



DECOMPOSITION OF POLYVINYL CHLORIDE, POLYPROPYLENE AND MELAMINE USING THERMOGRAVIMETRIC ANALYZER

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ABSTRACT

Thermogravimetric Analyzer (TGA) is a tool for analyzing thermal where the mass change of test material is measured in proportion to temperature rise and time function (with constant temperature rise rate). TGA is usually used to determine the material characteristics such as polymer. The loss curve of the polymer mass can be used to determine the decomposition of the material, the point of loss of weight, and to calculate the activation energy. This research uses Q500 series Thermogravimetric Analyzer (TGA), with 3 (three) types of polymer materials i.e. PVC, Polypropylene, and Melamine. There are also tests of the above-mentioned polymer types which have been pre-treated thereby further referred to as PVC (x), PP (x), and Melamine (x). The results showed that the heat treatment given before the TGA test had a negative and significant impact on PVC and PP polymer materials, but not significantly against Melamine. Obtained activation energy value from each test material that is $E = 66.27$ kJ/mol for PVC (x) and $E = 63.93$ kJ/mol for PVC. $E = 62.30$ kJ/mol for PP (x) and $E = 69.55$ kJ/mol for PP. $E = 47.40$ kJ/mol for Melamine (x) and $E = 46.14$ kJ/mol for Melamine.

Keywords: PVC, polypropylene, melamine, decomposition, TGA, activation energy.

1. INTRODUCTION

Polymers are widely used non-metallic engineering materials due to their superior properties such as light, corrosion-resistant and chemical, low cost, low electrical and heat conductivity, noise suppression, design conformance and manufacturing especially for low-temperature applications. [1].

Degradation or termination of the polymer chain, by thermal means can be done in various ways, such as heating or exposure of polymers to heat sources, such as the sun, fire, hot water and so on.

High temperatures are indeed one of the weaknesses in the most fatal use of polymers. An example is the use of black plastic bags when exposed to heat (e.g. from frying oil), can be decomposed, degraded into shape. [2].

Such cases also occur in some less precise polymers used as Feeding Bottle materials, melamine tableware, and Styrofoam feeding containers.

It should be noted that in addition to the use of polymer products in high temperatures, in some types of polymers there is also degradation when exposed to sunlight and other radiation. [3].

The research on polymer is done by [4] which discusses kinetics for the management of polymer waste that can be recycled and mix it with coal to be a source of energy. The same is done by [5], which examines the mixture of plastic and coal as the utilization of scrap plastic that can be utilized as part of energy mixed with coal. Another pyrolysis study on plastic waste is also carried out by [6]. A polymer study of human organs was performed by [7] who said that the majority of victims suffered acute kidney injury, nephrolithiasis and urolithiasis. It happens to baby milk containing melamine. While [8] states melamine is very limited in quantities in food.

Therefore, it is necessary to conduct more in-depth research on polymer characteristics, especially

decomposition analysis that occurs in polymer units exposed to sun exposure for long periods of time. Changing the behaviour of the polymer material composition can be understood by using the Thermogravimetric Analyzer (TGA) tool.

TGA is usually used to determine the characteristics of materials such as polymers. By calculating the change in weight associated with the temperature change. The weight loss curve can be used to determine the material decomposition, the point of loss of weight, and to calculate the activation energy of the material.

This paper aims to identify polymer products that are subjected to heat treatments in accordance with daily usage errors, and or polymer products exposed to direct and prolonged exposure to sunlight using TGA tools. It is also discussed about the thermal decomposition of the polymer by looking at the shape of the curve formed and taking into account and analyzing the activation energy of the specimens tested.

The polymers consist mostly of monomers in the form of hydrocarbon bonds produced from cracking of petroleum, for example Ethylene or ethane, which then react with other elements such as terephthalic acid with addition reactions.

