



## Study of The Photostabilization Of Polystyrene In The Presence And Absence Of Schiff Base Derivatives

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### Abstract

The initiated photodegradation of polystyrene films notice able all around were examined (for 400 hrs.) in the being and absence of Schiff bases for benzoxazin product compounds by quickened weathering analyzer. The adding of (0.1% wt/v) of organic compounds to polystyrene films (thickness, 25 $\mu$ m) diminished the degradation of the polystyrene. The rate of degradation was trailed by an expansion in absorption of carbonyl for polymers utilizing viscosity, I.R., and UV spectra estimation. As per the results, the initiated degradation instruments of polystyrene films were recommended under the exploratory term utilized utilizing temperature 45 °C, radiation of UV at  $\lambda = 313$  nm, illumination force  $3.49 \times 10^{-5}$  einsteins.dm<sup>-3</sup>.S<sup>-1</sup>.

**Key words:** photodegradation, photostabilization, polystyrene, Schiff bases

### 1. Introduction

Polystyrene (PS), is the most critical substances since the recent plastic production, has been utilized everywhere throughout the world, because of its low-cost and exceptional physical properties. Presentation to bright (UV) radiation may cause considerable degradation of numerous materials. The radiation of UV causes photooxidative which brings about breaking of the polymer chains, results radicals and diminish the molecular weight, making weakening of mechanical characteristic and leading to useless substances, after an unusual time<sup>(1)</sup>. The synthesized Schiff bases were used as photostabilizers for polystyrene against photodegradation. Polystyrene polymeric films containing synthesized Schiff bases (0.5% by weight) were irradiated ( $\lambda_{max} = 365$  nm and light intensity =  $6.43 \times 10^{-9}$  ein·dm<sup>-3</sup>·s<sup>-1</sup>) at room temperature. All the additives used enhanced the photostability of polystyrene films against irradiation compared with the result obtained in the absence of Schiff base. The Schiff bases can act as photostabilizers for polystyrene through the direct absorption of UV radiation and/or radical scavengers<sup>(2-12)</sup>. Recently, we have reported successful polymeric films photostabilization processes by the use of various additives at low concentrations<sup>(13-18)</sup> as part of our continuing interest in the field of polymeric materials<sup>(19-21)</sup>. The point of this work considers the photodegradation polystyrene in presence of

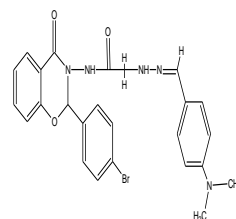
organic compounds and compared with polystyrene (control).

### 2. Experimental

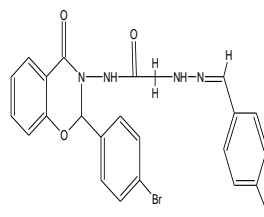
#### 2.1. The chemicals were used:

a- Polystyrene (commercial) (purity 99%).

b- *N*-[2-(4-bromophenyl)-4-oxo-2*H*-1,3-benzoxazin-3(4*H*)-yl]-2-[(*2E*)-2-(*N,N*-dimethyl chlorobenzylidene)hydrazino]acetamide (1), was synthesized and characterized according to method described previously<sup>(22)</sup>. IR. Spectra data: (C-H)ar 3046, (C-H)al. 2922,2860, (C=N) 3398.



c. *N*-[2-(4-bromophenyl)-4-oxo-2*H*-1,3-benzoxazin-3(4*H*)-yl]-2-[(*2E*)-2-(4-chloro benzylidene)hydrazino]acetamide (2), was synthesized and characterized according to method described previously<sup>(22)</sup>. IR. Spectra data : (C-H)ar 3047, (C-H) al.2939, (N-H) 3452, (C-CL) 623.



**2.2. Ultraviolet visible spectrophotometry (U.V):**

The U.V spectra was recorded on spectrophotometry type the Hitachi U-2000 in the ( $\lambda=200-600$ ) nm

**2.3. Infrared spectrophotometry (IR)**

IR spectra between (600-4000)  $\text{cm}^{-1}$  was recorded by A Pye-Unicam SP<sub>3</sub>-100 infrared spectrophotometer.

