The Effect of Blending Ratio of the Chemically Modified Tapioca Starch Coating Material on Its Physical Properties

by

Afifi Aznan

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

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(DR KU ZILATI KU SHAARI)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or person.

AFIFI AZNAN

ABSTRACT

Encapsulation of urea fertilizer through polymeric membranes to control the release rate of urea fertilizer gradually can maximize the efficiency of nutrient release for plant uptake and minimize environmental pollution. A biodegradable chemically modified tapioca starch film for coating the urea fertilizer will be prepared.

The effect of blending ratio of the chemically modified tapioca starch (CMTS) coating material on its moisture absorption, swelling rate, degradability and water retention ability were investigated. The optimum blending ratio of polyvinyl alcohol-tapioca starch-formaldehyde-urea formaldehyde which poses the best quality of coating material based on the moisture absorption, swelling rate, degradability and water retention ability will be selected for further studies.

In order to investigate the quality of the controlled release fertilizer encapsulated by CMTS, a deep research will be recommended to study the nutrient release pattern and the efficiency of controlled release material.

ACKNOWLEDGEMENTS

This project cannot have been a success if there are no guidance, ideas, assistance, support and advice from many. Without the help of my supervisor, Dr. Ku Zilati Ku Shaari, this dissertation would not have been possible. It is to my supervisor that I owe my deepest gratitude. First and foremost, I express my sincerest gratitude to Dr. Ku Zilati Ku Shaari for persevering with me as my supervisor despite her many other academic and professional commitments. Her wisdom, knowledge and commitment to the highest standards inspired and motivated me.

She has made available her generous help and guidance in a number of ways in spite of her other commitments and busy schedule as a senior lecturer. Lastly, I would like to thank my family and friends for their never-ending support and encouragement throughout the entire course of completing this project.

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CHAPTER 1

INTRODUCTION

1.1. Background of Study

Fertilizers are one of the most important products of the agro-chemical industry because fertilizers are the foundation for the increase of crop yield and offer the material security for sustainable agriculture[1-2]. The effectiveness of soil-applied fertilizers depends mainly on their ability to maintain a sufficient concentration of the nutrients within the plant root zone for a desired period of time. In most commercially available fertilizers, the concentrations of the fertilizer active ingredients rapidly diminish prior to sufficient plant uptake due to degradation (e.g., chemical, photochemical and biological), volatilization, leaching, adsorption or land immobilization. In order to increase the effectiveness of conventional fertilizers, relative large dosages are often applied, thus, increasing the environmental risk. In order to overcome this crisis, controlled release fertilizer has been developed, and used to improve the efficiency of fertilizer use, prevent and alleviate the environmental pollution from loss of fertilizers[3]. Many studies have been done; but mainly focused on the selection of coating film materials. The coating film materials developed can be divided into two main varieties, inorganic minerals and organic polymer. Inorganic minerals such as silicon and sulphur can be easily found with low price. And the coating film remaining in the soil after nutrient release may be decomposed naturally, which not only supply some minor nutrients and improve soil structure, but also show the environmental friendly characteristics. However, the concentration may not be high enough, leading to bad control of nutrients in soil. In contrast, the use of organic polymer as coating film has shown good control of nutrients. However, the organic polymer coating film comes with high cost due to the sophisticated technical process. Furthermore, the organic polymer coating film is not easy to decompose naturally, leading to a risk of soil pollution[2]. Therefore, the study on the new potential material for controlled release material is required in the development of cheap and environmental friendly coating film materials with good nutrient release is necessary and crucial. For this project, the tapioca starch will be studied to investigate the potential of this organic polymer in the controlled release application.

1.2. Problem Statement

Problem Identification

The high cost and environmental hazard issues of the use of synthetic polymer in controlled release fertilizer are the drive force to come out with new alternative which more cost effective and safe.

Significant of the Project

This project can benefit the development of agricultural sector as well as preserving the Mother Nature where if the tapioca starch which is a biomass-polymer coating film is proven to be more efficient as a controlled release material for urea coating, the production cost will be reduced since the tapioca starch can be easily found in Malaysia and good for environment.

1.3. Objective

There are two main objectives of this research.

1.3.1. To formulate a controlled release coating material from tapioca starch known as Chemically Modified Tapioca Starch (CMTS)
1.3.2. To investigate the effect of blending ratio of coating material on:
    1.3.2.1. Moisture content
    1.3.2.2. Swelling rate
    1.3.2.3. Degradation
    1.3.2.4. Water retention in soil

CHAPTER 2

LITERATURE REVIEW

2.1. Controlled Release Materials

There are two varieties of coating materials which are inorganic minerals and organic polymer. Table 1 below shows the comparison between those two.

Table 1: Comparison between Inorganic Minerals and Organic Polymer[2]

Inorganic Minerals	**Organic Polymer**
Silicon, Sulfur, Gypsum, Phosphates, Zeolete, Bentonite, Maifanitum, Diatomite, etc.	1. ***Natural macromolecular*** (eg: starch, fibrin, natural rubber, etc.) 2. ***High molecular synthetic material*** (eg: polyethylene, polyvinyl chloride, etc.) 3. ***High molecular semi-synthetic material*** (eg: ethyl cellulose)
Advantage	
1. Cheap and available 2. Environmental friendly – decomposed naturally 3. Improve soil structure – supply minor nutrients	1. Good control of nutrients in soil
Disadvantage	
1. Bad control of nutrients in soil – not enough concentration	1. High cost – sophisticated technical process 2. Not easy to decompose naturally – soil pollution

2.2. Starch

Starch is a biodegradable natural macromolecular polymer with excellent biocompatibility and non-toxicity. It is often compounded with other polymers or used alone in the fields controlled release technology; starch is a kind of water soluble macromolecule, it dissolves and leaves pore that accelerate the release rate [2, 4].

Regarding this project, tapioca starch is selected since it easily available in Malaysian market.

2.3. Conceptual Model of Nutrient Release from Coated Fertilizers

The nutrient release process of a coated controlled release fertilizer (CRF) begins with the penetration of water mainly in vapour into the core of fertilizer through the coating. The vapour condenses on the solid core and dissolves part of it, thus inducing a build up of internal pressure. At this stage, there are two possibilities happen. First, if the internal pressure is exceeding the membrane resistance, the coating will rupture so that the content of the granule will release instantaneously; this is called the ‘failure mechanism’ or ‘catastrophic release’. Anyhow, if the membrane resists the internal pressure, the fertilizer will release through diffusion driven by concentration gradient across the coating or through mass flow driven by pressure gradient or through the combination of both. This is called ‘diffusion mechanism’ [5-6].

The graphical explanation can be shown in the Figure 1 below.

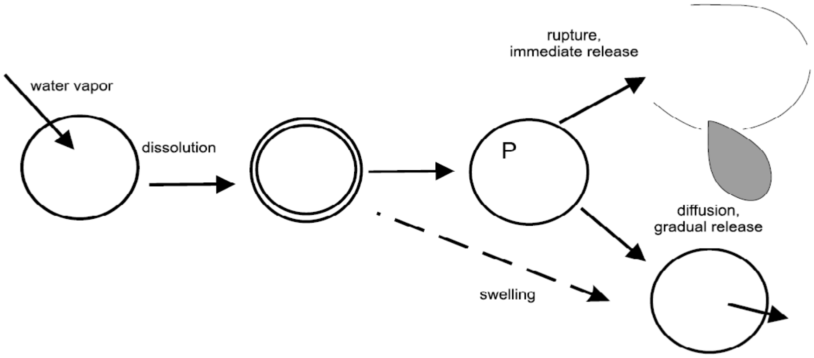

Figure 1: Stage of release from polymer-coated granule [7]

2.4. Water Retention

The application of controlled release fertilizer is influenced by the water retention property that poses by the coating material. The hydrophilic polymer like tapioca starch is capable of swelling and retaining huge volumes of water in the swollen state. The hydrophilic polymer have a potential to be commercialize in agricultural applications since it has shown encouraging results as they have been observed to help reduce irrigation water consumption, lower the death rate of plant, improve fertilizer retention in soil and increase the plant growth rate [8].

