**International ACADEMY OF SCIENCE,
Engineering and Technology**

IASET Connecting Researchers; Nurturing Innovations

AN IMPROVEMENT STUDY OF PHYSICAL PROPERTIES OF POLY VINYL CHLORIDE USING ZINC CHLORIDE SALT

HAMEED K AL-DULIAMI

Department of Chemistry, College of Education for Pure Sciences, University of Al Anbar, Ramadi, Iraq

ABSTRACT

The operation of physical properties improvement for polyvinyl chloride PVC, using zinc chloride salt ($ZnCl_2.6H_2O$), as supporting material for the synthetic polymer, is considered the purpose of applied at this investigation, for the purpose of improving, enforcing the texture, besides increasing. It's durability and the resistance towards the external effects. the supported polymer had been studied by many ways, where firstly different weight percents of the salt has been used, which were (0.025-0.4%) many physical measurements have been taken to follow the changes over the surface of the polymer, moreover it's texture. These were via calculating the increments of hydroxyl coefficient (I_{OH}), and the carbonyl coefficient (I_{CO}), using infrared spectroscopy (I.R) and the visible ultraviolet (UV-Vis) to follow the changes at the constant of dissociation (K_d), parameter which used to illustrate the effect of salt addition, it has been found that the salt used. Led to increments at the polymer stability towards photo oxidation resulting from its exposure to environmental conditions, this had been detected due to the decreasing values of both (I_{OH}, I_{CO}) in addition to (K_d).

A continuation, the supported samples were investigated by using viscometer technique, via calculating turnover the average viscous molecular weight quantum yield, degree of fractionation and the average chain scission. The obtained results showed decrease at the average viscous molecular weight, the other variables which imply a good indicator for the increments of photo stability of the polymer. Finally the samples were followed, before and after the addition of the salt, via using the morphological technique to know the amount of energy absorbed by the samples, as well knowing the changes occurred on the surface after the irradiation

KEYWORDS: Zinc Chloride, Poly Vinyl Chloride, Improvement

INTRODUCTION

The majority of studies, aimed at industries and techniques that are ambient –friendly, most of countries, took different ways to protect the environment from the pollutants that have an effect on the atmospheric climate [1].

Among these techniques, is the use of polymers; characterized by simple synthesis, transportation, cost in addition to its harmless towards the ambient, One of which is polyvinyl chloride PVC, which is considered to be one of the many polymers of high resistivity towards the chemical corrosion, bacteria, fungus, besides it's good properties, such as the physical and the chemicals ones [2]. Around 50% of the produced PVC around the world is used at construction industry because it's manufacturing simplicity, low price and simple construction, never the less, there is fear of its effect on the environment, which is due to its instability towards height and heat, releasing hydrogen chloride from its structure. Moreover, there is a probability that the polymer could release also vinyl chloride to the water circulating through the PVC pipes, besides that the same factor could affect the food- conservation cans.

There is another danger emerges from that some chlorinated organic compounds may be resulted from PVC due to high heat (DCE, TCE) [3,4].

In general PVC would irritate the skin, there is an impression that PVC could be accumulated leading to cancer. For all above mentioned reasons many researchers had investigated many chemical additives to improve its general character is this, making it more reissuing towards external factors, depending on the fact it's easy mixing with other chemical [5] at the present study ($ZnCl_2.6H_2O$) had been added at different weight percents to the PVC. Many tests had been applied to select the best weight percents to improve PVC quality.

Finding new additives to improve the tested PVC quality, especially resistivity towards heat and sunlight.

EXPERIMENTAL

Purification of Chemicals

Commercial PVC (Germany) was used, it is purified by dissolving into tetrahydrofuran (THF), then precipitated by methanol, this process was twicely repeated. Then it has been dried under vacuum using the desiccators, at room temperature for 24 hrs. The molecular weight had been determined visco metrically, it was of the order (6.2×10^4) g/mol. $ZnCl_2.6H_2O$ was dried under vacuum, it was of analytical grade (fluka).