Classification of polymers

Polymers can be classified by their origin, monomer type, heat resistance and formation reaction [9]. Based originally, polymers are distinguished into natural polymers and artificial polymers. Natural polymers have been developed for thousands of years, such as starch, cellulose, cotton, rubber, wool, and silk. Artificial polymers may be regenerated polymers and synthetic polymers. The regeneration polymer is a modified natural polymer, for example, rayon, which is synthetic fiber made from wood (cellulose). Synthetic polymers are polymers made from



simple molecules (monomers) in the plant and are not present in nature. These polymers include all types of plastics, fibers, synthetic rubber and nylon. Meanwhile, based on the type of monomer constituents, the polymer is divided into homopolymers and copolymers. Homopolymers are formed from monomers of a kind, for example polyvinyl chloride, whereas Copolymers are formed by two or more different types of monomers. Based on its resistance to heat, Polymers are divided into 2 i.e. thermoplastics and thermosetting. The thermoplastic polymer when heated will melt and after cooling will harden, the process may occur repeatedly, so it can be re-formed in various forms through different molds to obtain the new polymer. Examples: Polyethylene, Polyvinyl chloride, Polypropylene, Polystyrene. The thermosetting polymer is a polymer that has a heat resistance property, if the polymer is heated it is hard to melt, so it cannot be reshaped. This polymer arrangement is permanent in the first printed form.

Based on the article [10] can be known together that internationally has arranged the code for plastic packaging. This code was issued by The Society of Plastic Industry in 1988 in the United States and adopted by institutions developing code systems, such as ISO (International Organization Standardization).

Generally the sign is on the base, triangular, inside the triangle there will be a number, as well as the name of the plastic type under the triangle, with examples and explanations as follows:

Vinyl (Polyvinyl Chloride or PVC) is produced from two main types of raw materials: petroleum and salt (NaCl). The process of cracking / breaking up ethylene dichloride molecules produces vinyl chloride gas ($\text{CHCl} = \text{CH}_2$) and hydrochloric acid (HCl). Finally, through a process of polymerization is produced a giant molecule with a long chain (polymer): polyvinyl chloride (PVC), which is a fine white powder. PVC can be found on cling wrap, and bottles. The reaction that occurs between PVC and food packed with plastic is potentially harmful to the kidneys, liver and weight.

Polypropylene (PP) is the best choice for plastics, especially for foods and beverages such as food storage, drinking bottles and most importantly baby bottles, created in 1957, is a cheap alternative to polyethylene replacement. In addition to bottles, most of our food packaging is made of plastic no. 5 this. In fact, this is the most common plastic in the non - bottle form. Polypropylene is a polymer plastic that is easily formed when it is hot. Polypropylene has high chemical resistance, but its impact strength is low.

Melamine with chemical structure $\text{C}_3\text{H}_6\text{N}_6$ is a polymer compound which is a combination of formaldehyde (formaldehyde) monomer and phenol which, when the melamine composite component in a balanced composition looks safe, but should be aware of frequently in the manufacture of melamine, the mixing process is often uncontrolled. If the composition between formaldehyde and phenol is unbalanced then the residue occurs, i.e. formaldehyde monomer or phenol which is not perfectly united. The rest of the formaldehyde monomers are harmful to the health of the body. In addition, melamine compounds

are susceptible to heat and ultraviolet rays that can depolymerize melamine into formaldehyde and phenol monomers. Although resistant in the temperature range of 120°C to 30°C below zero, but because it absorbs heat, melamine cannot stand exposed to heat too high. Especially exposed in the long term. Therefore melamine cannot be used in microwave. Here the danger of melamine for the health of the body.

Thermal decomposition and thermogravimetric analysis

Thermogravimetric analysis (TGA) is an analytical technique for determining the thermal stability of a material and the fraction of volatile components by calculating the weight changes associated with temperature changes. The weight loss curve can be used to determine the point of loss of weight.

Activation energy is the minimum energy that must exist in the chemical system to carry out a chemical reaction. The activation energy was introduced by a Swedish scientist named Svante Arrhenius in 1889. Activation energy can also be defined as the minimum energy required to initiate a chemical reaction. The activation energy of a reaction is usually denoted by E_a in kilo Joules per mole (kJ/mol).

