

A new UV Stabilizer and Anti Oxidant Chemically Bonded with Polyethylene from Polyresorcinol Prepared by a new Method

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ABSTRACT

Polyresorcinol (PRE) can be used as U.V stabilizer additives for polyethylene (PE) which gives result's better than chimassorb (Ciba) used at Sidpec company. Which after

150 hr inside weathering ometer for chimassorb the decrease in percent elongation at break are 12%, and for 0.06% PRE is 3.8%. But for 0.03% PRE is 2 %, for chimassorb the decrease in percent elongation at break is 33.8%, and for 0.06% PRE is 12%, but for 0.03% PRE is 2.5%. Finally after 300 hr inside weathering ometer, the decrease on percent elongation at break for chimassorb is 57.22%. In case of 0.06% PRE the percent elongation at break is decreased by 28.5%, this mean that PE with 0.06% PRE are still have a resistance to weathering condition's but PE containing 0.06% chimassorb are completely degradable after 300 hr.

Before xenon test the compound of (PE+PRE) have low initial percent elongation at break which may be due to cross linking of (OH) groups with PE and not due to degradation as confirmed by DTA and FTIR. PRE are efficient UV stabilizer than chimassorb, and PRE used as anti oxidant.

Thermal analysis was studied for the compounds, DTA curves shows addition of PRE to PE cause increase in melting point of PE from 127.85 °C to 136.9 °C, also cause increase the energy of melting from 79.73 J/g to 107.5 J/g.

1. INTRODUCTION

The past few decades have seen most of man's greatest scientific and technological achievement, such as in the field of aeronautics and space exploration, automotive industry, computer science....etc. But without any doubt, the great development in material science is behind all this especially in the field of polymers and synthetics. Of all plastics known, polyethylene (PE) comes in the number one position in volume production on a world wide basis because it is used in many industries such as wire insulation, tubing, rod, tab, coating on rope, film casting, surface coating, proofing of paper, clothes, wood. Most of polyethylene applications are subjected to solar radiation, as a result PE needs to be stabilized against UV.

PE has considerable uses as a container for nuclear reactors but it has limitations of being unsuitable for use at high temperatures, due to its high hydrogen content of polyethylene relative to its weight it is identified by NASA as a promising radiation shielding material against galactic cosmic rays and solar energetic particles,..... etc. But on the other hand, PE is the least stable polymer, if it is exposed directly to heat or hot material, but it is also unstable towards any form of energy capable of initiating degradation chain of reactions such as photoinitiation by ultraviolet radiation, gamma radiation or any other high energy radiation. As a result we need to increase stability of PE.

Most of the compounds that display good thermal stability contain aromatic nuclei, which are the simplest organic structures resistant to thermal decomposition or oxidation. Polyphenylenes and polyhydroxyphenylenes (polyphenols) are considered as one of the best classes known to have high thermal stability i.e. can withstand high temperature applications. Further evidence supporting the use of polyphenylenes as temperature resistant polymers is that oligophenyls (terphenyls to sexiphenyls) have been used as high temperature lubricants, hydraulic fluids, heat transfer agents, and as coolants for nuclear reactors. Besides to their high temperature applications they could be used as semiconductors, insulators, radiation shielding materials and in LEDs (light emitting diodes).

The objective of this work is to synthesize polyresorcinol (PRE) by a new method where aluminum chloride is used as a primary catalyst, ferric chloride as a secondary catalyst and resorcinol as the monomer, study the structure of the synthesized polymers take place by IR and to study addition of PRE to PE as UV stabilizer we prepare a compounds of (PE+0.06%PRE) as duple shape and a disc, and thermal stability of the compounds are studied by DTA.

2. Materials and Method

2.1. Materials

1. Resorcinol : Molecular weight (110), Melting Point (111 °C), Boiling Point (276.5 °C), Solubility In water (229g/100g) at 30°C.

2. Aluminum Chloride : Molecular weight (133.34), Melting point(192.6°C) at 2.3 atm, Solubility in water (69.9g/100g)at 30°C.

3. Ferric Chloride (FeCl₃ .6H₂O): Molecular weight (270.32), Melting point(37°C), Solubility in water (91.9g/100g)at 30°C

4. High Density Polyethylene (HDPE) : Density (957gm/cm³), Melt index (8.5), Melting point (127.85°C), Soluble in toluene

5- Chimassorb : Molecular Weight (> 2,500), Melting Range (100 - 135°C), Solubility (less than 0.01% in water at 20°C).

