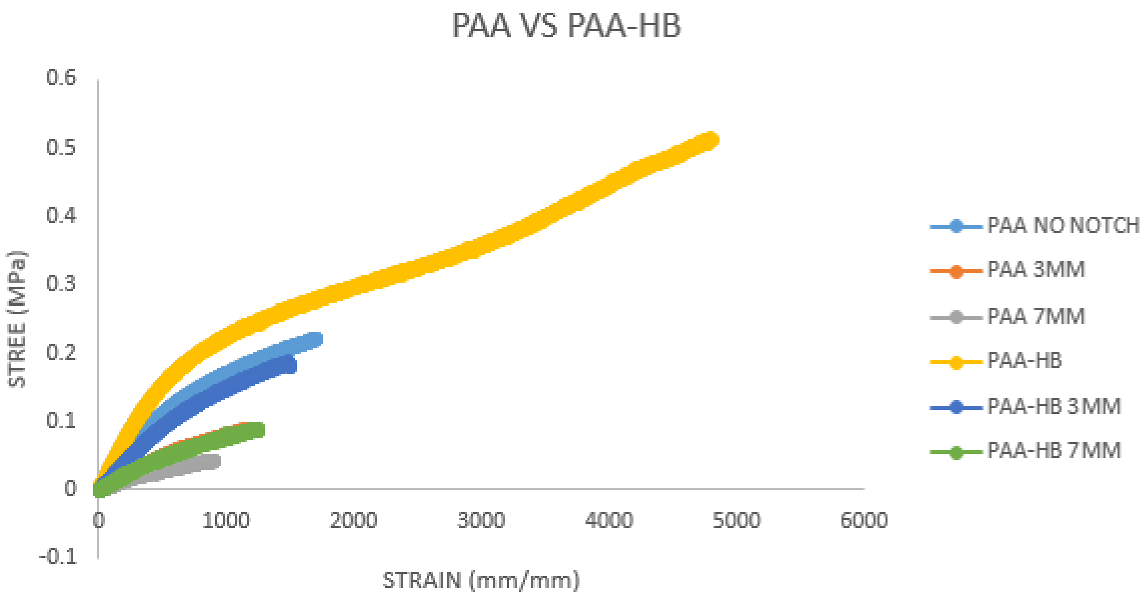


Figure 30 PAA VS PAA-HB FOR STRESS AND STRAIN

Figure 31 PAA VS PAA-HB FOR LOAD AND EXTENSION

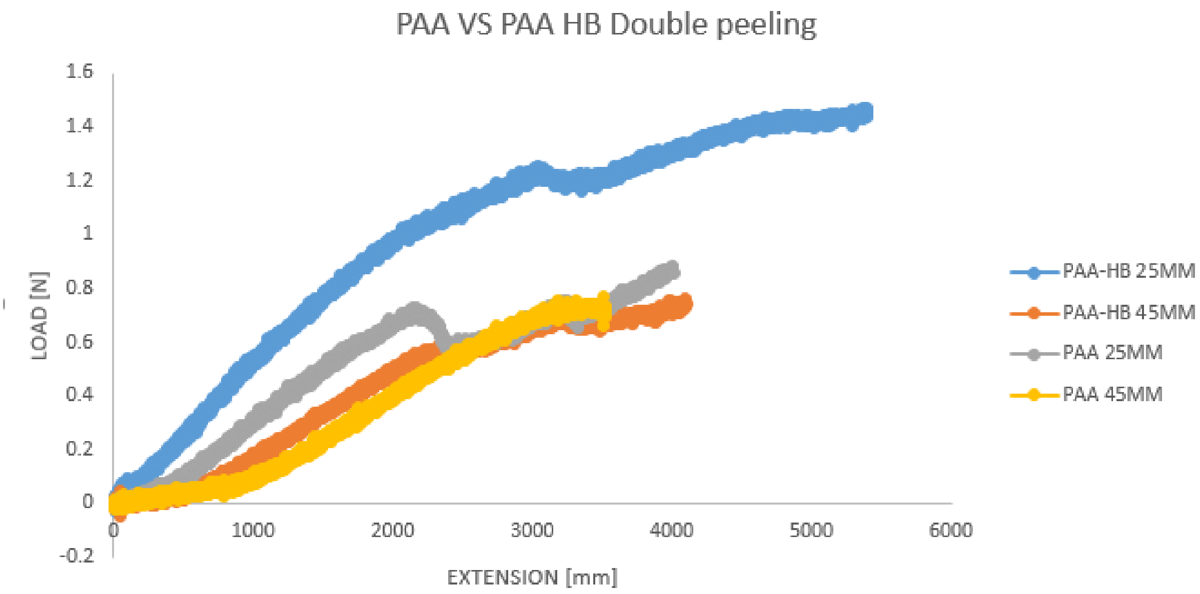


Figure 32 PAA VS PAA-HB DOUBLE PEELING FOR LOAD AND EXTENSION

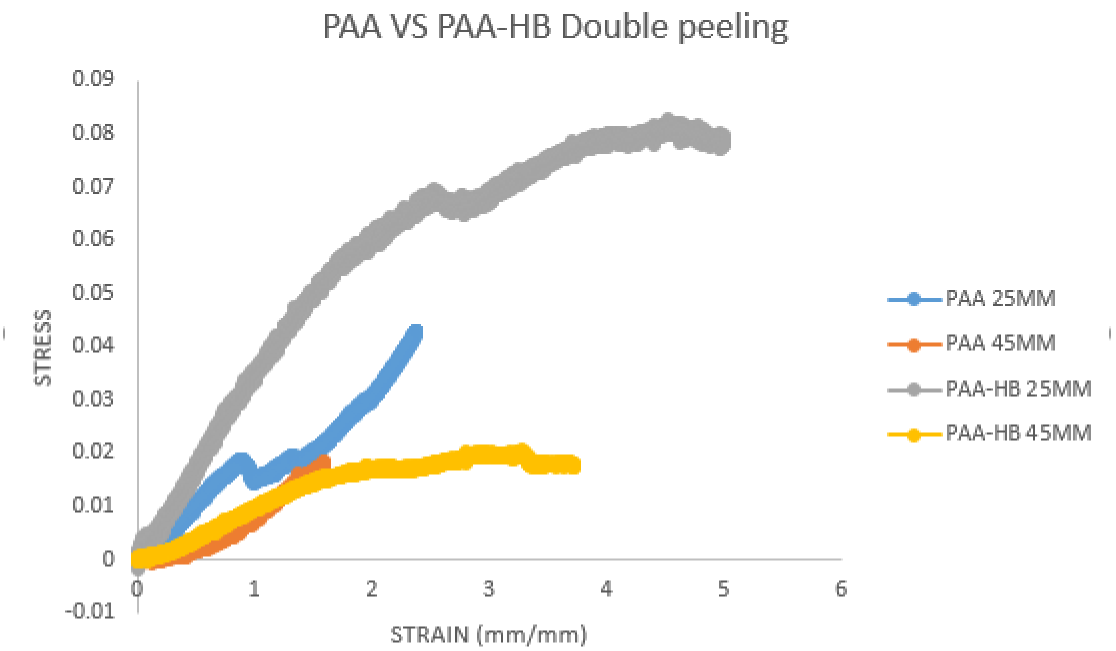


Figure 33 PAA VS PAA-HB DOUBLE PEELING STRESS AND STRAIN

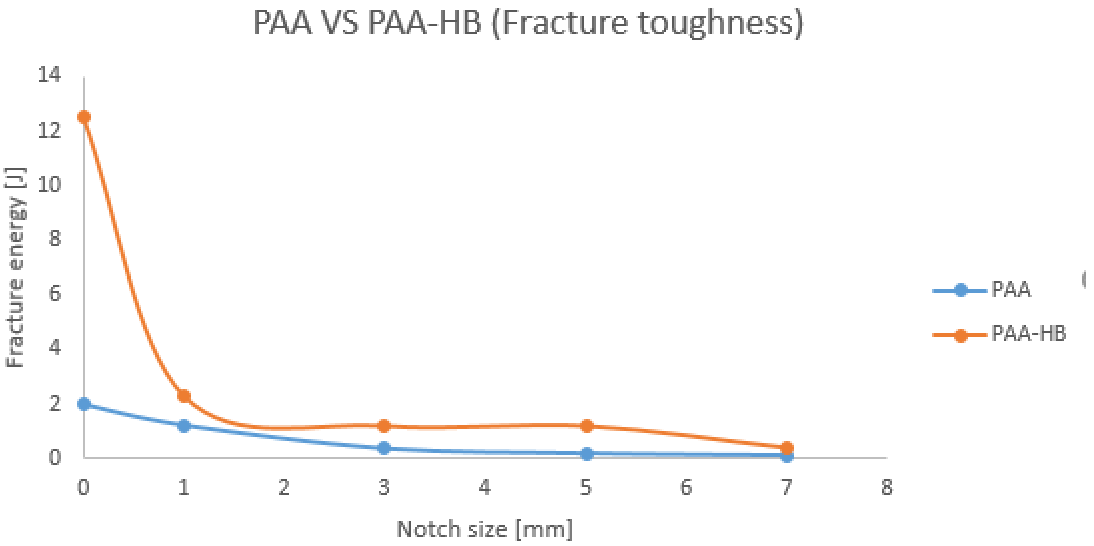


Figure 34 PAA VS PAA-HB FRACTURE TOUGHNESS

4.5 Water swelling behaviour

As mentioned above that the water absorbing test was conducted both on the conventional and its hybrid hydrogel. The aim of the experiment was to figure out whether the hybrid hydrogel can deliver the same results for water absorption so that its application could not be limited due to this. The picture below shows the difference between the dry state and swallow state hydrogel for both materials.

