The Study of the possibility of using expired ultraviolet stabilizer (Tinuvin 770) in polypropylene

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Abstract

TINUVIN 770 is a light stabilizer for stabilization of polymers, especially polypropylene against UV light that used worldwide. This compound has a high stability in dry conditions, away from direct sun light and in acidic condition is resistant to degradation and decomposition. The purpose of this research is the examination of the possibility of using expired TINUVIN 770 that besides the economic savings for the petrochemical industry, replace the applied method of using in expired materials in similar cases entering dozens toxic chemicals in Eco. This research is based on the identification methods of polymer additives such as high performance liquid chromatography coupled with ultraviolet spectroscopy(HPLC-UV), gas chromatography coupled with mass spectrometry(GC-MS) and comparison of the results obtained for the studied case (expired) and sample with date as the standard. Initially, DSC tests was performed on each sample to determine their thermal behavior. The FT-IR Spectrum of both samples was obtained. By UV-scan determined that both samples have UV absorbance in 270nm. The samples were analyzed by HPLC-UV, in this wavelength, and the same results were obtained for the two samples. Using GC-MS and comparison of the results obtained for the sample and standard it was proved the usability of expired TINUVIN 770.

Keywords: TINUVIN 770, light stabilizers, degradation of polymers, polymer additives

Introduction

Polymers due to exposure to weather and sunlight, depending on its nature lose their mechanical and physical properties (Pervez Zad, 2008). Often, these reactions as "polymer degradation reactions" recognizes (Haddadi Asl, 2000) polymeric materials easily during processes and their employment undergo to degradation processes as consequences of physical agents such as heat, light, high energy radiation, mechanical deformation and of chemical agents such as oxygen, water, ozone, atmospheric pollutants (Partini, 2006). Properties of polymers due to their high molecular weight and therefore, anything that causes a change in the molecular weight of the polymers, can significantly alter the properties of polymers and is lead to polymer degradation. Structural irregularities and hydro peroxides are thread important factors degradation and oxidation reactions (Allen and Edge, 1999). Degradation due to (UV)-radiation is called photodegradation. The(UV)-radiation is one of the most important factors determining the polymers lifetime (Diepens, 2009).The degradation of PVC has been widely studied since 1940[6n].

Photo degradation mechanism of polymers

Physical and chemical changes induced photo degradation are appear as discoloration, loss of gloss and gloss, wear and loss of tensile strength and impact strength (Kriston, 2010). When light is absorbed by the polymer, Norrish reactions can occur, which lead to changes in molecular structure resulting in degradation. The Norrish I reaction leads to chain cleavage and radicals that might initiate the photo-oxidation. The Norrish II reaction is a non-radical intramolecular process, in which hydrogen is transferred, leading to chain cleavage. For polyamides and polyesters the most important photolytic reactions are the Norrish I and II reactions. In Figure 1 both reactions are shown (Allen and Edge, 1999). Noriish II is a non-radical process in which hydrogen transfer, leading to the breaking of the chains Noriish I and II process for polyamides and polyesters are shown in Figure 1.

Stabilizing polymers against UV light

Inhibition of degradation of plastics induced by light and oxygen has considerable technical and economic importance (Sótonyi, 2004). Plastics can be found in increasing number of products that are used today. Initially used in consumer appliances, plastics are often used as a material of choice in many products, due to their relative, low cost, ease of manufacturing, and light weight. When used as a structural material and especially for outside use, industrial plastics require additives to provide polymeric stability from the effects of temperature and light (Plante, 2011). Polymers stabilization is defined as removal of various photochemical and photophysical processes that occur when they light oxidation.

Polymeric stabilizers are used in a broad range of processes and products, from pharmaceuticals and engine lubricants to formulated foods and shampoos (Ofer & Tam, 2012). Stabilizers can prevent degradation of polymers by chemical reactions (Bart, 2005). For example Antioxidants perform by eliminating oxidation during and after processing when materials are exposed to an energy source (Jessica, 2008). Usually the different types of stabilizers are molten mixed into the polymeric mass, via polymer extrusion (Carlos, 2011). Some types of stabilizers are as follows thermal stabilizers, UV Absorber decomposer peroxide stabilizers, retardant excited state, light stabilizers, etc (Jessica, 2008). Different stabilizers are used to prevent photodegradation of polymers That the HALS[1] are the most important groups of this stabilizers. HALSs are usually derivatives of 2,2,6,6-tetramethyl piperidine or 1,2,2,6,6 pentamethyl piperidine. In many resins they are used as both radical scavengers and antioxidants to protect the material against photo degradation (Przybytniak, 2005).

