PHOTO-OXIDATIVE DEGRADATION OF ABS COPOLYMER

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ABSTRACT

PHOTO-OXIDATIVE DEGRADATION OF ABS COPOLYMER

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Acrylonitrile-butadiene-styrene (ABS) polymer is one of the most popular copolymer having an elastomeric butadiene phase dispersed in rigid amorphous styrene and semi-crystalline acrylonitrile. Due to double bonds in the polybutadiene phase, ABS copolymers are very sensitive to photo-oxidative degradation. Photo-oxidation of butadiene rubber phase results in the formation of chromorphores and these chromorphores act as initiators in photo-oxidative degradation and after a while ABS starts yellowing.

In this work, the relationship between the UV light and the yellowing of ABS samples was also investigated with respect to time. In this study, pure, light stabilized and commercial ABS samples were aged under UV light. As the UV light intensity increased from 800 to 2800 $\mu W/cm^2$, yellowing of the samples were increased for pure ABS. This increase in yellowing of the samples was about 27 times higher compared to lower energy.

In this study, UV stabilizers IRGANOX 1076 (sterically hindered phenolic antioxidant), IRGAFOS 168 (hydrolycally stable phosphite stabilizer) and TINUVIN P (hydroxyphenol benzotriazole) were used alone or in combination with each other. Pure ABS samples, commercial ABS samples and UV stabilized ABS samples were aged under the same UV light. UV aging degradation was followed by measuring the yellowness of the samples at certain time intervals. Yellowness of the samples was followed by using Coloreye XTH Spectrometer. Degradation in ABS, however, was followed by using FTIR with an increase in the peak area of carbonyl groups in the ABS matrix.

Both color analysis and the FTIR analysis showed that combination of the IRGANOX 1076 and IRGAFOS 168 stabilizers gave the best stabilization. This revealed that combination of phenol and phosphate containing stabilizer is the most useful combination to prevent photo-oxidative degradation of ABS copolymer.

Additionally, vegetable oil was applied to the surface of a new set of ABS samples and these samples were aged for 700 h. Yellowing tendency of these samples was compared with the yellowing tendency of ABS samples that are directly aged for 500 h. It was clearly observed that samples with oil smeared had more resistance to UV radiation with respect to others. This shows that oil acts protective layer to the UV light and oxygen and slow down the photo-oxidative degradation.

Lastly some commercial ABS samples were compared to each other with respect to their yellowing tendency. Commercial ABS samples coded as K, L, A, B, C and D were aged under UV light at about 500 h. Sample A showed the best resistance against the yellowing among the other commercial ABS samples.

Key words: ABS, UV-aging, photo-oxidative degradation, yellowing, light stabilizers.

ÖZ

ABS POLİMERİNİN FOTO-OKSİDATİF BOZUNMASI

Güzel, Aylin
Yüksek Lisans, Polimer Bilimi ve Teknolojisi
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Poli(**A**krilonitril-**B**ütadien-**S**itiren) (ABS) en revaçta olan mühendislik plastiklerindendir. ABS elastomerik bütadienin sert amorf sitiren ile yarı kristal yapı gösterebilen akrilonitril kopolimeri içinde dağılımı ile elde edilir. ABS özellikle polibütadien fazının içerdiği çift bağlar nedeniyle UV ışınları altında oksidatif bozunmaya karşı çok duyarlıdır. Foto-oksidatif bozunma süresince kromofor grupları oluşmaktadır. Oluşan kromoforlar fotokimyasal bozunmayı hızlandırmakta ve bir süre sonra polimerde sararma gözlenmektedir.

Bu çalışmada UV ışın yoğunluğu ile sararma ve oksidatif bozunma arasındaki ilişki incelenmiştir. Saf ABS'de yapılan bu çalışmada UV ışık yoğunluğunun 800μW/cm^2'den 2800μW/cm^2 'ye çıkmıştır. Bu durum neticesinde ABS'deki sararma yaklaşık olarak 27 kez artmıştır.