Sampling

The specimens were prepared as films, via dissolving PVC at constant concentration (10% w/v) of the polymer solution dissolved in (THF) 40 ^0C, of this stock solution were mixed 1mL of the used salt ($ZnCl_2.6H_2O$) as stabilizer of weight ratios (0.025-0.4 %) respectively, then it has been casted using glass flakes resulted into PVC films of (60 ±5) micron as thickness, measured by micrometer, (Q. U. Vtester-Q. panel, company, USA) then the films were cut to parts of (1.5x3)cm for the purpose of measurements.

Irradiation of Samples

The specimens were irradiated by using an accelerated irradiator assembled in the laboratory supplied with a power supply of (125 Watts) end a light filter of were length 356 nanometer for 125 hrs at many stages. The samples were placed vertically and parallely to the lamp to ensure the light fall tube vertically over the films, with changing the positions of the films periodically to ensure the coincidency of the light.

Spectral Studies

The changes occurred in the polymeric films were followed by fourier-transformer infrared (FT-IR), measuring the growth level of I_{OH}, I_{CO} as means of PVC degradation behavior under light of fact, beside the U.V measurements to know the absorbed bands intensity which calculated before and after the irradiation [6].

Morphological Study

The study of the morphology plays an assisting role to describe the degradation state, which the molecules reflect on the polymer surface due to the effect of high energy light (U.V) leading to a change in the colour of the surface, or may be alternating the colour totally, which reflected into a loss of the electrical, physical and the mechanical properties, which cause a softness, pitting on the external surface [7]. Reflective images for the polymer surface were taking via photomicroscope of enlarging capacity (x100) (NIKON, JAPAN).

RESULTS AND DISCUSSIONS

PVC considered to become more soft with temperature increasing, and hardening with its depression, as all plastic do, which referred to thermoplastics. Recent studies confirmed [8] that it affected by U.V which is near to the visible

radiation limited by the sunlight which posses photons of high energy, that could irritate the polymeric molecules and the impurities, especially chromopheric groups to be excited and transferred to high levels creating free radicals attacking the polymeric chains leading to its partition (photo degradation) [9].
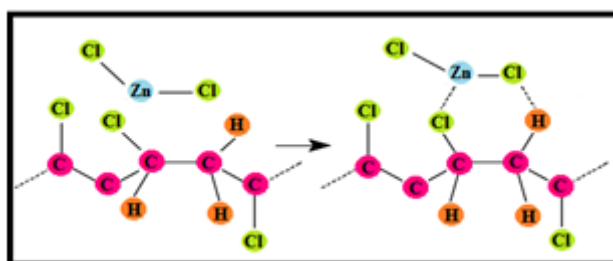
Which affect negatively on the physical and the mechanical properties of the plastic materials of external use. A lot of research had been done in the field of physical properties improvements of polyolefin, especially towards the light, using different chemical (organic and inorganic), besides the degradation, In this study ($ZnCl_2.6H_2O$) was used as an improving, packing of the polymer due to many reasons, of which surface homogeneousity, availability, hazardless and cheapness.

U.V-Visible

Indicated a drop down at the rate of photo degradation of the packed PVC films with the used salt in comparison with the untreatedfilms, where the stabilits of the films increasing with the amount of the saltadded as the decrease at the absorption reveal, which may be attributed to that an increase of the salt concentration prohibits the implementation of oxygen in to the polymer surface, resulting in to decrease into the photo oxidation degradation, which illustrated in table 1. These results had been confirmed by calculating the constant of dissolution (degradation) k_d, as figures (2, 6) show, in such a way that the highest additions gave the lowest k_d values, as table 2 reveals.

IR Spectra

Treated and untreated samples were investigated, using the growth of coefficients of I_{OH}, Ico as indicators. For both stability and photo degradation rates at the present system, therefore the changed had been noticed and then explained, where figure (1a,b,c) involves un treated PVC film of thickness (60 ±5 micron) before irradiation and after 125 hrs of irradiation in the presence and absence of the used salt. The figure illustrates many changes, where a change had been noticed at the light band clearly at a region above (3000 cm^{-1}), generally this band appears for both hydroxyl (and polymeric hydro peroxides [10] the change occurred at this band, is the intensity. For three samples, in such a way that the untreated film, it appears, weaker occulted due to the presence of few hydroxyl groups due to thermal oxidation before irradiation, or may be due to moistureduring measurements or samples handling[11]. For the same sample after 125 hrs of irradiation a clear wide–band had been noticed, which may be of hydroxyl or hydroperoxides formed as a result of degradation of PVC because of irradiation [12]. while concerning the sample that has $ZnCl_2.6H_2O$,the band once again decreased and located mid-way between the two previously mentioned bands, which could be a cause of rebinding of the degradated segments via coordination bonds between these segments and the salt, resulting into a decrease at the hydroxyl groups presence, or impedes its mobility. Also irregularity at the band intensely appeared at (1200-1650cm^{-1}), which could be of carbons. Revealing its strength after 125 hrs of irradiation, then turns to decrease after irradiate sample packed. This could imply that coordination bonds had been formed between $ZnCl_2$ and chlorine atom of the polymer. Leading to decrease at the presence carbonyl groups, this facilitates the mechanism of the polymer stabilization as the following scheme clarify.