In 1889 Arrhenius proposed an empirical equation which gives the basic value of the relationship between the activation energy and the rate of the reaction process. The Arrhenius equation describes the effect of temperature on the reaction rate constant:

$$k = Ae^{-E/RT}$$

A = frequency factor or Arrhenius factor

E = Activation energy (J/mol)

R = Gas constant (8.314 J/mol °K)

T = absolute temperature (°K)

The equation is then rewritten by [11] as follows:

$$\ln k = \ln A - \frac{E}{RT}$$

The second equation is a straight line equation with the X axis being $1/T$ and the Y axis is $\ln k$, the slope of the line equal to $(-E_a/R)$. Therefore, the activation energy can be calculated.

2. METHODS AND MATERIALS

The test was carried out on polymer materials i.e. Polyvinylchloride (PVC) Pipes, Feeding bottle Polypropylene (PP), and Tableware (Melamine). The test material was first filed into a powder then sieved with a 60 mesh sieve, ready test.

The tool that will be used during the process of this research is Thermogravimetric Analyzer Q500 series.

TGA is a device that serves to analyze the mass change of a material to the temperature change. Used in conjunction with TA Instrument Controller and related software, to create a thermal analysis system.

TGA measures the amount and rate of mass change in a material, either as a function of rising temperature, or isothermally as a function of time, in



atmospheric pressure, can be used to characterize any material that exhibits a change in weight and to detect phase changes due to decomposition, oxidation, or dehydration. This information helps scientists or engineers identify changes in weight percentage and chemical structure, decomposition, and material efficiency.

The first TGA test was carried out on a new PVC pipe and a PVC tube that was almost 5 years old exposed to sunlight during its use, hereinafter mentioned to as PVC (x). The second TGA test was performed on a Polypropylene (PP) -based baby bottle and baby bottle of the same base which was first given a heat treatment by boiling with boiling water ± 5 minutes (referring to the same treatment when the feeding bottle was cleaned by the baby's parents) which shall hereafter be referred to by PP(x). The third TGA test was done on the tableware in the shape of a melamine-based bowl and the same base bowl which was first given a heat treatment by filled / boiled with boiling water temperature $\pm 100^\circ\text{C}$ which would then be called Melamine (x).

3. RESULTS AND DISCUSSIONS

The data generated by the TGA test is a graph of the comparison between the temperature change and the loss of mass of the material under test, this graph is commonly referred to as the thermogram. These thermograms can be converted into Excel programs so we can calculate the activation energy of each polymer tested.

Tests performed on the above specimens are Thermogravimetric Analyzer (TGA), by calculating the change in weight to the temperature changes obtained by curves referring to the point of loss of weight, material decomposition, and energy of material activation.

The data generated by the TGA test is a graph of the comparison between the temperature change and the loss of mass of the material under test, this graph is commonly referred to as the thermogram (Figures 1, 2 and 3). These Thermogram can be converted into Excel programs so we can calculate the activation energy of each polymer tested.

As previously mentioned, TGA testing is performed on the above polymer specimen. The test is also carried out on the test material which is firstly given a heat treatment; this is done to obtain the comparison of the curve that occurs which refers to the comparison of the decomposition process and the amount of activation energy required, and the effect of heat treatment on each type of polymer.

TGA testing is done by using inert gas (Nitrogen), maximum temperature 900°C and Heating rate (Ramp) constant $50^\circ\text{C}/\text{min}$.

Polyvinylchloride Pipes (PVC)

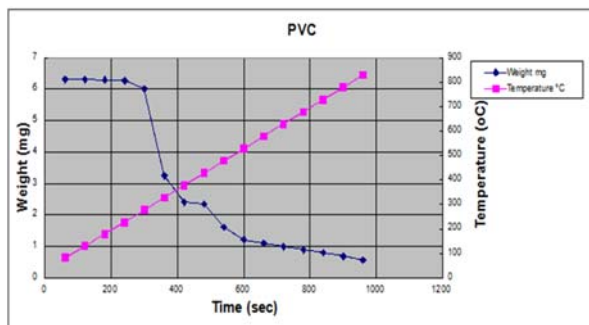


Figure-1. Graphic TGA PVC.