The function mechanism of HALSs

HALS are divided into two categories of "good" and "bad". Good HALS include: HALS NH, HALS RN, HALS NO, HALS NOH, HALS NOR and optimum performances in polymers on summary are scavenging carbon and oxygen free radicals, light excited species Quenching, disable light metal ions and other degradation primers. Thus, the mechanism for HALS Considering bad HALS (such as HALS nitrosonium) and the synergistic and antagonistic interactions of HALSs with other additives such as phenols and acids are studied (Ohkatsu, 2008).

Tinuvin 770(a light stabilizer)

TINUVIN 770 is a light stabilizer for stabilization of polymers, Specially polypropylene against UV light that used worldwide. This stabilizer is belonging to HALS, is used worldwide as a light stabilizer of polyethylene, polypropylene(PP), polycarbonate, polyurethane, polystyrene, polyamides, polyacetals, and acrylonitrile polymers. The chemical name of Tinuvin 770 is

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[1] hindered amine light stabilizers

bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate, its chemical name and structure is shown in Figure 2 (Sótonyi, 2004; Ohkatsu, 2004).
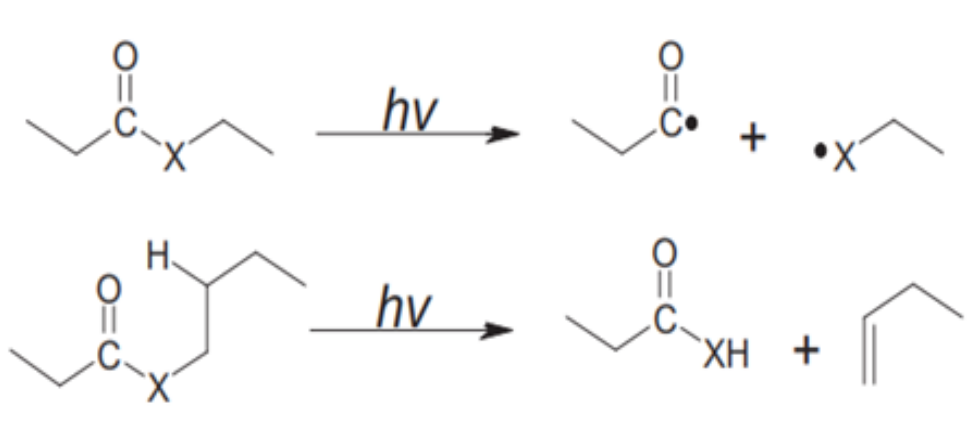

Figure 1: Norrish I (top) and Norrish II (bottom) reactions for polyamides (X=NH) and polyesters (X=O)[5].
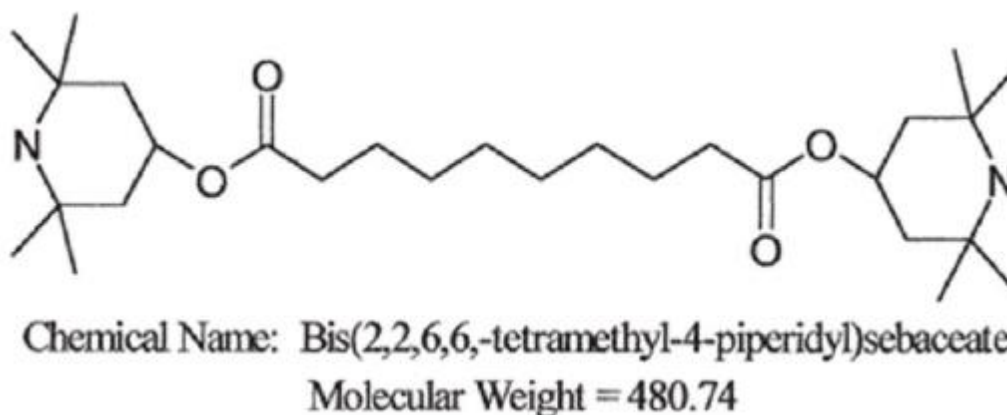

Chemical Name: Bis(2,2,6,6,-tetramethyl-4-piperidyl)sebaceate

Molecular Weight = 480.74

Figure 2: Chemical name and structure of Tinuvin 770.