**2.4. Film preparations**

A solution of polystyrene (5%) in chloroform was added to 0.1% solution of 1 or 2. A thickness (25 $\mu\text{m}$ ) was calculated by a micrometer type (2610, Germany), polystyrene without and with 1 or 2 were resulted by molding of solutions into horizontal glass coat. Polymers were dehydrated in vacuum for 24 hrs after solvent evaporation.

**2.5. Irradiation**

For irradiation of polystyrene films, the accelerated weather-o- meter, was used. The films were put aloof from the UV.lamps at  $\lambda=313$  nm . and temperature ( 45 °C).

**2.6. Thermo gravimetric analyses (TGA)**

were carried out using a TA Instruments Q500, operating under nitrogen and under air environments, with a 10 °C temperature ramp rate.

**2.7. Analysis**

I.R and U.V-Vis. spectrophotometer were used to follow the photodegradation of the polymer film. ( $I_{\text{CO}}$ ) were studied by relationship of the infrared absorption peak at 1750  $\text{cm}^{-1}$  for (C=O) and indication peak at 1440 $\text{cm}^{-1}$  for (C=C) bond for benzene.

$$\text{Carbonyl index (Ico)} = \frac{\text{Area of bsorption peak at } 1750 \text{ cm}^{-1}}{\text{Area of absorption peak at } 1440 \text{ cm}^{-1}}$$

To study the modify in the spectra of U.V-Visible through irradiation, the ultraviolet-visible spectrophotometer was used and this was used in calculating the rate of photodecomposition of the sensitizers 1 &2 by monitoring the increase in absorbance at  $\lambda=455$  nm and 435 nm respectively with irradiation time. The photodegradation rate constant for additives ( $k_d$ ) was calculated using the first order equation<sup>(7)</sup>.

$$\text{Ln}(A_{\infty} - A_t) = \text{Ln}(A_{\infty} - A_0) - k_d t \dots(1)$$

Where ( $A_t$ ) is the absorption intensity after irradiation time (t),  $A_0$  is the absorption intensity of the polymer film containing additive before irradiation and ( $A_{\infty}$ ) is the absorption intensity at infinite irradiation time.

**2.7. Determination of Viscosity Average Molecular Weight ( $M_v$ ) Using Viscometry method**

To determinate the molecular weight of the polymers the viscosity property was used using Mark -Houwink relation<sup>(8)</sup>

$$[\eta] = K (\overline{M}_v)^{\alpha} \dots\dots(2) .$$

where,  $[\eta]$  = intrinsic viscosity

K and  $\alpha$ : are constants for a polystyrene at a used temperature in a used solvent.

The viscometer type Ostwald U-tube was used to measur the intrinsic viscosity of a polymer solution. To made the solutions of polystyrene, the films was dissolved in a chloroform (g/100mL) and the run times of polystyrene (t) and pure solvent ( $t_0$ ),were calculated respectively. The relative viscosity ( $\eta_{\text{rel}}$ ) which is given by the ratio of the run time for the solution (t) to the flow time of the clean solvent ( $t_0$ ) was studied from equation (3)

$$\eta_{\text{rel}} = \frac{t}{t_0} \dots\dots(3)$$

The specific viscosity ( $\eta_{\text{sp}}$ ), which is the relative increment in viscosity of the solution over the viscosity of the solvent is :

$$\eta_{\text{sp}} = \frac{(\eta - \eta_0)}{\eta_0} = \eta_{\text{rel}} - 1 \dots\dots(4)$$

The Huggins relation<sup>[8]</sup> was used to calculate the intrinsic viscosity ( $[\eta]$ ) is the limiting viscosity number or (the reduced specific viscosity).

$$[\eta] = \left[ \left( \sqrt{2} / C \right) (\eta_{\text{sp}} - \ln \eta_{\text{rel}}) \right]^{1/2} \dots(5) .$$