For the purpose of enhancement the obtained results, the coefficients of absorption growth of both I_{CO}, I_{OH} had been calculated before and after the addition of the salt of the polymer films which are tabulated in the tables 3 and 4, which are calculated using the base – line method [13]. It has observed that these coefficients decreased as the concentration of the additive increased in comparison with the untreated films, which may be attributed to the fact that the increments of the additive may impedes the increased in comparison with the un treated films, which may be attributed to the fact that the increments of the additive may impedes the action of the light on the polymer surface as figures 7,8 demonstrate, where could notice the best stabilization concentration of the added salt was (0.4%) through shielding the radiation, and hence protecting the formation of the free – radicals and partitioned material due to the formation of charge transfer complexes, through the stoppage of their reacting [14].

Molecular Weights Determination

Showed that the average viscous molecular weight generally decreased as time of irritation increased. This due to the polymeric chains degradation as tables (5, 6) figures out. This decrease reduced at thepresence of the added salt figure 9, insuch of away that the decrease was so fast at the beginning of the irradiation due to the cleavage of bonds at the weak places along the polymeric chain, then becomes slower [15]. Figure 10 illustrates the proportional relationship between the rate of decrease of the average viscosity molecular weight (dMv\dt) and square viscosity molecular weight $(Mv)^2$ which improves, that the rapture was random, a fact which demonstrated though proportional relationship between the average of the chain scission (s) and the degree of partition (α) with time as in figure 11,12 respectively [16]. Via which one could deduce that the values of (s) and (α) for the supported films were less than the pure films, another indicator of salt efficiency towards quenching the photo degradation.

Table 7 demonstrates that quantum yield of chain scission of the improved film, is less than that of the pure film [17].

Surface Study

Selected regions of the polymer surface had been irradiated, to follow the changes before and after the irradiation. the best packing was at (0.4%) figures (15, 16), where it's clear that there are less defaults in comparison with the pure films figures (13,14), fact that proves that the added salt acted as stabilizer and improving agent for the polymer, which enable it to resist climatological conditions, especially the UV light and heat which consider with the obtained results via the previously mentioned ones, that of I.R (UV – Vis).

REFERENCES

1. T. Ayako and H. Hirose, Polymer Deg. Stab., (1999), Vol. 63, p 441.

2. E. Wilkes, A. Daniels, W. Summers, "PVC handbook", Akron- Ohio, USA, (2005).

3. E. Plinke, N. Wenk, and others, Mechanical Recycling of PVC wastes, Basel Milan Lyngby, January 2000.

4. Clayton Huggett and Barbara C. Levin, National Bureau of Standards, National Engineering Laboratory, Center for Fire Research, Gaithersburg,, USA, (1987), Vol.11, P.131-142.

5. Mr. A. W. Barnes, (ICI Plastics Division, Welwyn Garden City, Hertfordshire), Proc. roy. Soc. Med. April 1976, Volume 69.

6. S.I. Skuzina and A.I. Mikhailov, Institute of Problems of Chemical Physics Russian academy of Science, High energe Chemistry, (2010), Vol: 44, No: 1.

