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THERMAL STABILIZATION OF POLYVINYL CHLORIDE USING LEAD STEARATE AND COBALT STEARATE METAL SOAPS

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ABSTRACT

Polyvinyl chloride (PVC) has been proven to be non-resistant to heat, deteriorate, discolour and become brittle when they degrade. Therefore, the aim of this study is to apply lead and cobalt metal soaps of stearic acid as a thermal stabilizer in polyvinyl chloride to prevent degradation and also to determine the better stabilizer between lead stearate (PbSt) and cobalt stearate (CoSt). To stabilize polyvinyl chloride, lead stearate and cobalt stearate metal soaps were used and the amount of weight loss was measured. The study was carried out by heating a mixture of polyvinyl chloride and the metal soap in different proportions. To fully characterize the stabilization, the effect of time on the thermally stabilized polyvinyl chloride was also evaluated. The results showed that, metal soaps obtained from the same fatty acid with different metal ions displayed different stabilization ability as metal soaps obtained with the different fatty acids but the same metal ion. In conclusion, after they were subjected to the same conditions, lead stearate proved to be a better stabilizer compared to cobalt stearate. Also, when time was varied on stabilized polyvinyl chloride, it proved that time contributes to the degradation of polyvinyl chloride even when it is stabilized.

Keywords: Degradation, Heat, Heat Resistance, Polymeric Materials, Stearic Acid, Stearate Metallic Soaps

INTRODUCTION

Polyvinyl chloride is undoubtedly among the most frequently used plastics; it is widely applied in many branches of the national economy including industry and building [1]. Its advantages include comparatively high chemical resistance, low production costs, and an almost universal possibility of application as pastes, lattices, solutions, films, boards, and various extruded or molded pieces [2].

Polyvinyl chloride has played a key role in the development of the plastics industry over the past 40 years and continues to be a polymer of major importance. The reasons for its enormous versatility and range of application is derived from a combination of the basic structure which gives rise to a relatively tough and rigid material and its ability to accept a range of plasticizers and other additives which can modify its physical characteristics to produce a range of flexible products [3].

PVC has been proven to be non-resistant to heat and deteriorate, discolor and become brittle when they degrade [4]. Degradation during service life, or after careless disposal, is a chemical change that drastically reduces the average molecular weight of the polyvinyl chloride polymer. Since the mechanical integrity of a plastic depends on its high average molecular weight, wear and tear inevitably weakens the material. A great disadvantage of PVC is its rather low thermal stability. It is well known that PVC splits off hydrogen chloride at high temperatures; during this process polyene sequences are formed and the polymer is discolored. Up to about 220 °C hydrogen chloride is the only volatile degradation product. In the presence of oxygen, in addition to the dehydrochlorination, oxidation reactions can occur, which can also initiate chain scissions [5,6]. During the thermal degradation of PVC, three effects are known, which are, acceleration of the dehydrochiorination, bleaching of the degraded polymer and lowering of the molecular weight [7].

Thermal degradation is an intrinsic property of PVC and can be in form of oxidation, ultraviolet damage, thermal degradation, ozonolysis, e.t.c. During thermal degradation, the PVC is degraded on a chemical level leading to chain scission that can adversely affect the mechanical properties such as strength and malleability as well as appearance and color. Changes in synthesis conditions or special treatments that eliminate structural irregularities and improve the stability of the PVC can be used but cannot completely eliminate its degradation so stabilizers must be used [8].

When PVC is heated (170~180°C), chlorine and hydrogen in the molecules are eliminated and release of hydrogen chloride becomes evident. Once such decomposition starts, unstable structures are formed in the molecule, which further accelerate HCl elimination and decomposition [5]. As PVC is heated to soften during the extrusion or molding process, prevention of hydrogen chloride elimination due to heat and subsequent decomposition is required.

Thermal degradation has been handled in a commercially satisfactory way by the gradual development of a range of stabilizers, lubricants and other processing aids and the high quality material which has resulted has led to massive utilization of PVC by industry [9].

Stabilizers (metal compounds) are essential to prevent the chain reaction of decomposition [10]. They can also impart to the PVC enhanced resistance to daylight, weathering and heat ageing and have an important influence on the physical properties and the cost of a formulation. They are invariably supplied in the form of application - specific blends of which the main constituents are metal soaps, metal salts and organometallic compounds. The choice of heat stabilizer depends on a number of factors including the technical requirements of the PVC product, regulatory approval requirements and cost.

