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A Novel Approach To Control Corrosion Behaviour On Bio Materials Using Taguchi Method (design Of Experiments)

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by

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Abstract

In the present work, the Taguchi method, from the design of experiment (DOE) has been used to optimize the dip testing method to test the corrosion resistance of bio degradable materials such as PLA (Polylactic acid)and PCL (Polycaprolactone). A L9 (9) orthogonal array of Taguchi design was used, which involves nine experiments for three parameters (pH, sample, temperature) with three levels was used. Corrosion resistance in various pH change of HCL solution was evaluated by dip tests at various temperatures. Analysis of variance (ANOVA) is performed on the obtained measured data and S/N (signal to noise) ratios. The lower the better response variable was selected to obtain the optimum conditions. The optimum conditions providing the lowest weight change potential were estimated. The optimum conditions provided the lowest weight change potential. As a result, the optimum process parameters were determined. The conditions have been identified which achieve less corrosion. As a result of Taguchi analysis in this study, the factor with the most influencing parameter on the corrosion resistance is to be known to show most significant effect. The percentage contributions of pH, sample and temperature to the corrosion rate are to be seen respectively. Consequently, the Taguchi method was found to be the best promising technique to obtain the optimum conditions for such studies. Moreover, the experimental results obtained confirm the adequacy and effectiveness of this current approach.

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Chapter 1: Introduction

Corrosion is the deterioration of a material (often a metal or a polymer) due to interaction with its environment. Bio materials are the materials used to make devices to replace a part or a function of a living body in a reliable and safe manner. The use of Bio materials are used about fifty years old and it has experienced steady and strong growth over its history it deals with both bio chemistry and material science [1]. Corrosion on bio degradable polymers such as both plastics and various other compositions is in many cases similar to metals but in other cases it looks very different. Corrosion attacks on polymers are often hard to discover, the material may look normal but can in fact be embrittled and have lost its mechanical strength or some of its chemical properties such as its roughness, strength etc.

In Bone grafting materials are required when a portion of the bone is missing or it is needed to replace a portion of damaged bone [1]. The bone replacement may be classed by their materials characteristic; permanent and temporary. The former bone, implant for missing bone, is able to use as permanent one. In contrast, the letter bone, auxiliary implant, is necessary to remove it after the treatment is complete [2]. The process of grafting costs a lot because it is usually composed of metal substitutes such as magnesium, stainless steel or titanium alloy. Thus, the method using metal has a bit of a problem [3]. The problems are that the strength of metal is higher than original bone and some kinds of metals have toxicity when it is destroyed in the human body [4]. When the strength of transplanted aid is bigger than bone, the original one would be broken instead of a stronger one. For these reasons, grafting as temporary is preferred more. Nevertheless, it needed a secondary operation to eliminate or replace it. Therefore, biodegradable materials have emerged as a major interest in order to solve these problems [5].

Mechanical stressed polymers applied in chemical environments may initiate cracks on the surfaces. These cracks can thereafter propagate through the material either as a result of the mechanical

stresses or in combination with continuing chemical attack. Corrosion of polymers can be divided into either chemical reaction or physical interaction. Bio degradable Polymeric materials have wide applications; therefore, there are many factors that can lead to corrosion in these materials. Because the lifetime of a polymeric material cannot be accurately foreseen in a specific corrosive atmosphere, it is necessary to clearly understand the compositions and reaction mechanisms of polymeric materials. Hence corrosion test (dip testing) is done and Taguchi method is used to determine the statistical data to prove the best bio material which has less corrosion rate or degradation rate compared to other materials. The Biodegradable Polymers that have been taken into account are PCL (Polycaprolactone) and PLA (Polylactic acid). Among the biodegradable polymer, PLA and PCL are promising biomaterials owing to their properties. Both materials have good biocompatibility, sensible mechanical strength, heat reactive and are able to be fabricated [5].

The best way to improve or estimate the corrosion rate or quality of Bio parts is by using a statistical model approach such as Taguchi method

Bio materials are classified into four types such as shown in the picture

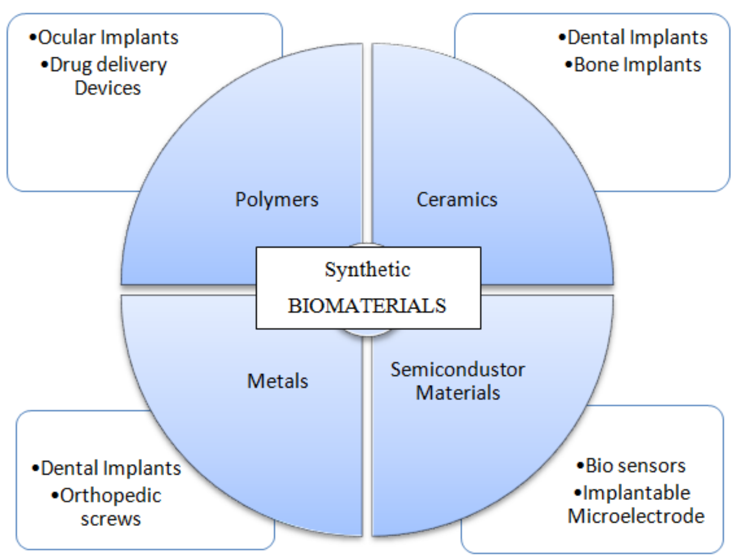


Figure 1.1 Classification of Bio materials

Methods of additive layer manufacturing include stereo lithography (SL), digital light processing (DLP), and selective laser sintering (SLS), fused deposition modeling (FDM), and multi jet modeling (MJM). The method of FDM is one of the 3D printing methods to build and support a layer using a method to dissolve the semi liquid thermosetting polymers. When the materials of printing have the property of thermosetting, the dispenser is able to be pushed it out. This method has various advantages, such as the equipment and maintenance costs being low since the structures and devices of the program are simple compared to other methods of printing techniques. It also has been developed based on the open soured, RepRap, and can be applied to variety of materials. Consequently, when the precision of controlling device is increased, it can be applied to a wide range of industries to strengthen the surface roughness of the model.

That being so, blended PCL and PLA were prepared by FDM printing method in this study. By comparing the mechanical behaviors of blended PCL and PLA, it can be adopted for more diverse purposes in terms of mixing ratio between them and area of interface.

1.1 PROBLEM STATEMENT IDENTIFICATION

As polymers do not corrode so easily it's very tough to find corrosion in these Bio materials so there are various types of corrosion tests to find the corrosion behavior in these materials. Types of constraints on materials that come into action are temperature, chemical interaction, moisture absorption/desorption so we choose dip testing method with the help of three variables that are temperature, pH (which shows the chemical concentration) and weight change in the material.

The use of proper design of experiments methodology has to be found out to solve the problem as we cannot implement too much iteration; we choose Taguchi method to find the best process parameter which affects the corrosion behavior of the material. In order to know the proper mixture of

the two samples we also need to do the mechanical testing of the material to determine the best suitable mixture ratio.

1.2 OBJECTIVE

Bio materials and Polymers in many cases similar to metals where as in some other cases they are quite different. These corrosion effects are hard to discover on polymers as the materials may look normal but can in fact be embrittled and have lost their strength.

The Objective of this study is to identify the best bio material based on surface energy, the bioactivity, and corrosion behavior at acid state.To 3d print the required amount of bio samples and to test the mechanical behavior to find out the proper ratio of these two materials, also to use Design of experiments (Taguchi Method) in order to find the best optimizing parameters to achieve lower corrosion rate to analyze the variance and to find signal to noise ratio.

1.3 CONTRIBUTION

As corrosion in bio materials is very limited the corrosion due to chemical reaction is taken into consideration in the present study, where the weight change is found out and lower weight change has to be considered the best.

In the present study as we have chosen three different variables with one response variable by using the manual method we need to conduct twenty seven iterations where by applying the design of experiments we can achieve much accurate results in just nine iterations. The use of Taguchi method and its promising effects are shown in the study.

1.4 Scope and Limitations

The scope of this paper is to deal with the Taguchi design and Design of experiments (DOE) for the bio samples. Also as we need to find the best bio mixture based on their mechanical behavior, the use of DOE is shown as the promising technique in any field of study.

As bio materials field of study is very limited further more study has to be done on various other biomaterials samples.

1.5 Thesis Outline

Basically the complete thesis discusses three topics mostly the mechanical and corrosion behavior of the two bio materials and the application of design of experiments to the study.

As such the paper is also been divided into five chapters

Chapter 1 “Introduction” presents the general idea on problem statement, objective, contribution, and scope and limitation.

Chapter 2 “Literature Review” studies of fused deposition modeling bio materials thermodynamic concepts and corrosion effects on bio materials are shown. Here, an analysis of the existing methodologies applied to the target scenario is presented.

Chapter 3 “Methodology” proposes and explains a new method of experimental procedures, samples preparation and implementing design of experiments to find the best optimizing parameters to reduce the corrosion effect on bio materials.

Chapter 4 “Case Study” illustrates how the proposed methodology is applied to a real case scenario.

Chapter 5 “Conclusion” summarizes the complete theory and describes the area to be enriched within the findings of this thesis.

Chapter 2: Literature Review

2.1 FUSED DEPOSITION MODELING FOR BIO MATERIALS

Fused deposition modeling (FDM) is a layer by layer filament extrusion process of thermoplastic materials which is an additive manufacturing (AM) technique. The use of these bio materials in the field of 3D printing is very attractive for the tissue engineering applications especially in the field of fabrication of scaffolds [7]. Apart from traditional techniques the additive manufacturing provides better porous control and high reproducibility of the design compared to the past techniques used [8].

In the field of Biomedical, applications include the printing of these bio materials which are more complex compared to other polymeric materials because of their mechanical and chemical behavior. Polylactic acid (PLA), polycaprolactone (PCL) and other copolymers or composite materials derived from them is bio degradable so as to achieve appropriate characteristic AM technique is preferred [9],[10]. In order to increase their accuracy the structures made of bio polymers reduction on the scale of fabrication is essential. This information has been analyzed for the ABS materials and the most common materials used in FDM but not for the bio materials used in tissue engineering. The study shows results to allow establish a simple method to discard a complete range of these operating conditions in manufacturing these bio materials with the use of micro FDM technique.

The pre processing is similar to that of normal printing process and the production process has to be changed based on the required temperatures of the thermoplastic which has to be set into ultra fine beads along the extrusion path. Later the post processing is similar to that of normal materials [11]. During the printing the variables which are to be evaluated during the simulation are shear strength and pressure so as the mechanical testing has to be done on the materials before printing them as they are the essential variables that affect the degradation and morphological characteristics of the extrudate.

2.2 THERMODYNAMIC CONCEPTS

The heat flow of the composites with different composition of PCL was analyzed by simultaneous thermal analyzer (STA 6000, PerkinElmer) to confirm whether PCL and PLA exhibit miscible or immiscible behavior. The scan speed is constant to 2˚C/min by using argon gas, which has 20ml/min. The setting temperature of blended PCL and PLA was determined by performing STA results. The results of STA, Figure 2.1, each peaks of PCL and PLA represented the points of their melting temperature (T_m) [12]. In Figure 2.1, it is also confirmed that the T_m peaks of PCL and PLA are coexisting when the mixing ratio is 50:50. It provides that those materials are immiscible. The crystallization peak appeared in the range from 90˚C to 100˚C in both conditions PLA 100% and mixed condition by half. It is common phenomenon in PLA state and it will harder when crystallization takes place [13].

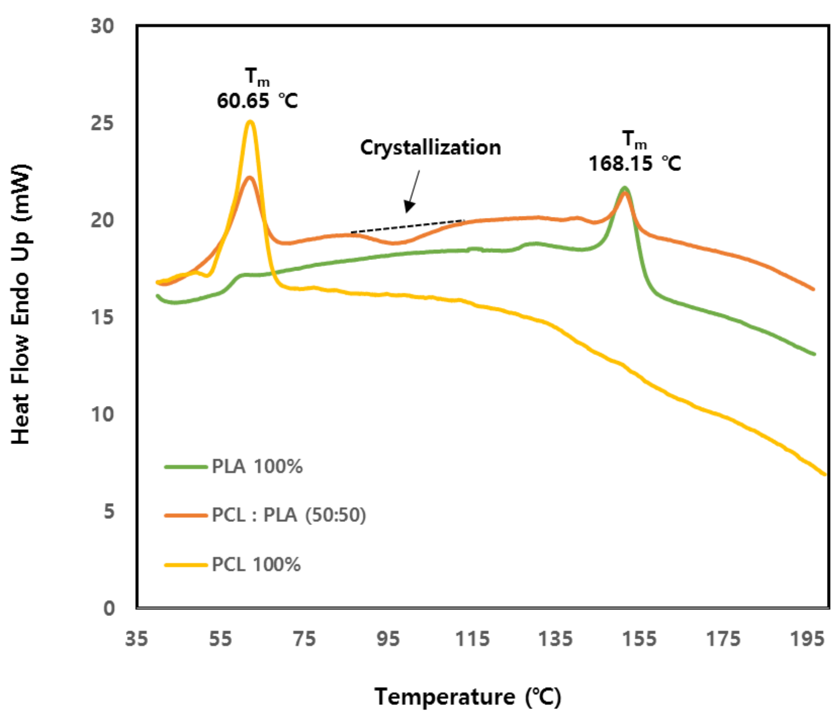
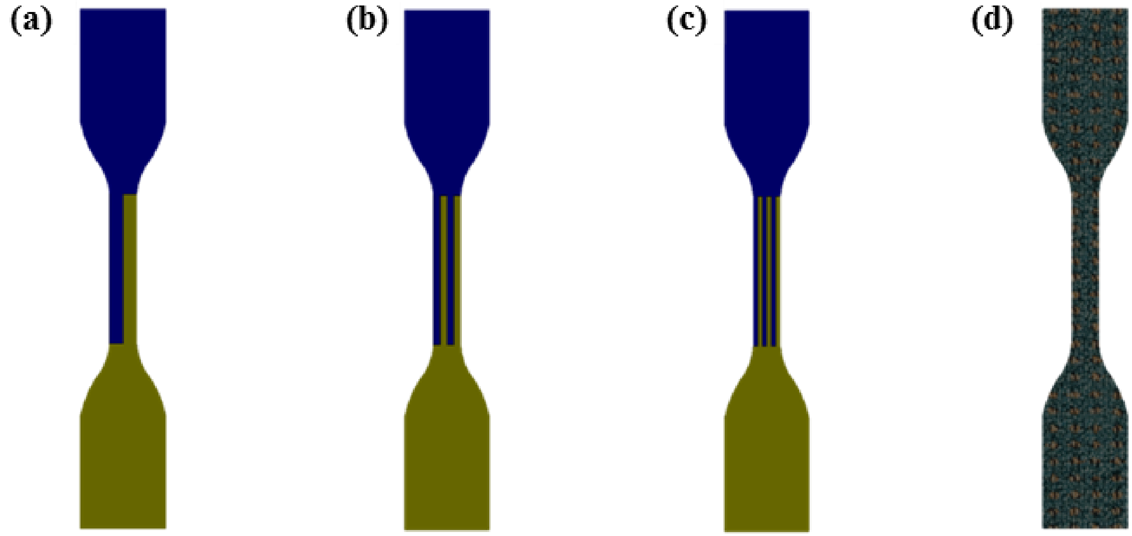


Figure 2.1. Results of STA measurement 100% of PLA, 50% ratio of PLA, PCL, and 100% of PCL

In general, the immiscible materials have positive value of ΔG_{mix}, if not, it would be negative. In case of polymer, it is negligible the figure of ΔS owing to high molecular weight. The dissimilar components can be expressed by the relationship governing mixture using Equation1. It equation provide the effect of mixing with Gibbs free energy.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S$$

Where the ΔG_{mix} is free energy mixing, ΔH_{mix} is the enthalpy of heated mixing, and ΔS is the entropy of mixing. Ordinary, the exothermic $\Delta H_{mix} < 0$ or endothermic $\Delta H_{mix} > 0$ depends on the basis of whether they give off or absorb heat. When the materials are mixed, the point of ΔS always has a positive number. The Figure 2.1 illustrates that both PCL and PLA act endothermic reaction. The Gibbs free energy can be also described like this; when the materials are favorable, or spontaneous reactions get $\Delta G_{mix} < 0$ and if not, it would be $\Delta G_{mix} > 0$. The delta entropy can be represented by $\Delta S = k \ln \Omega$. Where k is Boltzmann's constant and Ω (omega) represents number of cases when the different materials are to be arranged separately, randomly, in a system. The high number of entropy means that lots of substances are occupied in a system. For example, number of cases has one at same kind of substances, and then entropy will be 0. Therefore, the omega is able to be considered as interface area. Based on this mechanism, when the interface area is going up, free energy mixing will be lower and become more favorable [14].