Bu çalışmada üç değişik UV-ışık kararlı kılıcısı, IRGANOX 1076 (sterik olarak engellenmiş fenolik antioksidant), TINUVIN P (hidrolik olarak fosfitli kararlı kılıcı) ve IRGAFOS 168 (hidroksi-fenolbenztriazol) ayrı ayrı veya karışım olarak kullanılmıştır. Saf ABS, UV ışık kararlı kılıcı içeren ABS ve ticari ABS örnekleri aynı UV ışığı altında yaşlandırılmıştır. UV yaşlandırması UV ışınlaması zamanına karşı örneklerde renk değişimi (sararma olarak) takip edilmiştir. Bu renk değişimi Coloreye-XTH spectrometre cihazı ile, kimyasal bozunma ise FTIR’da analiz edilerek ABS’nin matriksindeki karbonil gruplardaki artışlar takip edilmiştir.

Hem renk değişimi hem de FTIR ile takip edilen foto-oksidatif bozunma sonucunda fosfitli ve fenollü kararlı kılıcıların ABS için en uygun olduğu belirlenmiştir.

Sararma yoğunlukla örneklerin yüzeyinde gerçekleştiğinden yeni bir set ABS örnekleri hazırlanarak bunların yüzeyine nebati yağ sürülmüştür. Yüzeyleri yağlanan bu örnekler 700 saat kadar UV lambası altında yaşlandırılmıştır. Bu örneklerin sararma oranları daha önce 500 saat UV ışığına maruz bırakılan örnekler ile karşılaştırılmıştır. Bu karşılaştırmada yüzeyine yağ uygulanan ABS örneklerinin daha az sararmış olduğu görülmüştür. Bu da yağın UV ışığına ve oksijene karşı koruyucu bir tabaka gibi görev yaptığını ve foto-oksidatif bozunmayı yavaşlattığını göstermektedir.

Son olarak ticari ABS örnekleri arasında foto-oksidatif bozunmaya karşı dayanıklılık açısından bir karşılaştırma yapılmak istenmiş, kendi aralarında K, L, A, B, C ve D olarak adlandırılan bu örnekler 500 saat süre ile UV ışığına maruz bırakılmıştır. Ticari ABS örneklerinde en az sararma A örneğinde gerçekleşmiştir.

Anahtar Kelimeler: ABS, UV yaşlandırması, foto-oksidatif bozunma, UV ışık kararlı kılıcısı.