Many diverse agents have been used to stabilize plastics including traditional derivatives of heavy metals (e.g cadmium) but lead metallic soap (lead metal salts of fatty acids not lead metals) has been proven to be a more suitable stabilizer. They are good heat absorbers that absorb energy from heat by reversible inter-molecular proton transfer thereby reducing the rate of degradation [11].

Therefore, the aim of this study is to prevent chain scission and chain reaction of decomposition in PVCs, by applying lead and cobalt metal soaps of stearic acid as a thermal stabilizer in polyvinyl chloride to prevent degradation and also to determine the better stabilizer between lead stearate and cobalt stearate. This study is also geared towards producing PVCs that can't be degraded by heat even after been exposed to the exact amount/degree of heat enough to degrade it.

EXPERIMENTAL

Freshly prepared reagents were used for the polyvinyl chloride stabilization. All other solvents used were of analytical grade and were used without further purification.

Preparation of Lead Stearate soap

Exactly 9.2 g of the stearic acid was weighed. Then 50ml of hot ethanol was measured into a beaker. The weighed stearic acid was then dissolved in the measured ethanol and the mixture was treated with 20 ml 20% (w/v) sodium hydroxide solution. Then 100ml 30% (w/v) solution of lead oxide salt was slowly added to the same beaker. The mixture was continuously stirred during the addition. Then the precipitated soap of lead stearate was washed twice with 25ml of hot water then it was air dried [10].

Preparation of cobalt stearate soap

About 50 ml of hot ethanol was measured into a beaker then 9.2g of the stearic acid was weighed, the stearic acid was dissolved in the ethanol. The mixture was then treated with 20ml 20% (w/v) sodium hydroxide solution. Then 100ml 30% (w/v) solution of cobalt chloride salt was slowly added. The treated mixture was stirred continuously during the addition. Then precipitated soap of cobalt stearate was washed twice with 25 ml hot water and then air dried [10].

Determination of weight degradation of PVC (Blank)

The thermal degradation/stabilization study of PVC was made as a function of time and heat. A crucible was weighed and its weight was recorded. Exactly 1g of PVC was weighed into the crucible. The crucible was re-weighed to ensure that the PVC in it was exactly 1g. Then the crucible was labeled 'blank' and exposed to heat in an oven for 15minutes at 160^{o}C. The sample was allowed to cool on a desiccator for 20min. The experiment was carried out in triplicate and weight loss was determined and recorded [1].

Weight Stabilization of PVC with lead stearate

Crucibles (4) were weighed and each of the weights was recorded. PVC of weight 0.2, 0.4, 0.6 and 0.8g respectively was weighed into the 4 different crucibles. Exactly 0.8, 0.6, 0.4, and 0.2g of lead stearate soap were added into each of the same 4 different crucibles making 20%, 40%, 60% and 80% PVC respectively. They were all labeled accurately and each PVC and lead stearate was mixed thoroughly to obtain a homogeneous mixture. Each of mixture was exposed to heat in an oven for 15minutes at 160^{o}C then brought out of the oven. Each sample was allowed to cool in a desiccator for 20min. The experiment was carried out in triplicate and weight loss was determined and recorded [1].

Weight stabilization of PVC with cobalt stearate

Crucibles (4) were weighed and recorded. Then varying weights of PVC were measured into the 4 different crucibles (0.2, 0.4, 0.6 and 0.8 g respectively) also varying weights of cobalt stearate soap (0.8, 0.6, 0.4, and 0.2g respectively) was added differently to each crucible making 20%, 40%, 60% and 80% PVC respectively. They were labeled accurately. All were thoroughly mixed till each of the mixture was homogeneous. Each mixture was heated in an oven for 15minutes at 160^{o}C then brought out of the oven and left to cool in a desiccator for 20min. The experiment was carried out in triplicate and weight loss was determined and recorded [1].

Effect of varying time on 20% stabilized PVC with cobalt stearate

To the 80% cobalt stearate, 20% PVC was weighed into an already labeled crucible. The crucible containing the mixture was put in an oven for 30 min. It was cooled in a desiccator for 25min. Then the weight was recorded and the extent of stabilization was calculated. The same process was repeated for 45 and 60min. The experiment was carried out in triplicate.