7. Taraq Abdul Jalal, Anbar University Journal of Pure Science,(2007) Volume 1, No: 2, 2007

8. W. Mareehall, Polyester Synthesis and Chemical Aspart, (2007), pp3, 77.

9. Herrera-Franco P., J. Valadez - Gonzolez, A. Composites B., (2005), Vol. 36, P 597.

10. C. Decker and K. Zahonily, Polym. Deg. Stab., (1999), Vol. 64, P. 293.

11. C. G Smith. and Others, Analysis of Synthetic Polymer and Rubbers, Analytical Chemistry, (1993), Vol. 65.

12. O.Chiantore, G. Camino, L. Costa, N.Grassise, Polym. Deg. Stab.,(1981) Vol.3, p 209-219.

13. W. Harris and B. Kratochvil, "An introduction to chemical analysis" New York, (1981), P. 572.

14. R. Walter, A. Marco, Polymer Degrdation and Stability, 93, pp276-280.

15. R. Chandra and S. P. Handa, J. Appl. Polym. Sci., (1982), Vol. 27, P. 1945.

16. R. H. Boyd, Thermal Stability of Polymer, Vol. I, R. T. Conley Ed., Dekker, New York, (1970), p. 75.

17. R. Chandra, B. P. Singh, S. P. Handa, polymer J., 1981, Vol. 22, P. 523.
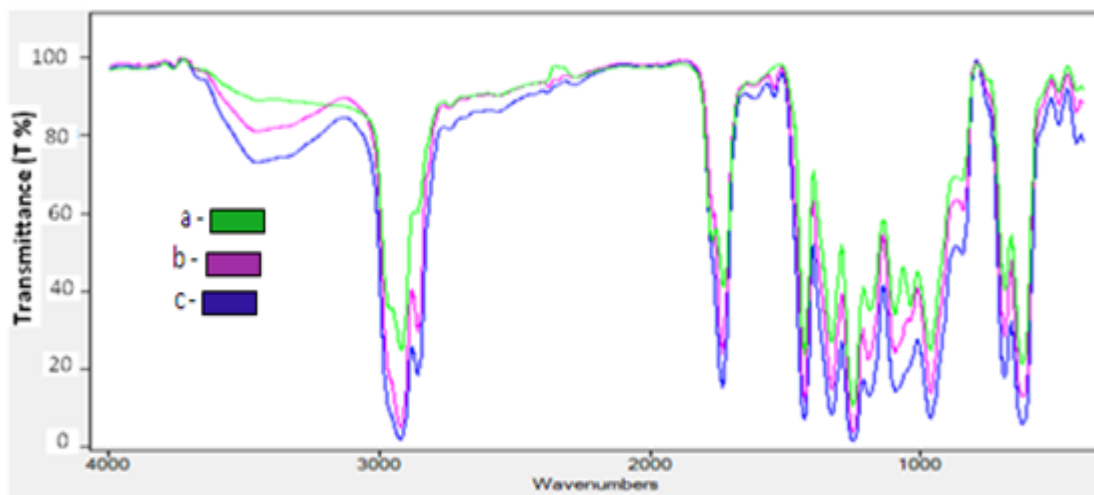
APPENDICES

Figure 1: I. R Spectra for PVC (60 ±5) Micron a) Additive Free before Irradiation b) with 0.4% ZnCl$_2$ after 125 Hrs Irradiation c) A Free after 125 Hrs Irradiation

Table 1: Absorption Values for PVC Films of (70 ±5) Micron with Different Concentrations of ZnCl$_2$ at ƛ = 286 nm, (U.V –Vis.)

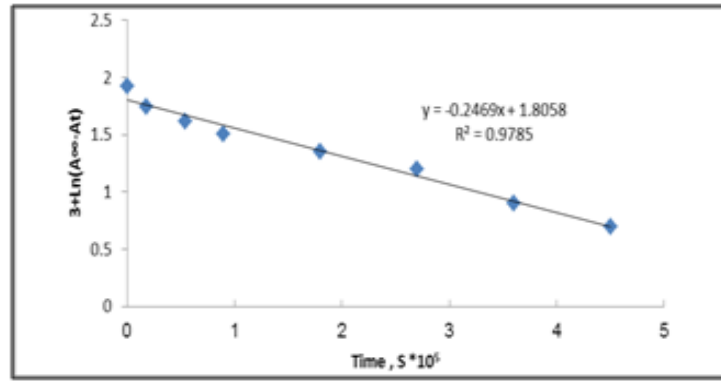| Time \ Hrs Irradiation Con. %	Absorption							
	0.0	5	15	25	50	75	100	125
PVC	0.301	0.364	0.419	0.464	0.501	0.559	0.604	0.673
PVC + 0.025	0.230	0.286	0.319	0.345	0.378	0.405	0.447	0.470
PVC + 0.050	0.227	0.269	0.283	0.322	0.340	0.363	0.408	0.429
PVC + 0.100	0.213	0.255	0.263	0.298	0.326	0.335	0.370	0.408
PVC + 0.200	0.208	0.223	0.240	0.276	0.293	0.304	0.336	0.378
PVC + 0.400	0.201	0.215	0.226	0.246	0.265	0.288	0.318	0.342