Where , C = concentration of polystyrene solution (g/100 mL). By using equation (1), the viscosity average molecular weight of polystyrene before and after degrdation were calculated

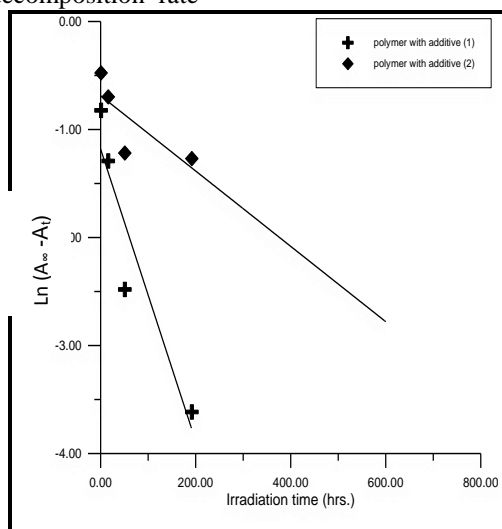
**3. Results and discussion**

The spectra of polystyrene (control) irradiated with several time has been used to study the photodegradation of polymer films. The absorbance is decreased after 600 hrs. of irradiation, the decrease rate is comparatively bigger than in the ( $\lambda= 230-325$ ) nm. this is due to the separation of chain bonds in polystyrene.

In this study, the degradation of polystyrene films was studied with photosensitizers (1 and 2) . From the results obtained, the absorbance of the polystyrene with 1 and 2 at  $\lambda= 435-455$  nm

slightly decrease with time of irradiation because the dissociation of photosensitizers (1 and 2). Figure (1) show the variation of  $\ln(A_t - A_\infty)$  of polystyrene and sensitizers 1 & 2 with irradiation time at  $\lambda=313$  nm at wave length ( $\lambda = 455$  nm), ( $\lambda = 435$  nm) respectively. A straight line is obtained which indicates primarily a first order reaction and the decomposition rate constant ( $k_d$ ) for sensitizers was calculated from the slope value. The photodecomposition rate

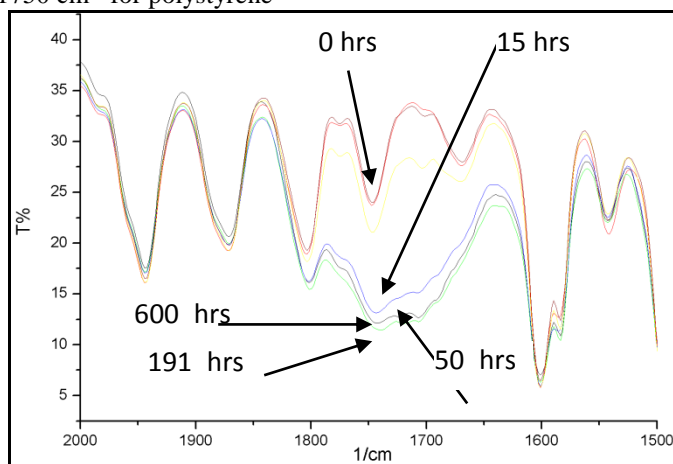
constant ( $k_d$ ) was calculated and it has been found the ( $k_d$ ) sensitizer 2 ( $k_d = -5.8 \times 10^{-5} \text{ min}^{-1}$ ) is higher than ( $k_d$ ) for sensitizer 1 ( $k_d = -2.25 \times 10^{-5} \text{ min}^{-1}$ ). It is concluded that the photodegradation rate of polystyrene with sensitizer 2 is higher than polystyrene with sensitizer 1. From the results obtained from kinetic and electronic spectroscopy, the sensitizer 1 was more stable compared with sensitizer 1.