The water retention of the tapioca starch can be measured by the water swelling ratio. The water swelling ratio of the polymer can be calculated as follows [4, 9]:

$$WSR = [(W_1 - W_0)/W_0] \times 100\%$$

Where W0 denote the weight (g) of tapioca starch which is dried at 80°C until a constant weight achieved; W1 is the weight of fully swollen tapioca starch. All the experiment will be done in triplicates.

2.5. Diffusion

The release studies of the tapioca starch through diffusion will be investigated in this project. Since tapioca starch is a kind of water soluble macromolecule, it shown that the release of nutrient is increased as the content of starch increased [4].

The diffusion of urea through tapioca starch coating can be shown in the Figure 2 below:

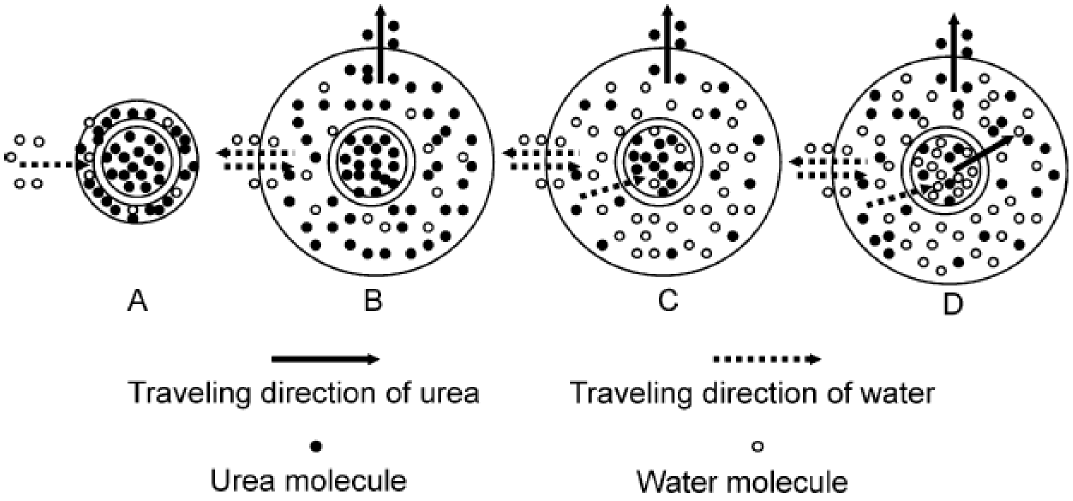

Figure 2: Nutrient release pattern through controlled release coating film by diffusion

The diffusion of the tapioca starch coating can be measured by dissolution rate which can be calculated as follows [10]:

$$D = 100 \times \frac{\text{mass of urea dissolved in 7 days}}{\text{total mass of urea in the sample}} \qquad (1)$$

Since the dissolution rate is a function of the starch content of the coating material, the tapioca starch content will be fixed. The urea content is obtained by refrectometry.

2.6. Multilayer of Coating Material

The controlled release fertilizer may influenced by the layer of the coating. Thus, the effect of number or starch coating layer will be investigated.

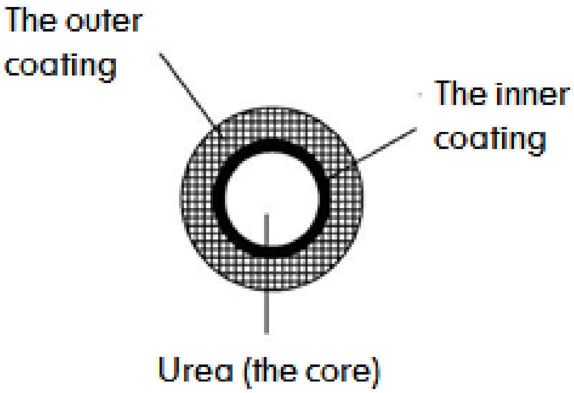

Figure 3: Cross-sectional schematic view of multilayer coated urea

Besides, the coated urea can be mechanically damage during packaging, transport and application. If the coating is damaged, the controlled release function is lost and the urea becomes readily soluble. This accelerated release could lead to short-term crop damage and long-term of fertilizer[6].

CHAPTER 3

METHODOLOGY

3.1. Materials

The polyvinyl alcohol (PVA) powder, tapioca starch powder, formaldehyde and urea formaldehyde (UF) are prepared.

3.2. Preparation of CMTS Coating Film

3.2.1. Six conical flask were labelled as O, A, B, C, D and E

3.2.2. Polyvinyl alcohol, tapioca starch, formaldehyde and urea formaldehyde were mixed in the conical flask at various weight ratios as shown in the Table 2 below

3.2.3. 95 wt% of distilled water were added into each conical flask

3.2.4. The solution were placed in a water bath with shaker for one hour until the mixture were completely gelatinized; constant temperature at 80°C and effective shaking condition

3.2.5. The solution were distributed into a levelled PET mould

3.2.6. The solution were allowed to be treated in a hot air oven for overnight at 50°C

3.2.7. The dried CMTS coating films were removed from the PET mould

3.2.8. The CMTS coating films were stored in polyethylene bags before use in further studies

Table 2: Blending ratio for sample O, A, B, C, D and E

Sample	Weight Ratio			
	Polyvinyl Alcohol	Tapioca Starch	Formaldehyde	Urea
A	10	30	5	3
B	10	40	5	3
C	10	50	5	3
D	10	60	5	3
E	10	70	5	3

3.3. Moisture Absorption Test

3.3.1. The coating films with the dimension of 2cm × 2cm were placed in a hot air oven for 24 hours at constant temperature of 80°C
3.3.2. The samples were taken out from the hot air oven
3.3.3. The samples were placed in a desiccator for 10 minutes
3.3.4. The initial weight of each sample were measured and recorded
3.3.5. The samples were kept in a relative humidity cupboard with constant 50% relative humidity for 24 hours
3.3.6. The final weight of each sample were measured and recorded

3.4. Swelling Rate Test

3.4.1. The coating films with the dimension of 2cm × 2cm were placed in a hot air oven for 24 hours at constant temperature of 80°C
3.4.2. The samples were taken out from the hot air oven
3.4.3. The initial weight of each sample were measured and recorded
3.4.4. Each sample was placed in a filter spoon
3.4.5. The filter spoons containing samples were immersed in distilled water
3.4.6. Every 1 hour, the filter spoons were removed from the distilled water
3.4.7. Excess water were removed from the filter spoons using tissue
3.4.8. Weight of each sample together with the filter spoon was measured and recorded every an hour until the sample was completely swollen

3.5. Biodegradation Test

Thermogravimetric analysis was performed on the samples to determine the changes in weight in relation to change in temperature. The procedure proposed for conducting TGA using PerkinElmer STA 6000 (Simultaneous Thermal Analyzer) was followed where the heating rate was set to 10°C/min and heated to the maximum temperature of 800°C.

3.6. Measurement of the Water Retention of CMTS in Soil

3.6.1. 2 grams of each sample was well mixed with 200 grams of dry soil in a plastic beaker

3.6.2. 200 grams of distilled water were added into each mixture

3.6.3. The initial weight of each beaker was measured and recorded

3.6.4. The beakers were maintained at room temperature

3.6.5. The weight of each beaker was measured and recorded every three days in 30 days period of time

CHAPTER 4

RESULTS AND ANALYSIS

4.1. Moisture Absorption Test

The effect of tapioca starch content was studied throughout the moisture absorption test. Based on the Table 3 below, the moisture content increases as the increase of tapioca starch content and Sample E shown the highest value of moisture content compared to the rest. It is indicated that the introduction of tapioca starch cross-lined with PVA by formaldehyde is proven as a good soluble material. The PVA helps to increase the polarity, crystallinity and hydrophilicity of the CMTS coating material due to the number of –OH in PVA[11]. However, the optimum moisture content of CMTS coating material needs to be investigated synchronising with the diffusion rate of urea fertilizer through the CMTS coating material since it is reported that as the moisture content increases, the CMTS coating material will biodegraded faster.