	(a)	(b)	(c)	(d)
Interface Images				
Interface Area (mm^2)	≈ 117	≈ 414	≈ 2970	> 2970

Figure 2.2 Designs of Tensile Strength Samples.

As seen in Figure 2.2 we see that the sample from (a) to (c) were designed by printing dual nozzle printing method by using 100% of PCL and PLA (a) 1 overlapped, (b) 2 overlapped, (c) 3 overlapped, and (d) Melt blended pellet type.

As mentioned above, PCL and PLA are not mixed since they blended polymers. In other words, when it premixed not regularly in a powder state, it begins getting more interfaces than any other conditions. The mechanical behavior between different interfaces could be described in terms of thermodynamic concept. The samples of tensile strength were designed to get the same ratio with a different amount of interfaces. The ratio of four samples was fixed on the halved ratio, because at this point it had the maximum value of ΔS. In order to confirm the effects between interface area, it was controlled by changing the number of overlapping gauge length shown as figure 2.2. The interface area is also calculated to compare like the chart in the figure 2.2. When the number of interfaces is higher, the

interface area increases dramatically. If do so, in this study, intensity of tensile strength is able to be compared according to increasing the interface area.

2.3 CORROSION EFFECTS ON BIO MATERIAL

Corrosion effects on both Bio materials and Polymeric materials is in many cases similar to metals, but in other cases it looks different .Corrosion effects on these bio materials are hard to find out as the corrosion can be in many forms .In fact the material may look normal but may lose its embrittled properties or there may be a change in its mechanical or chemical behaviors.

Mechanical assisted corrosion continues to be a serious concern for metallic biomaterials in all applications but as seen in biomaterials made from polymeric materials chemical interaction comes into play as a serious concern.

Surface modifications are often performed on the biomaterials to improve corrosion resistance, wear resistance, surface texture and biocompatibility [15, 16]. All these modified surfaces should be tested for its corrosion behavior invariably apart from improving other desired properties. A thorough understanding of the interactions which take place at the atomic level between the surface of the implant, the host and the biological environment including all types of micro motions of the bio materials kept inside the human system should be studied carefully in a greater detail in order to obtain bio materials which can sustain for a longer period in the human system [17]. The field of corrosion in bio materials is young and fertile as man knows less about them new bio material mixtures are made to understand much more complicated study and hence the mission will continue [18].

Chapter 3: Methodology

3.1 Experimental Procedures

The samples are prepared using 3d (three dimension) printer first set of samples are used for the mechanical testing to determine the best suitable bio material mixtures and based on the mixture ratio the second set of samples are printed for the chemical testing to obtain the weight loss values to determine the corrosion effect .Taguchi method is applied on the obtained set of values.

3.2 Sample Preparation

The pellets type of PCL (M_n=80,000, Sigma-Aldrich) which has a low melting point (≈65˚C) and having a glass transition temperature (T_g≈-60˚C) was used. The PLA 4043D (M_n≈60,000, Open Source Printing) that is melted high temperature (≈170˚C) and a glass transition temperature (T_g≈65˚C) is around 60˚C were also performed with PCL.

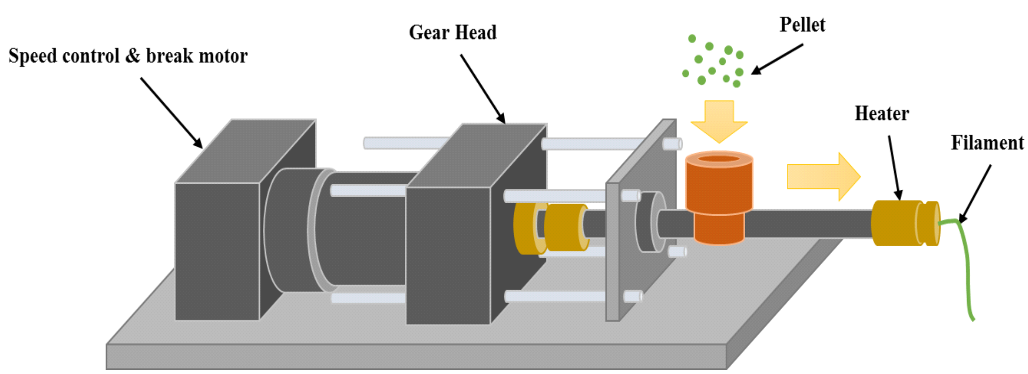


Figure 3.1 Schematic diagram of a filament extruder for extruding blended PCL-PLA pellet

Extruded filaments were printed for samples of tensile strength test using three dimension printers which is fused deposition modeling (NP-Mendel, Open creators). The specific conditions of printing process are to be followed [19].

The Figure 3.1 illustrates the specimen of tensile strength, which was designated by type Ⅳ of the American Society for Testing and Materials (ASTM) D368. It was identified by tensile strength machine (Dual column testing system Instron 5969, Illinois Tool Works Inc.).

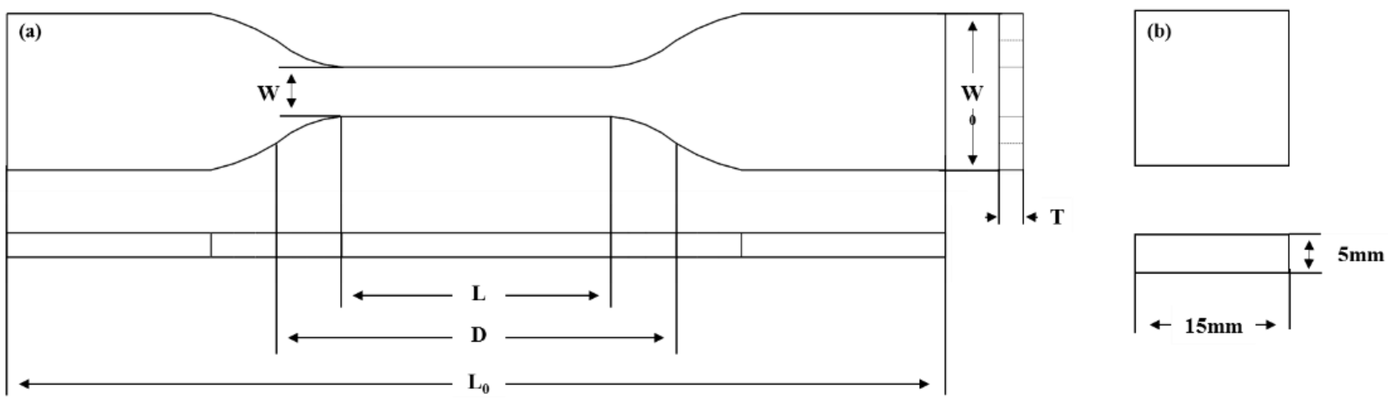


Figure 3.2 Test sample for mechanical testing

The dimensions of Figure 3.2 are as the length overall (L0), Distance between grips (D), Length of narrow section (L), Width of narrow section (W), Width overall (W0), and Specimen dimension for thickness (T)

In hardness case, the cuboids' types of samples were set in order that the polymer samples were analyzed by a nano-hardness test. It was designed 15x15x5mm (Width x Length x Height) then it was polished to produce the flat surface. If the surface is not flat, the polishing work is needed because the measured intensity of the oblique line is not perpendicular to the sample surface when the indenter strength measures the strength.

3.3 EFFECT OF MATERIAL COMPOSITION

The partial rupture of the PCL and PLA in accordance with the interface can be found through Figure 3.1.

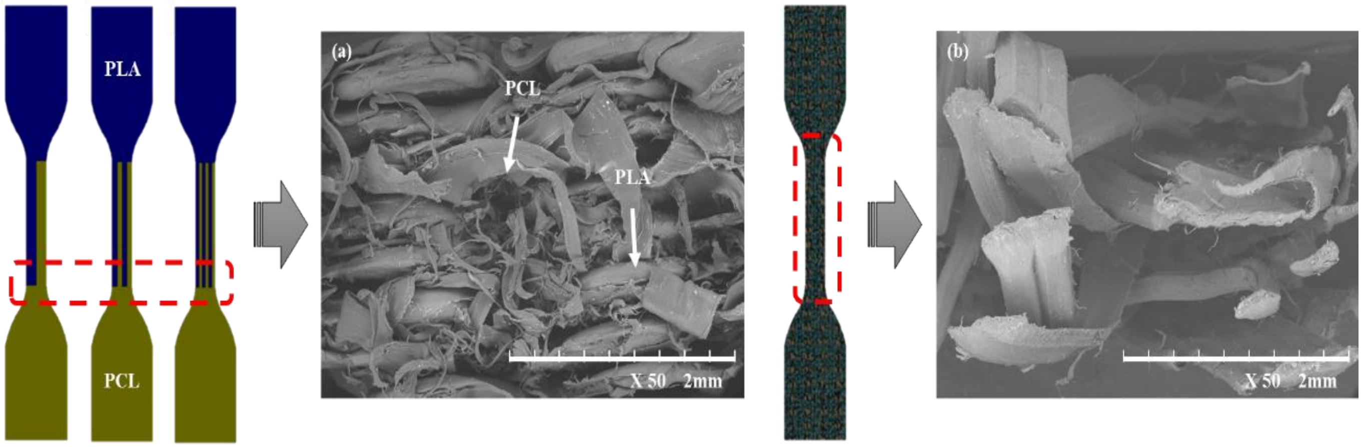


Figure 3.3 Effects of material composition

It illustrates the position of the fracture plane corresponding to the point where the interface is started on the 100% of PCL. Originally, the PCL that it has should be elongated when it was loaded, however, the PLA hold it to preventing at the beginning interface area. Then, the strength of fracture is concentrated at the weakest part. When the portion of pure PCL is pulled, it should be elongated. On the other hand, the bonding force of PLA holds the PCL and the tension rushes to the relatively weak parts [20]. Eventually the interfacial strength, which is the weakest part of the PCL, will break during the tensile strength test. In the other case, mixed randomly, has different. It ruptured the part among the gauge length. The results also said that the specimen failed at the point of poor interface, not following to the interface line. In Figure 3.3, the SEM images of dual type specimens shows that the PCL-PLA interfaces lines are highly ambiguous. These results demonstrate that the tensile strength is good at large interfaces in immiscible conditions because it makes some bond along to the interface line.

3.4 pH PREPARATION FOR DIP TESTING

The Bio materials used in the process are PLA 100% PCL 100% and PCL 50% and PLA 50% these are made to react with the chemical pH of values ranging pH 1,3 and 5. In order to obtain the pH value the distilled water are added with certain amounts of acidic or basic solution in order to get the required pH value the beaker must be kept stirring as shown in Figure 3.4 so as to avoid uneven mixing

of the solution. The pH meter is used to test the pH value of the solution once the required Ph values is obtained the liquid solution is used for the corrosion test of the materials .All acidic solutions have a pH values lesser than 7 and the basic solutions have their pH value greater than 7 in order to obtain the pH solution with pH values lesser than 7 certain amount of acidic solution are added and so on for the basic solution.

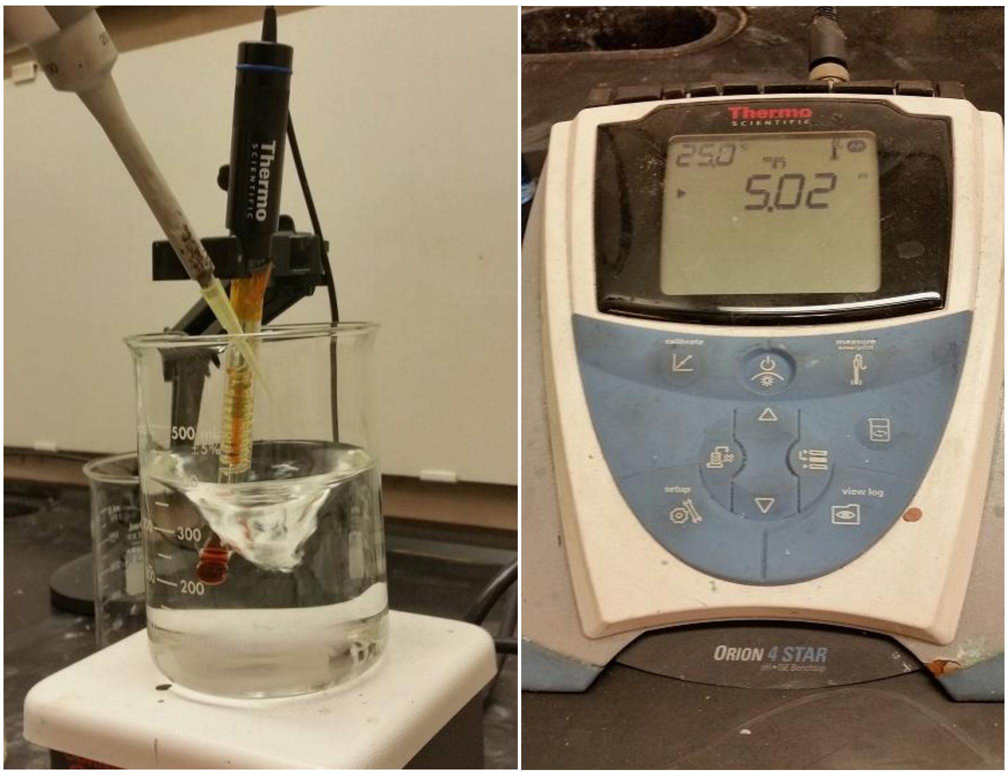


Figure 3.4 shows the ph meter used to calibrate the ph reading

3.5 TAGUCHI METHOD APPLICATIONS

A statically model is developed using Taguchi method to improve quality of material by estimating the corrosion behavior and likewise to determine specific material mixture and parameters required [21]. Taguchi is used to investigate how different parameters affect the mean and variance of a process performance characteristic, Taguchi method deals with the statistical quality process which helps us to have a product or process work the way we want it to behave [22].It is best used when there

are an intermediate number of variables (3 to 50), few interactions between variables, and when only a few variables contribute significantly.

Variables Used in the Study

Three variables are used with three parameters (Independent Variables)

1. Temperature (25, 50, 75 in degrees Celsius)

2. Samples (100% PCL, 100% PLA, 50-50% PCL PLA)

3. pH value (1, 3, 5)

The response variable is Corrosion Rate

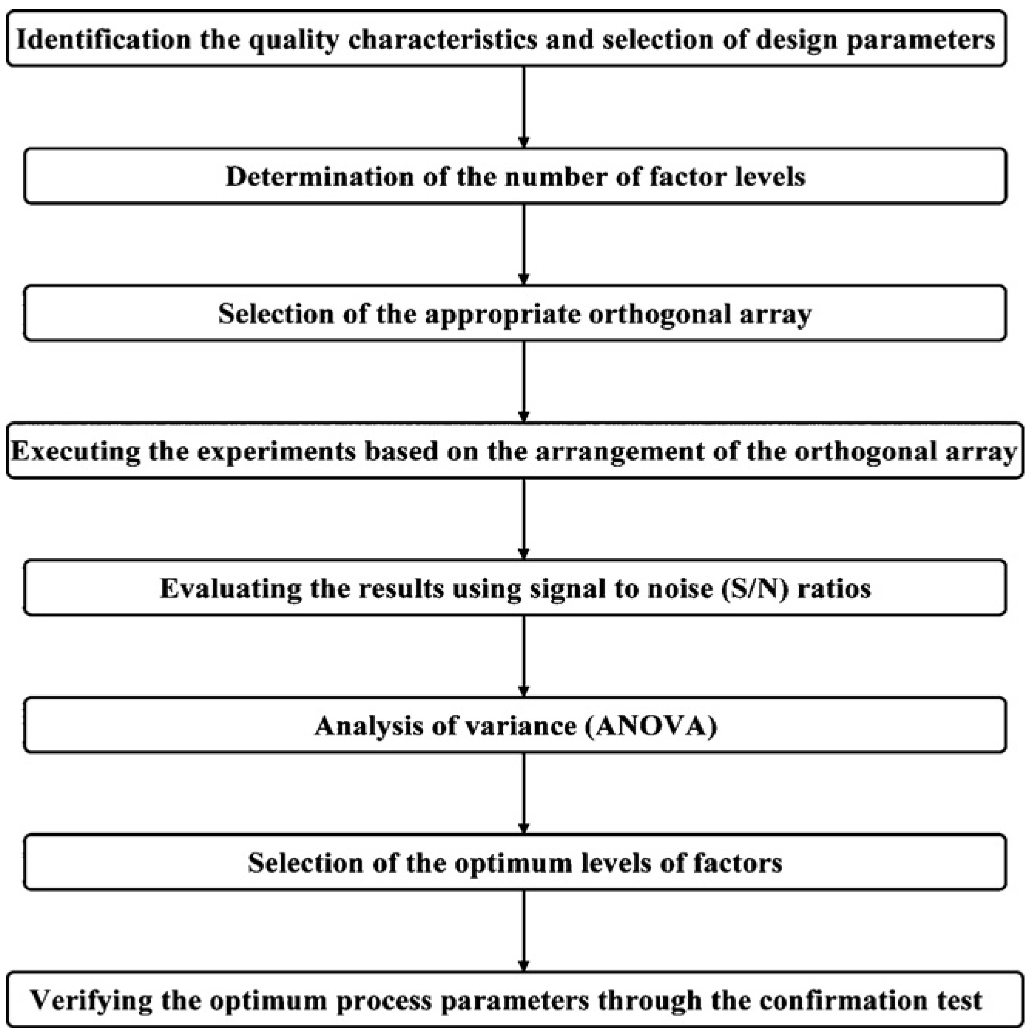


Figure 3.5: Taguchi method Summary

Selection of Orthogonal Array

Orthogonal array testing is a black box testing technique that is a systematic, statistical way of software testing. It is used when the number of inputs to the system is relatively small, but too large to allow for exhaustive testing of every possible input to the systems [23].