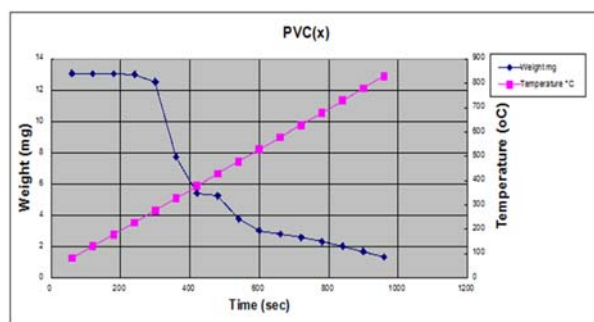


Figure-2. Graphic TGA PVC (x).

Graphs generated from the above Q500 TGA Analyzer tool can be translated into written data in data processing applications such as Microsoft Excel, so it can be further processed to obtain graphs of decomposition temperature relation with decreasing TGA mass and material degradation rate (dm/dt) (Figures 3 and 4).

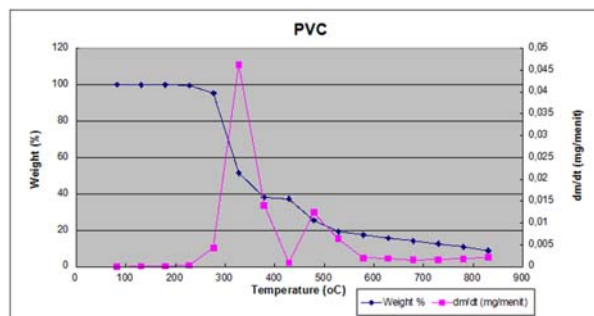


Figure-3. The relationship between PVC decomposition temperature with decreasing TGA mass and material degradation rate (dm/dt).

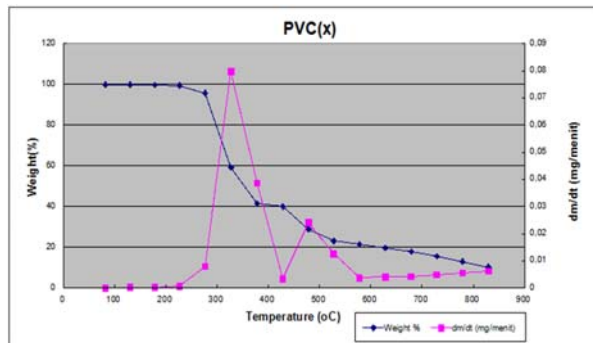


Figure-4. The relationship between PVC decomposition temperature (x) with decreasing TGA mass and material degradation rate (dm/dt).

By knowing the curve constraints we can graph the relationship of $\ln k$ to $1/T$, as shown in Figures 5 and 6, and by using the Trend line function, a Gradient of the curve will be used later to obtain activation energy for PVC and PVC(x). In addition to Gradient, the Trend line function also provides a R^2 value that is a level of confidence with a scale of 0 to 1 that can be used to ensure the curve constraint used is most appropriate, in this case the value of 0.8462 for PVC and 0.8565 for PVC(x) is the highest, so it is ensured that the upper and lower limits of the curve are eligible.

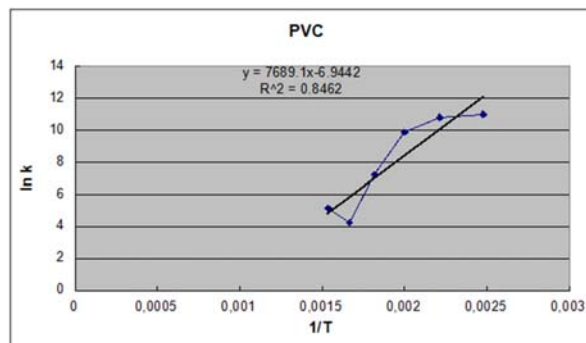


Figure-5. Relationship between $\ln k$ and $1/T$ for PVC materials.