Table 3: Effect of blending ratio of CMTS coating material on the moisture content

Sample	**Initial Weight, W_0 (gram)**	**Final Weight, W_t (gram)**	**Moisture Content, M_t (%)**
O			
A	0.280	0.291	3.750
B	0.249	0.260	4.627
C	0.123	0.134	8.980
D	0.129	0.142	10.506
E	0.070	0.079	12.857

4.2. Swelling Rate Test

The time required to reach the maximum swelling capacity of CMTS coating material with different blending ratio were studied, and the results are presented in Figure 4 below. CMTS samples with dimension of 2cm×2cm were immersed in an excess amount of distilled water, and the water absorbency was measured every one hour. The results shown the influence of blending ratio to the swelling rate and the samples reached its maximum swelling capacity after about two hours. Based on Figure 4 below, Sample C with 50wt% of tapioca starch ratio shows the highest swelling rate and the maximum blending ratio to absorb water. When the tapioca starch content is lower than 50wt%, the percent of water contents decrease because of the decrease of tapioca starch as soluble material. On the other hand, higher tapioca starch wt% results in the formation of more additional networks through cross-linking by formaldehyde and decrease the space for holding water. Besides, the result indicated that the Sample C had the highest initial swelling rate. It has been reported that the swelling rate of a superabsorbent is mainly determined by the swelling ability, surface area, particle size, and density of the polymer[8]. The high swelling rate for CMTS coating material with 50wt% is attributed to the fact that the use of formaldehyde as a cross-linker of tapioca starch and PVA loosen the polymeric network and increases the capillary effect. Furthermore, a high initial swelling rate is one of the most important factors for superabsorbent used in agriculture, for it could absorb more water during raining or irrigation.

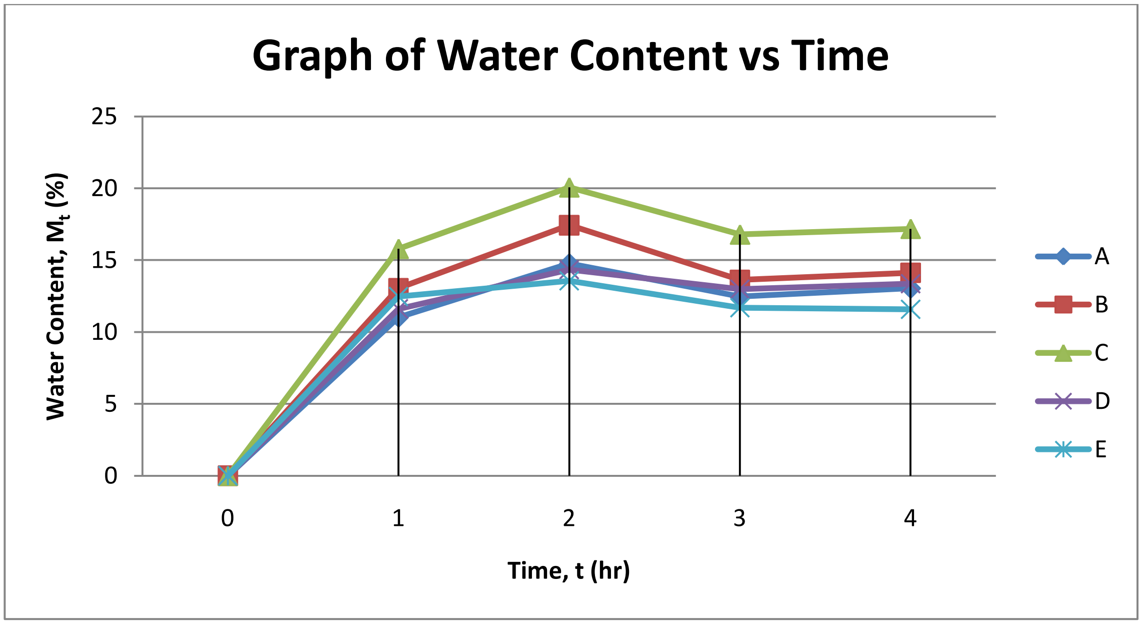

Figure 4: Effect of tapioca starch content on water content (Sample A, B, C, D and E)

4.3. Degradation Test

Thermogravimetric analysis has been conducted on the Sample A, B, C, D and E. Referring to Appendix B all samples were decomposed at temperature around 300°C to 310°C.

4.4. Measurement of the Water Retention of CMTS in Soil

Table 4: Effect of CMTS on the water retention in soil

SAMPLES	Evaporation Rate (gram/day)
Without sample	11.404
A	11.210
B	11.070
C	10.987
D	10.767
E	10.766

Based on Table 4 above, the evaporation rate decreases as the increase of tapioca starch content in the samples of CMTS coating material. The result is in good agreement with observations in the literature, which reported an exponential increase in the water holding capacity of a soil with increasing additions of hydrophilic polymers[8]. Therefore, CMTS could effectively store rainwater or irrigation water, and improve the utilization of water resources. Moreover, it was observed that the water flow rate through the soil was slowed when CNSW was added to the soil. Thus, the soil with addition of CMTS could hold much more water during the irrigation period compared to the soil without it and decrease water losses though infiltration and save water during irrigation. This is significant advantage of CMTS over normal slow release fertilizer.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

All in all, the CMTS coating material was successfully formulated. The effect of blending ratio of the Chemically Modified Tapioca Starch coating material on its physical properties are investigated throughout this project. First, the moisture absorption test shows that the moisture content increases as the tapioca starch coating increases. Second, the Sample C with 50wt% of tapioca starch content seen as the highest swelling rate with the maximum swelling capacity which is 20% moisture was achieved after about two hours. Third, the Thermogravimetric Analysis shown that all the samples decompose around 300°C to 310°C. Finally, the CMTS was proven to have an excellent water retention capability which can hold water since the evaporation rate of water in soil decrease as the tapioca starch content increase in the sample.

The study of controlled release material from CMTS is very impressive and can be seen as a good potential in agricultural sector since the tapioca starch shown excellent properties contributed to the improvement of controlled release fertilizer.

5.2. Recommendation

Throughout this project, there are few recommendations for further study:

5.2.1. The effect of blending ratio on the diffusion rate of urea fertilizer through the CMTS coating film
5.2.2. Morphology of the CMTS coating film
5.2.3. The effect of cross-linker content on the diffusion rate of urea fertilizer

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APPENDICES

A. Swelling Test

Table 5: Percent of water content for Sample A, B, C, D and E

Sample	**Water Content (%)**				
	W0	**W1**	**W2**	**W3**	**W4**
A	0	11.03	14.77	12.46	13.04
B	0	13.05	17.43	13.63	14.12
C	0	15.79	20.06	16.78	17.18
D	0	11.61	14.34	12.98	13.37
E	0	12.48	13.56	11.68	11.58