Effect of varying time on 60% stabilized PVC with lead stearate

About 60% PVC (0.4 g PbSt and 0.6 g PVC) was weighed into an already labeled crucible. The crucible containing the mixture was put in an oven for 30 min. It was cooled in a desiccator for 25min. Then the weight was recorded and the extent of stabilization was calculated. The same process was repeated for 45 and 60min. The experiment was carried out in triplicate.

RESULTS AND DISCUSSION

During thermal degradation of polyvinyl chloride, the evolution of HCl (dehydrochlorination) results in the formation of organic bond in the polyvinyl chloride molecule. Therefore, as long as the extent of degradation is low and dehydrochlorination is not accompanied by secondary reactions, the degree of stabilization in the degraded polymer should provide an assessment of level of degradation [12].

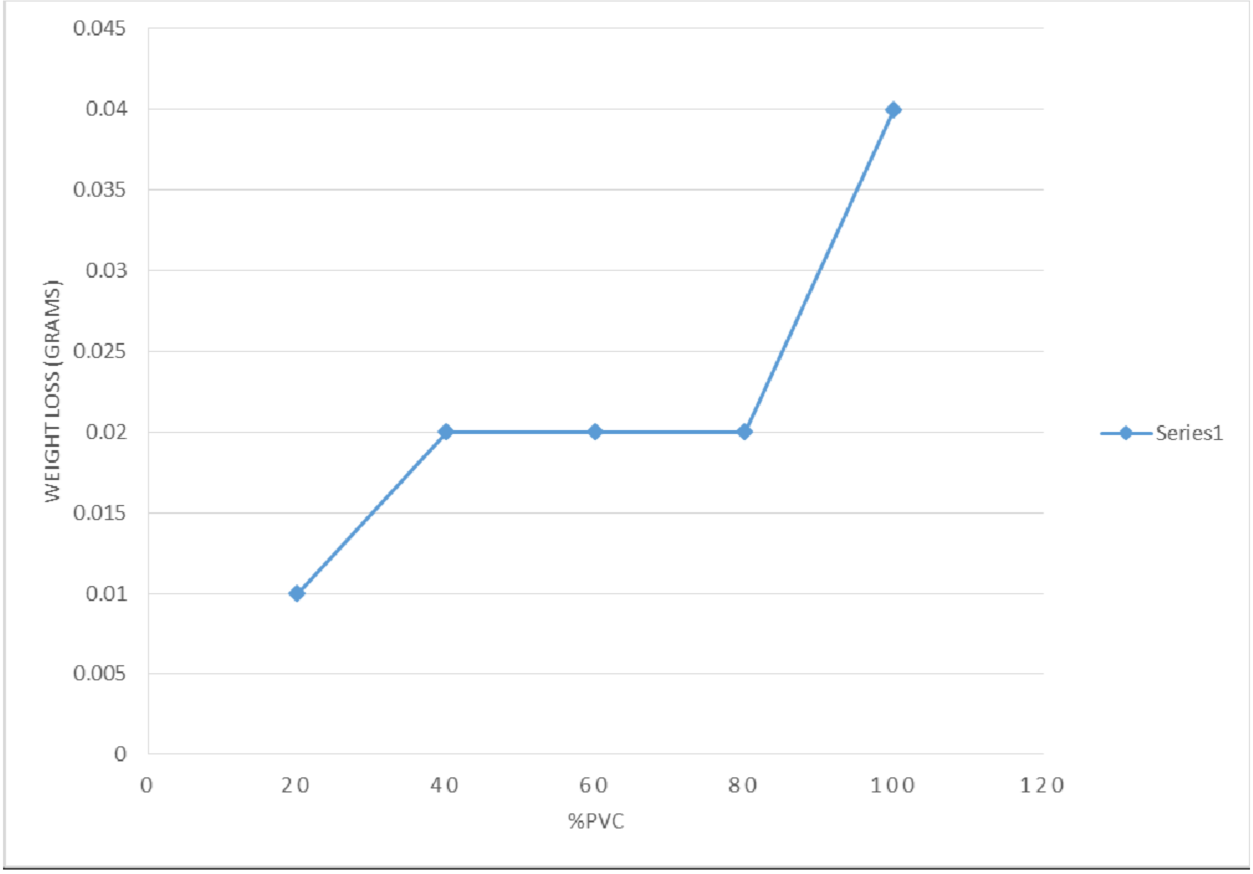

Figure 1: The stabilization of polyvinyl chloride using cobalt stearate (CoSt): Degradation at 160 °C for 15 minutes