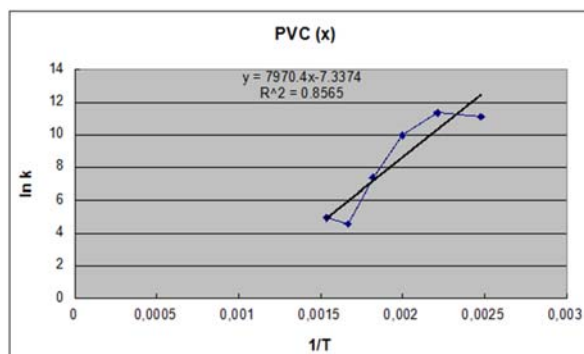


Figure-6. Relationship between $\ln k$ and $1/T$ for PVC material (x).

Feeding Bottle Polypropylene (PP)

The second TGA test was performed on a Polypropylene (PP) -based Feeding Bottle and Feeding Bottle of the same base which was first given a heat treatment by boiling with boiling water ± 5 minutes (referring to the same treatment when the Feeding Bottle was cleaned by the baby's parents) which shall hereafter be referred to by PP(x). The thermogram is shown in Figures 7 and 8).

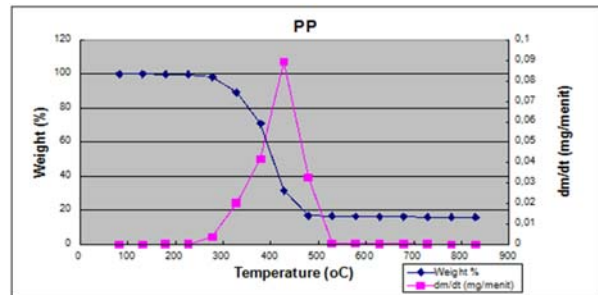


Figure-7. The relationship between the PP decomposition temperature and the decrease of TGA mass and the rate of material degradation (dm/dt).

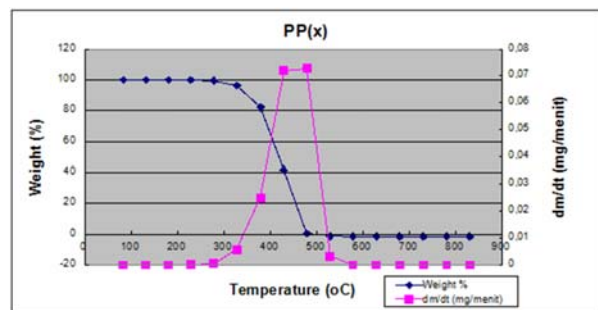


Figure-8. The relationship between the decomposition temperature of PP (x) with the decrease of TGA mass and the rate of material degradation (dm/dt).

By knowing the curve constraints we can graph the relationship of $\ln k$ to $1/T$, as shown in Figures 9 and 10, and by using the Trend line function, a Gradient of the curve will be used later to obtain activation energy for PP and PP(x).

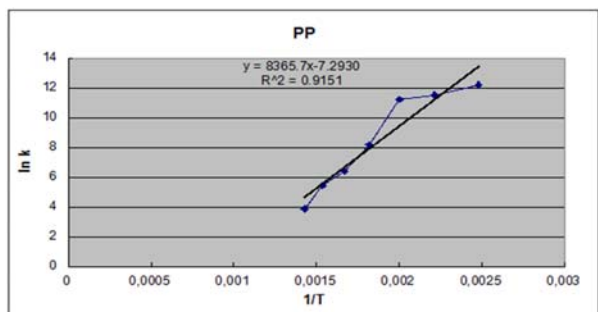


Figure-9. Relationship between $\ln k$ and $1/T$ for PP material.