Our goal in this study is use of expired material until In addition cost savings to the industry in terms of sanctions, the arrival of dozens of chemicals into the environment and to avoid it.

Methodology
Materials and Equipment
Expired Tinuvin770 existing in Maroon Petrochemical Co., and non-expired Tinuvin770 as a standard, both manufactured in SONGWON Co. of Korea was used. First, DSC testing was performed on two samples showed a melting point of expired sample and standard on the range located. Then FT-IR spectra were taken by infrared spectrometer Perkin-Elmer Spectrum RX1 model from both the expired sample and standard. Scanning of UV on both samples using UV-VISIBLE spectrophotometer VARIAN CARY100SCAN model was performed in Laleh Petrochemical Company and it was determined that the absorption range of two samples are conformed to one another. In all experiments, syringe filters manufactured in JETBIOFIL Co. of China, was used to filter the produced solutions. At the end, two samples analysis by means of HPLC-UV device manufactured by Waters Co. of America, Waters1525 model and with the C18 column and double pump QP5050 model, GC-MS device manufactured by the Shimadzu Co. of Japan. For this test, the solvent acetonitrile were obtained from the Merck Co. of German.

Results and Discussion

DSC[2] analysis

DSC test is the first performed experiment on the standard sample of Tinuvin770 and under studying expired sample. DSC, is a thermal test for Polymers that can be used to determine melting temperature, crystallization temperature, glass transition temperature, crystallization percent and etc.

As seen in Figures (3 and 4), the curves obtained for the standard and expired samples have a peak that indicate expected primarily transmission that is melting, and according to apparatus report the melting point of standard sample is 85.92 C°, and for expired sample is 85.54 C°, that both obtained numbers for melting temperature corresponded with the reported range in the MSDS provided by the manufacturer Co. for both samples (SONGWON Co. of Korea) 81-86 C°. This indicates that no change or degradation leading a change in the melting point, was happened in under studying sample.
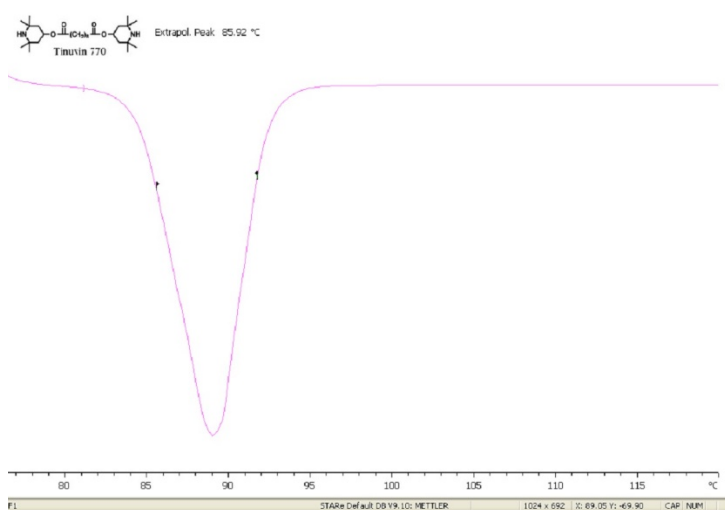

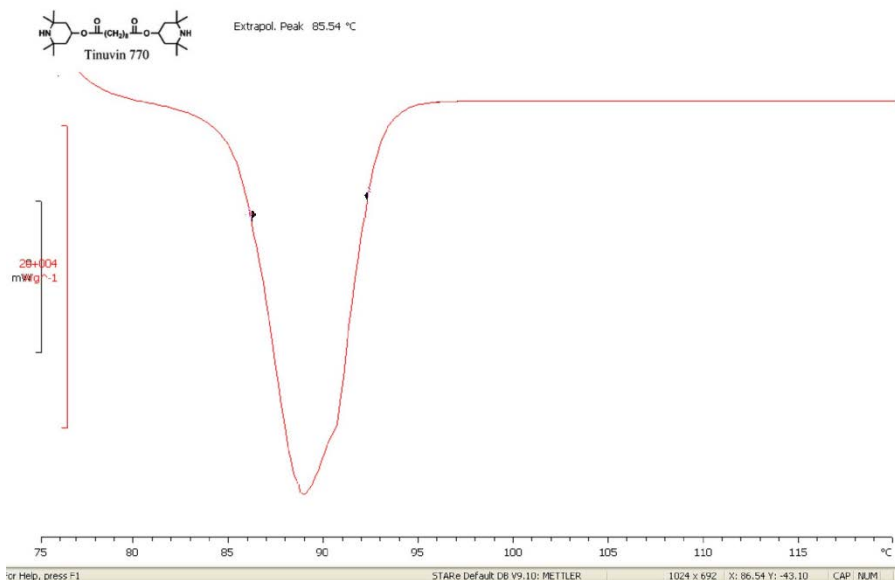**Figure 3: DSC curves of the standard Tinuvin 770.**

Figure 4: DSC curve of expierd Tinuvin 770.