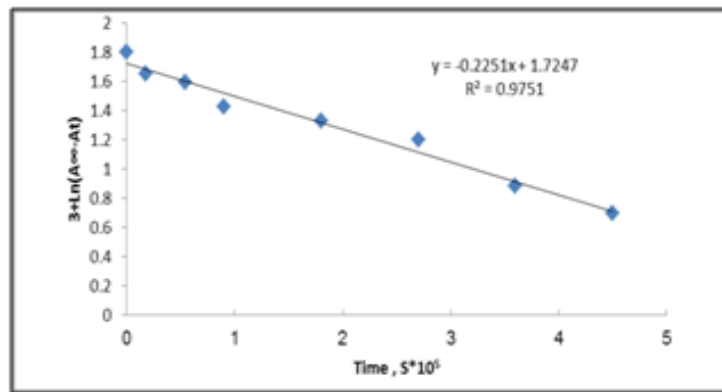**Figure 2: Relationship between Ln. of (0.025%) $ZnCl_2$ in PVC Film**

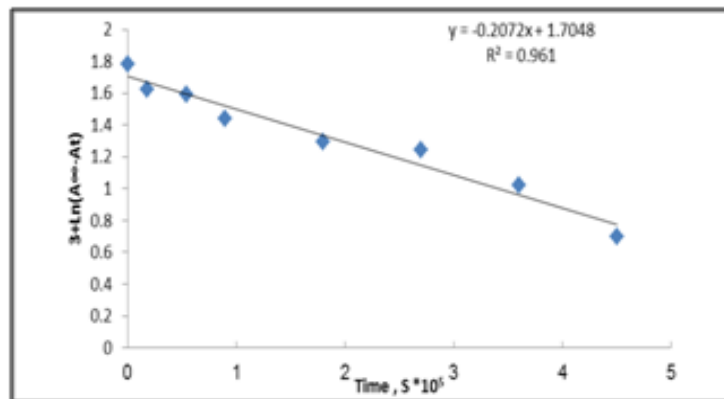**Figure 3: Relationship between in of (0.05%) $ZnCl_2$ in PVC Film of (60 ± 5) Micron Thickness**

Figure 4: Relationship between in of (0.1%) $ZnCl_2$ in PVC Film of (60 ± 5) Micron Thickness
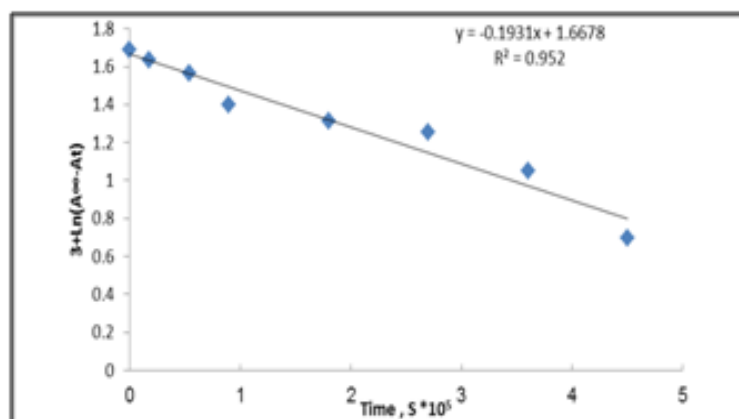