6- Irganoxe: Molecular Weight (646.9), Melting Range (180 - 186°C), Solubility (soluble in benzene and chloroform).

2.2. Apparatus and Instruments

1-Infrared Spectrophotometer (Jasco FTIR 460), England

Used for detecting the structure of the polymer. The instrument is based on the fact that functional groups and each position in the benzene or any chemical formula absorb a certain band of certain wave length.

2- Differential Thermal Analyzer, Shimadzu DTA-50, Japan

(Sample weight: 6.8 mg, cell: Platinum, Atmosphere: air, rate flow: 20.00 ml/min, heating rate: 5,10,20,40 °C/min, hold temperature: 500 °C)

3- Injection Machine (ARBURG 221K), Germany

Used to prepare the compound of polyethylene and polyresorcinol or polypyrogallol in the form of duple shape and disc.(Temp of zones 220°C, Pressure 1500 bar, Flow of injection 90cm/sec).

4- Weathering- Ometer (Ci – 3000) Atlas, Italy

(Radiation: 60 w/m², Humidity: 50%, Temp of chamber: 38 °C,). Used for simulate the environmental parameters of sunlight, temperature, and moisture in the form of rain, dew, and humidity. These parameters are controlled to replicate actual end use conditions, [ISO-4892, ASTM-G155].

5 - Material Testing (ZWICK), Germany

Used for measuring percent elongation at break, load Cell (5KN), ASTM D-638, force for tension=0.

2.3. Procedure of Polymerization

The conditions of polymerization were adjusted to achieve maximum percentage yield of the synthesized polymer.

1- Resorcinol or, aluminium chloride and ferric chloride are mixed in a molar ratio of (1:1:2 and 1:1:3), then the mixture is put in a dry stainless steel cone.

2 - The polymerization is carried at [temperature at 90, 130, and 150° C, time 2,4 and 6 hours, molar ratio resorcinol:AlCl₃:FeCl₃ (1:1:2 and 1:1:3),

- 3- The crude product is then extracted by ethyl alcohol in a Soxhlet apparatus until ethyl alcohol returned colorless and then the powder product is dried in air, this step removes the unreacted monomer (resorcinol).
- 4- The polymer is purified from the remaining catalysts by pouring it in concentrated hydrochloric acid (35%) and leaving it for 1 day.

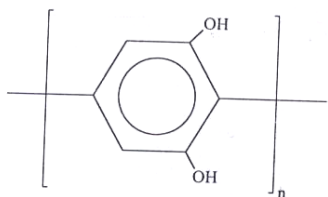
The actual yield is calculated as follows:

$$\% \text{ yield} = \frac{\text{Weight of polymer after purification}}{\text{Weight of resorcinol}} \times 100$$

3. Results and Discussion

3.1. Study the Structure of the Resulting Polymer

The structure of the obtained polymer has been characterized by the investigation of its infrared spectra IR spectra of polyresorcinol sample. The structure of the obtained polymer can be suggested as the following formula which is poly (1, 3 dihydroxy-2, 5 phenylene), [1]. Also we measure the hydroxyl group for the repeat unit by FTIR spectrum in fig (1), which is 0.29, and the theoretical hydroxyl group is 0.3, these mean repeat units contain 2(OH) groups.



Poly (1, 3 dihydroxy-2, 5 phenylene)