To My Family

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ABREVIATIONS

ABS: Acrylonitrile-Butadiene Styrene Polymer

PB: Polybutadiene

S:Styrene

AN: Acrylonitrile

SAN: Styrene-acrylonitrile

BR: Butadiene Rubber

UV: Ultraviolet

HALS: Hindred Amine Light Stabilizers

FTIR: Fourier Transform Infrared Spectroscopy

L: Lightness

+a: Redness

-a: Greenless

+b: Yellowness

-b: Blueness

h: Hour

ABS*: Pure ABS Sample Aged Under 2800µW /cm^2 UV Light

ABS**: Pure ABS Sample Aged Under 1400µW /cm^2 UV Light

ABS***: Pure ABS Sample Aged Under 800µW /cm^2 UV Light

Sample K: Commercial ABS Sample

Sample L: Commercial ABS Sample

Sample A: Commercial ABS Sample

Sample B: Commercial ABS Sample

Sample C: Commercial ABS Sample

Sample D: Commercial ABS Sample

LAB ABS: ABS sample supplied by METU polymer laboratory

Arçelik ABS: ABS sample supplied by Arçelik Bulaşık Makinaları A.Ş

CHAPTER I

INTRODUCTION

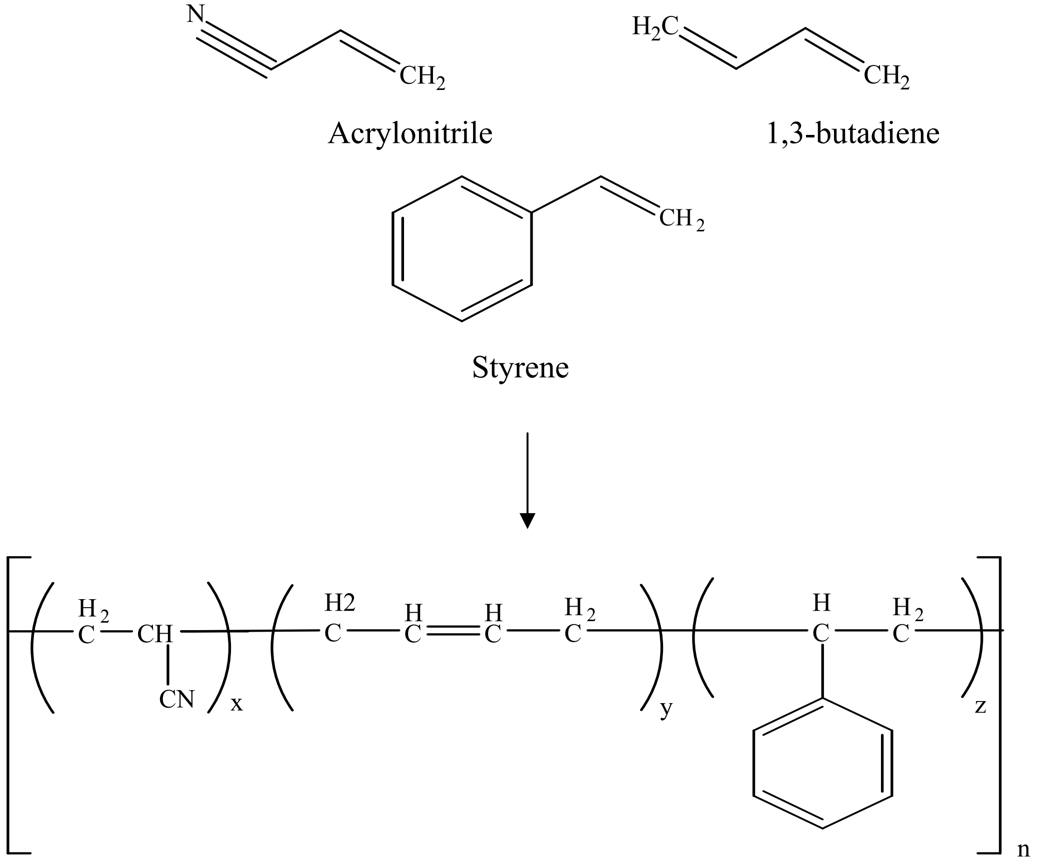
Polymers have been used since the beginning of time. Natural polymers, tar, shellac, tortoise shell etc., were processed with heat and pressure into useful articles like hair ornaments and jewelry. Natural polymers started to be chemically modified during the 1800s to produce many materials. The most famous of these were vulcanized rubber, gun cotton, and celluloid. Since then, the polymer industry has continued to grow and has evolved into one of the fastest growing industries in the world.

1.1 Acrylonitrile-Butadiene-Styrene Copolymer (ABS)

Styrene Acrylonitrile copolymers (SAN) have been available since the 1940’s but its limitations led to the introduction of a third monomer which was butadiene. Acrylonitrile-Butadiene-Styrene copolymer (ABS) become available in the 1950’s and the variability of these copolymers and ease of processing led to ABS becoming the most popular engineering polymer.

Poly(acrylonitrile-butadiene-styrene) ABS copolymers consist of an elastomeric component, polybutadiene (PB) dispersed in a copolymer of styrene (S) and acrylonitrile (AN). PB and the thermoplastic component (SAN) become compatible due to grafting of SAN on the elastomer chain. The resulting complex polymeric materials are phase-separated into B-rich and SAN-rich domains, but the specific morphology depends on the preparation method. In emulsion polymerization, a PB latex is further polymerized at ambient temperature in the presence of S and AN, leading to a dispersion of PB-g-SAN in a continuous SAN phase; the size of the rubber particles is in the range 0.1-1µm. In mass polymerization, S and AN monomers are grafted to linear PB chains at elevated temperatures, ~373K, in the absence of solvent; this process results in larger rubber particles typically 0.5-5 µm. ABS polymer can be modified by variation of the grafting conditions and monomer ratio, to produce a polymer suitable for specific application [1,10].