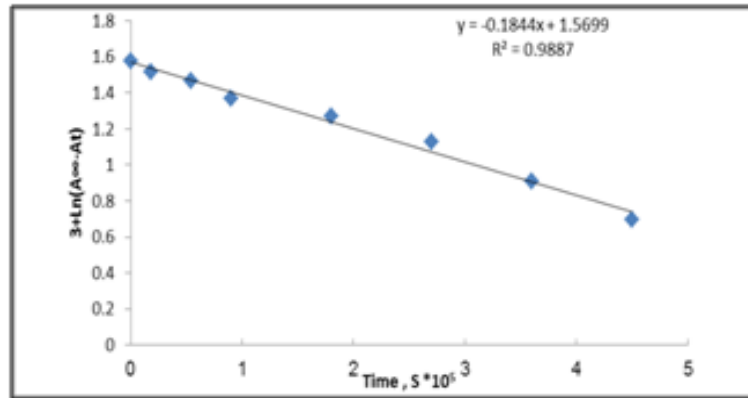**Figure 5: Relationship between ln of (0.2%) $ZnCl_2$ in PVC Film of (60 ± 5) Micron Thickness**

Figure 6: Relationship between in of (0.4%) ZnCl$_2$ in PVC Film of (60 ± 5) Micron Thickness

Table 2: Rate Constants of ZnCl$_2$ Degradation in PVC Film of (60$\pm$5) Micron Thickness

K$_d$ ×10^{-5}(Sec)$^{-1}$	Concentrations
0.246	0.025
0.225	0.050
0.207	0.100
0.193	0.200
0.184	0.400

Table 3: Carbonyl Index Values (I$_{CO}$) with Irradiation Time

Time \ Hrs Irradiation Wt% of Addition	Carbonyl Index (Ico)					
	0.0	25	50	75	100	125
PVC	1.392	1.721	1.949	2.413	2.807	3.304
PVC + 0.025 CoCl$_2$	1.356	1.573	1.785	2.110	2.580	2.957
PVC + 0.05 CoCl$_2$	1.307	1.512	1.681	1.967	2.330	2.630
PVC + 0.1 CoCl$_2$	1.269	1.476	1.612	1.783	2.088	2.345
PVC + 0.2 CoCl$_2$	1.214	1.412	1.506	1.613	1.785	2.010
PVC + 0.4 CoCl$_2$	1.158	1.266	1.329	1.483	1.615	1.834

Table 4: Hydroxyl Index Values (I$_{OH}$) with Irradiation Time

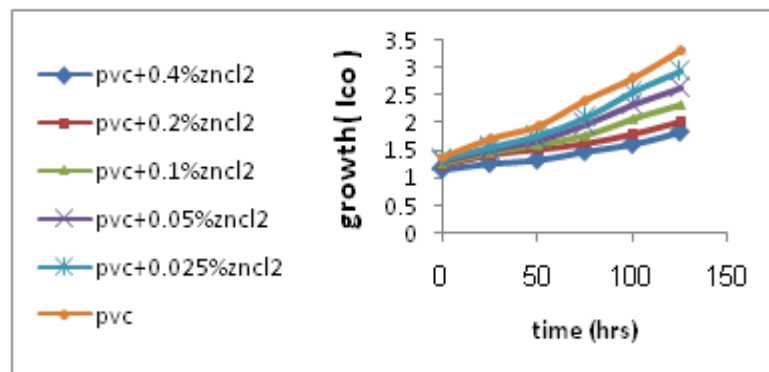| Time \ hrs Irradiation Wt% of Addition	Carbonyl Index (I$_{OH}$)					
	0.0	25	50	75	100	125
PVC	0.000	0.512	0.774	0.857	0.986	1.209
PVC + 0.025 CoCl$_2$	0.000	0.437	0.695	0.751	0.840	0.956
PVC + 0.05 CoCl$_2$	0.000	0.377	0.611	0.678	0.723	0.814
PVC + 0.1 CoCl$_2$	0.000	0.329	0.563	0.618	0.669	0.731
PVC + 0.2 CoCl$_2$	0.000	0.265	0.470	0.566	0.607	0.668
PVC + 0.4 CoCl$_2$	0.000	0.216	0.412	0.504	0.552	0.607