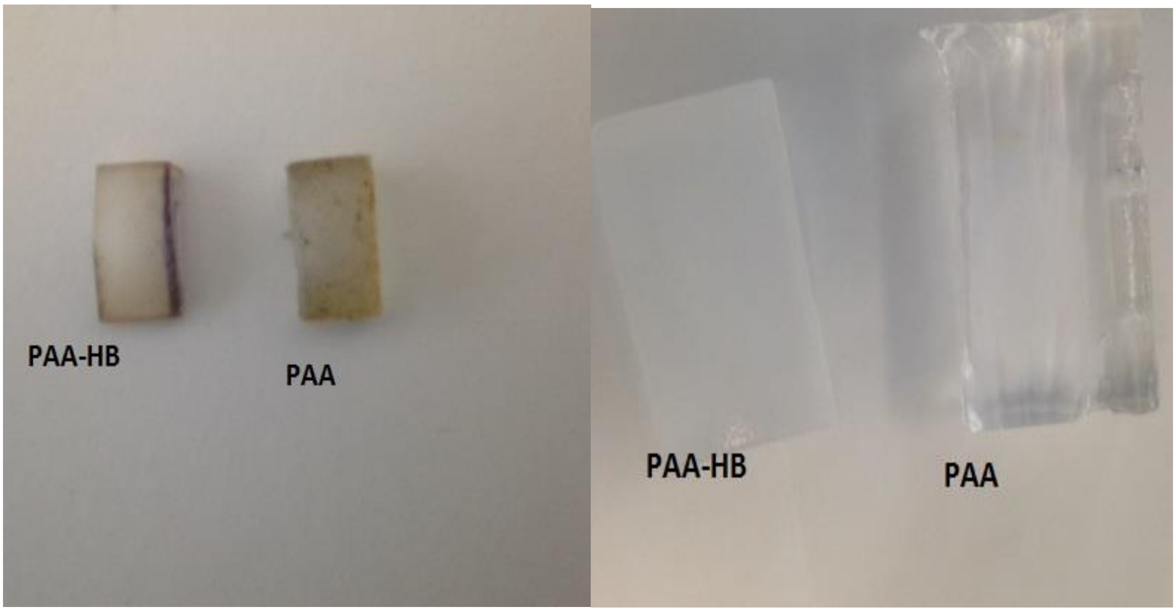


Figure 35 Both hydrogels are in dry stare (left image) and both hydrogel in swollen state (right image).

The experiment was conducted for three sample of each hydrogel so as to be sure about the results obtained. The samples used for this test was chosen of small dimension as it was expected to absorb a lot of was and was expected to huge increase in the size of the swollen hydrogel sample. As per the expectation, the size of the swollen hydrogel was huge as compared to the original size of the both hydrogel samples as shown in the figure 35.

4.5.1 PAA vs PAA-HB

The comparison was made for the water absorbing behaviour for PAA and PAA-HB hydrogel. For the comparison, the swelling ratio was calculated (from the previous mentioned formula) and then plotted against the time. As seen from the graph, the swelling ration for both the materials was plotted against time, which clearly suggest that the PAA-HB is better at water absorption properties as compared to conventional hydrogel (PAA)