[2] Differential scanning calorimetry

FT-IR[3] analysis

The FT-IR spectra obtained for Tinuvin770 standard sample is shown in Figure (5). This spectrum shows that the corresponding peak to the carbonyl group is formed within 1660-1850 cm-1 that is 1721cm-1. The corresponds peak to N-H tensile absorption as two broad peaks in range of 3300-3500cm-1 means 3323 cm-1 and 3423 cm-1 appeared, and the N-H bending absorption in 1500 cm-1 is observed as a poor peak. The N-H out of sheet bending absorption in 793 cm-1 is observed. Also, the spectrum shows that the bending absorption peak of methylene group (CH3) at 1378cm-1 and the bending absorption peak of methyl group (CH2) in long chain at 739cm-1 has appeared.
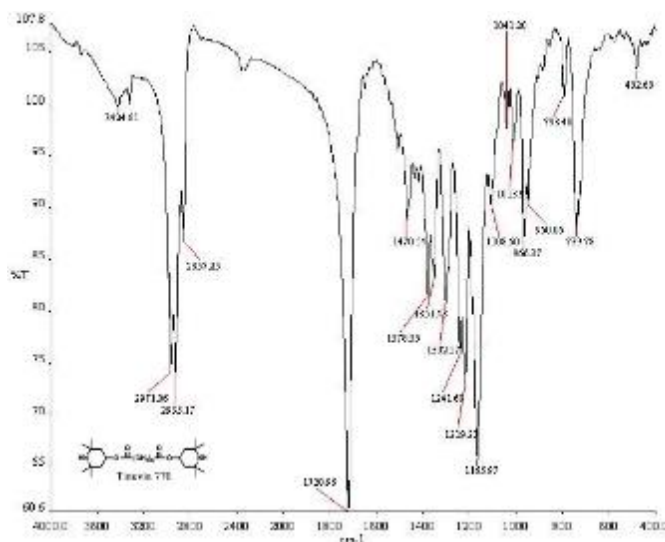

Figure 5: FT-IR spectrum of the standard Tinuvin 770

The FT-IR spectra obtained by analysis of Tinuvin770 expired sample is shown in Figure (6).
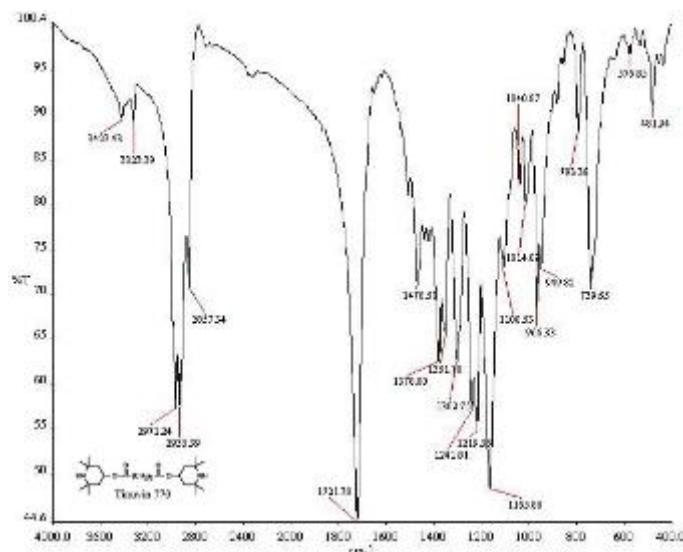

Figure 6: FT-IR spectrum of expierd sample of Tinuvin770.

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[3] Fourier transform infrared spectrometry

This spectrum shows that the corresponding peak to the carbonyl group is formed within 1660-1850 cm-1 means 1721cm-1. The corresponds peak to N-H tensile absorption as two broad peaks in range of 3300-3500cm-1 means 3323 cm-1 and 3423 cm-1 appeared, and the N-H bending absorption in 1500 cm-1 is observed as a poor peak. The N-H out of sheet bending absorption in near the 800cm-1, means 793 cm-1 is observed. And, the bending absorption peak of methylene group (CH3) at 1378cm-1 and the bending absorption peak of methyl group (CH2) in long chain at 739cm-1 has been appeared.