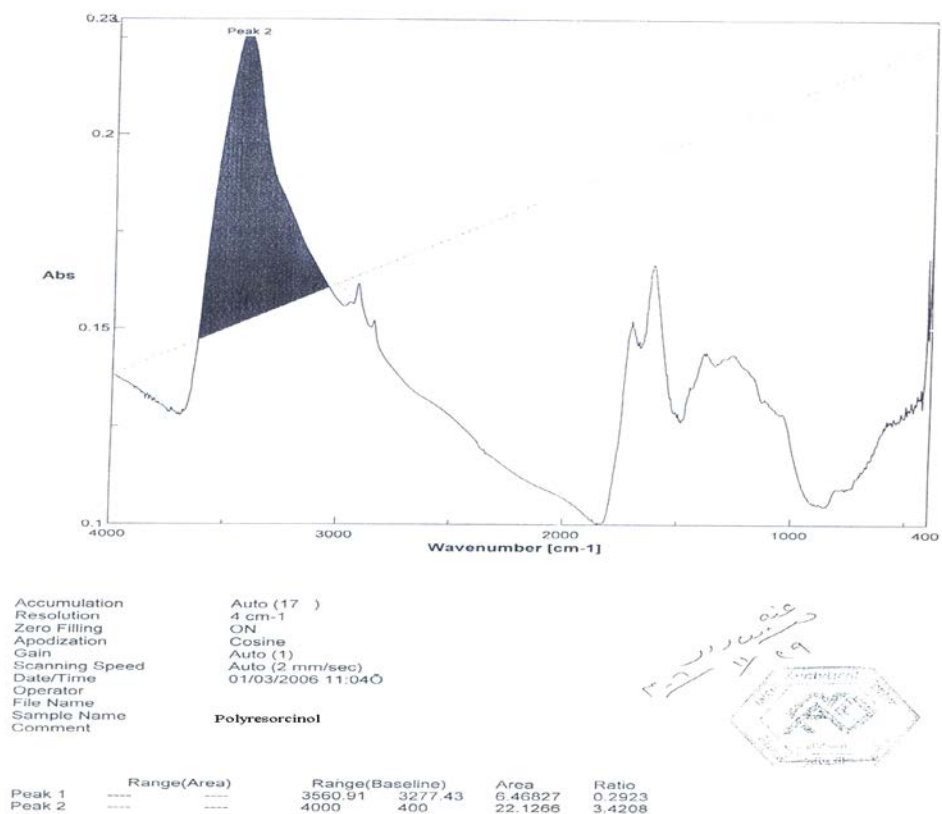


Figure (1): FTIR of Polysorcinol

Finally, we suggest that the mechanism of polymerization of resorcinol is the same as the mechanism suggested by Kovacic for polymerization of

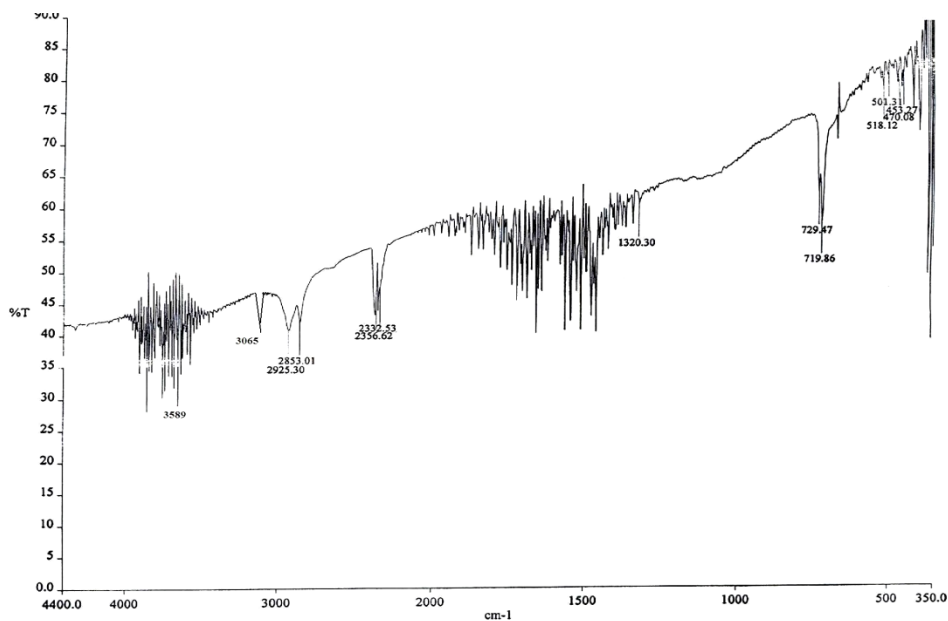
benzene to poly (p-phenylene) by $\text{AlCl}_3\text{-CuCl}_2$ which is radical cation initiation, entailing propagation via coordination of C_6H_6^+ with benzene nuclei [2].