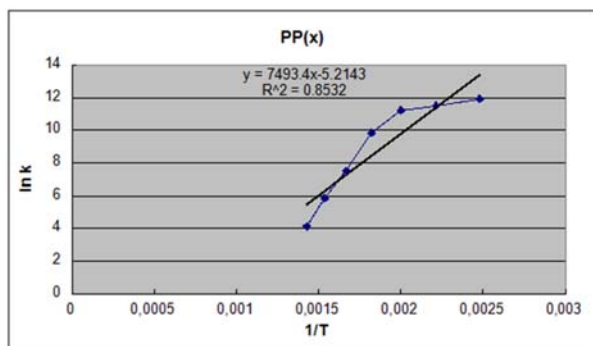


Figure-10. Relationship between $\ln k$ and $1/T$ for material PP (x).

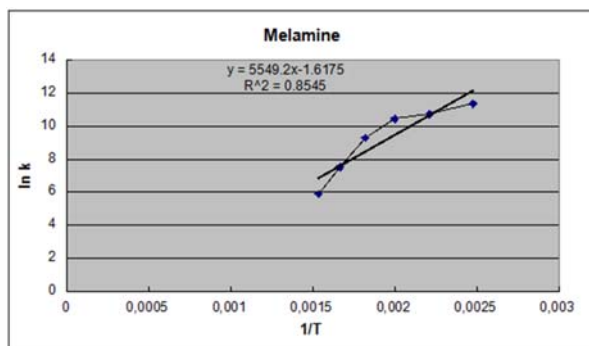


Figure-13. Relationship between $\ln k$ and $1/T$ for Melamine material.

Tableware/bowl (Melamine)

The third TGA test was performed on the tableware in the form of a melamine-based bowl and the same base bowl which was first given a heat treatment by filled/boiled with boiling water temperature $\pm 100^\circ\text{C}$ which would then be called Melamine (x). The thermogram is shown in Figures 11 and 12.

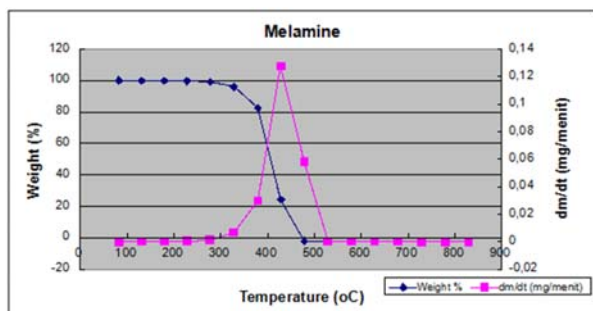


Figure-11. Relationship between Melamine decomposition temperature with decrease of TGA mass and material degradation rate (dm/dt).

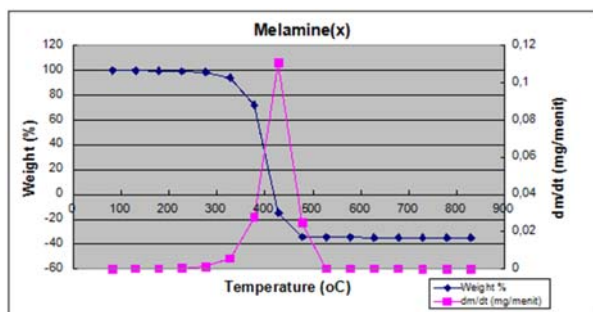


Figure-12. Relationship between decomposition temperature Melamine (x) with decrease of TGA mass and material degradation rate (dm/dt).

Figures 13 and 14 are Relationship between $\ln k$ and $1/T$ for Melamine material.

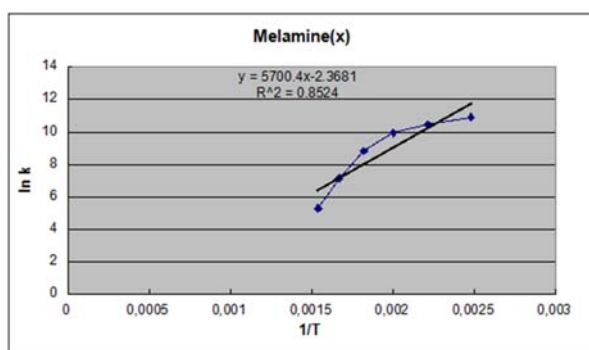


Figure-14. Relationship between $\ln k$ and $1/T$ for Melamine material (x).