By comparison of obtained FT-IR spectrums result for expired sample of Tinuvin770 and standard sample of Tinuvin770, concluded that both spectrums are related to one compound, and this result is achieved that, the degradation and changes due to expiring has not been happened in this sample. But, since the FT-IR results are qualitative, identification experiments or more quantitative separations experiments, are required.

UV-VIS[4] analysis

We used UV-VIS method in continuing our laboratory work. UV-VIS spectra of both standard and expired samples are interpreted and compared subsequently. UV-VIS visible ultraviolet Spectrum as a graph of absorbance against wavelength (in nm) is recorded. In this experiment, methanol was used as solvent that in the range of 800nm to 200nm hasn't ultraviolet absorbance, and 205nm is absorption cutoff point.

Therefore, the observed peak in the obtained spectrum, is related to UV absorption of the used sample. UV spectra of standard sample is shown in Figure (7). There are Carbonyl chromophore groups (C=O) in tinuvin770 structure. Carbonyl groups in unsaturated compounds containing atoms such as oxygen and nitrogen, have transfers from $n \rightarrow \pi^*$ type within 280-290nm that because so many of these transitions are forbidden transitions, resulting peak intensity is low. Standard sample of tinuvin770 shown poor absorption in 280-290nm area and its adsorption starts to increase in 270nm and reaches its maximum in 250nm. UV spectra of Tinuvin770 expired sample is shown in Figure (8).
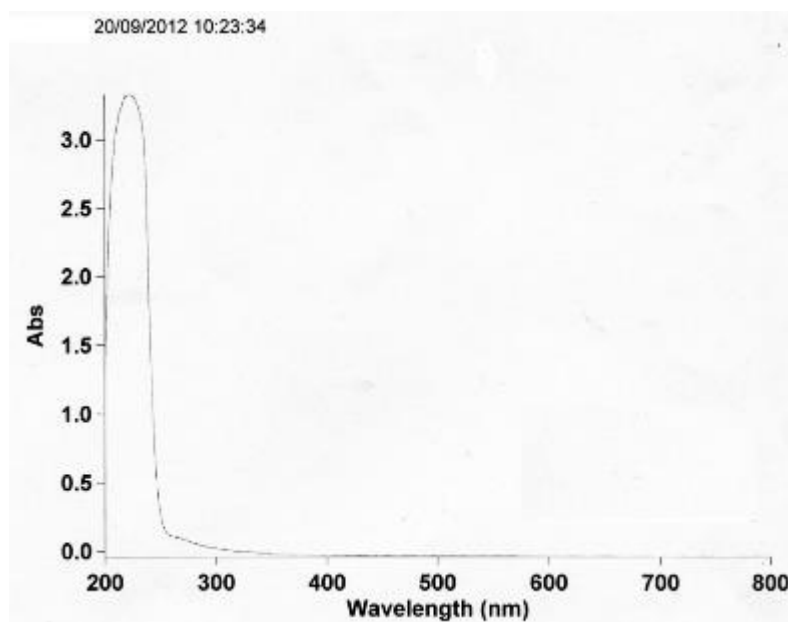

Figure 7: UV-VIS chromatogram of standard Tinuvin770.