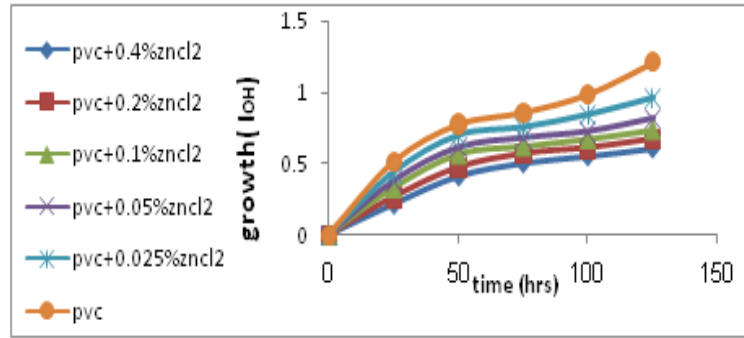**Figure 7: Relationship between Carbonyl Absorption Index with Time of Irradiation**

Figure 8: Relationship between Hydroxyl Absorption Index with Time of Irradiation Time

Table 5: Value Calculated from Measurement of Molecular Weight and Viscosity for Pure PVC Films

Time Irradiation	M_v	$(M_v)^2 \times 10^9$	$\frac{dMv}{dt} = \frac{Mvo - Mvt}{t}$	Degree of Polymerization P	$\frac{1 \times 10^{-4}}{P}$	Dag. Degree$\alpha \times 10^{-3}$	Ava. Chain Scission (S)
0.0	62812.143	3.945	∞	1004.994	9.950	0.0	0.0
25	46789.572	2.189	0.178	748.633	13.300	0.335	0.336
50	35831.023	1.283	0.149	573.296	17.400	0.745	0.748
75	30642.816	0.938	0.119	490.285	20.300	1.035	1.040
100	26934.752	0.725	0.099	430.956	23.200	1.325	1.331
125	23753.306	0.564	0.086	380.052	26.300	1.635	1.643

Table 6: Value Calculated from Measurement of Molecular Weight and Viscosity for Pure PVC with (0.05%) from Salt ZnCl₂

Time Irradiation	M_v	$(M_v)^2 \times 10^9$	$\frac{dMv}{dt} = \frac{Mvo - Mvt}{t}$	Degree of Polymerization P	$\frac{1 \times 10^{-4}}{P}$	Dag. Degree$\alpha \times 10^{-3}$	Ava. Chain Scission (S)
0.0	62812.143	3.945	∞	1004.994	9.950	0.0	0.0
25	53887.503	2.903	0.099	862.200	11.598	0.164	0.164
50	47912.175	2.295	0.082	766.594	13.044	0.309	0.310
75	44606.203	1.989	0.067	713.699	14.011	0.406	0.408
100	40107.744	1.608	0.063	641.723	15.583	0.563	0.565
125	35103.538	1.232	0.061	561.656	17.804	0.785	0.788

Table 7: Values of Quantum Yield of Chain Session for Pure an 0.05% ZnCl₂ Added Salt of (60±5) Micron Thickness for 100 hrs under $I_O=1.5 \times 10^{-8}$ Ein.dm^{-2}s^{-1} Light Intensity

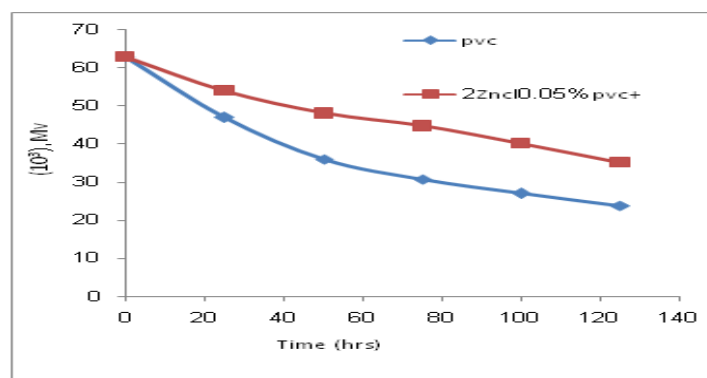| Φcs X10⁻⁴	Addition	S
1.962	PVC	.1
0.834	Zncl₂ + PVC	.2