ABS is an amorphous thermoplastic blend. The recipe is 15-35 wt% acrylonitrile, 5-30 wt% butadiene and 40-60 wt% styrene. Depending on the composition different properties can be achieved [2]. Monomers of ABS and the structure of the copolymer are given in Figure 1.1.



Monomers

Figure 1.1: Acrylonitrile-Butadiene –Styrene (ABS) Copolymer

ABS is a biphasic system having styrene-co-acrylonitrile in the continuous phase with a dispersed phase of butadiene rubber.

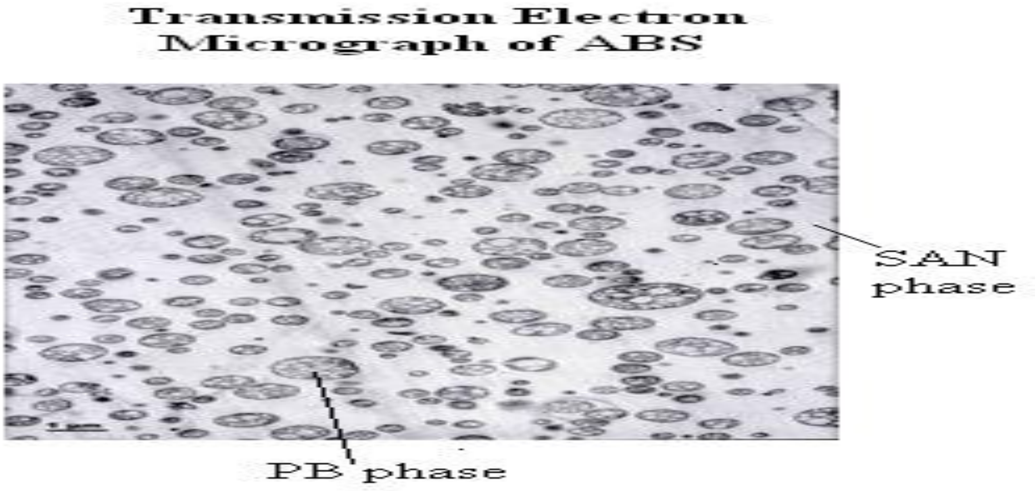


Figure 1.2: Transmission electron micrograph of ABS [3]

Every monomer in ABS produces its own specialty; acrylnitrile part increases thermal and chemical resistance of ABS, white butadiene part increases ductility and impact strength and styrene part gives the glossy surface and makes the ABS easily machinable and less expensive. The most amazing mechanical properties of ABS are its resistance and toughness. A variety of modifications can be made to improve impact resistance, toughness, and heat resistance. The impact resistance can be amplified by increasing the proportions of PB in relation to styrene and acrylonitrile although this causes changes in other properties. The relevant properties of ABS are given in Table 1.

Table 1: Typical physical and mechanical properties of a commercial ABS [11]

PROPERTY	**ABS**
PHYSICAL	
Density (g/cm^3)	1.04
Water Absorption, 24 h (%)	-
MECHANICAL	
Tensile Strength (MPa)	45
Tensile Modulus (MPa)	2344
Tensile Elongation at Break (%)	25
Flexural Strength (MPa)	75.8
Flexural Modulus (MPa)	2206
Hardness, Rockwell	R105
THERMAL	
Heat Deflection Temperature (°C) at 1.8 MPa	102
Melting Temperature (°C)	-
Max. Operating Temperature (°C)	60

ABS copolymer has resistance to aqueous acids, alkalis, concentrated hydrochloric and phosphoric acids, alcohols and animal, vegetable and mineral oils, but it swells in glacial acetic acid, carbon tetrachloride and aromatic hydrocarbons and is attacked by concentrated sulfuric and nitric acids. ABS is soluble in esters, ketones and ethylene dichloride.