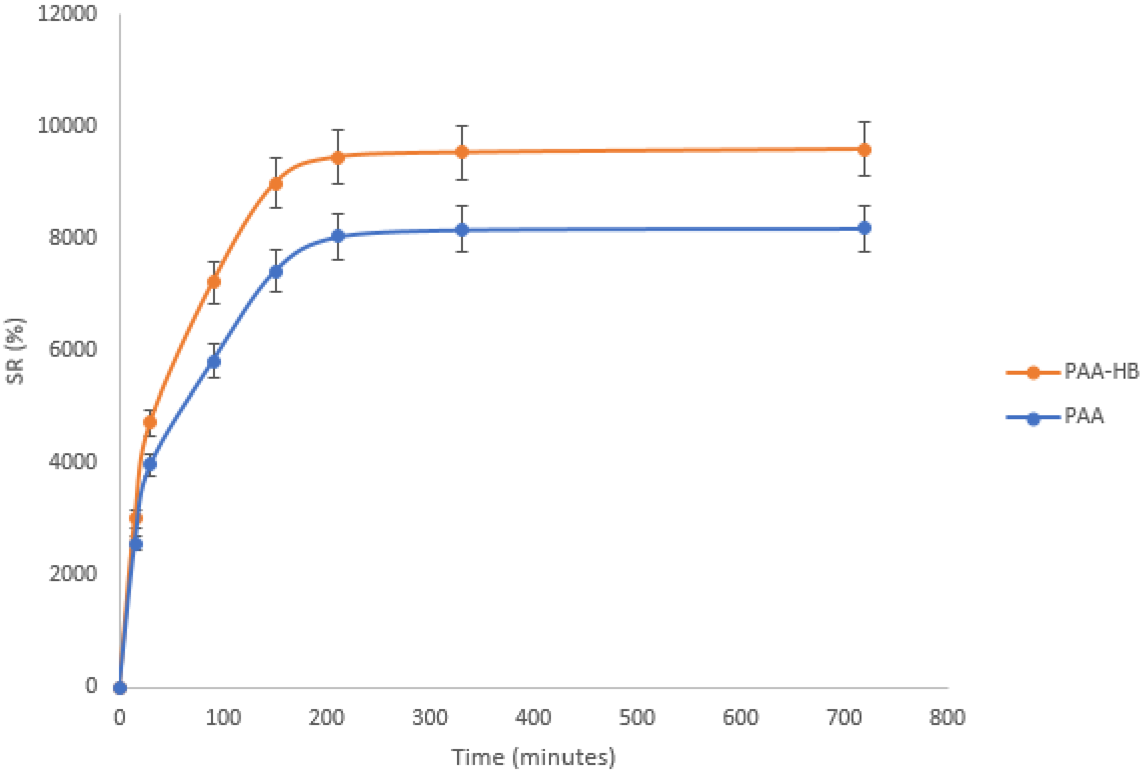


Figure 36 Water swelling behaviour for PAA and PAA-HB

As seen from the graph, the PAA-HB is clearly ahead of the PAA in case of water absorption properties. As seen from the graph, both the hydrogel starts absorbing water (distilled water) at much higher rate and after some time the water absorption rate decreases and at the end both the samples reach equilibrium (stage where no more water can be absorbed). The reading was taken till both the samples have achieved equilibrium state.

As the experiment started, both the hydrogel samples start to absorb water at much quicker rate. The first reading was taken after 30 minutes, at which both the samples were quickly absorbing water but the PAA-HB sample swelling ratio was higher than PAA swelling ratio. As the time passes, the absorption rate for both the material start to slow but PAA-HB was always ahead of PAA. The next readings were taken at 90, 150 and 210 minutes shows the slow rate of water absorption for both the samples. Form the 210 minutes, both the samples were at the equilibrium stare: which mean that both the samples were absorbing approx. no water. The last reading for this experiment was taken at 720 minutes, so as to make sure that both the sample have achieved equilibrium state.

4.6 Molecular interaction with FTIR

The FTIR (Fourier transform infrared spectroscopy) was used to describe the functional groups of the PAA and the PAA-HB. In the FTIR, each sample was placed on the central crystal of the ATR plate. The air was used as the reference for each scan for both the samples. The recording for the FTIR was done with the resolution of 4 cm^{-1}. 64 scans were used for the recording of the FTIR spectra.