Figure 9: Relationship between Average Molecules Weight Viscosity with Time of Irradiation for PVC with Thinness (60±5) Micron in Presence and Absence (0.05%) Concentration ZnCl₂
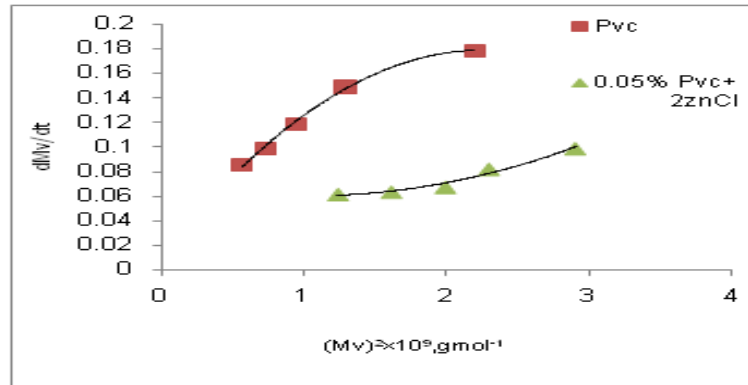
Figure 10: Relationship between the Rate at Decrease in Average Molecular Weight Viscosity (dMv/dt) and Square of Average Molecular Weight Viscosity of PVC Film with Thickness (60 ± 5) Micron in Presence and Absence (0.05%) Concentration of $ZnCl_2$
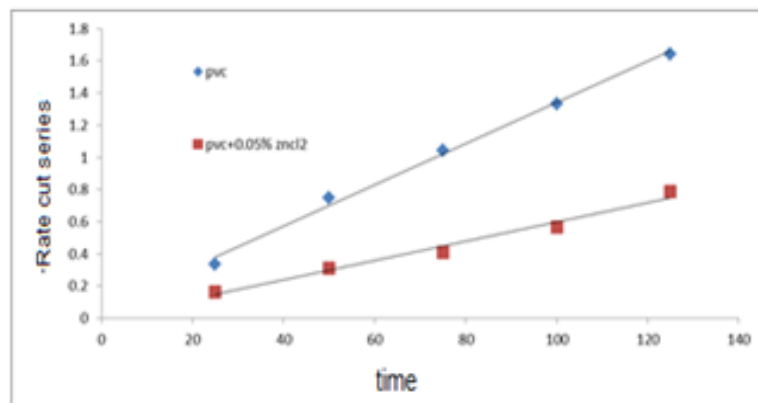

Figure 11: Relationship between Rate Cut Series with Time of Irradiation for (P.V.C) with Thinness (60+5) Micron in Presence and Absence (0.05) Concentration $ZnCl_2$
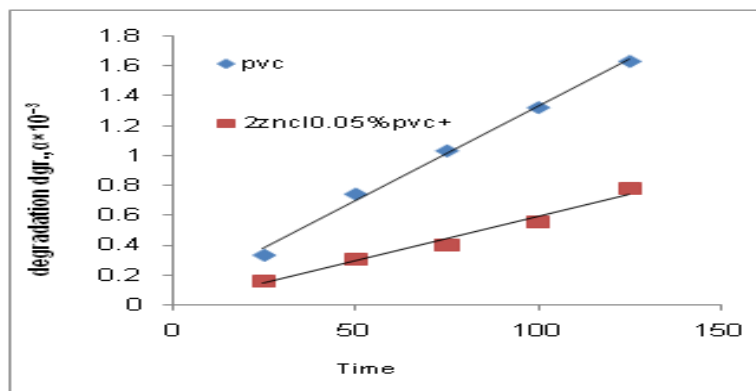

Figure 12: Relationship of Degradation Degree with Time of Irradiation for PVC Film by Thickness (60+5) Micron in Presence and Absence %0.05 Concentration of $ZnCl_2$
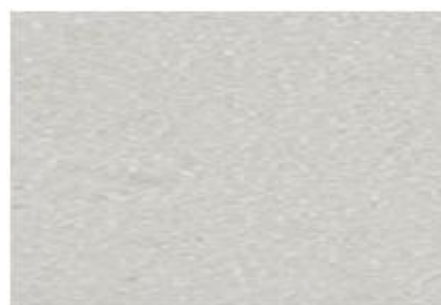

Figure 13: PVC before Irradiation

Figure 14: PVC after 125 Hrs Irradiation

Figure 15: PVC Contain 0.4% ZnCl$_2$ before Irradiation

Figure 16: PVC Contain 0.4% ZnCl$_2$ after Irradiation