After analyzing the TGA data from each material of the test material, the patterns produced on each graph and the curve that occurs, and the comparison of activation energy required in the heating process until the decomposition occurs in each material, obtained some facts that can be discussed further to get a conclusion that refers to the purpose of research.

PVC and PVC(x)

Based on the thermogram generated from the TGA test in Figures 1 and 2 it can be seen that the decomposition level in PVC and PVC (x) materials is divided into three levels of temperature: First level between 130°C to 378°C , second level between 378°C to 480°C and third level above 480°C . However, since the amount of activation energy obtained is to compare between PVC and PVC (x), so in this study only one curve rate comparison of material decomposition rate occurs at the first decomposition level between 130°C to 378°C .

In the comparison graph of decomposition temperature with decrease of TGA mass and material degradation rate (dm/dt) of Figures 3 and 4, the decomposition process can be seen clearly where the heating starts at the preparation temperature of 80°C and there is a very small and constant mass drop to a temperature of 227°C , this shows the release of water vapor present on the surface of the material, starting from this point 227°C the mass decrease begins to be apparent. The jumping peak dm/dt occurs at the next point i.e. 277°C to



328°C and still there is a massive decrease of mass up to the point 378°C. Thus the most significant decomposition process in PVC and PVC (x) occurs at temperatures of 227°C to 378°C. So there is no need to discuss the temperature above 378°C.

After obtaining the activation energy amount for PVC is $E = 63.93$ kJ/mol and for PVC (x) is $E = 66.27$ kJ/mol, indicating that the energy required until the decomposition of the material is greater in PVC pipe that has been exposed sunlight for ± 5 years rather than the new PVC. This is in contrast to the supporting journals and general knowledge of the material that in PVC pipe exposed to sunlight for a long time there will be material degradation.

PP and PP(x)

Based on the thermogram generated from the TGA test in Figures 7 and 8 it can be seen that the level of decomposition in PP and PP material (x) is divided into two levels of temperature, namely: The first level is between 130°C and 428°C and the second level is above 428°C. However, since the amount of activation energy obtained is to compare between PP and PP (x) then in this study only used a curve of comparison rate of material degradation that occurred at first decomposition level that is between 130°C until 428°C. Based on the comparison of the mass loss curve between PP and PP(x) it can also be seen that there is a shift in the time function on the graph of PP(x) where the decomposition image is steeper than the PP graph, this is due to material damage during the heat treatment, (x) more easily/quickly decompose.

In the comparison graph of decomposition temperature with decrease of TGA mass and material degradation rate (dm/dt) of Figures 9 and 10, the decomposition process can be seen clearly where the heating starts at the preparation temperature of 80°C and there is a very small and constant mass drop to a temperature point of 227°C, this shows the release of water vapor present on the surface of the material, starting from this point 227°C the mass decrease begins to be apparent. The jumping peak dm/dt occurs at the next point i.e. 277°C to 428°C and the dm/dt rate decreases again and becomes constant over the 428°C point. Thus the most significant decomposition process in PP and PP (x) occurs at temperatures of 227°C to 428°C.

After obtaining the activation energy amount for PP is $E = 69.55$ kJ/mol and for PP (x) is $E = 62.30$ kJ/mol, indicating that the activation energy required until the decomposition of the material is smaller in the infant treated PP (x) bottle by boiling water for ± 5 minutes rather than a new PP baby bottle. This shows that in PP (x) there has been material damage at the time of heat treatment, where it is possible to decompose the substances contained in the PP material at boiling time.