B. Degradation Test

Figure 5 until Figure 14 below show the result of Thermogravimetric Analysis

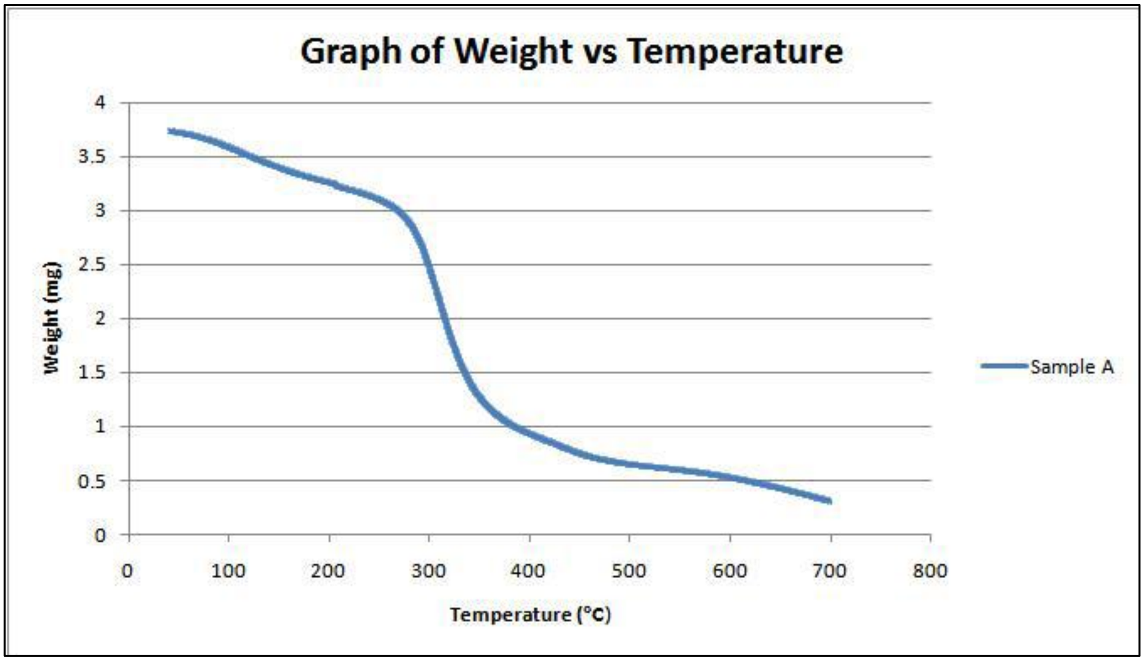

Figure 5: Weight changes in Sample A as a function of temperature

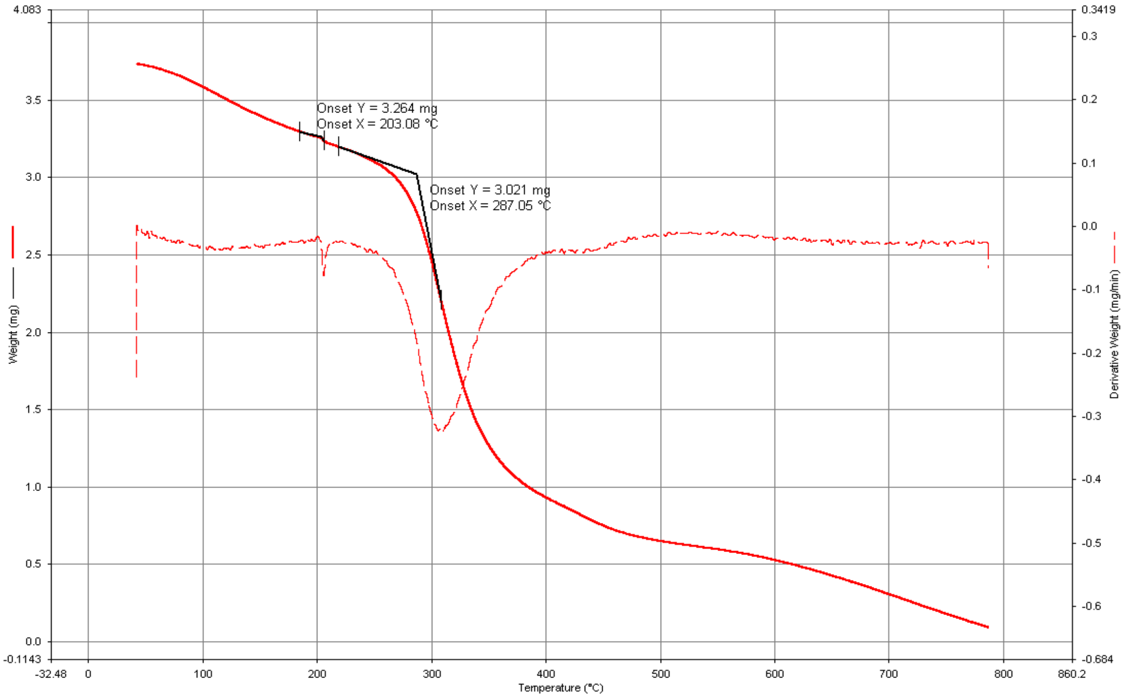

Figure 6: Thermogravimetric analysis of Sample A

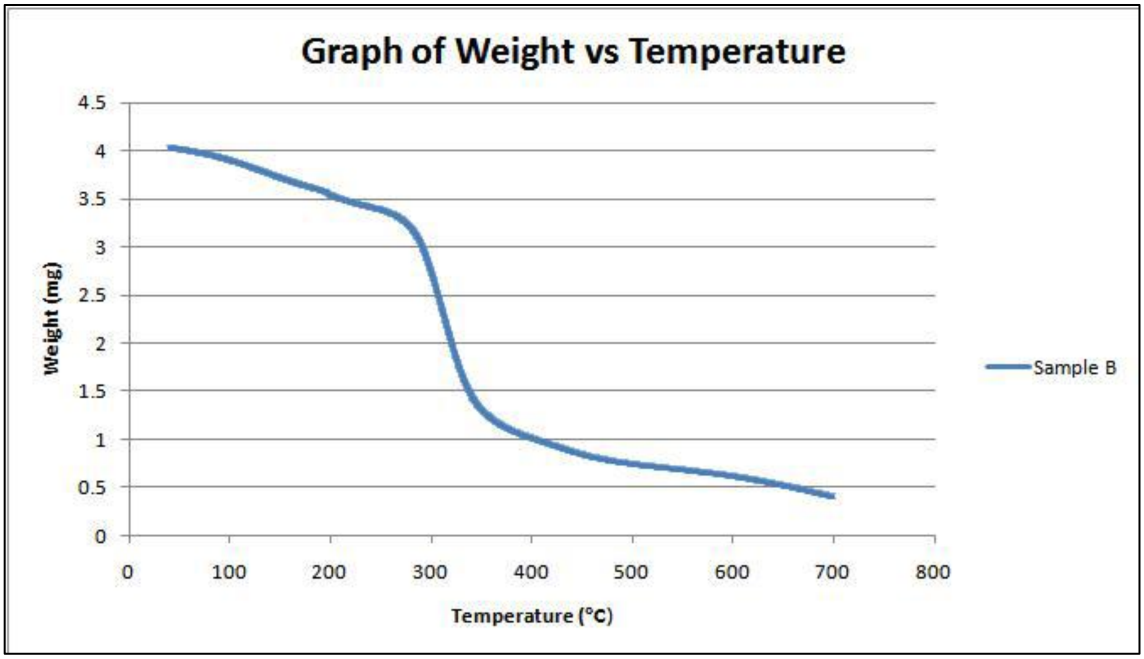

Figure 7: Weight changes in Sample B as a function of temperature