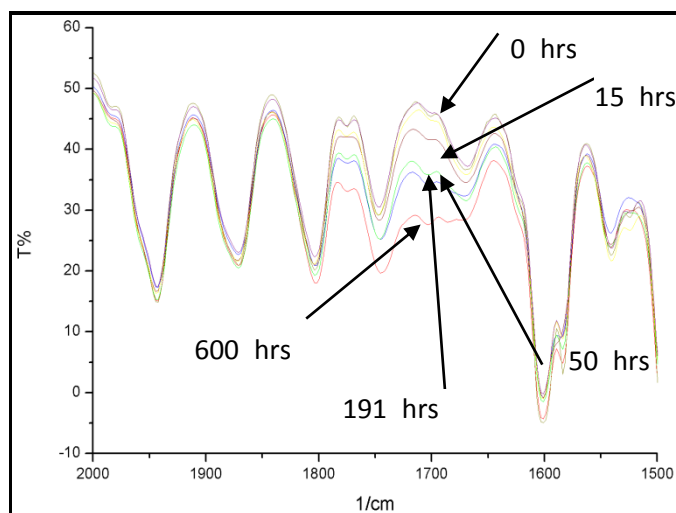
**Figure (1):**Logarithm change of absorbance with irradiation time for polystyrene with additive 1 & 2 at 435 nm

The FT-IR (fig.2) shows the high growth of carbonyl groups for polystyrene (control) after the (control) irradiated at ( $\lambda=313$  nm), while the FT-IR (fig.3) shows decrease in progress of (C=O) absorbance at  $1750 \text{ cm}^{-1}$  for polystyrene

with sensitiz (1), and with irradiation time this group strength decreases exponentially. The term carbonyl index ( $I_{CO}$ ) is expressed on carbonyl groups.

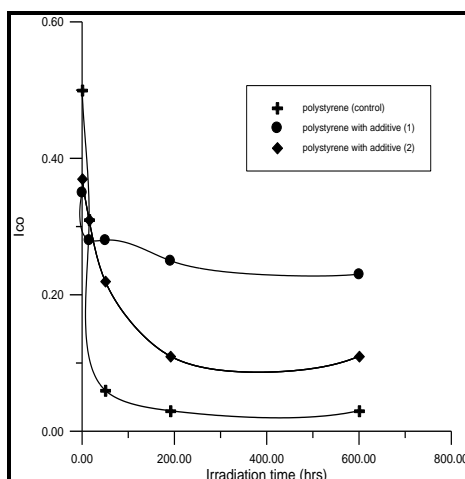


**Figure (2) :** The change in FT-IR spectra of polystyrene film (control) (thickness: 25  $\mu\text{m}$ )



**Figure (3) : The change in FT-IR spectra of polystyrene film and sensitizer (1) (thickness: 25  $\mu\text{m}$ )**

The correlation between ( $I_{\text{CO}}$ ) and the time of irradiation is established in figure (4).



**Figure (4) :The relationship among irradiation time and carbonyl index for polystyrene films without and with of sensitizers (0.1% w/v)**

It has been watched that the carbonyl index ( $I_{\text{CO}}$ ) deeply decreased with irradiation time for polystyrene film (control) while diminishing with photosensitizers (1) and (2). The mechanism of the degradation and formation of (C=O) of polymers are like general in literatures<sup>(25)</sup>.

So these photosensitizers (i.e 1 and 2) are presented photostabilizer for polystyrene, as the decrease in development of ( $I_{\text{CO}}$ ) with these compounds which are lower than polystyrene without two sensitizers. Previous figures, confirm that (1) act as good-photostabilizer of polystyrene parallel to sensitizer (2), where the aromatic ring of Schiff base contain electron releasing group in sensitizer (1) while in sensitizer (2) the

aromatic ring of Schiff base contain electron withdrawing group and also, the decreased in carbonyl index ( $I_{\text{CO}}$ ) with sensitizers 1 are lower than that for sample (control) or with sensitizers 2.