Table 3.1: Orthogonal Array table

	Number of Parameters (P)																													
Number of Levels	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
2	L4	L4	L8	L8	L8	L8	L12	L12	L12	L12	L16	L16	L16	L16	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32	L32
3	L9	L9	L9	L18	L18	L18	L18	L27	L27	L27	L27	L27	L36	L36	L36	L36	L36	L36	L36	L36	L36	L36								
4	L'16	L'16	L'16	L'16	L'32	L'32	L'32	L'32	L'32																					
5	L25	L25	L25	L25	L25	L50	L50	L50	L50	L50	L50																			

NOTE: X-axis: Determines the Number of Parameters (here we use 3)

Y-axis: Determines the number of Levels (here we use 3)

A L9 (9) orthogonal array of Taguchi design is selected based on the number of parameters and its factor levels.

Table used for application of Taguchi method

We have 3 parameters and each of them has 3 values. To test all the conceivable blends of these parameters called thorough (exhaustive) testing we will require an arrangement of 3^3 = 27 test cases. In any case, rather than testing the framework for every mix of parameters, we can utilize an orthogonal exhibit to choose just a subset of these blends. Utilizing orthogonal array testing,

Table 3.2: Design Matrix based on L9 array

PH Value	**BIO Material**	**Temperature (in degrees Celsius)**
1	1:0	25
1	1:1	50
1	0:1	75
3	1:0	50
3	1:1	75
3	0:1	25
5	1:0	75
5	1:1	25
5	0:1	50

The table represents that 1:1 = 100%PLA: 100%PCL

Chapter 4: Results

4.1 CONDITIONS OF 3D PRINTING

Extruded filaments were printed for samples of tensile strength test using three dimension printers which is fused deposition modeling (NP-Mendel, Open creators).

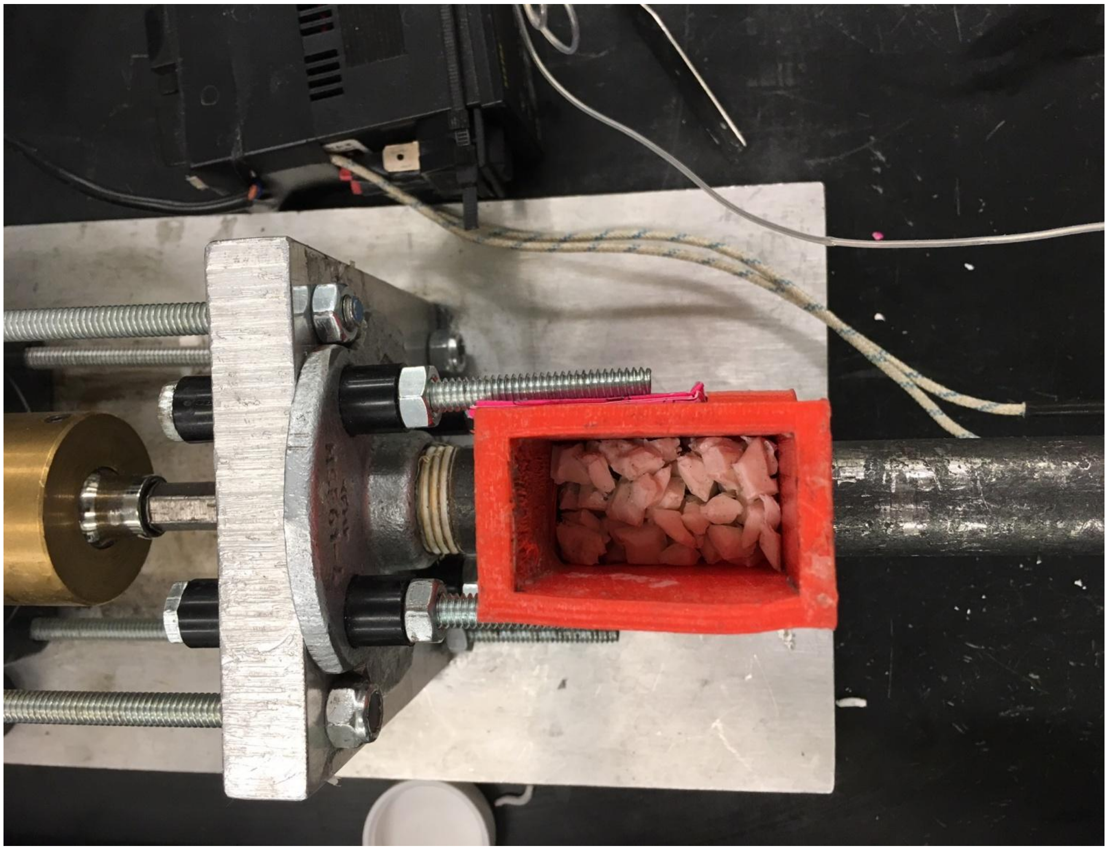


Figure 4.1 Pellets added to the filament extruder hooper

The extruded filaments were printed by using a typical melt spinning process which requires a constant mass flow rate of the molten polymer where the speed is maintained by a meter (shown in figure 4.3) attached to it with the help of a spinning pump generally positioned inside the spinning head [24]. The pellets of the required material a added into the hood of the extruder later the molten polymer is channeled into a number of individual slots or holes of the extruder which are defined with a specific shape or size [25].

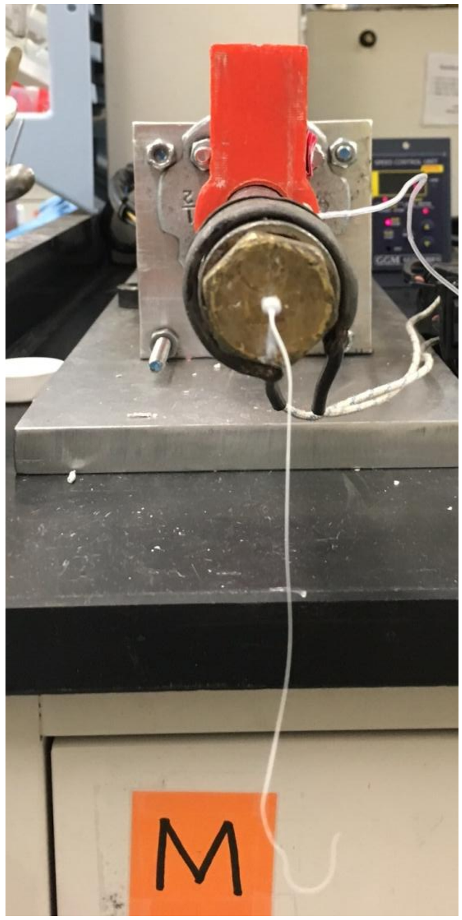


Figure 4.2 Extruding the material

In Figure 4.2 the PLA filament is been extruded with the speed control of 1000

Figure 4.3 Shows Speed control unit

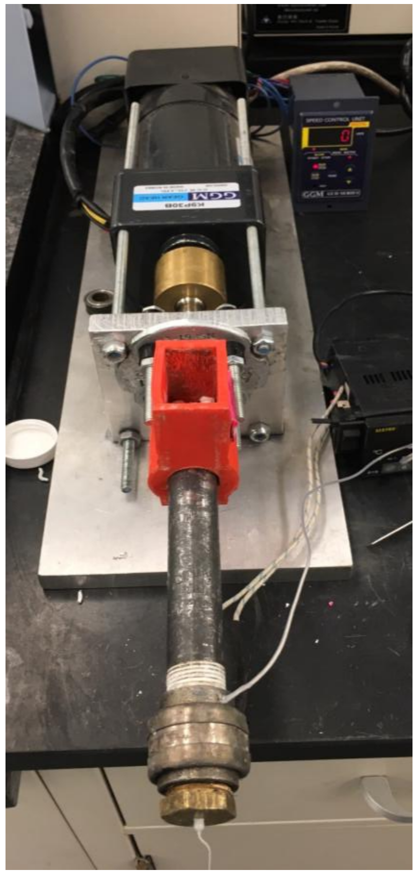


Figure 4.4 Overall picture of a filament extruder

Table 4.1 Specific Conditions of Printing Process

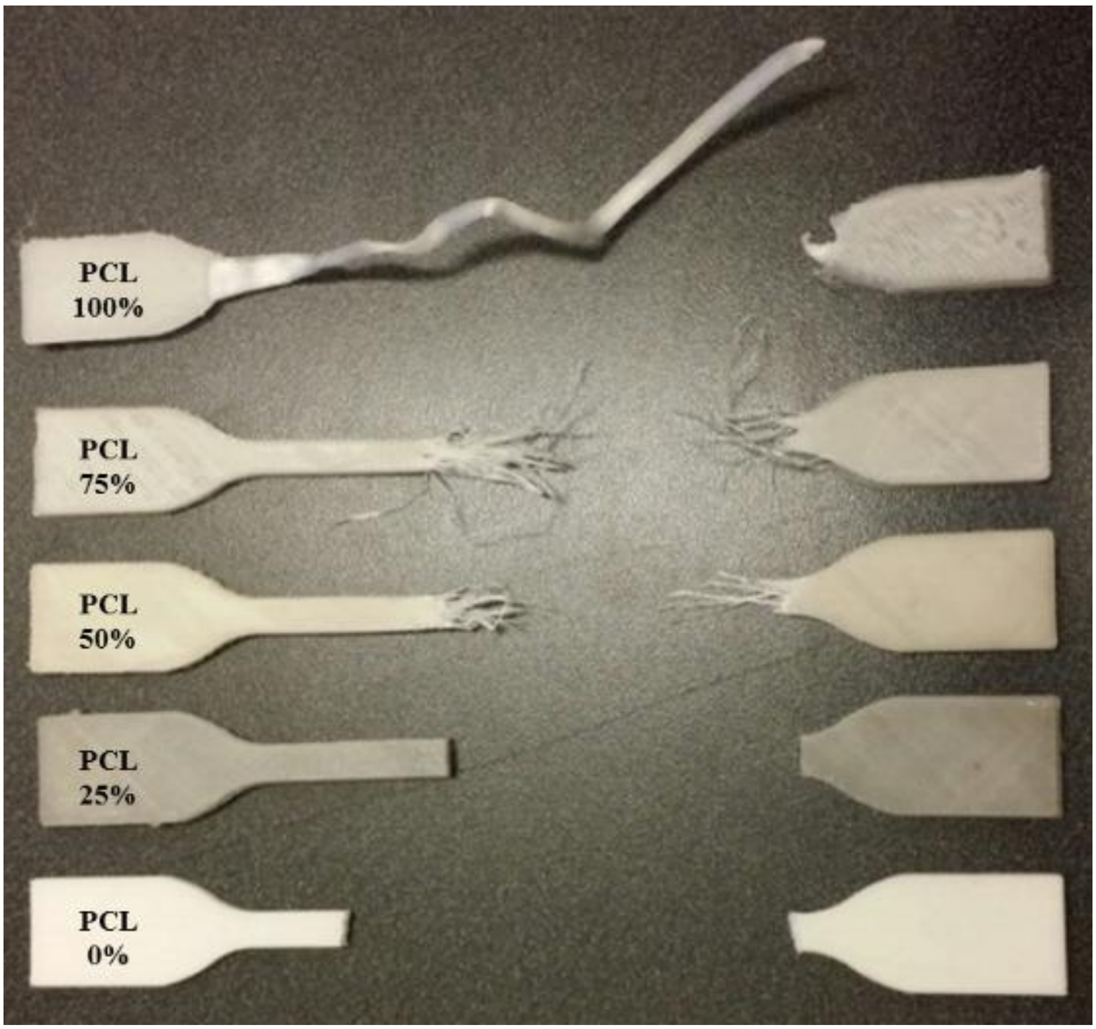
Classification	**Name of Materials or Process**	**Characteristics**
Printing Materials	Blended PCL-PLA	- Blending Amount: Range from 0 to 100wt% The ranges set about 25% apart
Conditions of Blending	Temperature Speed	- 80-160℃ - 2-3 rpm
Conditions of Printing	Nozzle Temperature Bed Temperature Speed Thickness	- 150-200℃ - 70℃ - 5mm/sec` - 0.5mm

The filament was added into the 3D printer to print the required bio material sample for the chemical test. The required printing conditions were shown in Table 4.1 where the conditions of the

blending should not be more than required temperature [26] that is 160 degrees Celsius .The bed temperature should be maintained 70 degrees and the thickness of 0.5mm is taken .

4.2 MECHANICAL BEHAVIOR

For the mechanical testing the parts are to be printed as per the American Society for Testing and Materials (ASTM) D368 standards.



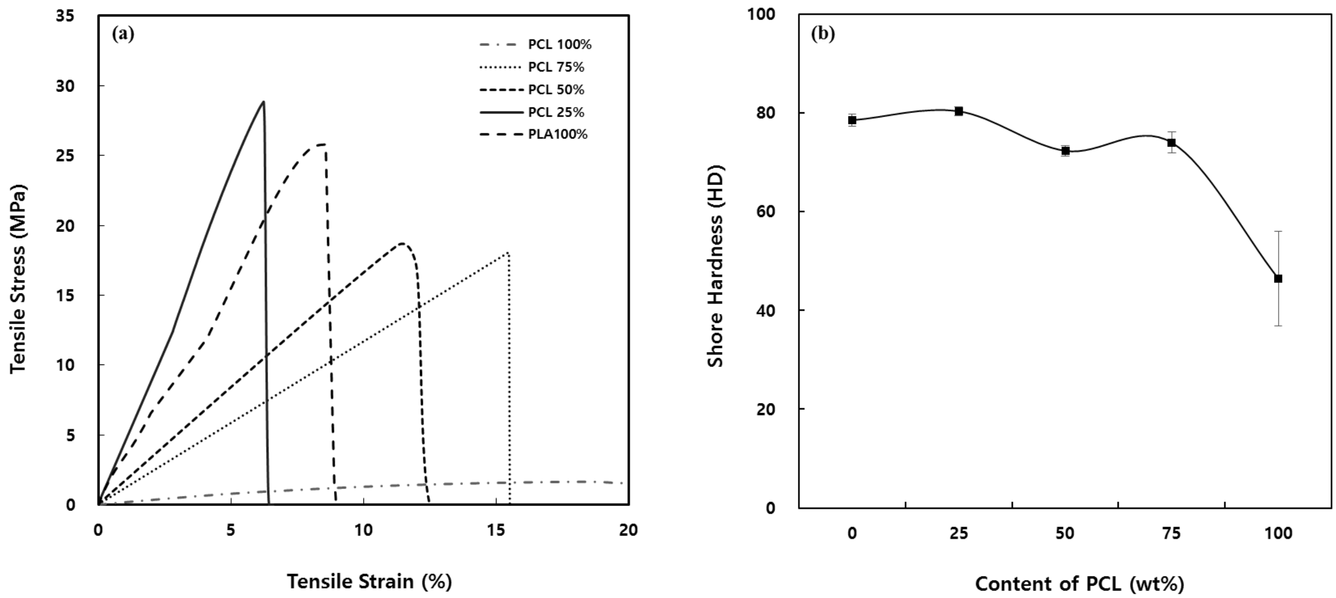


Figure 4.5 Tensile tested samples

Table 4.2 Results of mechanical test

Contents	Maximum Load (N)	Tensile strain at Maximum Load (mm/mm)	Tensile stress at Maximum Load (MPa)	Young's Modulus (MPa)	Maximum Tensile strain (mm/mm)
PCL 0%	**448.36**	**0.08**	**25.76**	**399.83**	**0.20**
PCL 25%	**529.20**	**0.06**	**28.84**	**577.27**	**0.08**
PCL 50%	**415.02**	**0.11**	**18.55**	**299.19**	**2.69**
PCL 75%	**374.47**	**0.17**	**18.50**	**241.02**	**4.02**
PCL100%	**270.59**	**8.43**	**12.71**	**94.53**	**8.63**

The above table shows (a) Tensile Strain-Stress Curve, (b) Shore Hardness, and (c) Fracture Images (left) PLA 100% (b) PCL 100%.