In Figure 1, the results obtained gave a graph that decreased gradually from 100% polyvinyl chloride to 80% polyvinyl chloride and 20% cobalt stearate (0.04 and 0.02g), then maintained that trend from 80% polyvinyl chloride to 20% cobalt stearate (0.02g), 60% polyvinyl chloride to 40% cobalt stearate and 40% polyvinyl chloride to 60% cobalt stearate. Then it decreased slightly for 20% polyvinyl chloride to 80% cobalt stearate (0.01g). This shows that polyvinyl chloride stabilizes better with cobalt stearate in the ratio of 1: 4 polyvinyl chloride to cobalt stearate with a weight loss of 0.01g. In Figure 1, a decrease in degradation was shown.

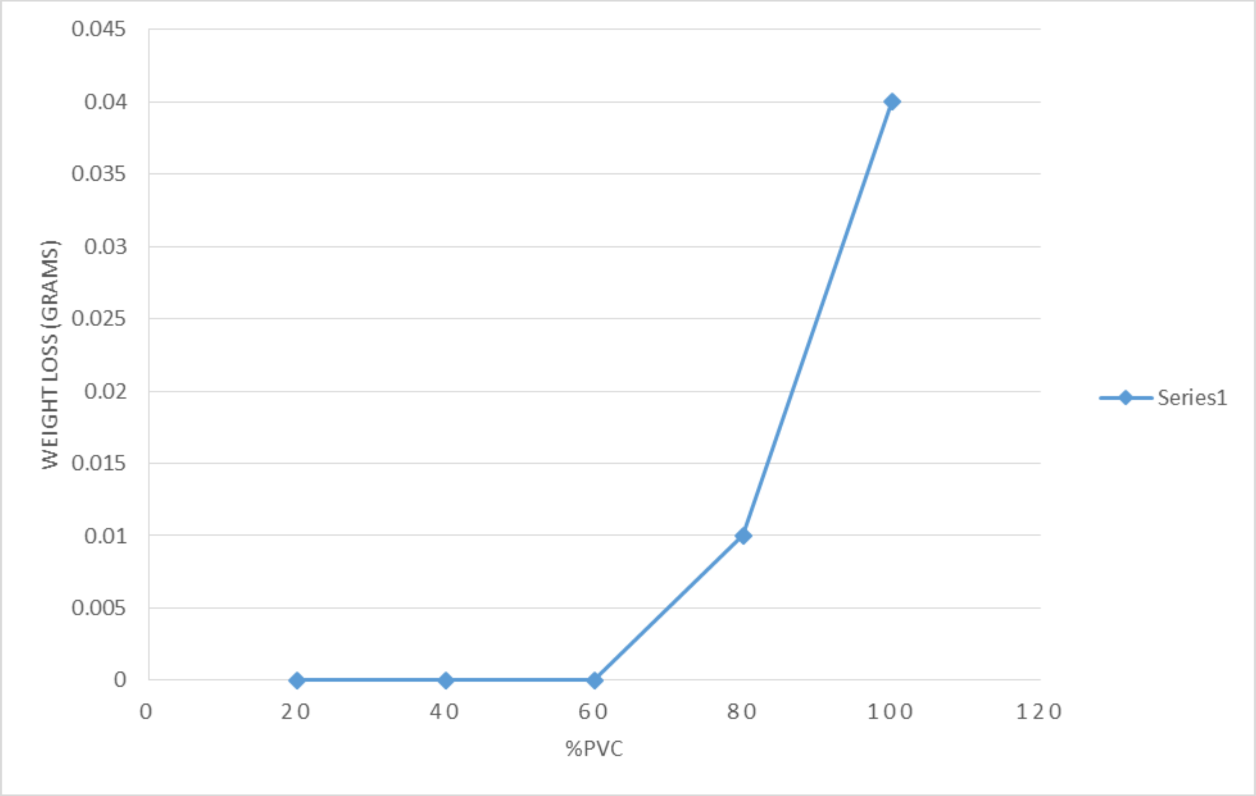

Figure 2: The stabilization of polyvinyl chloride using lead stearate (PbSt): Degradation at 160 °C for 15 minutes

In Figure 2, stabilisation of polyvinyl chloride using lead stearate at 160 °C for 15 minutes showed a decreasing trend. For 100% polyvinyl chloride, the weight loss was 0.04g then for 80% polyvinyl chloride to 20% lead stearate. The graph decreased steeply to 0.01g. For 60% polyvinyl chloride to 40% lead stearate, 40% polyvinyl chloride to 60% lead stearate and 20% polyvinyl chloride to 80% lead stearate the graph had a constant trend at 0.00g weight loss. The graph showed an increase in stabilization.