3.2. Properties of the Compound

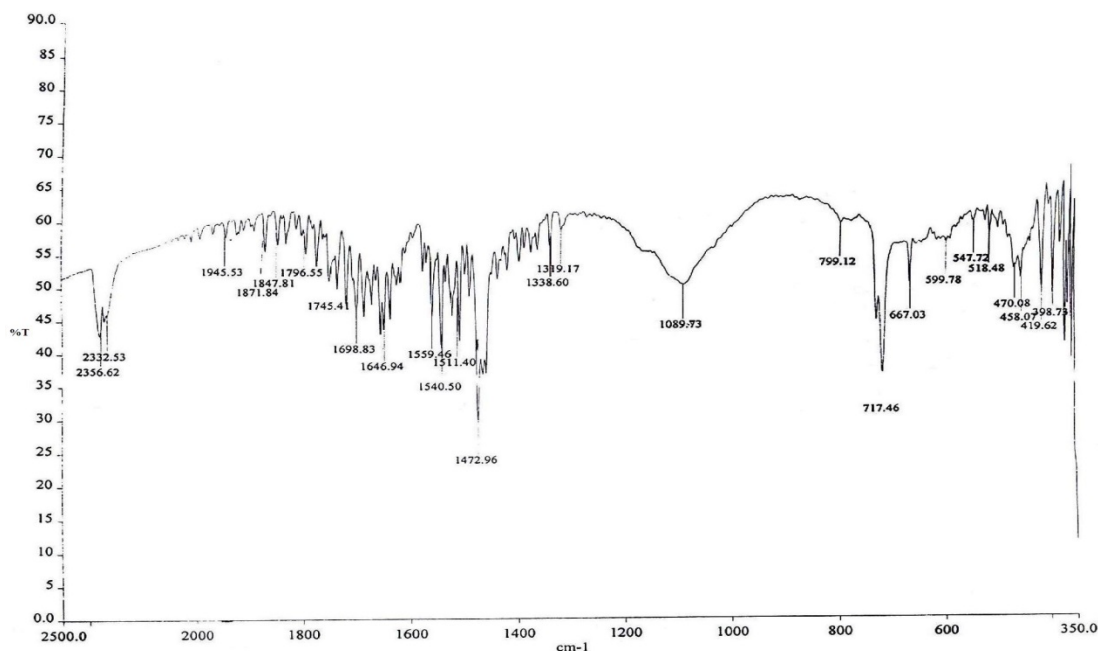
3.2.1. Fourier Transform Infra Red for Pure Polyethylene and its Compounds of (PE+0.06%PRE)

The structure of the prepared compounds has been characterized by the investigation of its infrared spectra which is shown in figure (2), this figures shows a peak at 1340 cm^{-1} which is characteristic of the alkyl CH. There is a peak at 2853 cm^{-1} , this peak lies in the range of ($2850\text{--}2900\text{ cm}^{-1}$), which is characteristic of the alkane C-H. This denotes the probability of cross linking between PE and OH of the PRE. There is a peak at 3065 cm^{-1} , this peak lies in the range of ($3030\text{--}3080\text{ cm}^{-1}$), which is

characteristic of the aromatic =C-H. A small peak at 3589 cm^{-1} due to the presence of OH group from PRE which mean that not all the OH is used in cross linking.



(Figure (2) : FTIR for a compound (PE+0.06%PRE)



(Figure (3): FTIR for HDPE

Fig (3) show FTIR of pure HDPE which doesn't show the peaks characteristic of alkane group which is present in FTIR of the compound of (PE+0.06%PRE).

3.2.2. Study of Differential thermal analysis (DTA)

Thermal analysis comprises a group of techniques in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme. In differential thermal analysis, the temperature difference that develops between a sample and an inert reference material is measured, when both are subjected to identical heat treatment [3, 4].

3.2.2. 1.Study of DTA for a Compound Containing PE with 0.06%PRE

Fig.(4) show The DTA of PE + 0.06%PRE show a peak at 136.9 °C, which corresponds to the melting point of PE. PRE cause increase in melting point of PE from 127.85 °C to 136.9°C, i.e melting point increases by 9°C, the presence of PRE of the compound increase the melting point of PE, the presence of PRE makes the compound stable till to 449.5°C. The energy of melting of PE on the compound is raised from 79.73J/g to 107.5J/g, (Fig. 5)due to the presence of PRE i.e PRE increases the energy for melting on the compound. The compound shows no decomposition up to onset temperature 403.54°C, with a Peak at 449.5°C and end set at 444.43°C.