The stress and strain curve of randomly premixed filament with PCL and PLA can be seen from Figure 4.5. The strength is improved according to increasing the percent of PLA except 25%, and the PCL 50% and 75% blend compositions show the similar mechanical behaviors. As increasing in

content of PCL, the value of Young's modulus and ultimate strength (UTS) were decreased but tensile strain was increased. The slope of the strain-stress curve indicates Young's modulus. The Young's modulus means the degree of deformation and elongated when stretched out the object to hold form either side. The stiffness is relative; therefore, when it is higher, it indicates the sample has more rigid and small deformation. The Figure 4.5 confirmed that the PLA exhibits brittle features while PCL shows the ductile behavior. Typically, immiscible blended materials have poorer mechanical behaviors than purse. The graph of PCL 25%, in particular, has high tensile stress compared with other samples. There are other cases the immiscible blend has strong mechanical property. It can be different depending on the blending process and the melt blending technique is one of these methods [27]. It is proved that the tensile stress and strain are able to be handled by controlling the loading amount of PCL.

The hardness tests were carried out with shore hardness tester. It could be converted to young's modulus; hence, the tendency of hardness can be expected that is similar with modulus. Figure 4.5 exhibits the hardness propensity and said that 25% of PCL is the most rigid as 80HD and pure PCL has weak hardness with around 46HD [28]. The PCL has lots of porous, and it effects on the condition of hardness it is expressed by wide variation. Except for the PCL 25%, intensity of hardness appears decline symptoms with increasing the amount of the PCL.

4.3 CHEMICAL BEHAVIOR

The Bio materials used in the process are PLA 100%, PCL 100% and a mixture of PCL 50% and PLA 50%; the printed parts are shown in the Figure 4.6 these are made to react with the chemical pH of values ranging pH 1, 3 and 5. In order to obtain the pH value, the distilled water is added with certain amounts of acidic or basic solution in order to get the required pH value and the pH meter is used to test the solution. Once the required pH values are obtained, the liquid solution is used for the test of the materials .All acidic solutions have pH values less than 7 and the basic solutions have their pH values

greater than 7. The parts are dipped into the solution for 7 days and dried out. The weights of the samples are noted down before and after dipping them into the solution.

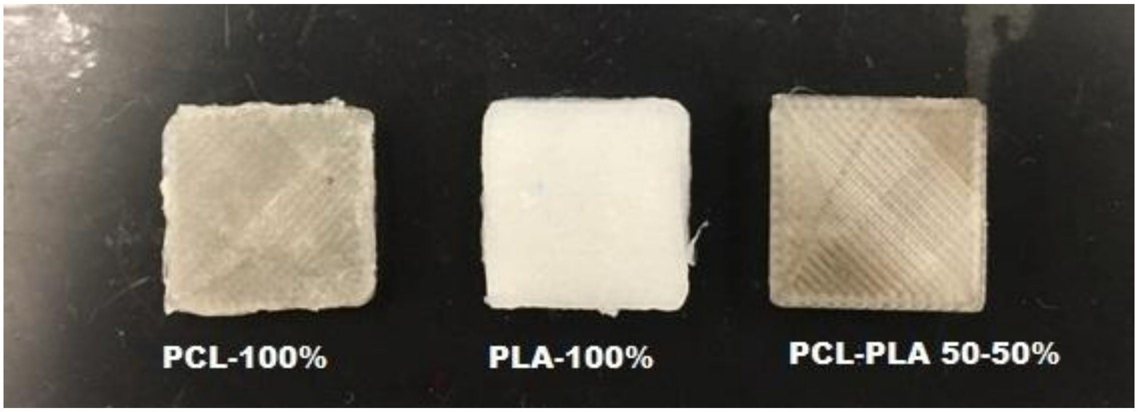


Figure 4.6 Test samples for chemical test

The pH solution are taken into a small container and the bio material sample are immersed into the solution each sample is immersed in the test solution in each jar samples for total immersion test are positioned in such a way that the sample is not touching the bottom of the jar [29]. Later the jars are kept in the incubator or heat chambers (shown in Figure 4.8) and required temperature are set that is 25, 50 and 75 degree Celsius, the samples are made to react for about 24 hours and the initial and final weight are noted down before and after the removal of the sample also the coupon initial and final weight are to be noted down.

Figure 4.7 Heat chamber

Figure 4.8 Sample beakers placed in the heat chamber

As shown in Figure 4.9 the sample weight must be noted down before immersing it into the solution and the weight is noted down ,before using the weighing instrument it must be tare to zero in order to avoid errors and the calibration readings must be corrected and adjusted.

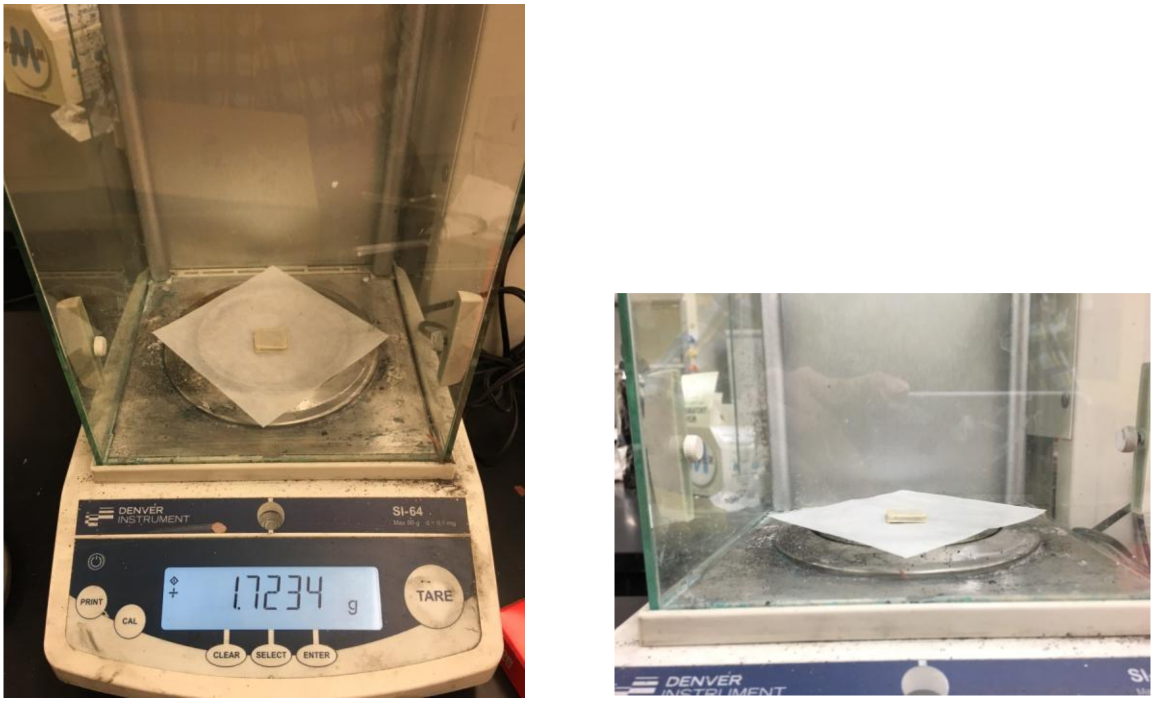


Figure 4.9 weighing instrument

The test samples are kept dry when taking the initial and the final readings also the coupons are dried before using them to prevent moisture and to make sure there are no errors in the readings and the values are accurate.

4.4 APPLICATION OF DESIGN OF EXPERIMENTS

A statistical model is developed using Taguchi method to improve the quality of material by estimating the corrosion behavior and likewise to determine specific material mixture and parameters required. As we have three variables with three parameters we choose a L9 method [30].

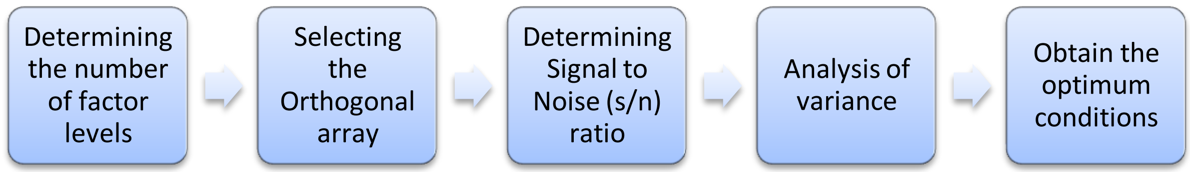
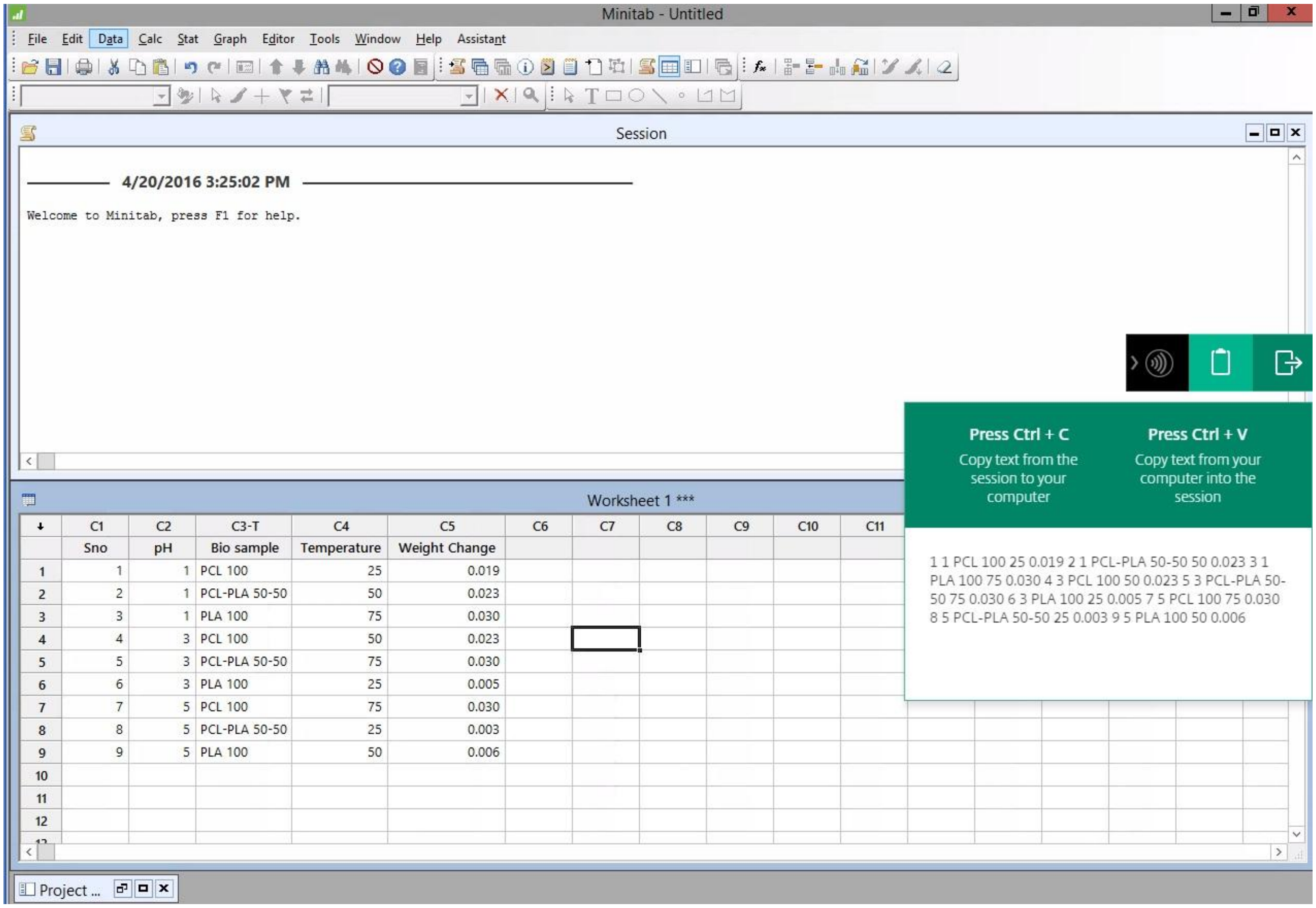


Figure 4.10 Design Of experiments process

Table 4.3 Design and data for the Taguchi design matrix

S no	pH	Bio Sample	Temperature	Weight Change
1	1	PCL 100	25	0.019
2	1	PCL-PLA 50-50	50	0.023
3	1	PLA 100	75	0.030
4	3	PCL 100	50	0.023
5	3	PCL-PLA 50-50	75	0.030
6	3	PLA 100	25	0.005
7	5	PCL 100	75	0.030
8	5	PCL-PLA 50-50	25	0.003
9	5	PLA 100	50	0.006

Using Minitab 17 statistical software the step wise procedure is shown below



↓	C1	C2	C3-T	C4	C5
	Sno	pH	Bio sample	Temperature	Weight Change
1	1	1	PCL 100	25	0.019
2	2	1	PCL-PLA 50-50	50	0.023
3	3	1	PLA 100	75	0.030
4	4	3	PCL 100	50	0.023
5	5	3	PCL-PLA 50-50	75	0.030
6	6	3	PLA 100	25	0.005
7	7	5	PCL 100	75	0.030
8	8	5	PCL-PLA 50-50	25	0.003
9	9	5	PLA 100	50	0.006

Figure 4.11: Shows the Addition of data into the Minitab excel

From the above Figure 4.11, initially the Minitab 17 software is opened and the values need to be copied into the clipboard before entering into the Minitab excel. Later on copying the obtained data into the clipboard it is added into the Minitab excel sheet as follows.