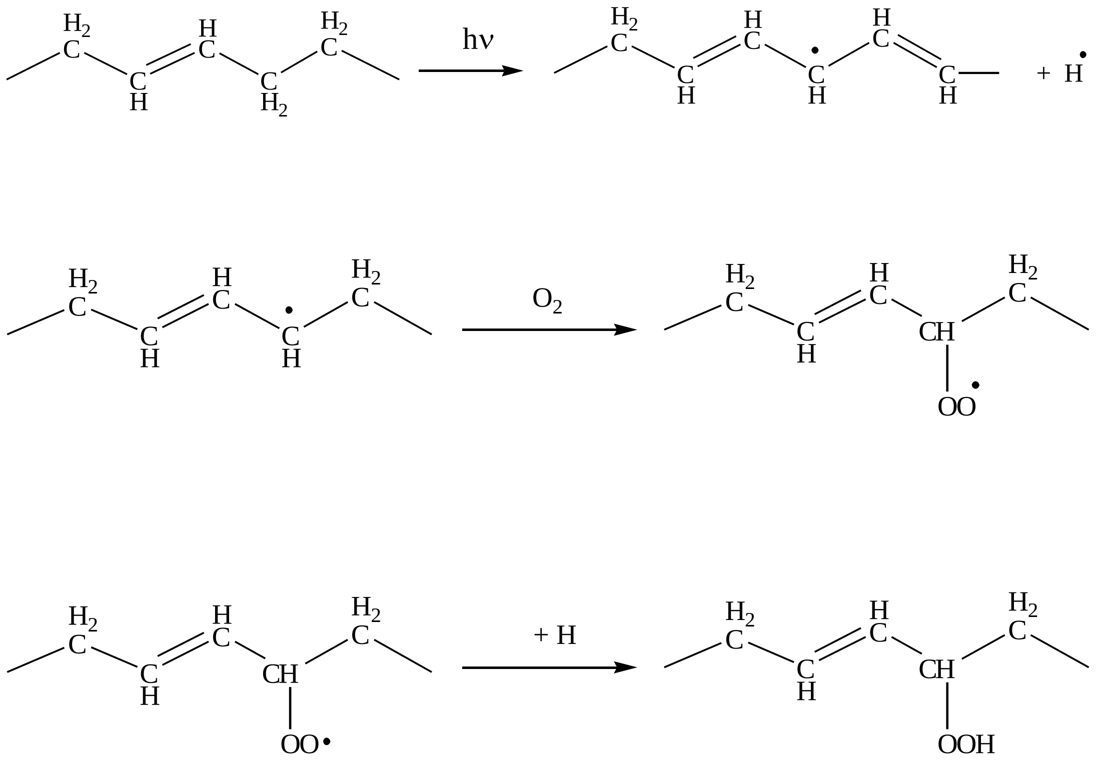
ABS copolymers are used to make light, rigid, molded products such as piping, musical instruments, automotive body parts, wheel covers, enclosures, protective head gear and toys.

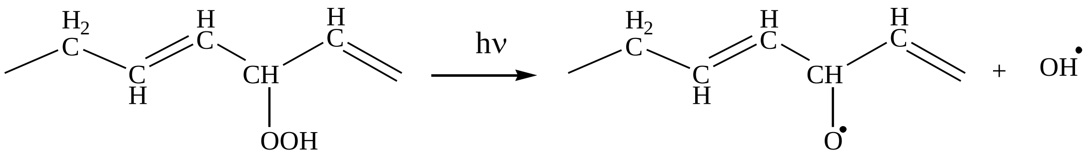
1.2 Degradation of ABS Copolymer

1.2.1 Photo-Oxidative Degradation of ABS Copolymer

ABS is very sensitive to photo-oxidative degradation. Especially PB phase is the major process involved in ABS photo-oxidation.

On radiation in the presence of oxygen, primary hydroperoxidation occurs in the α-position to the double bond of polybutadiene nodules [4]. Methylene bond formation occurs in the trans-1,4-polybutadiene and this produces an allylic radical polymer chain. This radical may undergo several reaction that yield hydroperoxides, ketones and esters [5]. Photochemical decomposition of polybutadiene with the formation of hydroperoxides is shown below [4].