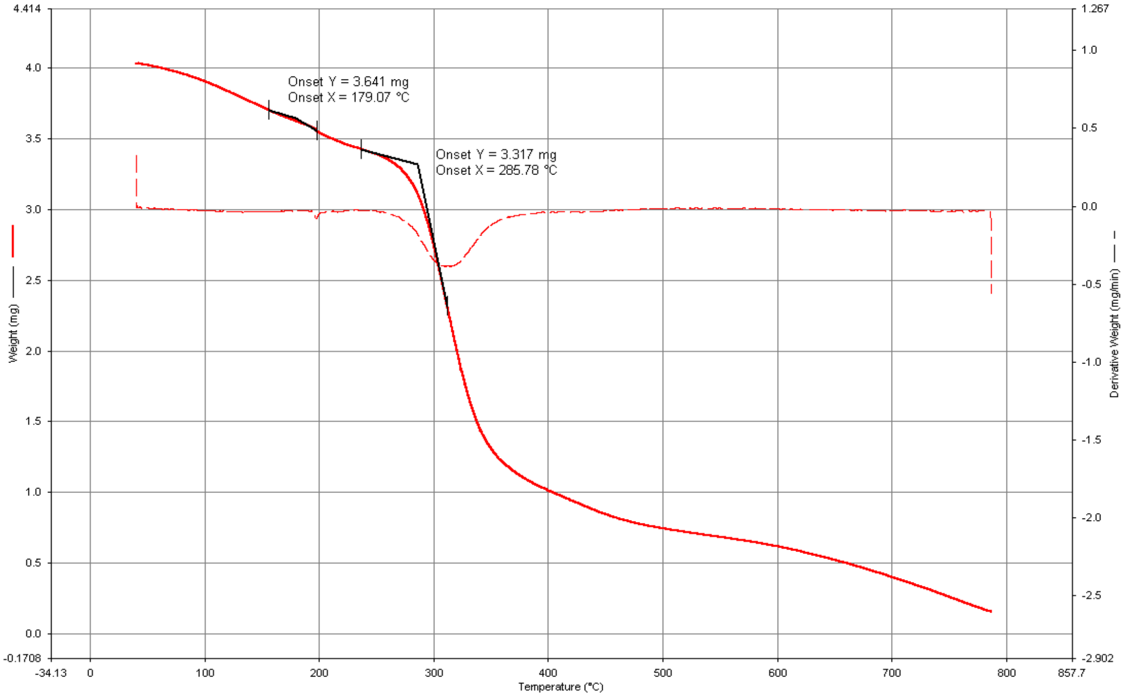

Figure 8: Thermogravimetric analysis of Sample B

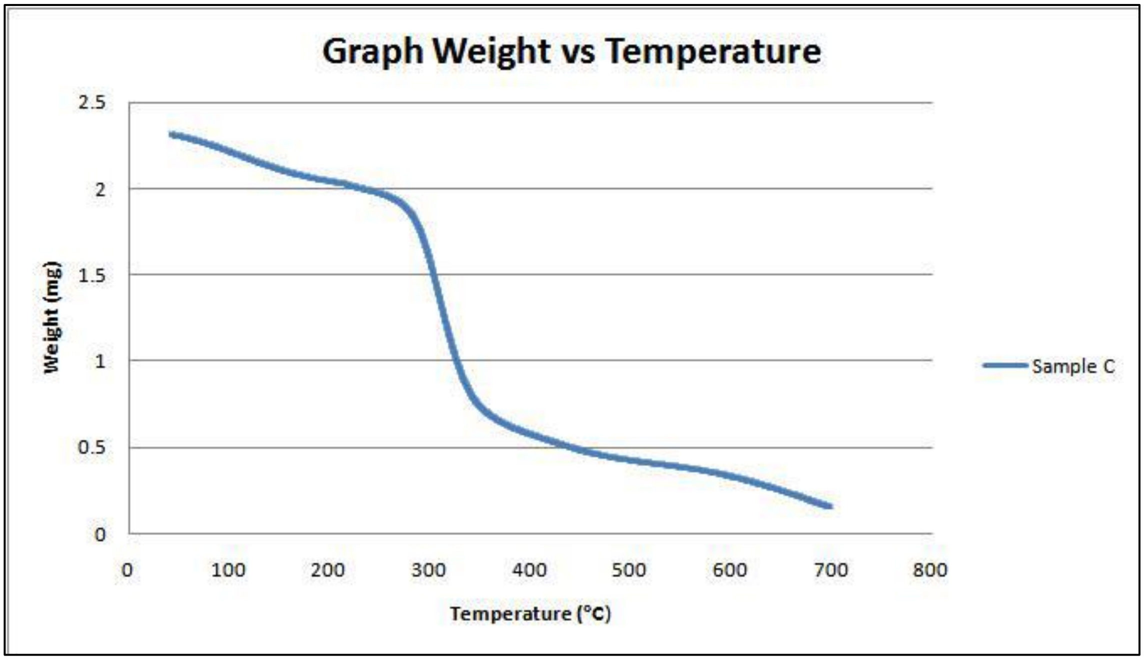

Figure 9: Weight changes in Sample C as a function of temperature

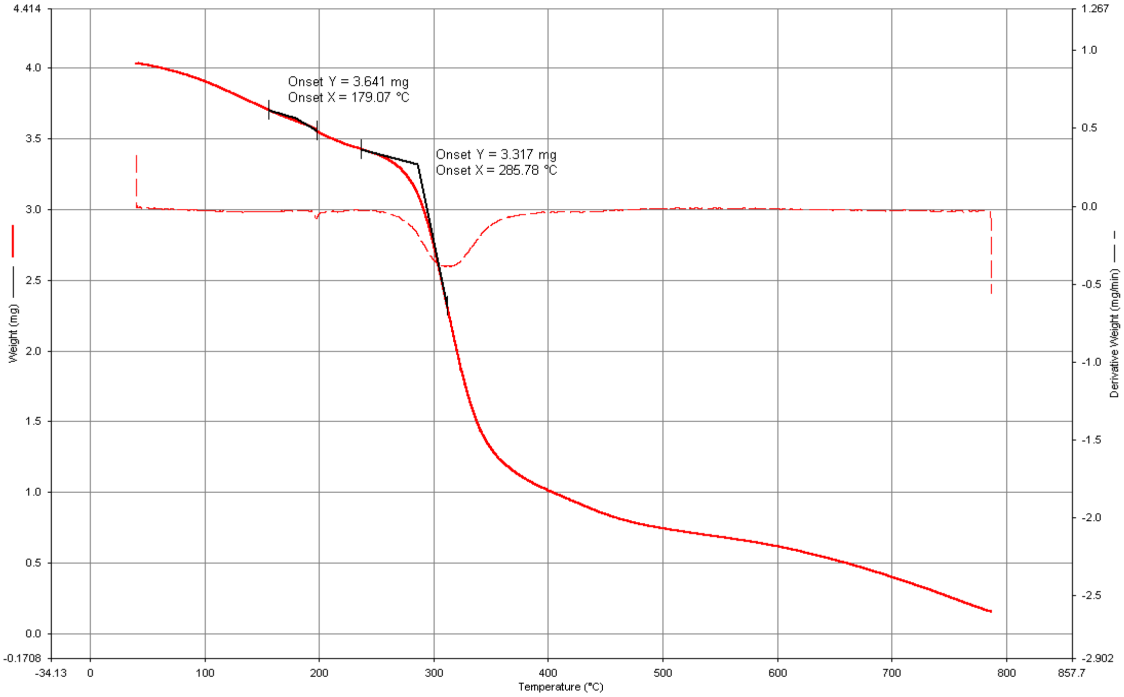

Figure 10: Thermogravimetric analysis of Sample C

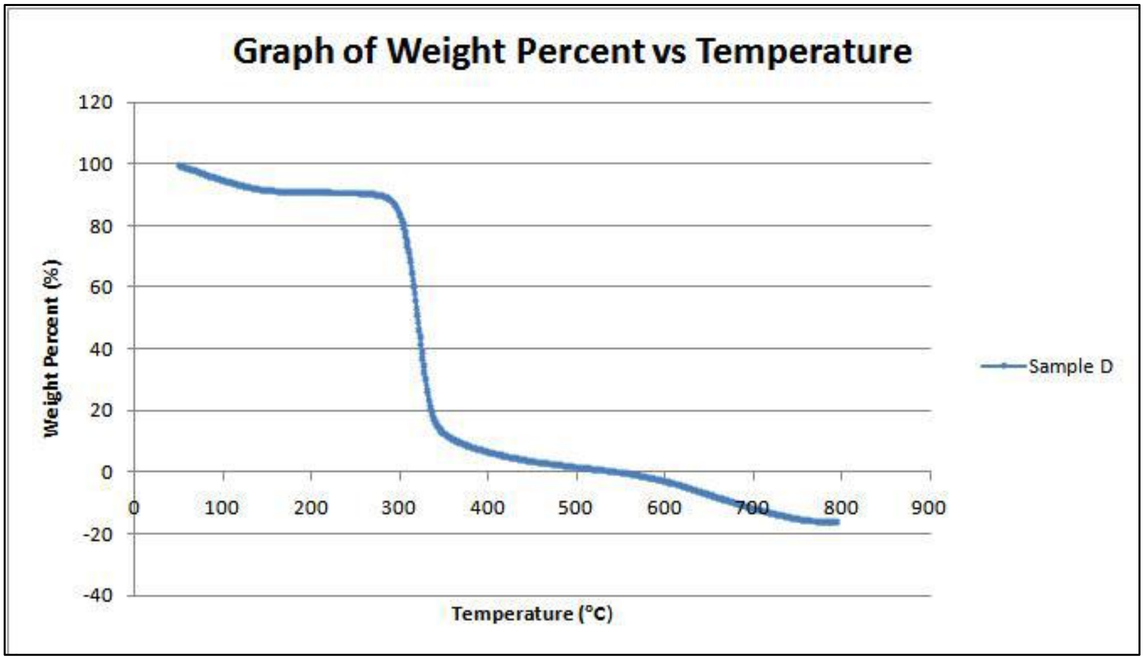

Figure 11: Weight changes in Sample D as a function of temperature