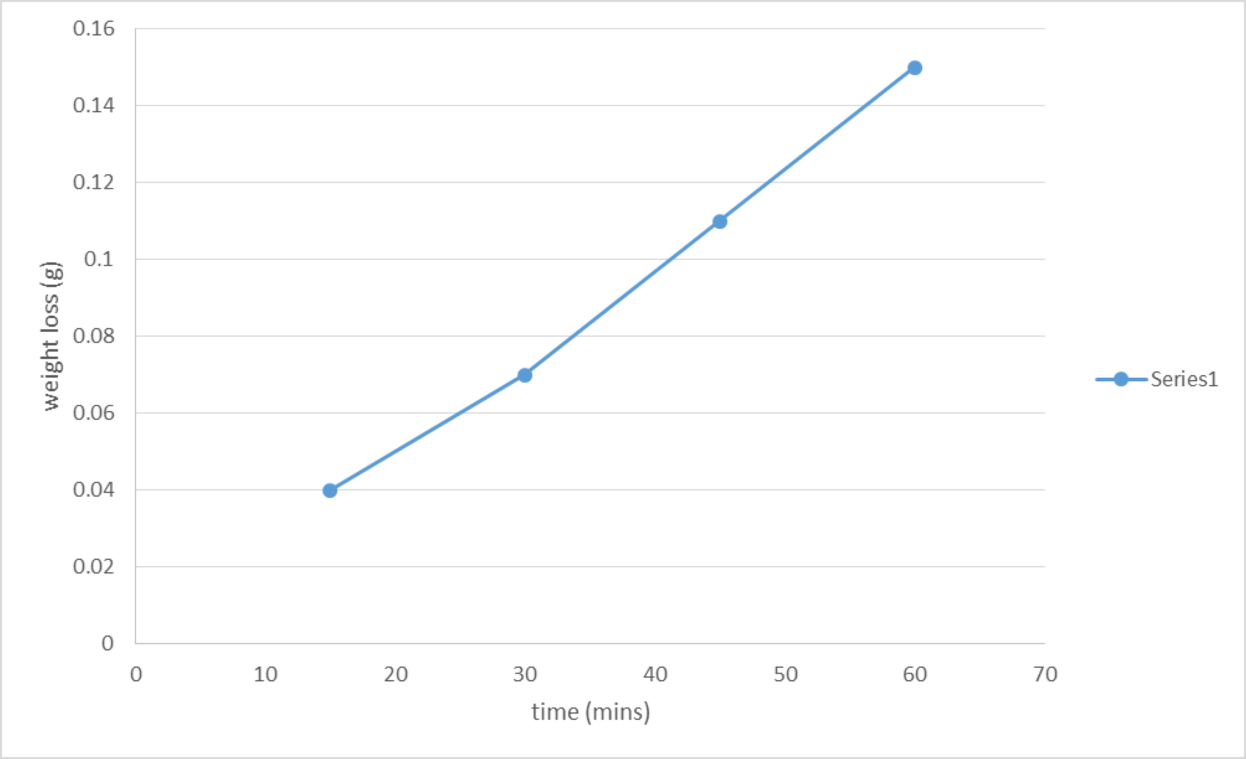

Figure 3: The degradation of polyvinyl chloride at 160°C

In Figure 3, the time effect on the degradation of polyvinyl chloride at 160 °C at a different time interval was shown. The graph has an increasing trend it grew from 15 – 30 min with 0.04g weight loss, 30- 45min with 0.07g weight loss, 30- 45min with 0.11g weight loss, 45-60min with 0.15g weight loss. This proves that polyvinyl chloride degrades with an increase in time at constant temperature [9].