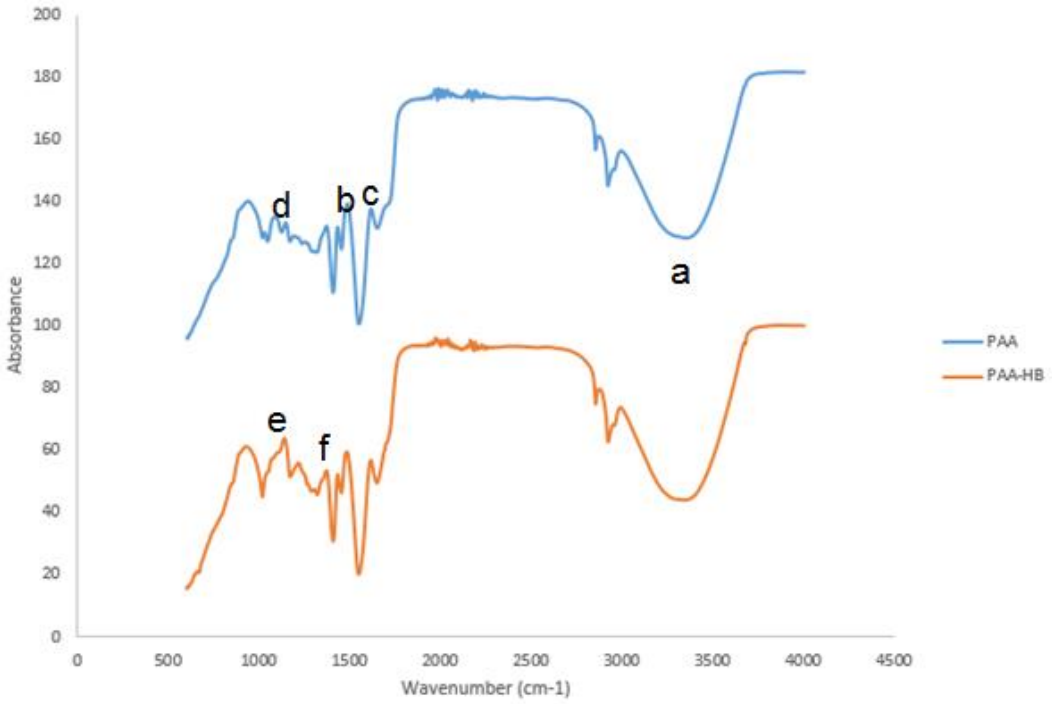


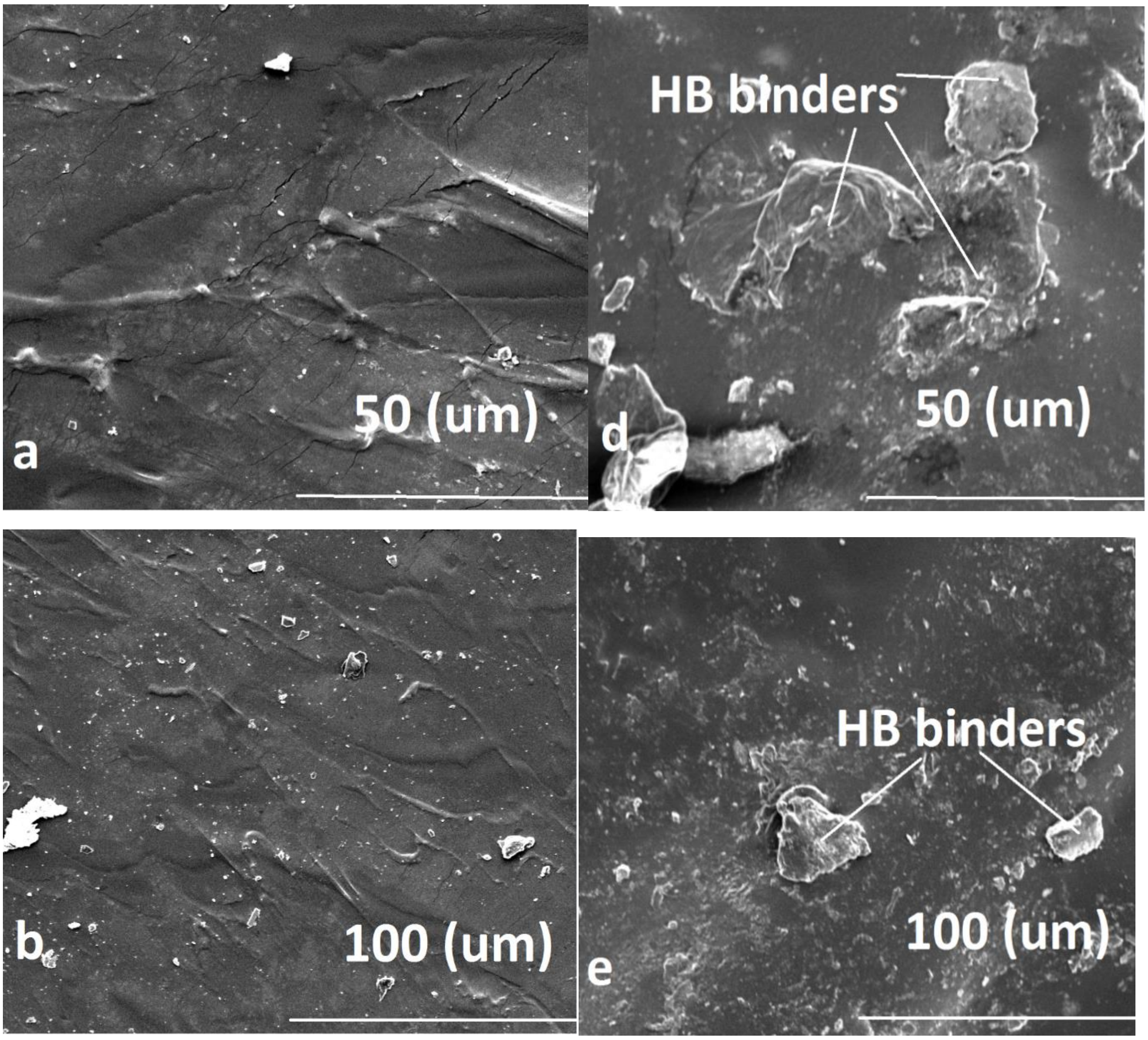
Figure 37 FTIR spectra for PAA and PAA-HB

From the FTIR spectra in case of the PAA, the peak (a) is observed around the 3500 cm^{-1}. This peak is due to the stretching of the water molecules in the PAA. At the (b) (approx.)1400 cm^{-1}, the –C=O asymmetric stretching variations were observed and the COO symmetric variations were observed (c) at the (approx.) 1600 cm^{-1} (Yu, et al. ,2015). At the (d) 1200 cm^{-1}, the variations for the COO- groups were identified

After the addition of the HB polymer in the PAA matrix, new peaks were absorbed around the (e) &(f) 1100 and 1300 cm^{-1}. These peaks were missing in case of the PAA hydrogel sample FTIR spectra. These peaks represent or were because of the C–O(–OH) stretching hydroxyl and O–C stretching of the ester group in case of the HB polymer (Linde, et al., 1990). These two peaks signify the additions of the HB polymer into the PAA matrix.