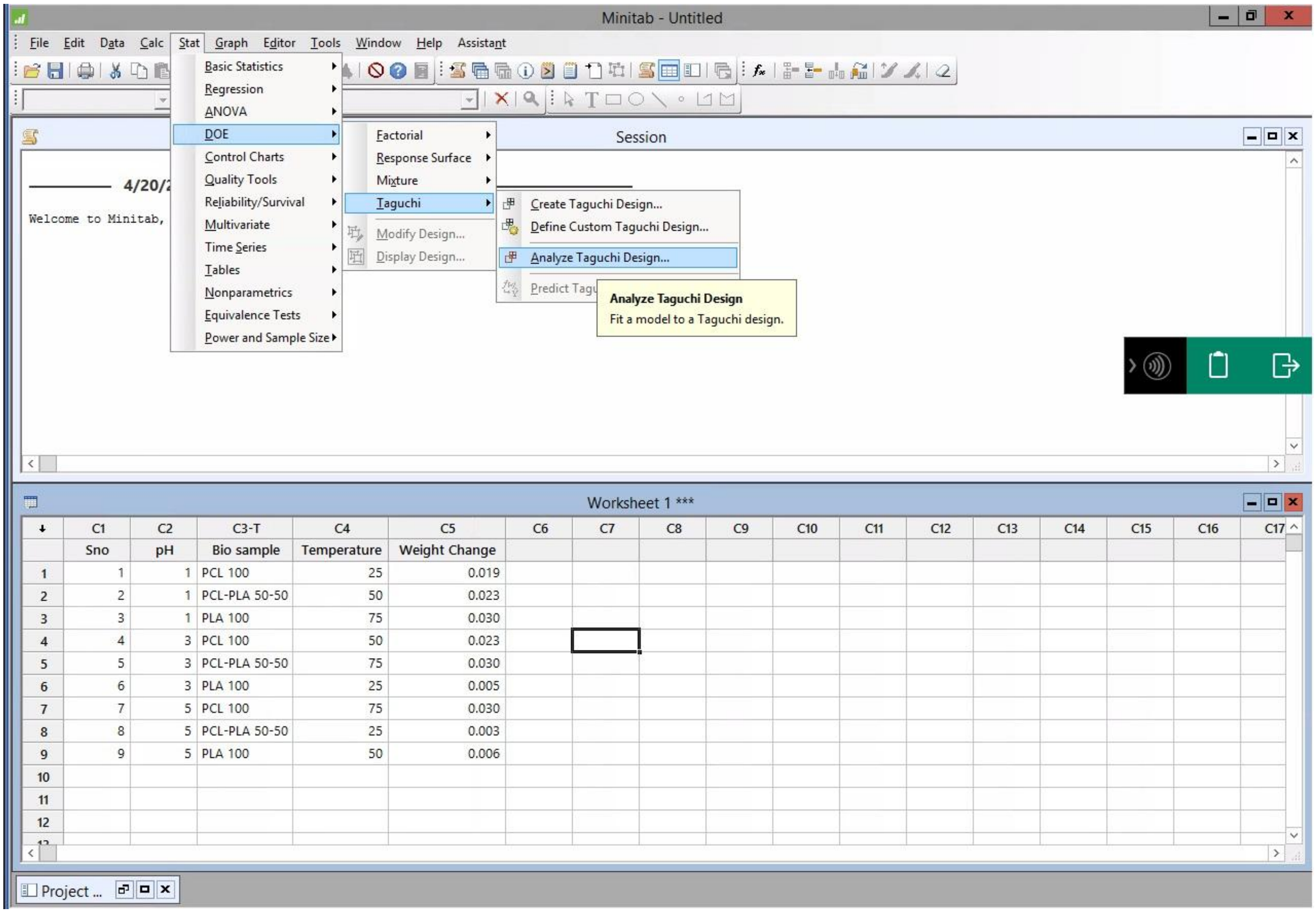


Figure 4.12 Pellets added to the filament extruder

Later Analysis of the Taguchi design needs to be done ,By selecting the Stats option then select as follows Stat > DOE > Taguchi > Analyze taguchi Design

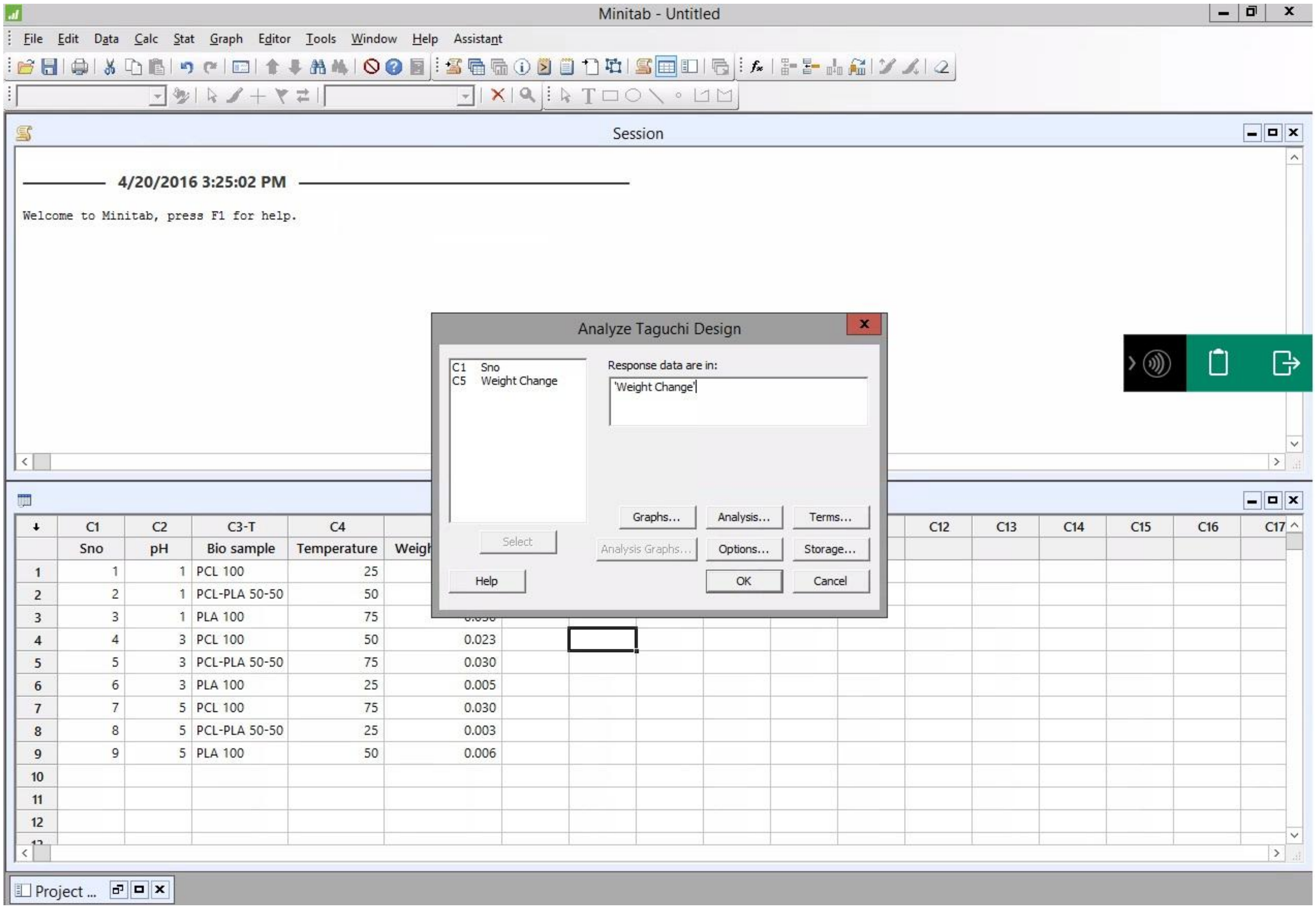


Figure 4.13 Weight Change is selected as response variable

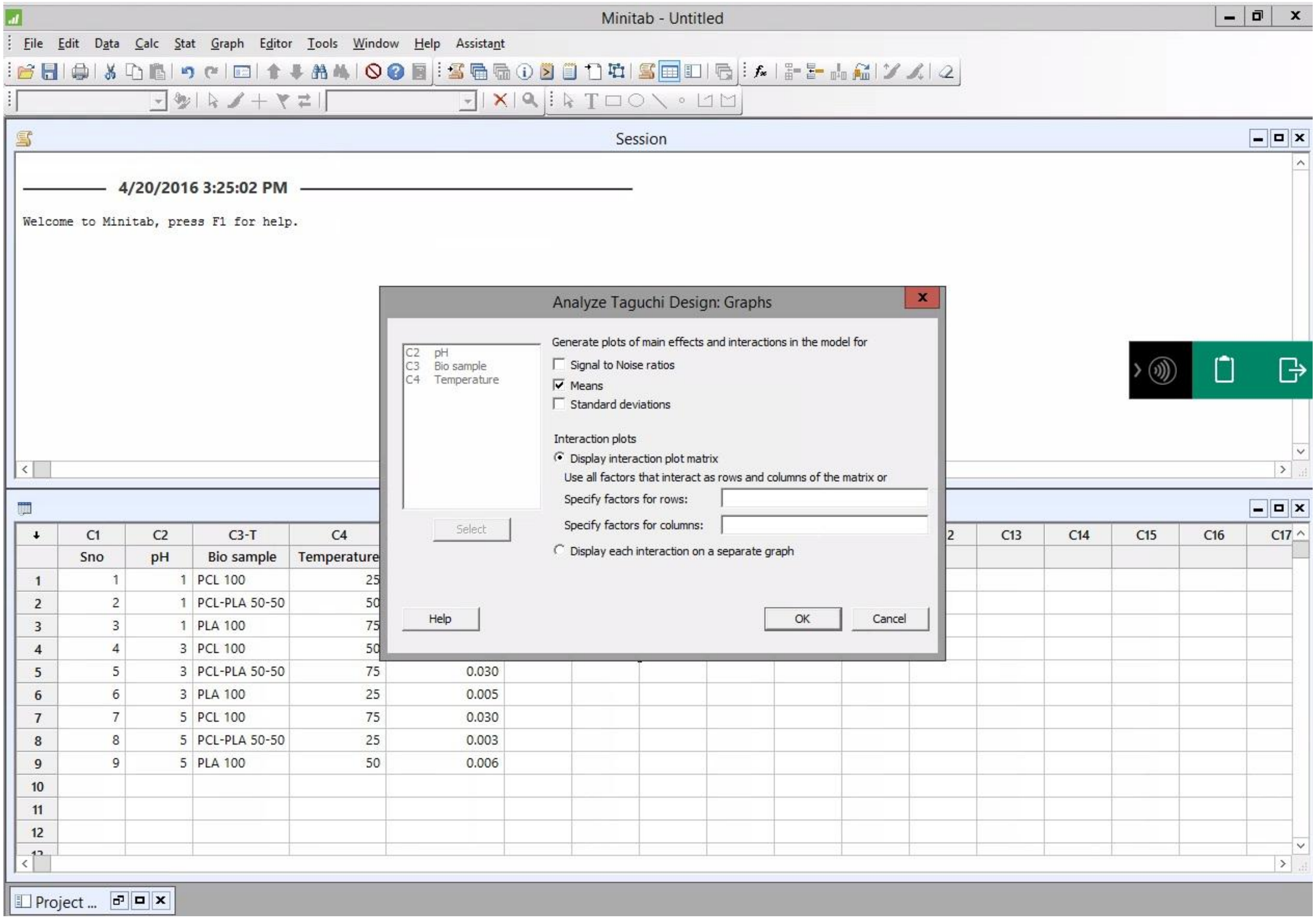


Figure 4.14 Pellets added to the filament extruder

In order to analyze taguchi design of the main effect plot signal to noise ratio is not selected yet as to show the interaction plots.

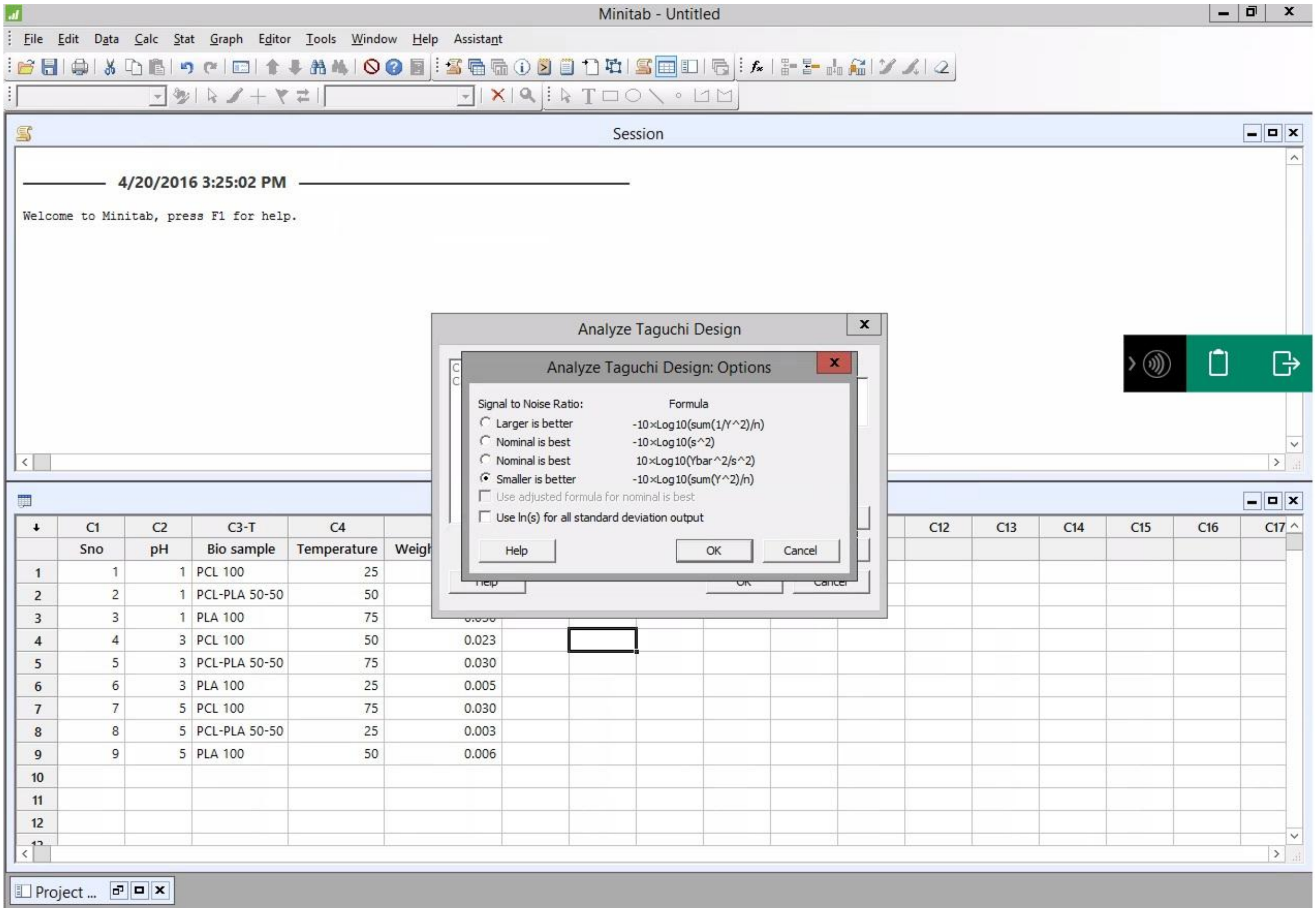


Figure 4.15 selection of s/n ratio

As we need to get the weight change value less and the parameters should be minimized to get the response variable equal to zero we need to choose smaller the better.

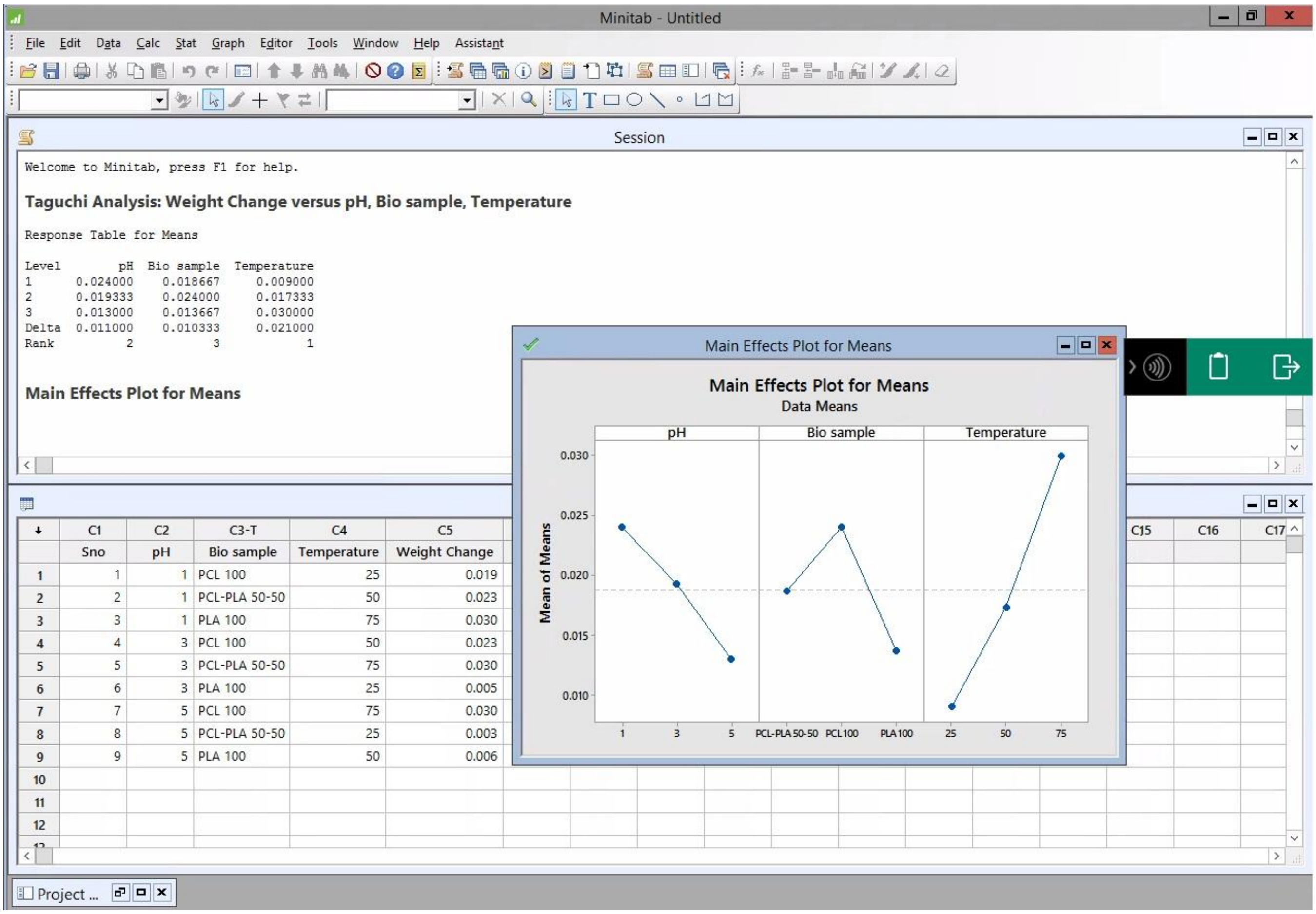


Figure 4.16 Main effect plot Graph

The main effect plot is achieved with x axis showing the three different variables pH (1, 3 and 5) Bio samples (PCL-PLA 50-50,PCL 100,PLA 100) and the Temperature (25,50,75) Y axis showing the Mean of means that is the respones variable weight change.