Melamine and Melamine (x)

Based on the thermogram generated from the TGA test in figures 11 and 12 it can be seen that the level of decomposition in Melamine and Melamine (x) material is divided into two levels of temperature: First level between

130°C to 428°C and second level above 428°C. However, since the amount of activation energy obtained is to compare between Melamine and Melamine (x) then in this study only used one curve of comparison rate of material degradation that happened at the first decomposition level that is between 130°C until 428°C. Based on the comparison of the mass loss curve between Melamine and Melamine (x) it can also be seen that there is a shift in the time function on Melamine graph (x) where the decomposition image is steeper than Melamine graph, this is due to material damage during heat treatment, so Melamine (x) more easily/quickly decompose.

In the comparison graph of decomposition temperature with decrease of TGA mass and material degradation rate (dm/dt) of 11 and 12, the decomposition process can be seen clearly where the heating starts at the preparation temperature of 80°C and there is a very small and constant mass drop to a temperature of 227°C, this shows the release of water vapor present on the surface of the material, starting from this point 227°C the mass decrease begins to be apparent. The jumping peak dm/dt occurs at the next point i.e. 277°C to 428°C and the dm/dt rate decreases again and becomes constant over the 428°C point. Thus the most significant decomposition process in Melamine and Melamine (x) occurs at temperatures of 227°C to 428°C.

After obtaining the activation energy quantity for Melamine is $E = 46.14$ kJ/mol and for Melamine (x) is $E = 47.40$ kJ/mol, indicating that the energy required until the material decomposition is slightly larger in the Melamine bowl (x) that have been treated with heat by pouring it with boiling water into it instead of a new Melamine bowl. This indicates that Melamine is not significantly affected by the heat treatment. However at a certain temperature point in this case is the point 277°C, Melamine (x) first decomposes than Melamine which is not heat treated. This temperature is close to melamine boiling point of 300°C.

4. CONCLUSIONS

Based on the results of TGA research on PVC, PVC (x), PP, PP (x), Melamine and Melamine (x) then obtained the following conclusion:

The required activation energy to material decomposition is greater in PVC pipe that has been exposed to sunlight for ± 5 years than the new PVC. Namely $E = 66.27$ kJ/mol for PVC (x) and $E = 63.93$ kJ/mol for PVC.

Point 1 shows the non-homogeneity of PVC (x) sampled, i.e. PVC pipe that has been used for 5 years, left under open conditions where contamination of impurities may occur.

The required activation energy until the material decomposition is smaller in the infected PP (x) infant bottle by boiling with boiling water for ± 5 minutes rather than the new PP baby bottle. Namely $E = 62.30$ kJ/mol for PP (x) and $E = 69.55$ kJ/mol for PP.

The activation energy required in the PP (x) material is less than that of PP due to damage to PP (x) material during heat treatment, where it is highly possible to decompose the substances contained in PP (x) material at the time given heat treatment.



The required activation energy until the material decomposition is slightly greater in the heat-treated Melamine (x) bowl by pouring it with boiling water into it instead of the new Melamine bowl. Namely $E = 47.40 \text{ kJ/mol}$ for Melamine (x) and $E = 46.14 \text{ kJ/mol}$ for Melamine.

At a temperature point of 277°C , Melamine (x) first decomposes than Melamine which is not heat treated. This means that Melamine (x) decomposes faster after being treated for the first time. Further testing is necessary if this applies repeatedly to subsequent heat treatment.

In terms of heat treatment that occurs in everyday activities it can be seen that the PVC pipe need to be coating or coating to prevent the occurrence of contamination of impurities that would affect the mechanical strength of the material. Should also be considered to avoid direct contact on the installation of PVC pipe to sunlight. Similarly how sterilizing PP Feeding Bottles that have been done by parents of babies is less precise, because by boiling a bottle of newly purchased milk with boiling water will cause the decomposition of the substances contained therein. For later use any bottle of milk will be more susceptible to material degradation by high temperatures. For basic food/beverage ingredients Melamine is not too affected by the heat treatment given by pouring boiling water into a melamine bowl. It should be taken into account that used in this study is food grade labeled melamine tableware. However, although little, the effect persists and is advised to limit the use of melamine tableware.

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