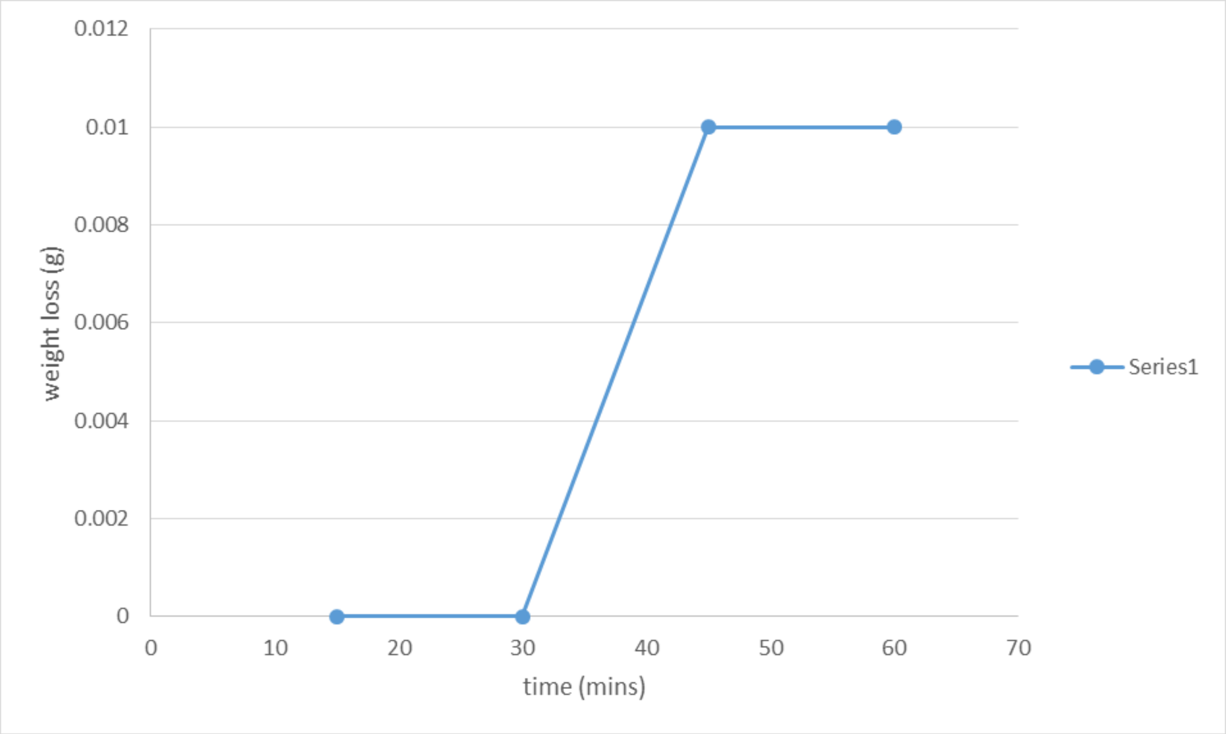

Figure 4: The effect of time on PVC stabilized (60%) with lead stearate

In Figure 4, the effect of time on the most stabilized ratio of polyvinyl chloride to lead stearate at constant temperature of 160 °C was shown. From Figure 2, polyvinyl chloride stabilizes with lead stearate at 60% polyvinyl chloride to 40% lead stearate for 15 min. In Figure 4, the sample was still stable for 15-30 min then degraded from 30-45 min losing 0.01g weight but continues constantly in that trend from 45-60 min.