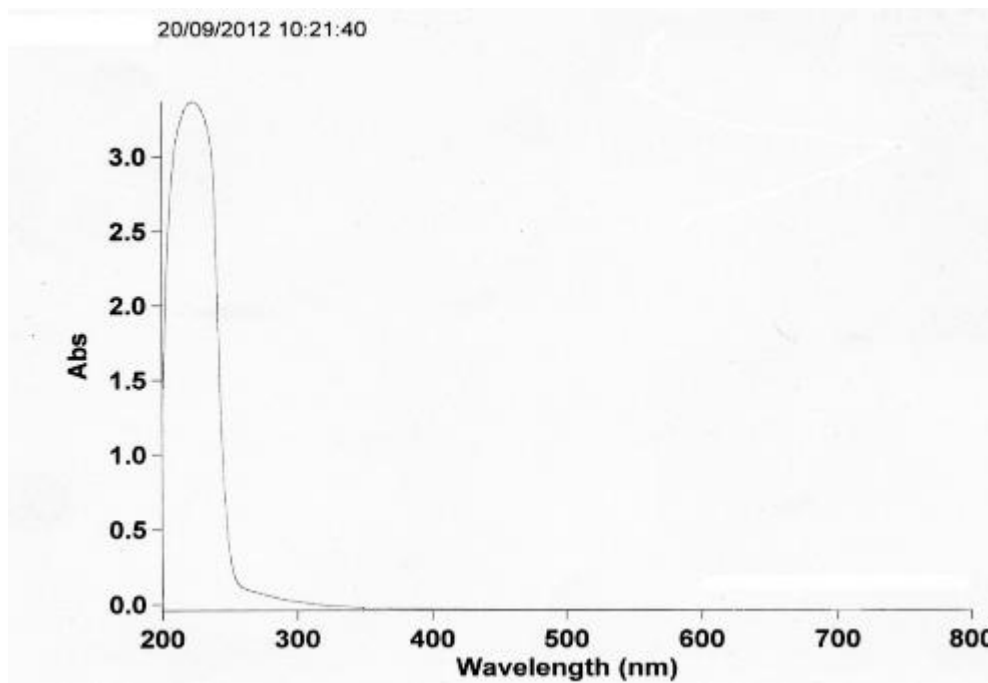[4]Ultraviolet - visible

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Figure 8: UV-VIS chromatogram of expired Tinuvin770.

The corresponding peak of the Carbonyl chromophore group (C=O) of expired sample Tinuvin770 like standard sample, in the 280-290nm area was weak and begins to increase from 270nm. The summit peak is located in 250nm. Therefore, we conclude that, has not been happened any changes in chromophore groups of expired sample. For this reason, two samples have the same absorption.

HPLC-UV[5] analysis

Then, 200ppm solutions of standard and expired samples in acetonitrile were analyzed by HPLC-UV. According to the chromatogram, retention time, that is the interval time from injection to reach the summit peak, is equal to 5.4 minutes (Figure 9). Retention time is a way to identification of the material peak. But a way to quantitative identification is calculating the area under each peak. The area under each peak (absorption bands) was proportional to the amount of studying material, and determined by integrators of the stability system.
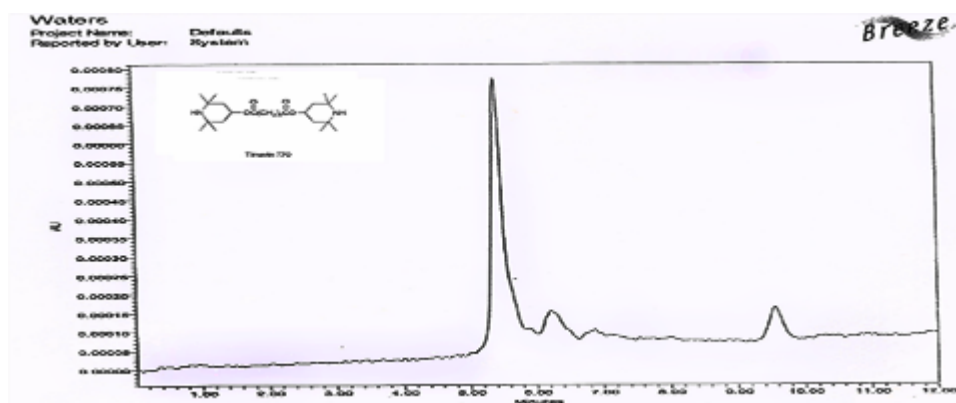

Figure 9: HPLC_UV chromatogram of standard Tinuvin 770.

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[5] High-performance liquid chromatography coupled by Ultraviolet - visible