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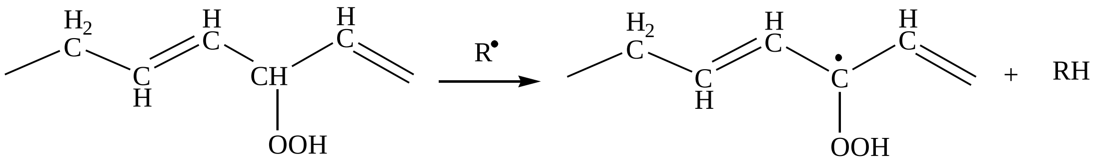
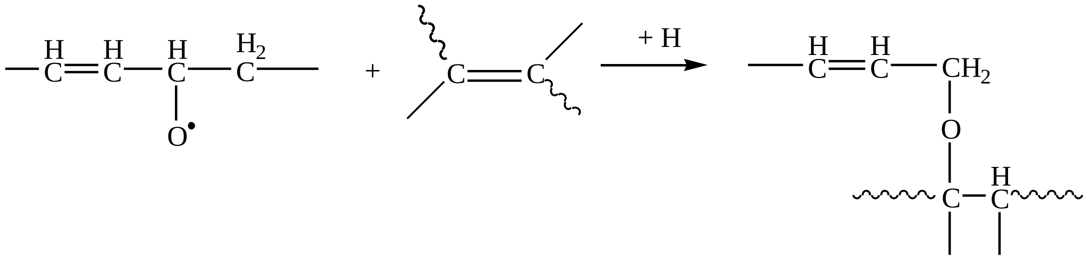
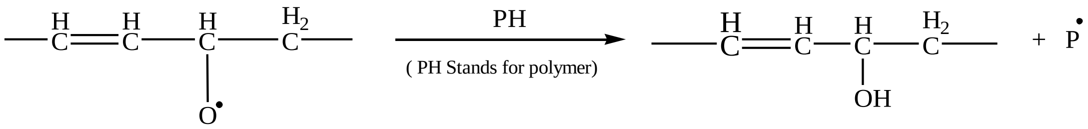


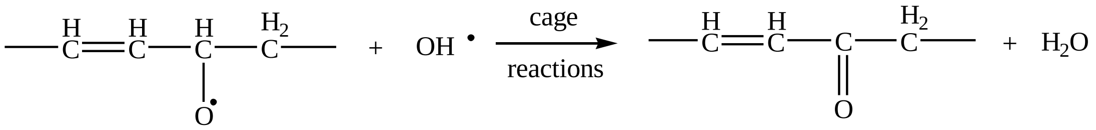
Radicals that are formed during the degradation of polybutadiene phase are precursor of various photoproducts. Some of those photoproducts are given below.

Crosslinking

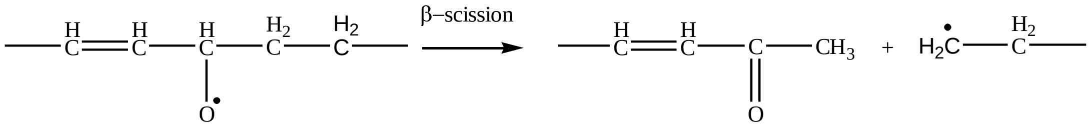


Other Reactions





Chainscission Reactions



These degradations affect the molecular weight of the copolymer and crosslinking leads to an increase in molecular weight whereas the chain scission has the opposite effect. Due to this molecular weight change, viscosity and free volume of the copolymer changes and because of free volume change the polymer's microstructures changes.

1.2.2 Discoloration

Discoloration, which is caused by various factors such as light, heat, moisture, γ-rays, pH extremes, contaminants, is one of the most important problems for commercial polymers. Discoloration is usually due to combination of two or more factors so it is difficult to assign which one is the base reason for discoloration and discoloration is often related to the coupling of radicals with degradation peroxy radicals [5]. Although most discoloration shows itself as yellowing, pink and grey discoloration are also possible.

Types of yellowing associated with degradation are thermal yellowing, photochemical yellowing and radiolytic yellowing.

In ABS, the butadiene rubber phase (BR) has such high sensitivity towards oxidation relative to other components so BR part plays the determining role in yellowing of ABS copolymer.