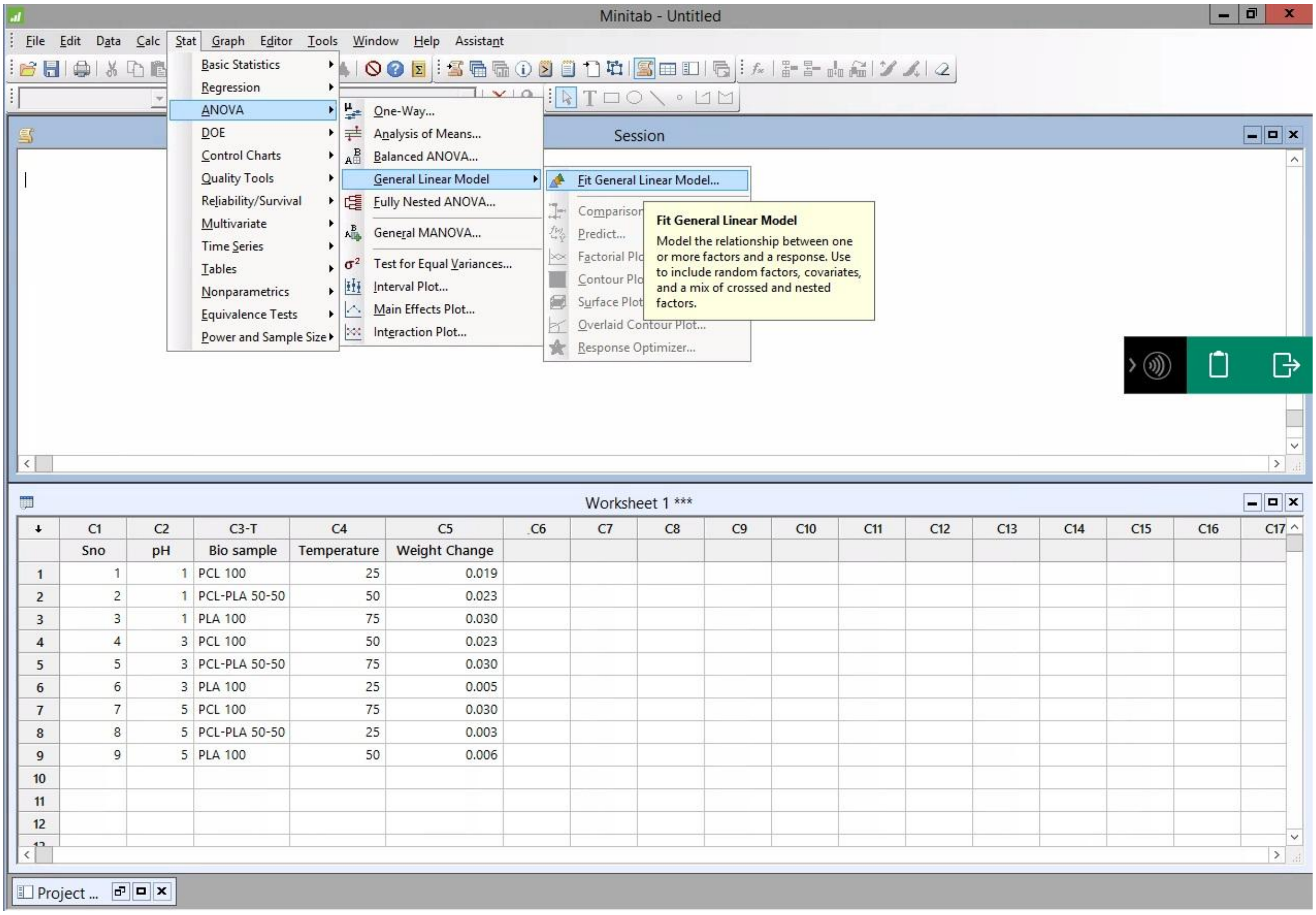


Figure 4.17 General linera model is used to perform ANOVA

To Fit general linear model to achieve ANOVA (analysis of the variance) use Stat > ANOVA > General Linear Model > Fit General Linear Model

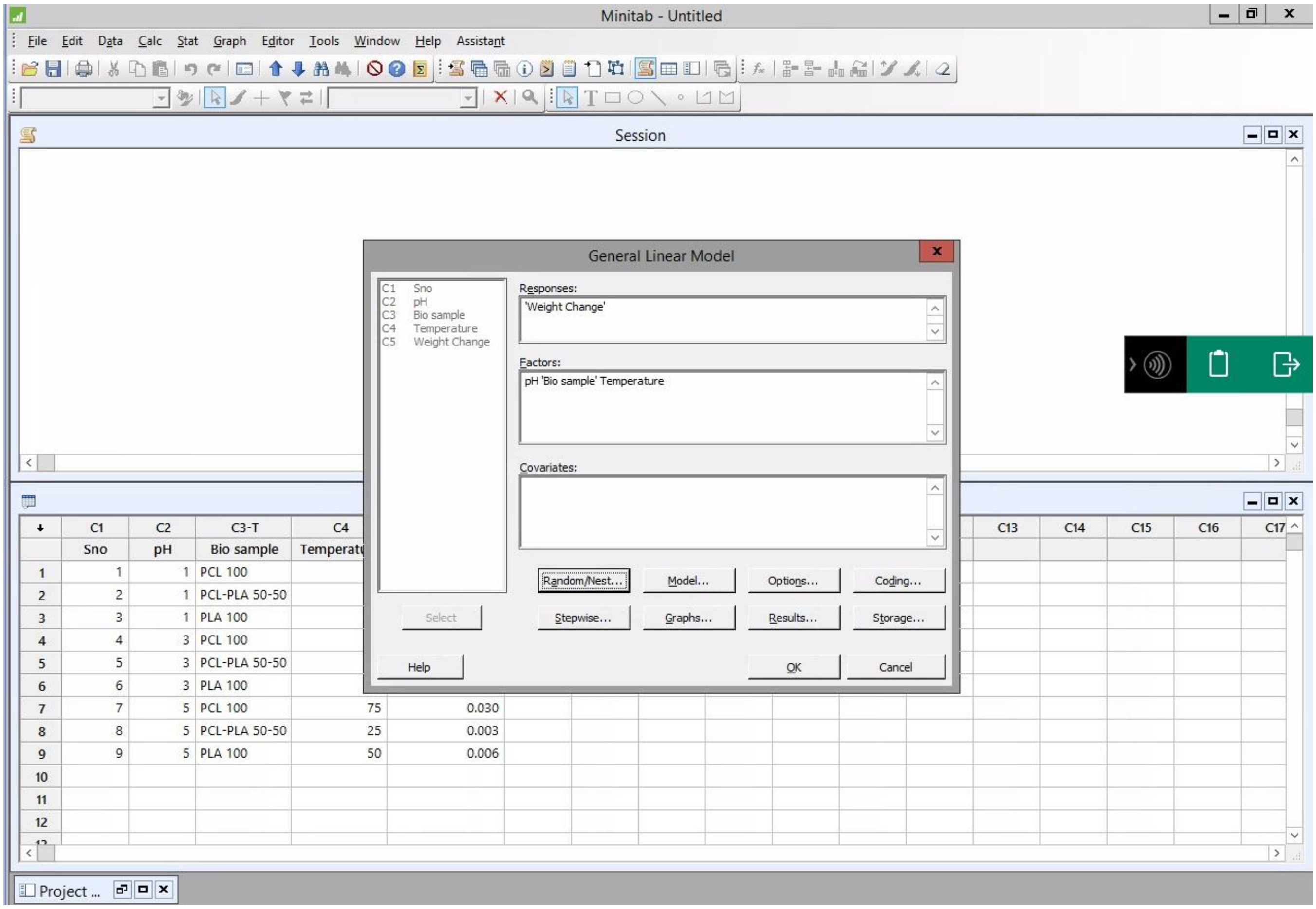


Figure 4.18 Selection of variables

Using GLM(general linear model), we can enter our response column in the Responses field and our three factors in the Factors field without the need to specify one factor as the row and one as the column factor.

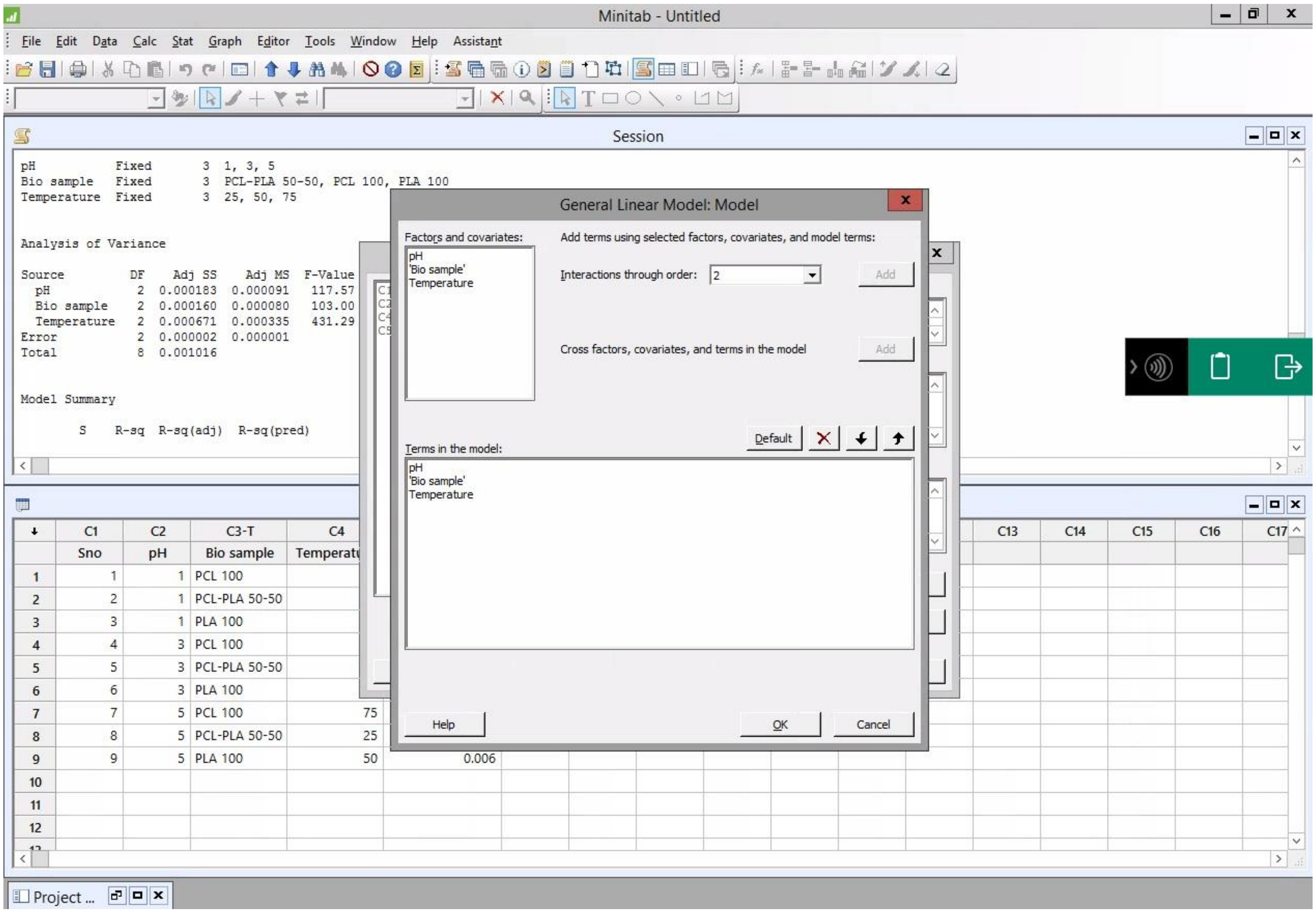


Figure 4.19 General linear model

As in Minitab 16's Two-Way ANOVA option also shows the two-factor interaction, so in Minitab 17 we need to manually add the interaction by clicking the **Model** button in the GLM dialog box. There we can highlight the factors listed on the left side .When we do that, the **Add** button on the right will become available.

3.2.1 Variance of the test samples

As seen in Fig.4.20. The plot between data means and mean of means show the effect of response data. As we choose lower the better or smaller the better pH 5 has much less effect on the bio sample, so as at 25 degree Celsius temperature it shows less effect. The Bio sample PLA 100% pure has good weight loss resistance compared to other PCL and PLA-PCL composition.

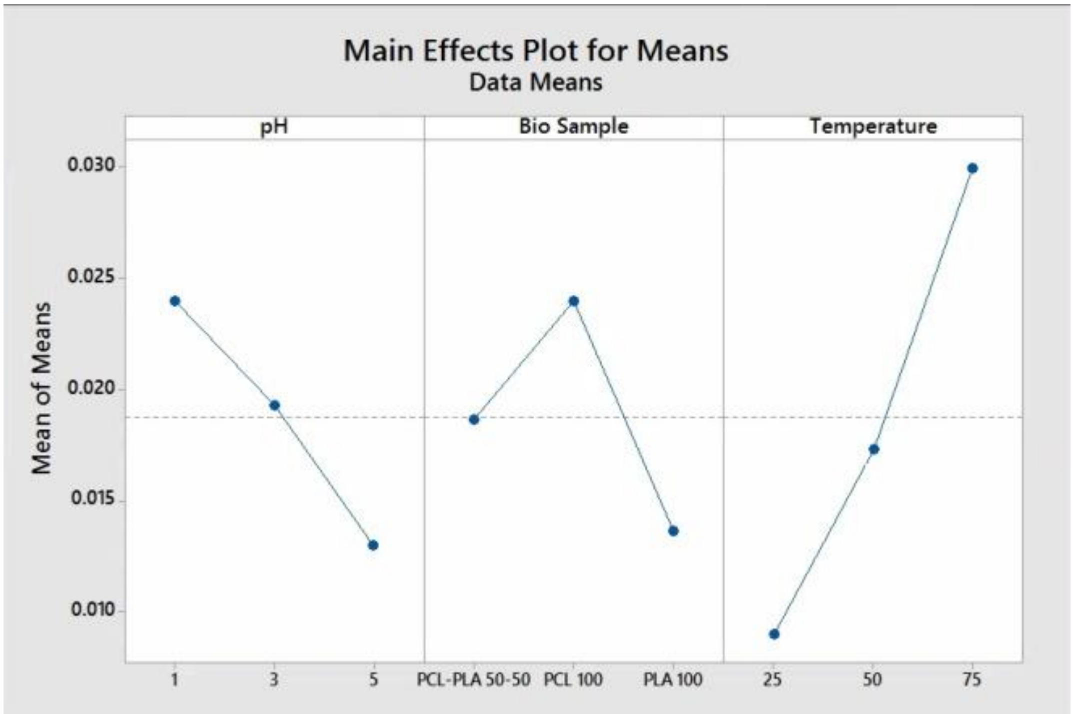


Figure.4.20. Main effect Plot for means versus Mean of Means Plot

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
pH	2	0.000183	0.000091	117.57	0.008
Bio Sample	2	0.000160	0.000080	103.00	0.010
Temperature	2	0.000671	0.000335	431.29	0.002
Error	2	0.000002	0.000001		
Total	8	0.001016			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0008819	99.85%	99.39%	96.90%

Figure.4.21. Analysis of variance (ANOVA) from Minitab

As seen in Fig 4.21 both pH and Temperature are significant at 95% confidence interval from general linear model. The higher the R^2 value, the better the model fits. The results of ANOVA indicate that R^2 of 99.85% means the model is best fit.