The retention time of the expired Tinuvin770 chromatogram, is 5.4 minute that is an indication of the lack of degradation in expired sample (Figure 10). Obtained under peak amounts for the standard and expired samples in four performed injection, are reported in Curve (1). According to the sameness of obtained retention time for two samples and a little difference between their area under peak (that could be caused by humidity or a lump of samples) the probability of being useless expired samples greatly decreased.
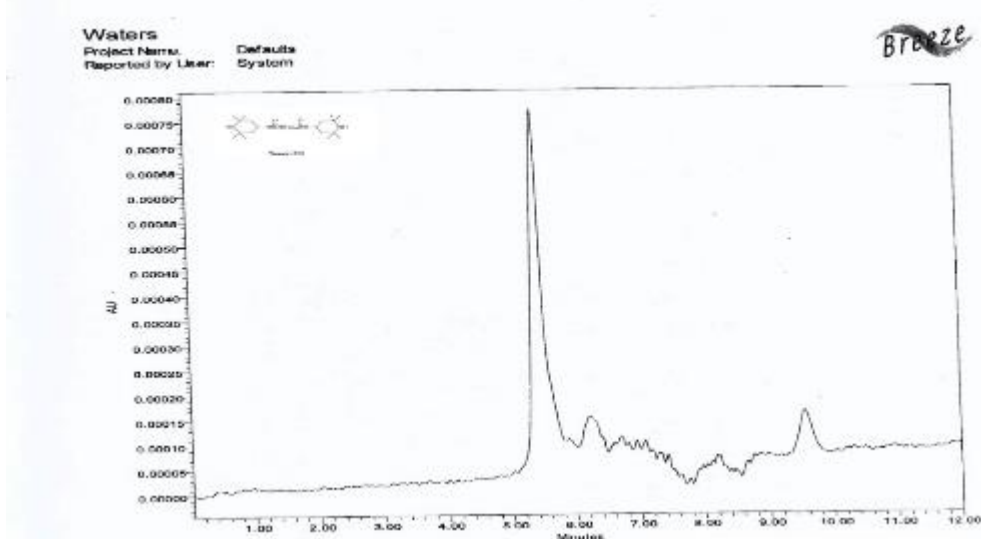

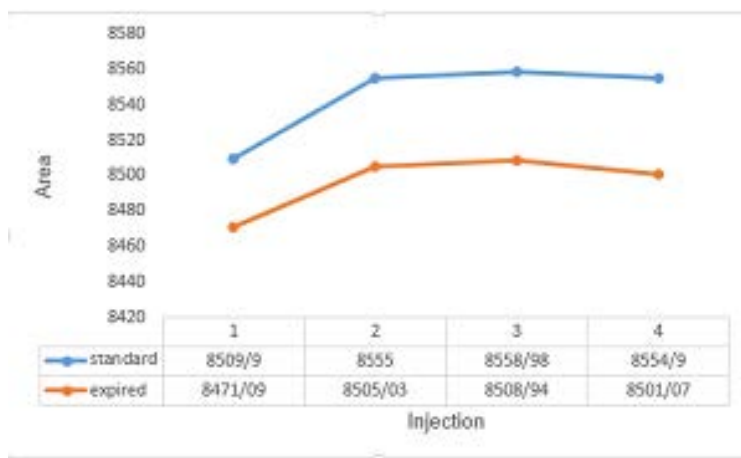**Figure 10: HPLC_UV chromatogram of expired Tinuvin 770.**

	1	2	3	4
standard	8509/9	8555	8558/98	8554/9
expired	8471/09	8505/03	8508/94	8501/07

Injection

Diagram 1: Comparison of area under the curve of the both sample in the HPLC-UV

GC-MS[6] analysis

Continuing, to being ensure of the obtained results, also a method of detection and isolation was used that is gas chromatography coupled with mass spectrometer (GC-MS). In gas chromatography the sample is carried by a flow of gaseous inert fluid phase into the capillary column containing a liquid stationary phase, which is adsorbed onto an inert solid surface. The area under each peak is proportional to the concentration of the studied compound. GC-MS chromatogram of the standard sample, respectively, are shown in Figures (11) and (12). In GC-MS chromatogram like HPLC-UV chromatogram, retention time and area under peak can be used to

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[6] gas chromatography coupled with mass spectrometer