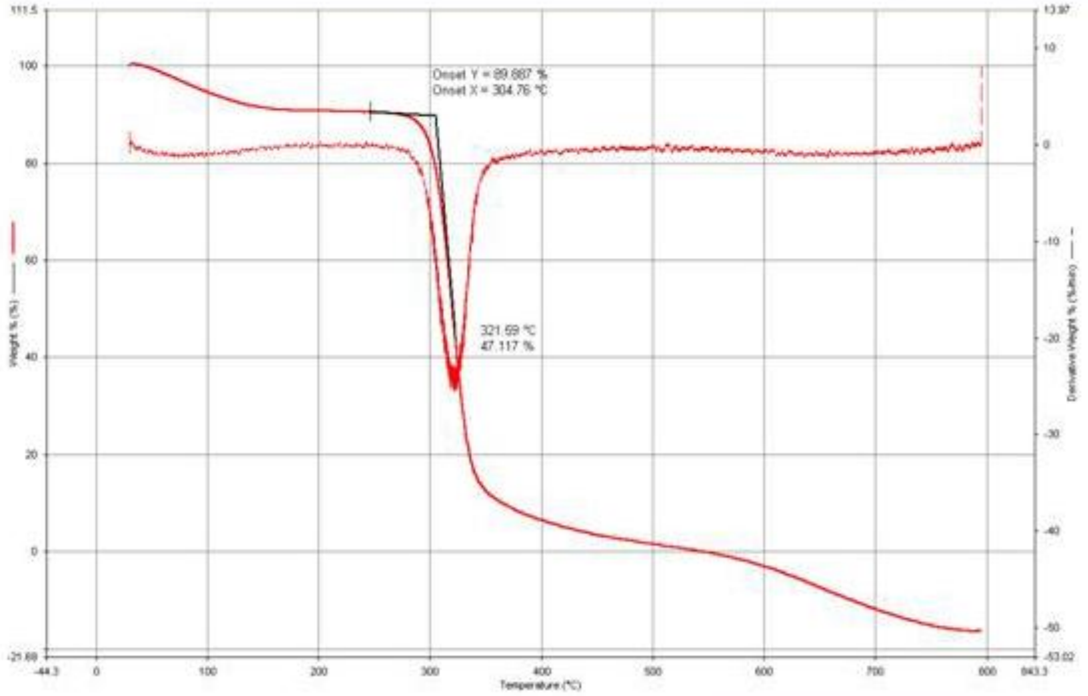

Figure 12: Thermogravimetric analysis of Sample D

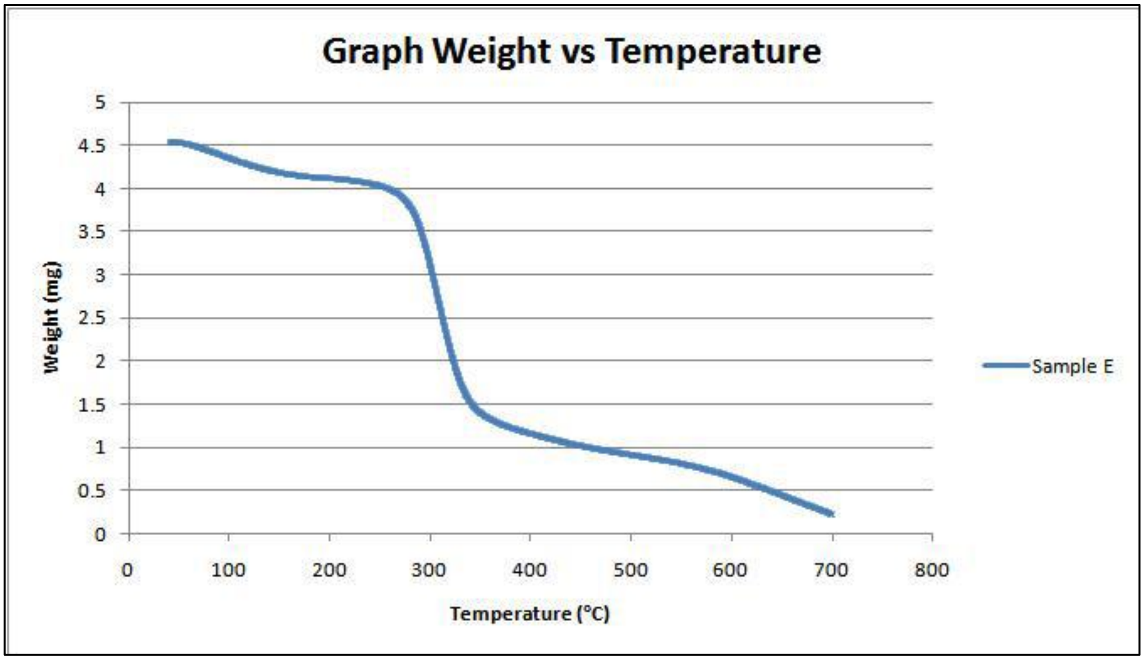

Figure 13: Weight changes in Sample E as a function of temperature

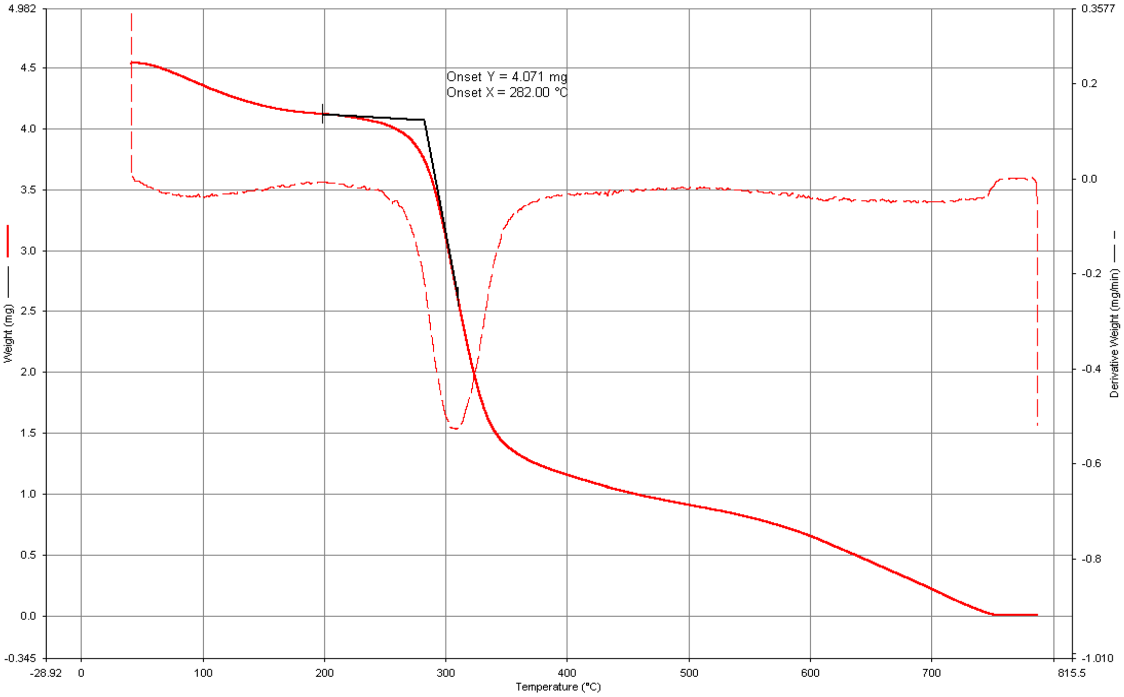

Figure 14: Thermogravimetric analysis of Sample E

C. Measurement of the Water Retention of CMTS in Soil

Figure 15 until Figure 20 show the water retention of CMTS in soil through the weight loss of water in soil.