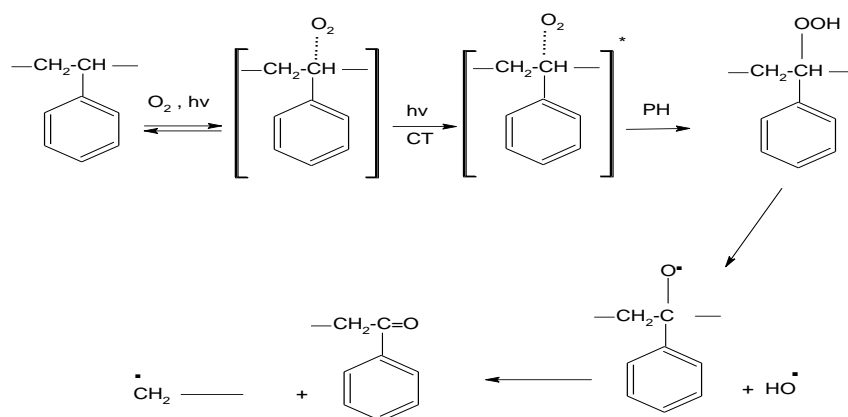
### 3.1. Molecular Weight Change During Photolysis

After irradiation time the changes in molecular weight are determined for solutions of polystyrene films by viscosity measurement with intensity of alight at  $3.49 \times 10^{-5}$  einsteins. $\text{dm}^{-3} \cdot \text{S}^{-1}$ , this is another indication of degradation, Table (1) show the data of  $\eta_{\text{ret}}$ ,  $\eta_{\text{sp}}$ ,  $\eta_{\text{red}}$  and Mn for polymers before and after radiation

Table (1) shows the polystyrene without sensitizes was higher degradation than

polystyrene with sensitizers, where there are high reduction in molecular weight through irradiation, but with sensitizers there are low

degradation for polystyrene and therefore the data of molecular weight was high.



PH : polymer molecule

**Scheme (1) : The photodegradation scheme in the presence of  $\text{O}_2$  for polystyrene**

**Table (1) The data of  $\eta_{\text{ret}}$ ,  $\eta_{\text{sp}}$ ,  $\eta_{\text{red}}$  and Mn for polymers unradiation and radiation**

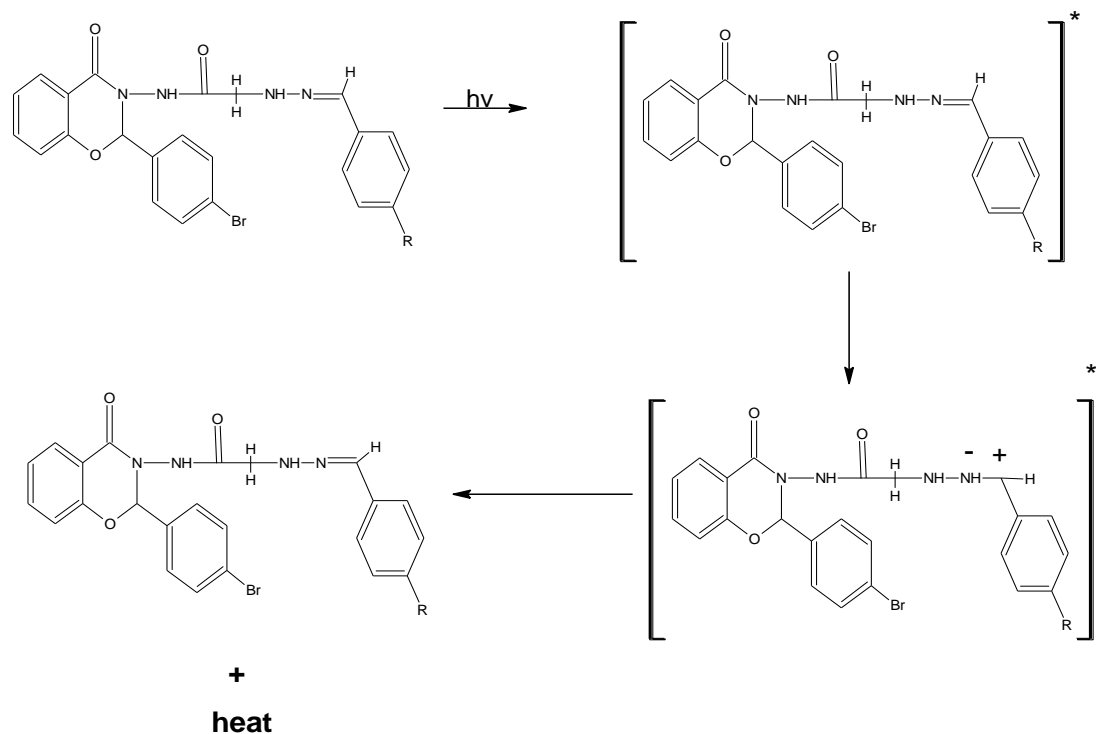
Polymer	$\eta_{\text{ret}}$	$\eta_{\text{sp}}$	$\frac{\eta_{\text{sp}}}{C}$ ( $\eta_{\text{red}}$ )	$\overline{\text{Mn}}$
<b>Poly styrene before irradiation</b>	2.45	1.45	18.75	31432
<b>Poly styrene after irradiation</b>	1.5	0.5	8.27	10705
<b>Poly styrene with sensitizer (1) after irradiation</b>	1.62	0.62	11.11	15787
<b>Poly styrene with sensitizer (2) after irradiation</b>	1.26	0.26	9.63	13080