determine the compound. As shown in Figure (11) retention time of standard Tinuvin770 is 27.089 min. It is observed that the retention time of the expired sample is 26.999 min (Figure 12). The comparison of GC-MS area under peak of the standard and expired samples was shown in Curve 2.
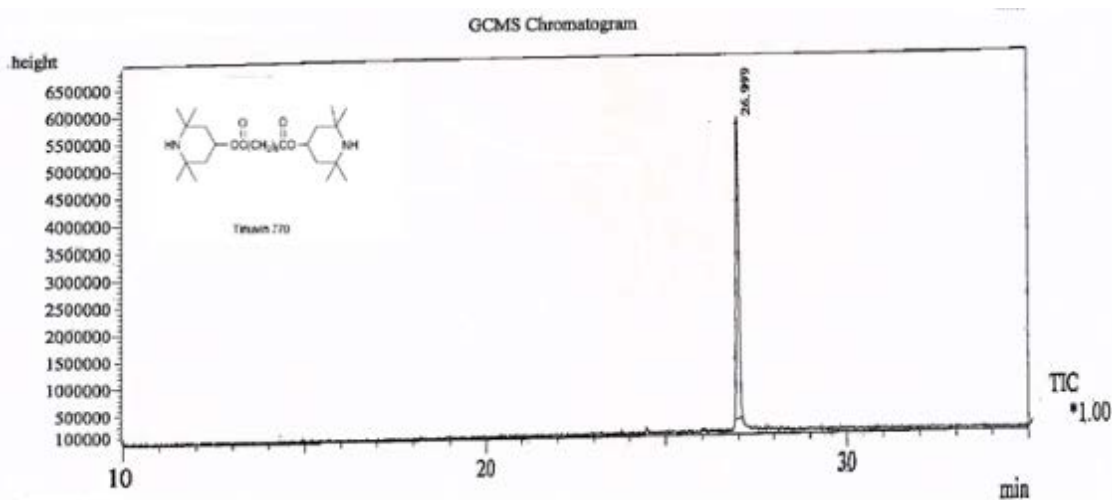

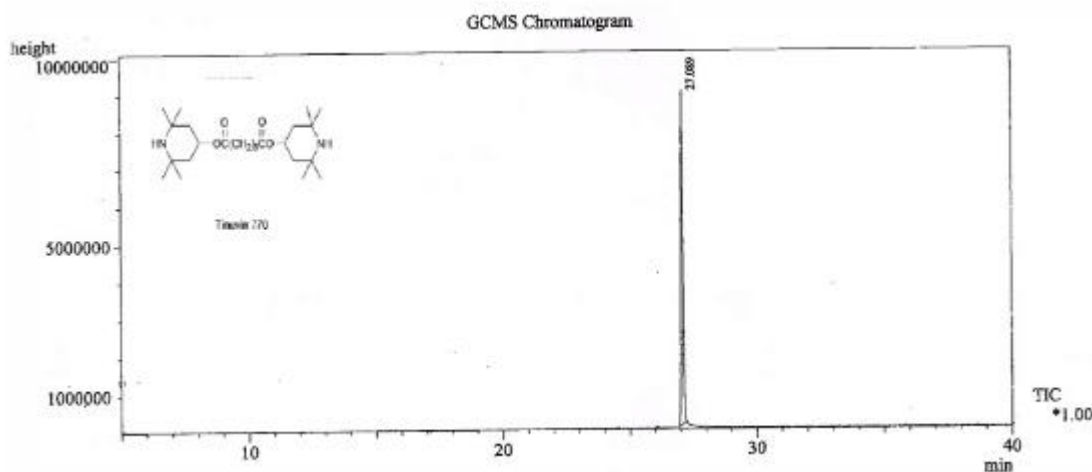**Figure 11: GC-MS chromatogram of standard Tinuvin 770.**

Figure 12: GC-MS chromatogram of expired Tinuvin 770.

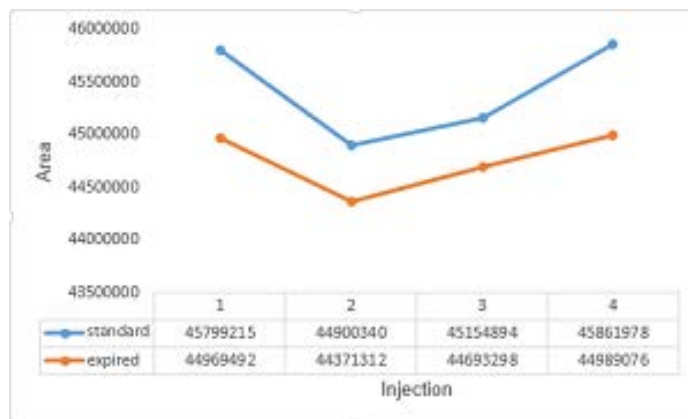|	1	2	3	4
standard	45799215	44900340	45154894	45861978
expired	44969492	44371312	44693298	44989076

Injection

Diagram 2: Comparison of GC-MS areas under the peak Tinuvin 770

Conclusion

The studies concluded that the light stabilizer Tinuvin770 after expire date, under appropriate conditions, away from humidity, ionizing radiations and high temperature (above Extruder system temperature), and because of being alkaline compound, it must be kept in free acidic environment. We can foresee that it retain its structure and functional characteristics and can be used in the stabilization of polypropylene and other polymers.

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