3.2.2 Identifying the best process parameters

Figure 4.23 shows rank order where Temperature plays a vital role in determining the means.

Taguchi Analysis: Weight Change 1, Weight Change 2 versus pH, Bio Sample, Temperature

Response Table for Means

Level	pH	Bio Sample	Temperature
1	0.022000	0.017167	0.007500
2	0.017333	0.021667	0.015333
3	0.011667	0.012167	0.028167
Delta	0.010333	0.009500	0.020667
Rank	2	3	1

Figure 4.22 Shows rank order of the variables

After conducting the second set of experiment weight change values are noted down

Table 4.4 Taguchi design matrix with both set of results

S no	pH	Bio Sample	Temperature	Weight Change 1	Weight Change 2
1	1	PCL 100	25	0.019	0.015
2	1	PCL-PLA 50-50	50	0.023	0.019
3	1	PLA 100	75	0.030	0.026
4	3	PCL 100	50	0.023	0.017
5	3	PCL-PLA 50-50	75	0.030	0.027
6	3	PLA 100	25	0.005	0.002
7	5	PCL 100	75	0.030	0.026
8	5	PCL-PLA 50-50	25	0.003	0.001
9	5	PLA 100	50	0.006	0.004

Taguchi Analysis: Weight Change 1, Weight Change 2 versus pH, Bio Sample, Temperature

Predicted values

```
S/N Ratio        Mean      StDev
  54.4231  -0.0026667  0.0010999


Factor levels for predictions

    Bio
pH  Sample  Temperature
 5  C                25
```

Figure 4.23 Predicted values of Signal to noise ratio and its optimum parameters

From the Figure 4.23 we can say that the best significant factors are pH value 5 , temperature 25 and the Bio sample C which is PLA 100% pure. They have less corrosion rate compared to that off other materials.

Both Figures 4.24 and Figure 4.25 show the interactions between both Bio sample or Bio material and Temperature change which shows that all the materials interact at a common temperature 75 degrees Celsius and the material PCL 100 and PCL-PLA 50-50 interact at temperature 50 degree Celsius and at 25 degrees the materials react unevenly so tests must be done in temperature range of 25 to 50 degree Celsius.

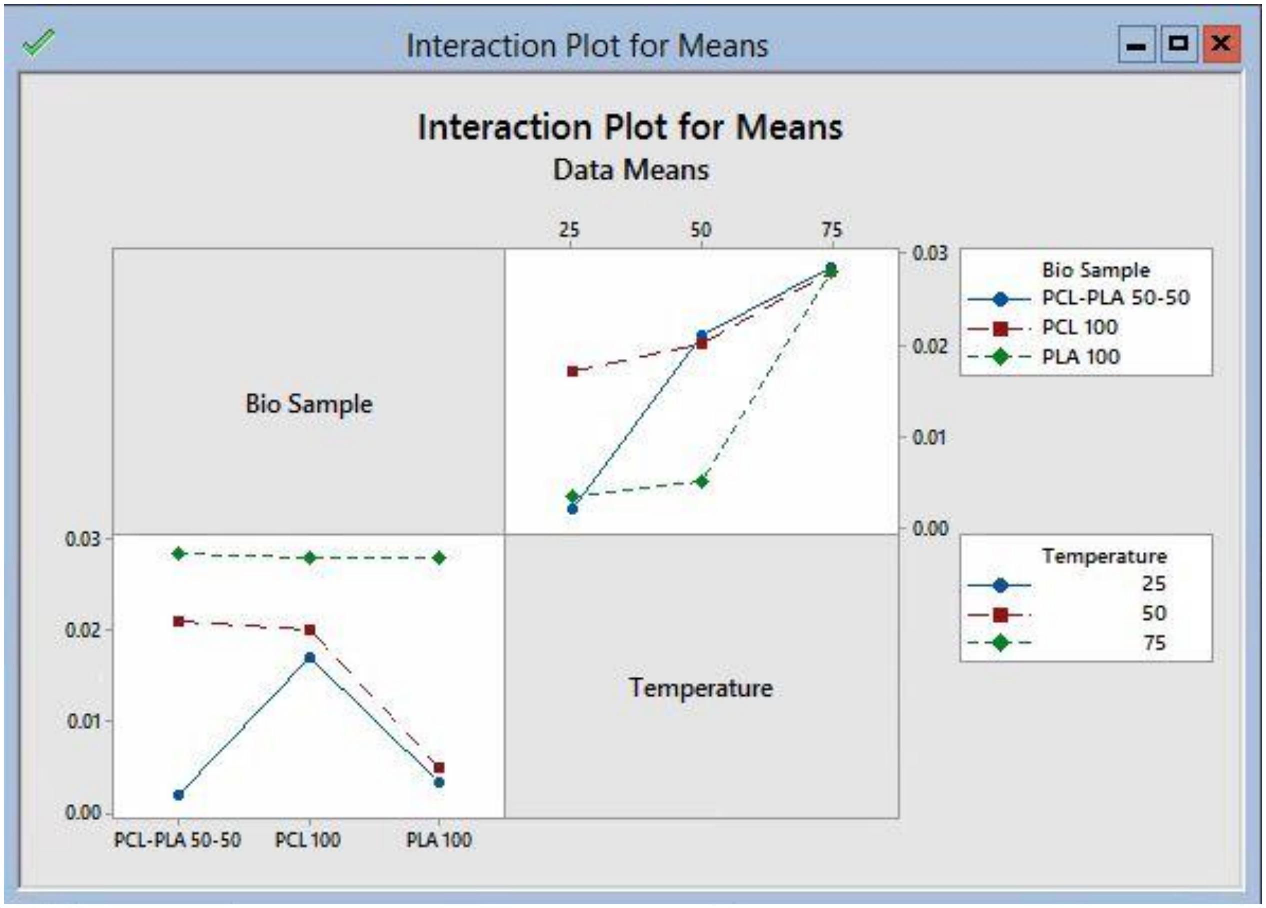


Figure 4.24 Interaction Plot for Bio sample and Temperature

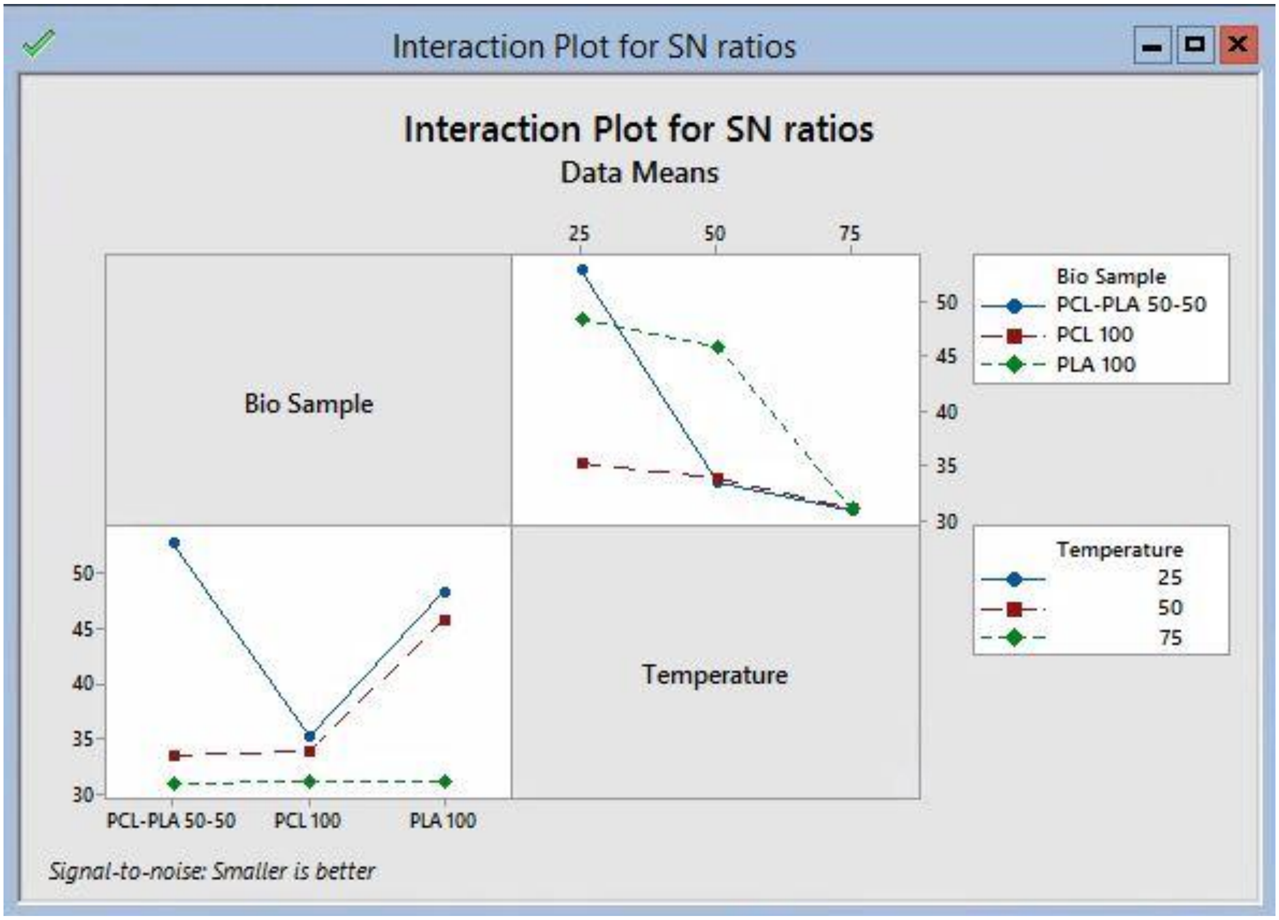


Figure 4.25 Interaction plot for S/N ratio of Bio sample and temperature

Also from the Figure 4.26 and Figure 4.27 the interaction plot shows the reaction of both pH and Bio sample or bio materials where the pH 1 effects PLA 100 more than remaining materials and PLA does no react much to remaining two pH values.

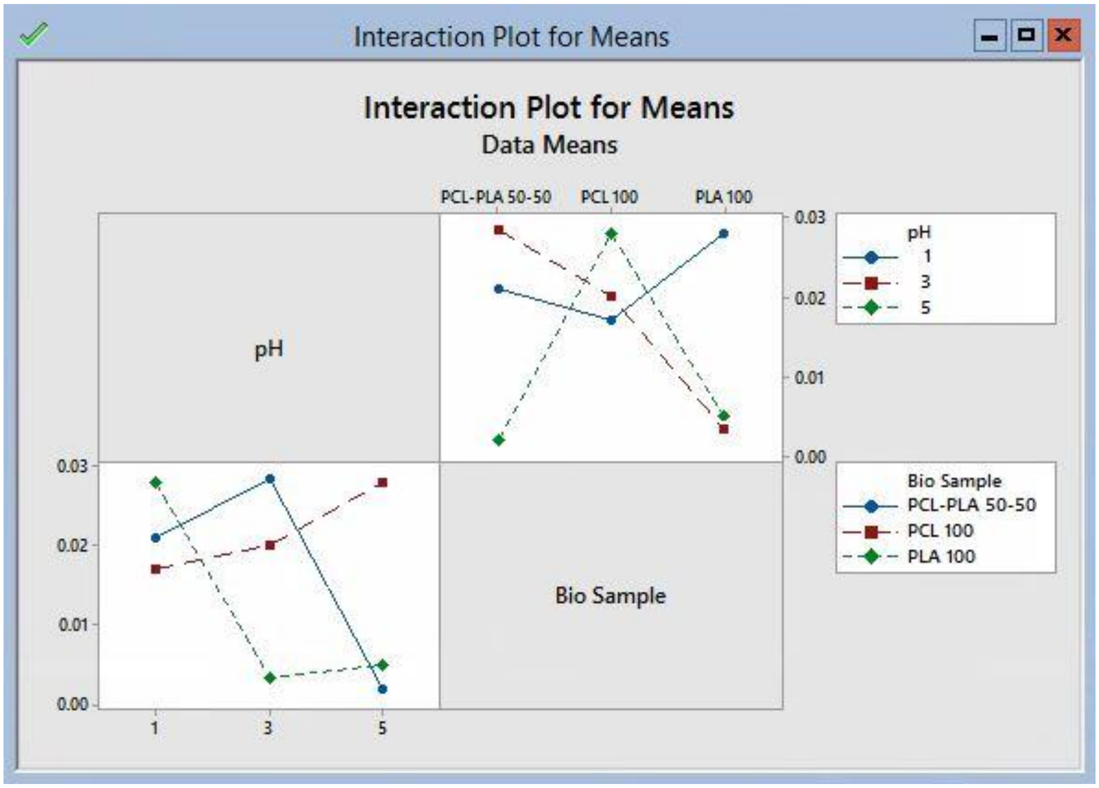


Figure 4.26 Interaction plot for Bio sample and pH change

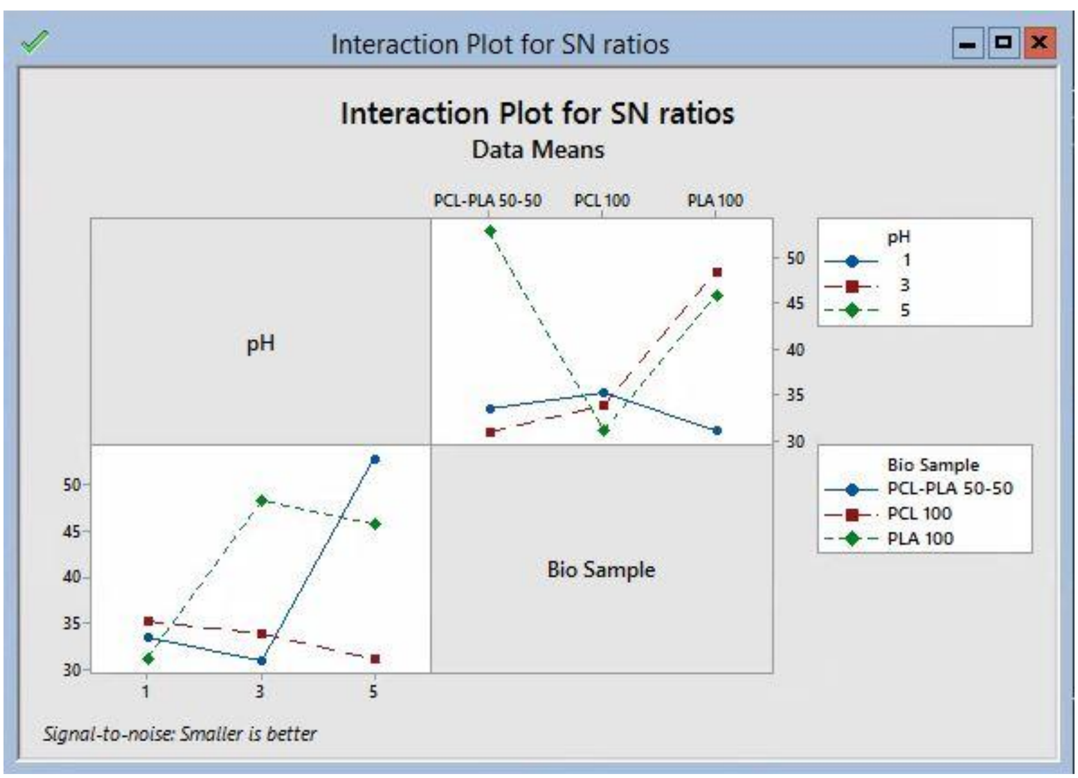


Figure 4.27 Interaction plot for S/N ratios of both pH an Bio sample

The interaction plot between pH and Temperature shows some constant range where at lower temperature there's no change in the pH compared to higher temperature ranges.