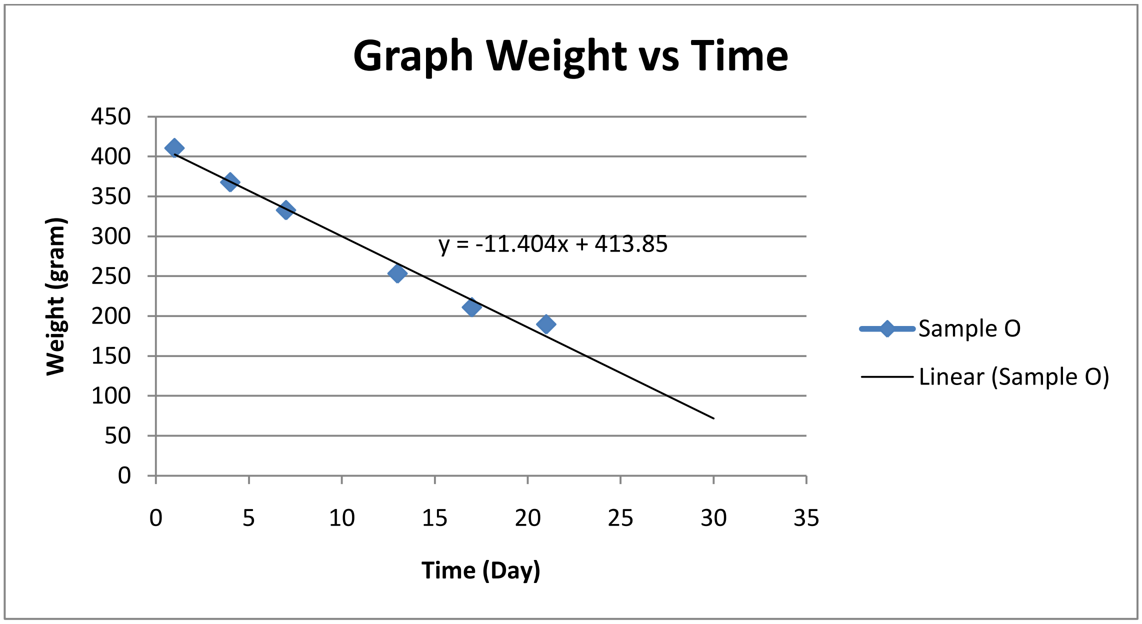

Figure 15: Weight loss of water in soil with respect to time

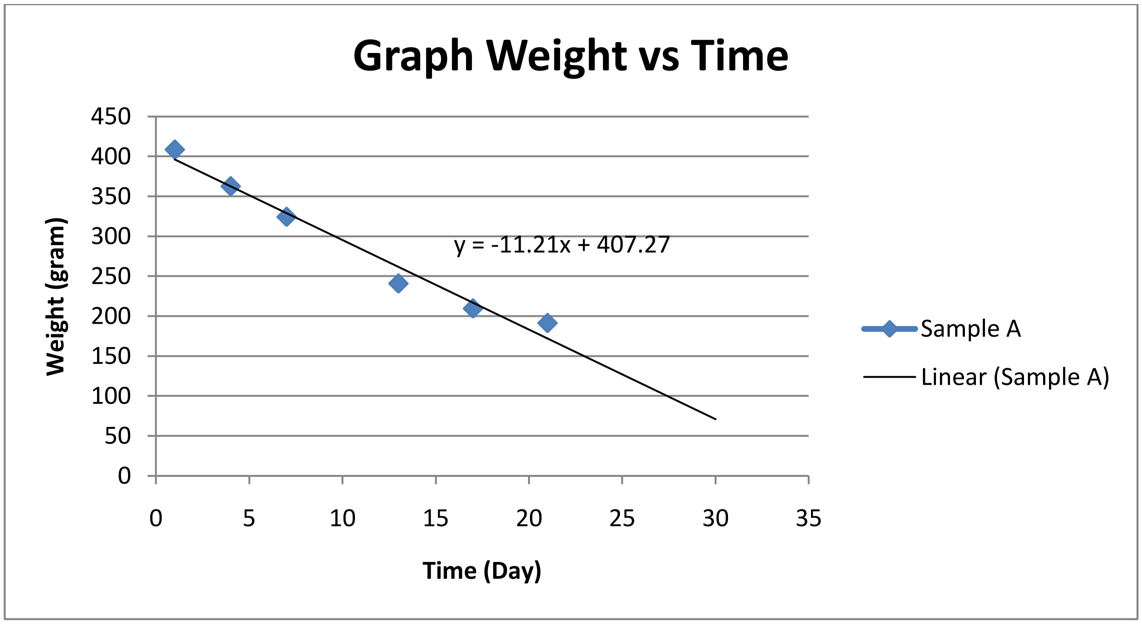

Figure 16: Effect of Sample A on the weight loss of water in soil with respect to time

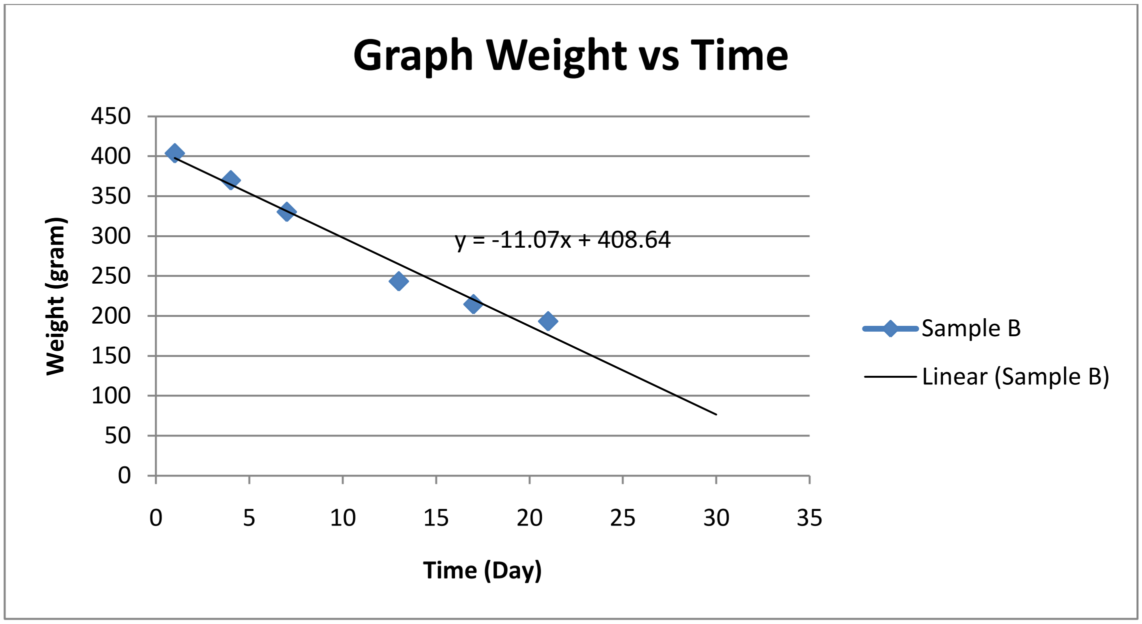

Figure 17: Effect of Sample B on the weight loss of water in soil with respect to time