the adjust within the carbonyl and molecular weight change as a indication for the evaluation, as shown in figures 2–4. The sensitizers stabilize polystyrene by various mechanisms, such as radical scavengers or uv absorbers screeners. as proposed in schemes 2.

### 3.2. Photostabilization mechanisms of polystyrene by means of Schiff bases compounds

From the results in this work, the efficiency of photostabilizers (schiff bases) as for polystyrene films can be orderly according to

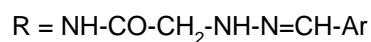
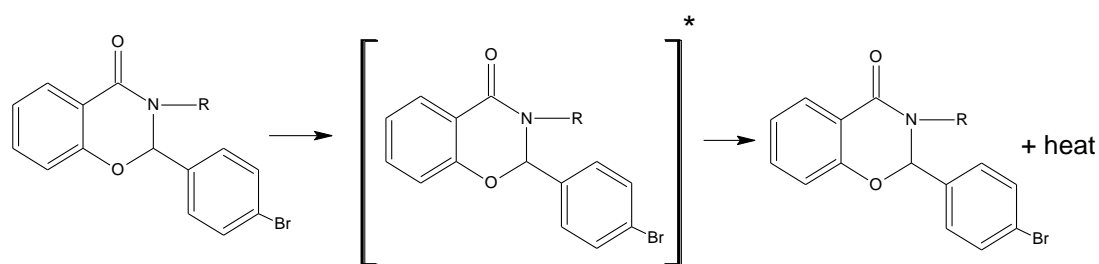




**Scheme (2) : The proposed mechanism of Schiff bases (1) and (2) as photostabilization, the “\*” indication for excited state**

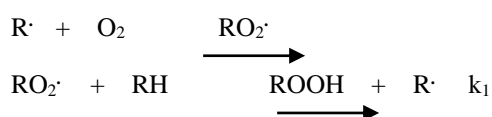
The rings of benzoxazin play a role in the mechanism of the stabilizing process by acting as UV absorbers. The UV light absorption by these added substances containing benzoxazin disperses the UV vitality to harmless heat

energy (Scheme 2). Besides, this ring plays a role in resonating structure conjugation of the radical in peroxide decay, as appeared in Scheme 3, which illustrate its role as a stabilizer.



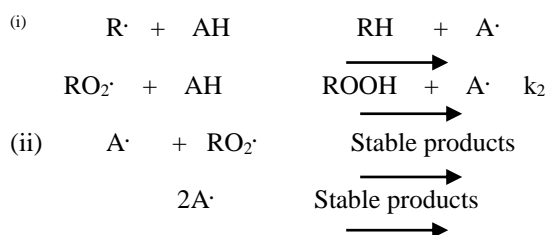
**Scheme (3): Suggested mechanism of the photostabilization of benzoxazin as a UV absorber. Where “\*” represent the excited state**

To explain the antioxidant mechanism we should consider the propagation, i.e. the



mechanism of oxidation of the free radicals formed:

These processes can be prevented by addition of antioxidants (AH) which operate mainly by two reactions: chain transfer (i) or termination (ii).