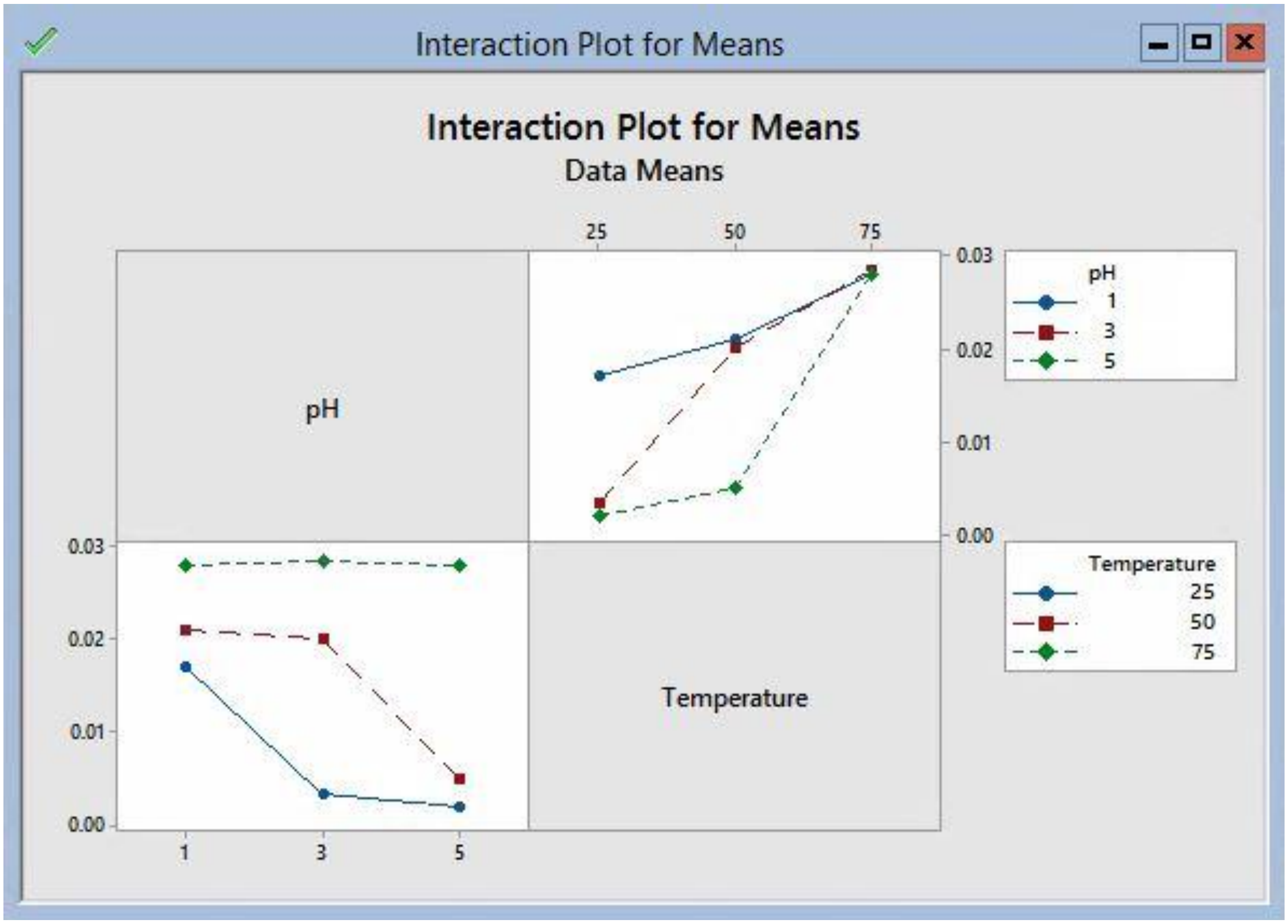


Figure 4.28 Interaction plot for pH and temperature change

The plot shows that at higher temperature all pH interact more which means there is change in the concentration levels as they react more.

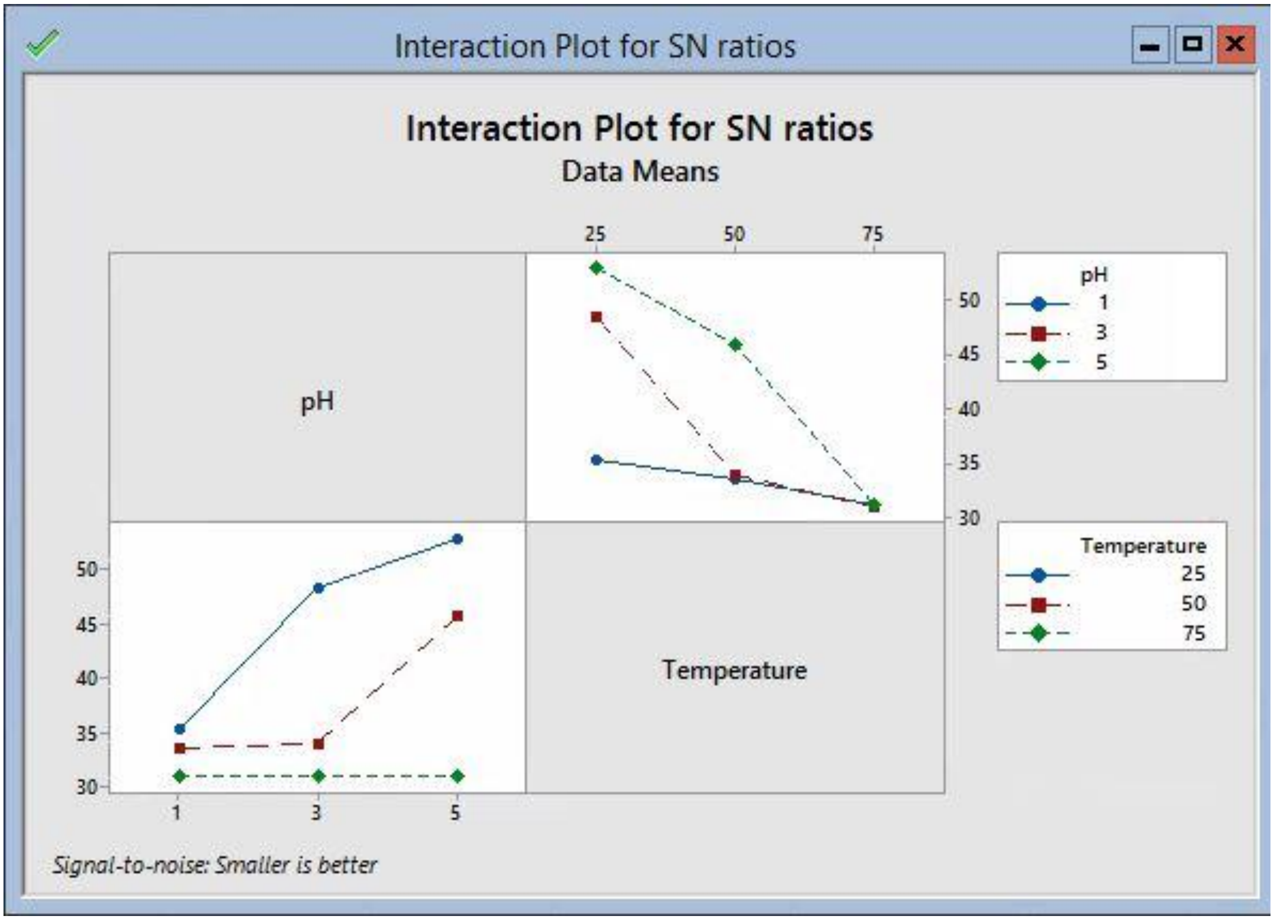


Figure 4.29 Interaction plot for S/N ratios of both pH and Temperature change

Chapter 5: Conclusion

The insights into the results obtained in the previous chapter and conclusions based on them were presented in this chapter. The purpose of this work is to determine the mechanical properties of the bio materials used and to estimate the parameters which effect the corrosion rate of the bio materials. The immiscible polymers PCL and PLA were manufactured by the melt blending technique, The blended pellets were extruded by the screw extruder and then the samples for the mechanical test and chemical were fabricated.

From the mechanical properties we determine that PLA 100% pure is harder material compared to that of PCL 100% and also PLA has rigid property and the PCL has shrinking property from the results we can see that mixture of PCL 25% and PLA 75% have highest tensile strength but in order to determine the corrosion behavior we choose the materials PCL100%,PLA 100% and PCL-PLA 50-50 mixture.

The results from the Taguchi design show us that the optimum process parameters are at Temperature of 25 degrees Celsius , pH 5 and the material with less weight loss is PLA 100% pure. Also we cn determine that temperature has more effect on the weight loss or corrosion rate of the bio sample than the bio sample itself.

Chapter 6: Future work

As in the current work the proposed methodology was applied to only three bio samples and with three different parameters in three different variables more changes can be done by selecting more number of parts and much more complicated orthogonal array to benchmark the taguchi method. It needs to be tested on wide variety of bio samples to completely validate the methodology through various process parameters. Also various other parameters can be taken into consideration to conduct much deeper sets of experiments and to achieve the best bio material in bio field.

References

[1] Schmalz, G., & Arenholt-Bindslev, D. (2009). *Biocompatibility of dental materials*. Berlin: Springer.

[2] F. Witte, (2010) The history of biodegradable magnesium implant, *Acta Biomaterialia, 69*(5), 1680-1692

[3] R.D. Erba, G. Groeninckx, G.maglio, M. Malinconoco, and A. Migliozzi, (2001) Immiscible polymer blends of semicrystalline biocompatible componenets: thermal properties and phase morphology analysis of PLLA/PCL blends, polymer, 42, 7831-7840

[4] H.S. Brar, M.O. Platt, M. Samtinoranont, P.I. Martin, and M.V. Manuel, (2009) Magnesium as a biodegradable and bioabsorbable material for medical implants, Biomedical Materials And Devices, 61(9), 31-34

[5] D.F Williams, (2009) , Biomaterials, 30, 5897-5909

[6] H. Cai, V. Dave, R.A. Gross, and S.P. Carthy, (1996) Journal of Polymer Science part B: Polymer Physics, 34 (16), 2701-2708

[7] Yeong, W., Chua, C., Leong, K., & Chandrasekaran, M. (2004). Rapid prototyping in tissue engineering: Challenges and potential. *Trends in Biotechnology, 22*(12), 643-652. doi:10.1016/j.tibtech.2004.10.004

[8] Vaezi, M., & Yang, S. (2014). Freeform fabrication of nanobiomaterials using 3D printing. *Rapid Prototyping of Biomaterials,* 16-74.

[9] Korpela, J., Kokkari, A., Korhonen, H., Malin, M., Närhi, T., & Seppälä, J. (2012). Biodegradable and bioactive porous scaffold structures prepared using fused deposition modeling. *Journal of Biomedical Materials Research Part B: Applied Biomaterials J. Biomed. Mater. Res., 101B*(4), 610-619. doi:10.1002/jbm.b.32863

[10] Hutmacher, D. W., Schantz, T., Zein, I., Ng, K. W., Teoh, S. H., & Tan, K. C. (2001). Mechanical properties and cell cultural response of polycaprolactone scaffolds designed and fabricated via fused deposition modeling. *Journal of Biomedical Materials Research J. Biomed. Mater. Res., 55*(2), 203-216. doi:10.1002/1097-4636(200105)55:23.0.co;2-7

[11] M.I. Sabir, X. Xu, Li. Li A review on biodegradable polymeric materials for bone tissue engineering application J. Mater. Sci., 44 (21) (2009), pp. 5713–5724

[12] Ramkumar, D. H., & Bhattacharya, M. (1998). Steady shear and dynamic properties of biodegradable polyesters. *Polym. Eng. Sci. Polymer Engineering & Science, 38*(9), 1426-1435. doi:10.1002/pen.10313

[13] Patrício, T., & Bártolo, P. (2013). Thermal Stability of PCL/PLA Blends Produced by Physical Blending Process. *Procedia Engineering, 59*, 292-297. doi:10.1016/j.proeng.2013.05.124

[14] Ornaghi, H. L., Bolner, A. S., Fiorio, R., Zattera, A. J., & Amico, S. C. (2010). Mechanical and dynamic mechanical analysis of hybrid composites molded by resin transfer molding. *Journal of Applied Polymer Science J. Appl. Polym. Sci.* doi:10.1002/app.32388

[15] Shard, A. G., & Tomlins, P. E. (2006). Biocompatibility and the efficacy of medical implants. *Regenerative Medicine, 1*(6), 789-800. doi:10.2217/17460751.1.6.789

[16] Kappelt G, Kurze P, Banerjee D. Method for producing a corrosion-inhibiting coating on an implant made of a bio-corrodible magnesium alloy and implant produced according to the method. US Patent 20080243242, 2008

[17] Arnold H, Deutchman ,RJ, Partyka RJ, Borel. Orthopaedic implants having self-lubricated articulating surfaces designed to reduce wear, corrosion, and ion leaching. US Patent 20080221683, 2008.

[18] Q. Fang, and M.A. Hanna, (1999) Rheological properties of amorphous and semicrystalline polylactic acid polymers, Industrial Crops and Products, 10, 47-53

[19] A.K. Matta, R.U. Rao, K.N.S. Suman, and V. Rambabu, (2014) Preparation and characterization of biodegradable PLA/PCL polymeric blends, procedia Materials Science, 6, 1266-1270

[20] T. Patricio, M. Domingos, A. Gloria, and P. Bartolo, (2013) Characterization of PCL and PCL/PLA scaffolds for tissue engineering, Procedia CIRP, 110-114

[21] Rao, R. S., Kumar, C. G., Prakasham, R. S., & Hobbs, P. J. (2008). The Taguchi methodology as a statistical tool for biotechnological applications: A critical appraisal. *Biotechnol. J. Biotechnology Journal, 3*(4), 510-523. doi:10.1002/biot.200700201

[22] O'connor, P. D. (1990). Quality through Design: Experimental Design, Off-Line Quality Control and Taguchi's Contributions, N. Logothetis and H. P. Wynn, Oxford University Press, 1990. Number of pages: 464, Price: £50.00. *Qual. Reliab. Engng. Int. Quality and Reliability Engineering International, 6*(2), 161-161. doi:10.1002/qre.4680060217

[23] Asafa, T., Tabet, N., & Said, S. (2013). Taguchi method–ANN integration for predictive model of intrinsic stress in hydrogenated amorphous silicon film deposited by plasma enhanced chemical vapour deposition. *Neurocomputing, 106*, 86-94. doi:10.1016/j.neucom.2012.10.019

[24] Anand, K. A., Jose, T. S., Agarwal, U. S., Sreekumar, T. V., Banwari, B., & Joseph, R. (2010). PET-SWNT Nanocomposite Fibers through Melt Spinning. *International Journal of Polymeric Materials, 59*(6), 438-449. doi:10.1080/00914030903538587

[25] Booy, M. L. (1963). Influence of channel curvature on flow, pressure distribution, and power requirements of screw pumps and melt extruders. *Polym. Eng. Sci. Polymer Engineering and Science, 3*(3), 176-185. doi:10.1002/pen.760030305

[26] Arai T and Aoyam H (1963), 'Die wall restriction on elastic shear deformation in viscoelastic fl ow of polymer melt', *Transactions of Society of Rheology* , **7** , 333–355

[27] B.A. Ibrahim, and K.M. Kadum, (2010) Influence of polymer blending on mechanical and thermal properties, Modern Applied Science, 4(9), 157-161

[28] Lim, L., Auras, R., & Rubino, M. (2008). Processing technologies for poly(lactic acid). *Progress in Polymer Science, 33*(8), 820-852. doi:10.1016/j.progpolymsci.2008.05.004

[29] Guide for Laboratory Immersion Corrosion Testing of Metals. (n.d.). doi:10.1520/g0031-12

[30] Summerscales, J. (1990). Taguchi methods (Proc 1988 European Conference) Editor: Professor A. Bendell Elsevier Applied Science Publishers, London, 1989 ISBN 1-85166-333-9 pp 212 xv. *Composites Manufacturing, 1*(1), 52-53. doi:10.1016/0956-7143(90)90277-4

Vita

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Symposium (2016): S. D.Kilari., N.Kim., & B.Tseng. (2016, April 9). A Novel Approach to Estimate Corrosion Effect in 3D Printed Bio Material's using Taguchi Method. Retrieved April 9, 2016, from http://engineering.utep.edu/sets/docs/SETS2016.pdf

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