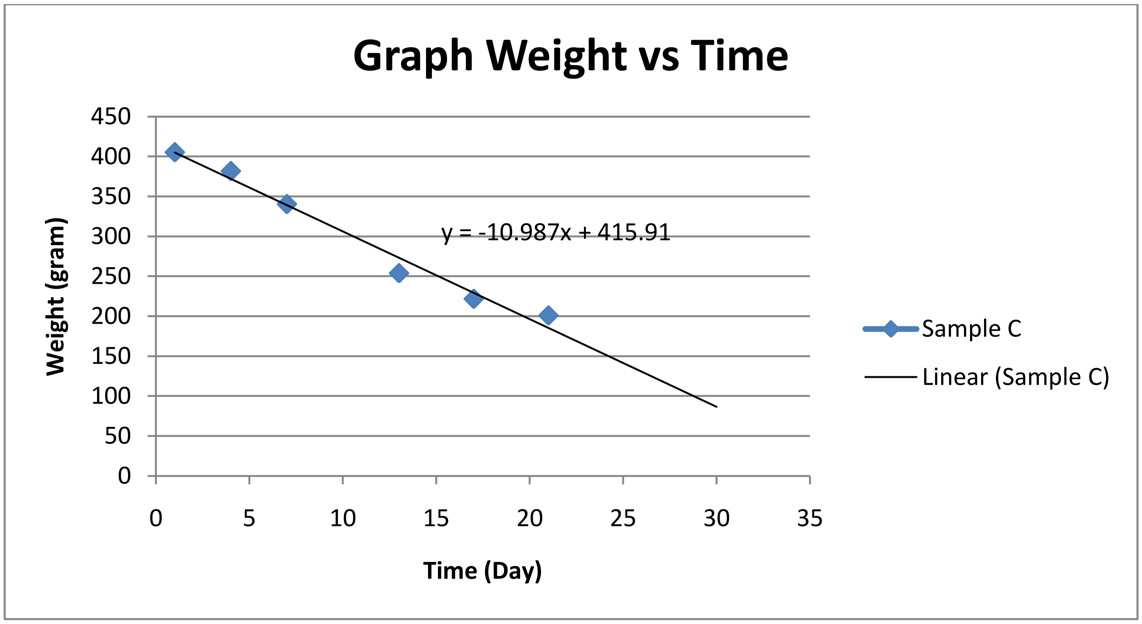

Figure 18: Effect of Sample C on the weight loss of water in soil with respect to time

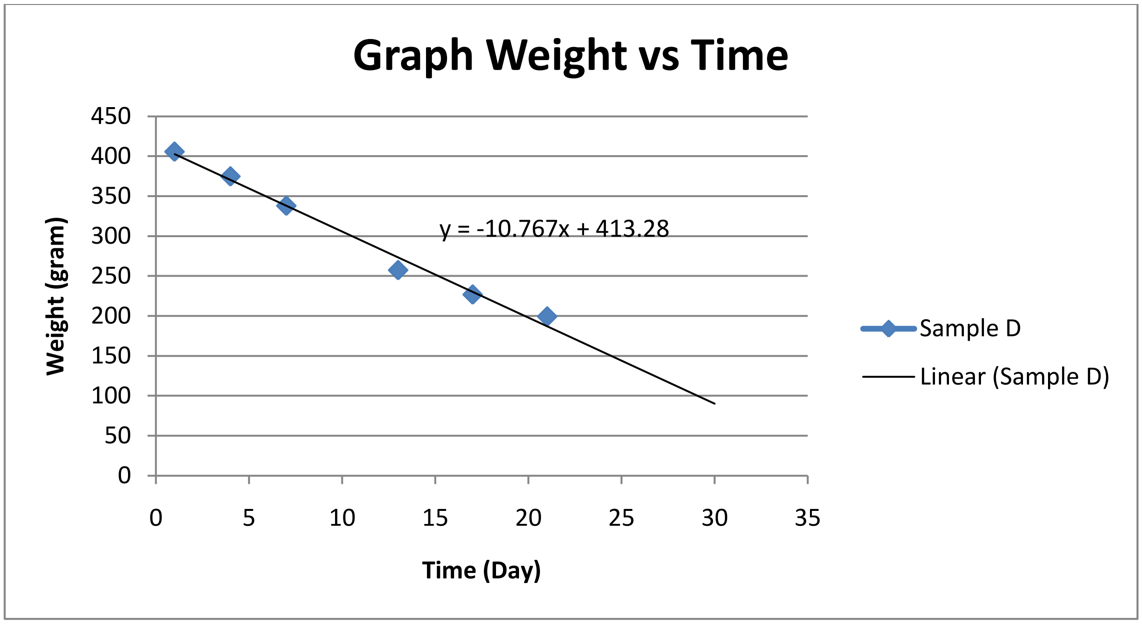

Figure 19: Effect of Sample D on the weight loss of water in soil with respect to time

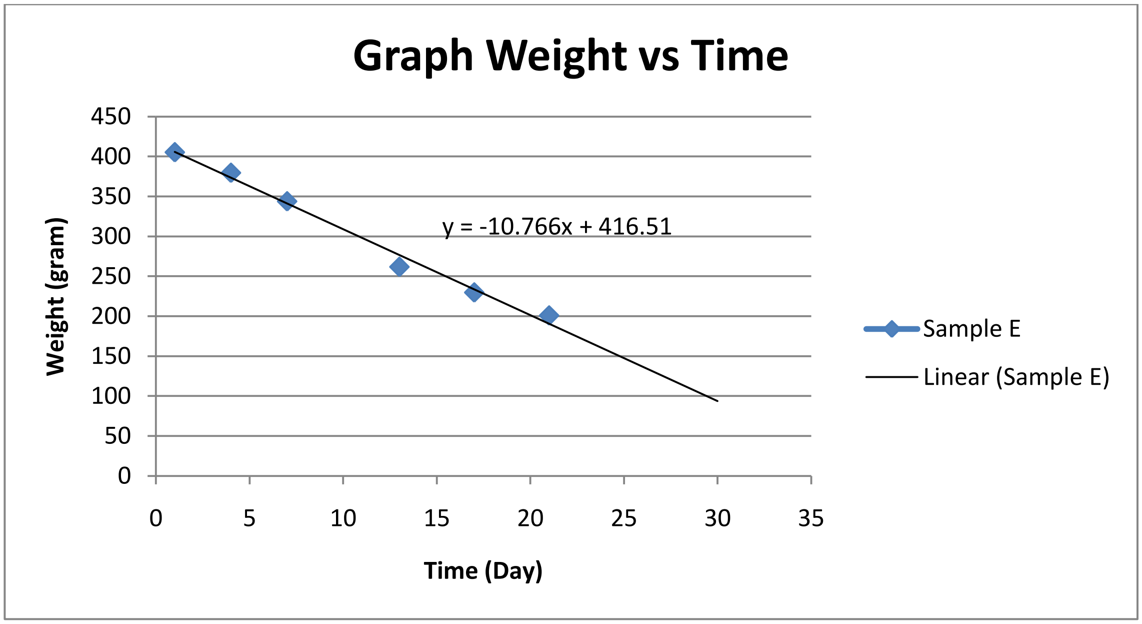

Figure 20: Effect of Sample E on the weight loss of water in soil with respect to time