Antioxidants react faster with peroxyradicals ( $\text{RO}_2\cdot$ ) than with ( $\text{R}\cdot$ ) radicals. The role of Schiff base as photostabilizer for polymers are similar for results in litretures<sup>(26)</sup>.

The photostabilization procedure might be expert with trade light stabilizers in addition to chalate complexes. The idea of the polymer and photostabilizer will decid the procedure and effectiveness of photoprotection of the sample film .

This strategy for stabilization consists of mixing the stabilizer into the polymer solution where the particles of the stabilizer diffuse into the polymer or dissolve in it. In order to apply this method, the stabilizers and the polymers must fulfil certain requirements. The stabilizer must be in a finely scattered shape to have the capacity to diffuse or to dissolve into the polymer mass. The compounds must be dealt with ahead of time by fine granulating to a positive size and blended with different added substances, encouraging the procedures of diffusion<sup>(27)</sup>.

### 3.3 Thermo Gravimetric Analysis (TGA)

TGA is an experimental technique in which the weight of a sample is measured as a function of sample temperature or time. The sample is typically heated at a constant heating rate. The results of a TGA measurement are usually displayed as a TGA curve in which percent weight is plotted against temperature. Different effects can cause a sample to lose, or even gain, mass, these include the following:

1. Evaporation of volatile constituents; such as desorption of gases and moisture
2. Thermal decomposition in an inert atmosphere with the formation of gaseous products
3. Oxidation of constituents.

### 3.4 Polymer/organic compounds

With incorporation of a variety of organic compounds in the polymer matrices, organic compounds are much different from the conventional composites. Schiff base filler particles have significant barrier effect to slow

down product volatilization and thermal transport during decomposition of the polymer, which assists composites with high thermal stability. For example influence of the content of Schiff base on the thermal degradation of poly styrene/ Schiff base composites were examined. TG curves (Fig 5), shows that thermal stability of PS/Schiff composites is higher than in pure PS. Improved thermal stability of composites with respect to the pure PS can be assigned to partially altered molecular mobility of the polymer chains due to their adsorption on the surface of the filler particles. Simultaneously, adsorption of polymer chains onto the surface of Schiff base filler particles results in restriction of segmental mobility and serves to suppress chain transfer reactions .Polymer adsorption on the surface of filler particles is a crucial step for explanation of changed thermal stability of polymer/Schiff base composites.

### 4. Conclusions

From the above results that extra of little sum (0.1% w/v) of sensitizer compounds, for example, 1 and 2 not well influences the photo processes in the polymer. The results indicate that photodegradation of the sample isn't effective within these compounds and 1 was high stabilizer for polystyrene and 2 was low for polystyrene. Estimation based on the viscosity average molecular weight ( $M_v$ ) plainly demonstrates a general reduction in molecular weight through irradiation, particularly without sensitizers. At longer presentation periods, degradation of polystyrene, proceed however are lessened with sensitizers. It is likely that at the initiation times of presentation, the random sample sequence scission occurs.

### 5. Acknowledgment

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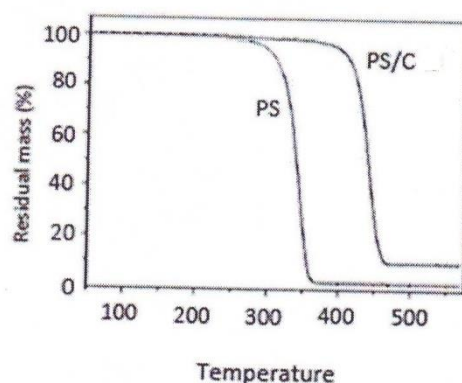


Figure (5): TGA curves of pure poly styrene and polystyrene/ C (Schiff base)

## 6. Conflicts of interest

There are no conflicts to declare”.

## 7. Formatting of funding sources

Self

## 8. References

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