4.7 Morphological (SEM)

PAA PAA-HB



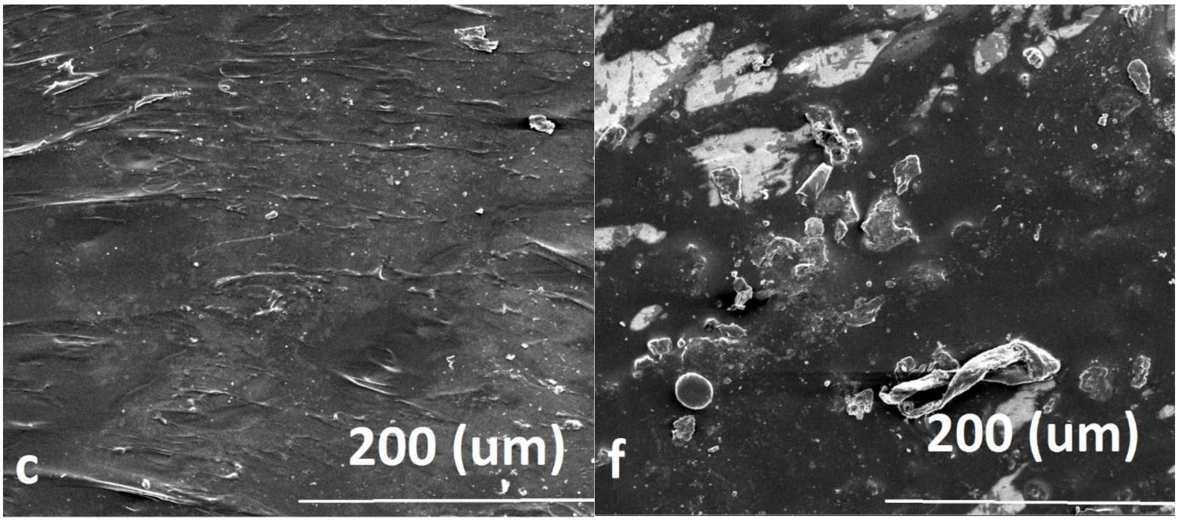


Figure 38 SEM images of PAA and PAA-HB at different magnification levels

The samples were observed by the SEM in order to understand the interaction between the PAA and HB. All the measurements shown in the Images are in µm. As it can be seen from the left side images (a, b and c) that the surface is relatively smooth, that surface is of the PAA hydrogel. As the PAA hydrogel does not contain any polymer for toughening that is why the surface of the PAA hydrogel is comparatively smooth. The small sections or the particle seen in the PAA hydrogel surface is due to the presence of water or may be due other substances like the (Noah, cross linker such as MBA).

On the other hand, the surface of the PAA-HB hydrogel is very much uneven as compared to the PAA. The surface of the PAA-HB hydrogel is shown on the right-side images (d, e and f). As shown in the different magnifications levels of the pictures the binders (particles) of the HB can easily be sported in the PAA solution. The binders of the HB in the PAA solution can be seen as the crystals spread all over the PAA surface as marked in the pictures. As it can be observed from the images of both the PAA and PAA-HB, it can be said that the PAA looks more homogenous whereas the PAA -HB shows the spread of the HB polymer uneven distributed (at µm level).

4.8 Results obtained from other methods of toughness

The results obtained from the double network hydrogel shows the elastic modulus from 0.1 to 1.0 MPa. The fracture toughness of the double network hydrogel is 1-10 MPa. And their fracture energy is 100 to 1000 $\mathrm{J\ m}^{\wedge 2}$. The mechanical properties obtained from the double network hydrogel are comparable to that of rubbers or soft tissues. The issue with the double network hydrogel is that it is very expensive to synthesize the hydrogel.

4.9 Limitations

While performing the mechanical testing for the hydrogel, there were few limitations encountered, which made the testing bit difficult. Due to these limitations, might have an impact on the output results. To get the accurate results, even the minute things were adjusted accordingly but still there were few things that might distort the end results. The limitations for the mechanical testing was different for each test performed. To eliminated these limitation or sources of error more number of samples were used during each mechanical testing. The possible sources of error are discussed below for each test performed.

4.9.1 For tensile testing

As discussed above, in tensile testing the tensile force was applied on the hydrogel samples. During the tensile testing, there were mainly three limitations that were encountered which might affect the results.

4.9.1.1 Slipping of sample

The main issue with the tensile testing is the slipping of the sample between the clamps of the Instron machine.

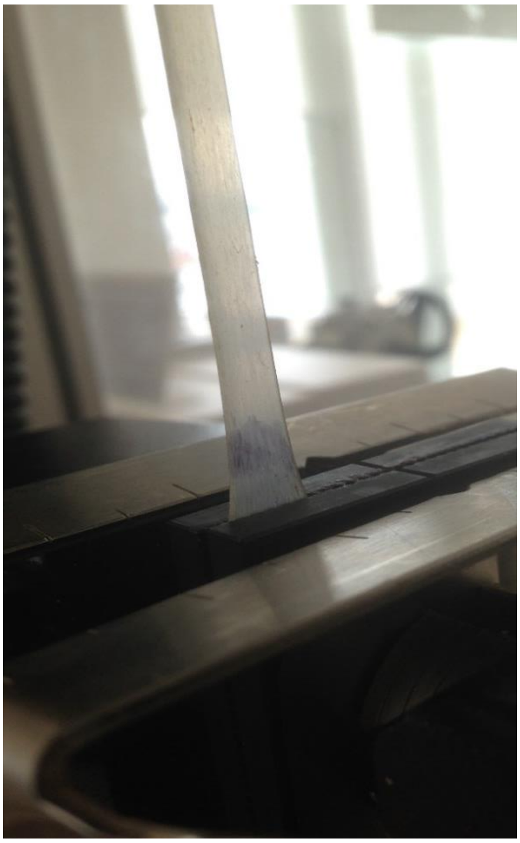


Figure 39 Slipping of sample

The slipping of the sample occurs when the grip of the clamps is weak and when the samples is under the tensile force it starts to slip. Another reason for the slipping is that, when the sample is placed in the tensile force, the thickness of the sample decreases due to which the samples starts to slip between the clamps.