File Name : RE.D1
Detector Type : Shimadzu DTA-50
Sample Name : PE+0.06%PRE
Weight : 6.8[mg]
Cell : Platinum
Atmospher : Air
Rate Flow : 20.00[ml/min]

Temp Program		
Rate	Hold Temp	Hold Time
[C/min]	[C]	[min]
10.0	500	0.0

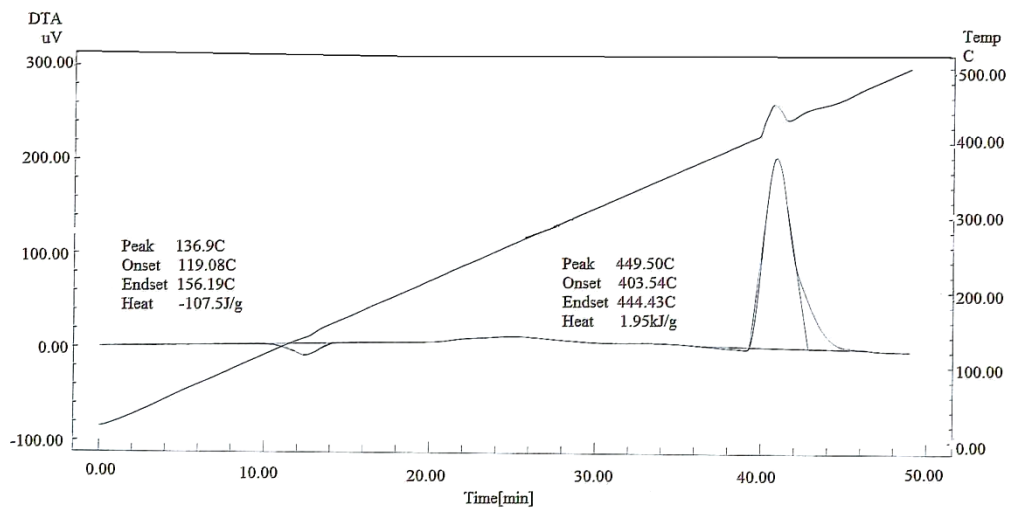


Fig (4): DTA of a Compound (PE+0.06%PRE)

File Name : PE.D0
 Detector Type : Shimadzu DTA-50
 Sample Name : HDPE
 Weight : 6.85[mg]
 Cell : Platinum
 Atmosphere : Air
 Rate Flow : 20.00[ml/min]

Temp Program		
Rate	Hold Temp	Hold Time
[C/min]	[C]	[min]
10.00	500	0.0

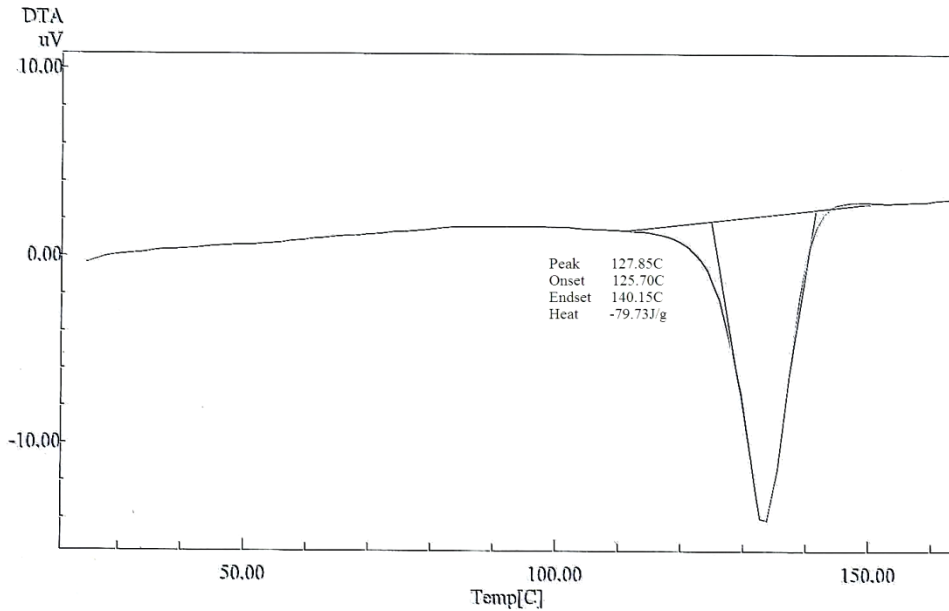


Fig (5): DTA of Pure PE

3.3. Study of using Polyresorcinol as UV Stabilizer to Polyethylene

One of the defects of polyethylene (PE), that doesn't withstand UV radiation with this reason UV stabilizer are added. The test of UV stabilization is carried out on weathering ometer, it's idea depends on simulation of weathering conditions which include UV radiation as it contains xenon lamp.