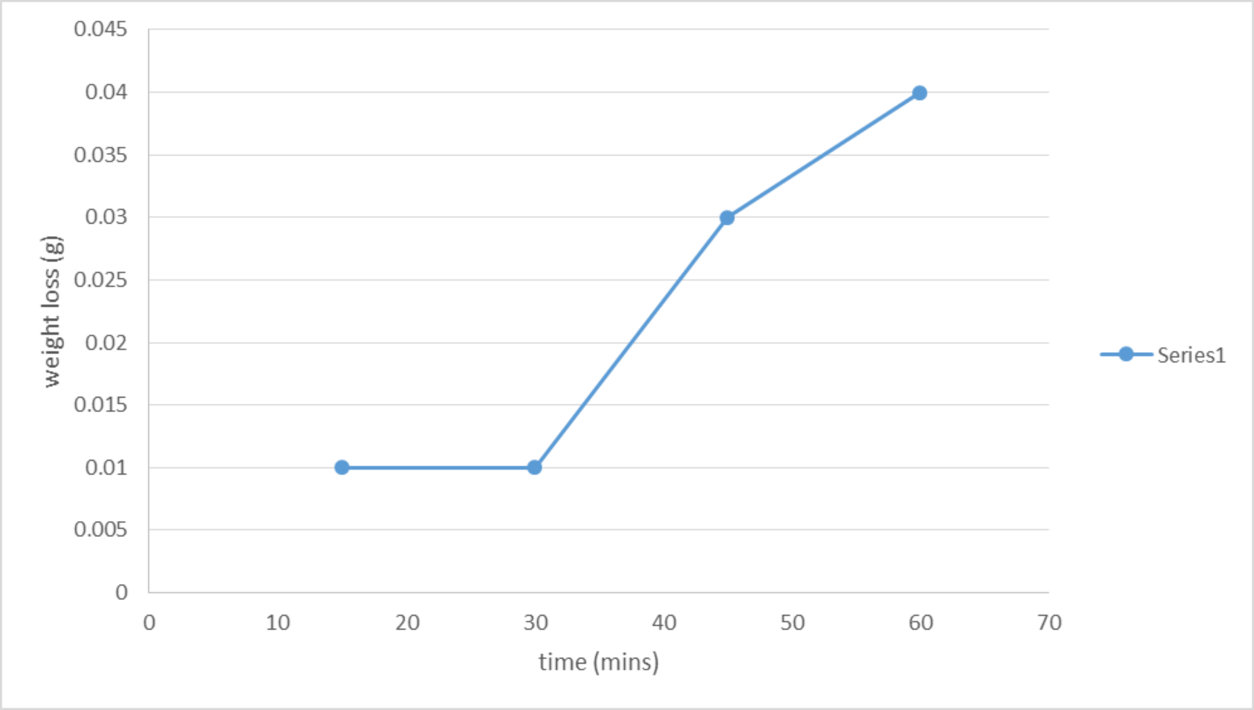

Figure 5: The effect of time on PVC stabilized (80%) with cobalt stearate

In Figure 5, the time effect of polyvinyl chloride stabilized with cobalt stearate was shown. In Figure 1, polyvinyl chloride stabilized best with 80% cobalt stearate to 20% polyvinyl chloride by degrading by just 0.01 g. Exposing the 80% polyvinyl chloride stabilized with 20% cobalt stearate to heat at varying time as shown in figure 4 to be constant from 15-30min (0.01 g) and grew for 30- 45 minutes from 0.01 g - 0.03 g then increased slightly for 45-30 min from 0.03 g to 0.04 g proving that there is an effect of heat at constant temperature on a stabilized polyvinyl chloride causing it to degrade [9].

The color intensity of the stabilized PVC was also studied using ultraviolet spectrophotometer with nitrobenzene at 420 nm. As shown in the appendix, the increase in the concentration ratio of polyvinyl chloride to lead or cobalt stearate showed an increase in color intensity of the mixture. This proves that the degradation of a metal soap and polyvinyl chloride affects it color intensity. This is shown in Tables 1 and 2 in the Appendix.

It should be noted that lead salts are toxic. The soluble salts of inorganic lead have been proven to be strong systemic poisons. These salts may accumulate within the body over a long period until toxic levels are reached. Though lead salts are good stabilizing agents for PVC its toxicity should not be trivialized.

CONCLUSION

The results obtained showed that lead stearate and cobalt stearate both had stabilizing effect on degradation of polyvinyl chloride when compared to polyvinyl chloride degraded in the same condition without any metal soap. When time was varied on stabilized polyvinyl chloride, it proves that time contributes to the degradation of polyvinyl chloride even when it is stabilized. Also, lead stearate is a better stabilizing agent on polyvinyl chloride compared to cobalt stearate after been subjected to same conditions.

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Conflict of Interests

No conflict of interest exists.

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APPENDIX

Table 1: Colorimetric analysis of PVC stabilized with cobalt stearate

PVC (%)	Absorbance Value
100	1.800
80	1.825
60	1.827
40	1.835
20	1.844

Table 2: Colorimetric analysis of PVC stabilized with lead stearate

PVC (%)	Absorbance Value
100	1.800
80	1.803
60	1.805
40	1.806
20	1.809