The speed of testing is very slow therefore, it is difficult to identify the slipping of sample. In order to detect the slipping, a mark is made on the sample (from where the sample is held by the clamps) and during the test, if the mark made on the sample starts to expand, it means the sample is slipping from the clamps. The example of sample slipping is shown in the figure 39, as the mark on the sample is expanding, during the tensile testing.

4.9.1.2 Sample damage by clamps

The second limitation in the tensile testing is due to the sample damage by the clamps. As the hydrogel is a very sensitive material therefore a little pressure might damage the sample. In order to avoid the slipping of the sample, the sample is held very tight (by increasing the clamp grip) which can damage the sample. If the sample is held tight by the clamps then the crack will propagate at the ends (where it is holded by the clamps) which shows that the sample was held tight. In the perfect case, the crack should start propagating from the middle of the sample.

4.9.1.3 Sticky sample

The third limitation that is observed in the tensile testing is the sticky sample. The stickiness of the sample is a major problem when it comes to the testing of the notched samples. As the sample are kept for a while after laser cutting, in the meantime the notches of the samples stick to each other, the sticking of the sample will affect the results obtained. Therefore, in order to avoid the notches to stick to each other, slice of paper was placed in between the notch so that the notch would not stick back. As shown in the figure 40, piece of paper placed between the notch in order to avoid the stickiness of the notch.

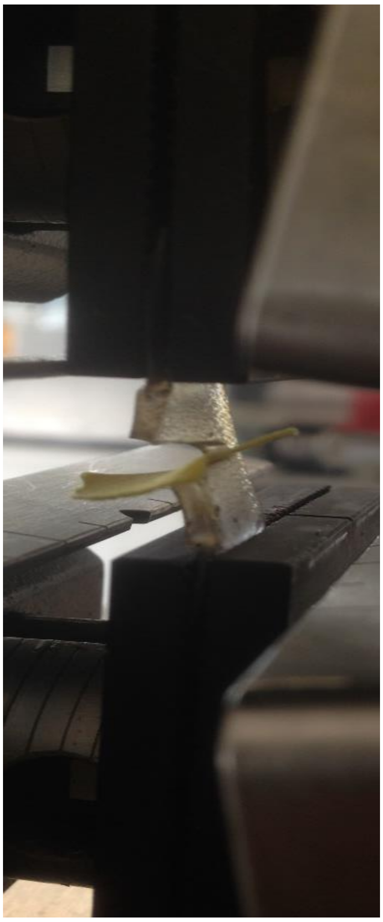


Figure 40 Paper strip placed at notch to avoid sticking

4.9.2 For double peeling testing

The major problem with double peeling test is that, there are no standards set for this test. The other big issue with the double peeling test is that it is very difficult to hold the sample in place (between the clamps of the Instron machine).

Theoretically, the crack should start propagating from the notch and should go all the way through the sample but practically the propagation of the crack is uneven, the crack starts to propagate in the upward or the downward direction as shown in the figure 41.

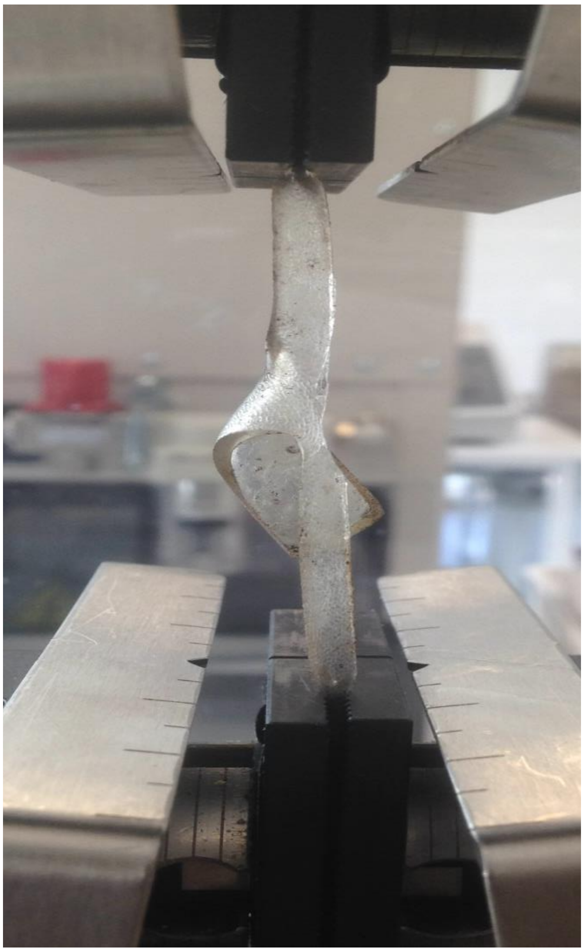


Figure 41 Uneven propagation of crack from notch

As seen from this figure 41, the cark is propagating in the downward direction instead of going all the way through the sample. Due to this, elongation of the sample decreases (because it early during the experiment as the crack is not propagating in the expected direction) and does not provide the appropriate results.