The idea of measurement depends on the fact that UV causes degradation of PE and this leads to increase rigidity and brittleness and so elongation at break decreases. The decrease on elongation at break with time is taken as a measure for UV stabilization. Table (1) shows the relation between percent elongation at break with time inside weathering ometer for our stabilizers compared with chimassorb used in Sidpec factory.

3.3.1. Effect of Time on Percent Elongation at Break When Using PRE as UV Stabilizers to PE

Chimassorb is used in Sidi kerir petrochemical company (Sidpec) as UV stabilizer. The aim of this work is to make a comparison between the efficiency of this additive and that of new additives. These polymers are (1, 3 dihydroxy-2, 5 phenylene) PRE. These additives are used in this study as UV stabilizers and anti oxidant for HDPE.

The value of percent elongation at break is taken as a measure of degradation on xenon test. This value is decreased with increasing time. The compound is considered failed when the decrease on percent elongation at break reaches 50% from the initial value. We shall consider two cases, the first case is the percent elongation at break of the compound before its introduction to weathering ometer and the other case is that when the compound is put into weathering ometer.

From table (1,2), it was shown that when 0.25% anti oxidant (Irganoxe) –which is used with chimassorb- was used in our compounds with the same concentration, the percent elongation at break is not affected. In other words the addition of anti oxidant has no effect on the compound this means that our UV stabilizer acts also as anti oxidant.

By using 0.06%chimassorb with anti oxidant the percent elongation at break is 1239% while it decreases by 8.3%, when 0.06%PRE is used under the same condition when 0.03%PRE without anti oxidant, the percent elongation at break is decreased by 14.6%, from that of chimassorb.

Table (1): Relation between Percent Elongation at break with Time inside Weathering Ometer for our Stabilizer Compared with Chimassorb used in Sidpec Company

Time inside Weathering Ometer, hr	Elongation at break, %, For Different UV stabilizer		
	0.06% chimassorb *	0.06% PRE *	0.03% PRE **
•	1239	1136	1057
100	1140	1132	1036
150	1090	1093	1030
200	820	1000	1031
300	530	813	

Polyresorcinol (PRE), Polypyrogallol (PPY), With using 0.25% antioxidant (Irganoxe) (*), Without using antioxidant (**)

This difference of the value of percent elongation at break for the cases of 0.03% and 0.06%PRE may be due to the increase of OH group due to the increase of concentration of PRE giving more probability for partial cross linking with PE, which leads to smaller decrease on percent elongation at break in the case of 0.06%PRE.

Generally the compounds of (PE+PRE) is accompanied by the decrease in percent elongation not due to degradation as confirmed by DTA study but may be due to partial cross linking of OH groups present in PRE, this is confirmed by the presence of a peak at 2853 cm^{-1} indicating C-H aliphatic in IR. This decrease of initial percent elongation at break of the compounds before introducing to the weathering ometer is itself an advantage because this decreases gives by this way dimensional stability of the compounds.

The UV is the factor affecting degradation at 300 hr, consequently PE losses elasticity and becomes brittle, and not suitable for usage. The use of PRE gives better results concerning reduction of percent elongation at break by 50% and increase economy due to omission of anti oxidant and decrease of the used concentration of PRE UV stabilizer by 50%. We recommend using the 0.03%PRE, without anti oxidant which is better than chimassorb used by the Sidpec company which is exported from Ciba.

Table (2): Relation between Percentage Decrease of Percent Elongation at Break and Time

Time Weathering Ometer, hr	Decrease of Percent Elongation at Break, %, For Different UV stabilizer		
	0.06% chimassorb *	0.06% PRE *	0.03% PRE **
100	^	0.35	2
150	12	3.8	2
200	33.8	12	2.5
300	57	28.5	

The percentage decrease of percent elongation at break is taken on the bases of the value of percent elongation at break at zero time.

REFERENCES

- [1] Safaa.M.Negm., S. A. El-Garf M.Sc., Thesis "Preparation of Zinc Powder - Polyresorcinol Composite and Study of its Radiation Stability and its Semiconducting Properties.", (2005).
- [٢] P.Kovacic and W.B.England , "Novel Pathway for Homopolymerization by Nuclear Coupling Via Aromatic Radical Cation Initiation.", J.Polymer.Sci., Vol.19, PP.359-362, (1981).
- [٣] [http:// www.ortonceramic.com/instruments/05Cdta.shtm1](http://www.ortonceramic.com/instruments/05Cdta.shtm1).
- [٤] [http:// www.inano.dk/sw256.asp](http://www.inano.dk/sw256.asp).