Another limitation for the double peeling test is that more number of sample are needed. As the propagating of the crack is uneven in case of double peeling, that is the result of double peeling cannot be easily trusted. In order to make sure, more number of sample are required for every single type of notch. By performing the sample experiment for the same size notch, the result can be trusted by analysing the results from majority of samples.

CHAPTER 5

CONCLUSION

As discussed, the hydrogel has the vast range of applications in many fields. The only limitation of hydrogels is their poor mechanical properties and because of it, the hydrogel applications are very limited.

Therefore, various studies have been conducted on providing the toughness to the conventional hydrogel. So as to increase their application in the various fields. As discussed, the limitation of hydrogel in the biomedical field is also the poor mechanical behaviours of the hydrogel. As many of the biomedical application of hydrogel are limited due to weak mechanical properties of the hydrogel for example, in the drug delivery, the hydrogel could be also to sustain the drug for the longer period of time if the hydrogel was more tough.

In this thesis, the tough hydrogel was prepared and then compared with the conventional hydrogel. The comparison was made by conducting various mechanical tests on both the hydrogels and then analysing the results. The mechanical tests that were conducted on the hydrogel were tensile testing, double peeling testing and the dynamic loading testing.

After analysing the data produced by these tests, it can be concluded that there is huge improvement in the mechanical properties of the hydrogel with the addition of the hyperbranched polymer. As there are no standards for the hydrogel therefore, the results of the tensile test were confirmed by performing the double peeling test. The dynamic loading test also indicate that the toughened hydrogel was also better at the repeated loading. This is very useful information for the applications of the hydrogel, especially for the applications in which the hydrogel has to go through many cycles of the load (repeated loading) for example in case of the artificial muscle, where it has to go through extension or compression for number of cycles.

As the aim of the thesis was to enhance the mechanical properties of the hydrogel (specially the fracture toughness, it can be seen from the obtained result that the fracture energy for the PAA i.e. conventional hydrogel is 8.25 J but for the PAA-HB the fracture energy is 38.75. The water swelling properties has also improved significantly as seen from the result, the water swelling rate was quicker for the PAA-HB as compared to PAA. The selling ration for the PAA-HB was about 9500 and for the PAA, the swelling ratio was 7800 approx. This result shows the significant increase in the mechanical properties as well as the water swelling properties of PAA-HB hydrogel as compared to the PAA or the conventional hydrogel.

As the hydrogel is well known for its water swelling properties therefore, it was made sure that the toughened hydrogel or the hybrid hydrogel has sufficient water absorbing properties. The toughened hydrogel shown good water swelling capabilities even better than that of the conventional hydrogel. Therefore, it can be said that the toughened i.e. PAA-HB hydrogel shows better mechanical properties than the PAA hydrogel and it also possess the conventional properties of hydrogel (water absorbing).

Chapter 6 Future work

The main focus of this thesis was to provide the toughness to the conventional hydrogel and then compare the mechanical properties of both the hydrogel. In this thesis work the enhancement provided to the conventional hydrogel was at the molecular level (by the hyperbranched polymer) but in the future the sub micro level enhancement can also be provided to the conventional hydrogel or the PAA-HB hydrogel. The sub micro level enhancement can be provided by the PVA polymer.

At present, there were mainly two difficulties that were faced during the synthesised of the PAA-HB PVA. The first difficulty was that, the PVA polymer was prepared by the process of electrospinning and from this process the PVA was collected at the aluminium foil but it is very difficult to extract the PVA from the aluminium foil. The PVA needs to be peeled off from the aluminium sheet but most of the PVA would be damaged or wasted during peeling it off from aluminium sheet. The second difficulty was that, the PVA needs to be placed on the prepared solution of PAA-HB before placing it into the oven but placing the PVA on the prepared solution was difficult as the PVA was available in bits and peace (as peeled from the aluminium foil) therefore, the spread of the PVA was uneven in the PAA-HB solution. Which means that the prepared hydrogel containing PVA is non-homogeneous therefore the mechanical results of this would vary a lot that is why the PAA-HB PVA was not considered in this thesis but it definitely has huge possibilities in future.

As discussed above, the toughened hydrogel or the hybrid hydrogel has huge scope in the biomedical field. Therefore, it is very crucial to make sure that the particular hydrogel is not harmful for our human body, this can be done by performing a biocompatible test on the hydrogel sample.

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