Discoloration of ABS can be attributed to the formation of photoproduct chromorphores during degradation. Chromorphores absorb energy in the UV visible spectrum and cause discoloration. According to literature, both the PB and SAN phases are said to form chromorphores upon oxidation which are responsible for fading and yellowing [5].

1.3 Stabilization of Polymers

Stabilizers are chemicals that are added to polymers in small amounts (1-2% weight) in order to inhibit or slow down the degradation of the polymers [6,21,22].

According to their mode of action they are classified as bellow;

- Light stabilizers
- Antioxidants
- Metal deactivators

1.3.1. Light Stabilizers

Free radicals form as a consequence of excitation of absorbing functional groups in the polymer due to exposure of light. Energy of the light and structure of the polymers are the parameters that affect the radical formation [15,20,22].

a) UV Absorbers

UV absorbers absorb the harmful UV radiation and dissipate it as heat. Thus, they do not lead to photosensitization [22].

b) Hindered Amine Light Stabilizers (HALS)

Hindered amine light stabilizers can be defined by the reaction between alkyl radicals and nitroxyl radicals. Hindered amine stabilizers are effective light stabilizer. Hydroxyl amine forms an intermediate reactive species (nitrone) which are capable of scavenging C-radicals [12,13,14].

1.3.2 Antioxidants

a) Hydrogen-Donors

After addition of H-donors; peroxy radicals offer more easily abstractable hydrogen by externally added hydrogen donor. Hydrogen abstraction from polymer backbone will not take place until all of the external H-donor is consumed [5,22].

Among H-donors aromatic amines, secondary aromatic amines and sterically hindered phenols are excellent H-donor but their application is limited to polymer due to discoloring and staining properties. Phenolic antioxidants are most widely used H-donor stabilizers and discoloration caused by oxidation products of phenol can be minimized by choosing the specific structure of phenolic antioxidants and by using suitable co-stabilizers.

b) Hydroperoxide Decomposers

A suitable hydroperoxide decomposer transforms hydroperoxides into non-radical, non-reactive and thermally stable products. Hydroperoxide decomposers stabilizes hydroperoxides into alcohols while they are oxidized in a stiochiometrical reaction.
Organic compounds of trivalent phosphorous and organic compounds of sulfur are widely used hyroperoxide decomposizers and they are generally used in combination with H-donors [17,22].

c) Alkyl Radical Scavengers

Scavenging alkyl radicals reacts with oxygen at extremely high reaction rate [6,22] and stop auto-oxidation immediately.

Acryloyl Modified Phenols

Acryloyl modified phenols are effective C-radical scavengers, especially during the processing of the styrene copolymers they prevent the crosslinking and degradation of the copolymer [16].

1.3.3. Metal Deactivators

Metal ions cause the decomposition of the peroxides by forming reactive radical and it forms stable complexes with metals [6].

1.4. Aim of the Study

The aim of this research is to understand and find a relationship between photo-oxidative degradation and yellowing of ABS copolymer. Furthermore, find a simple method for following the yellowing and the extent of yellowing. And finally it was tried to prevent yellowing of ABS copolymer by using different types of stabilizers.

CHAPTER II

EXPERIMENTAL

2.1 Materials

2.1.1 ABS Samples

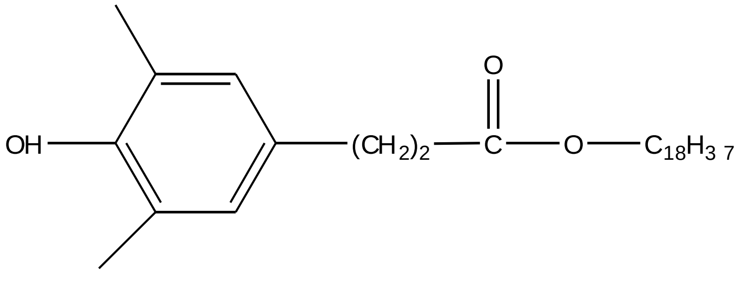
Granular commercial pure ABS samples and different types of granular commercial ABS samples coded as K, L, A, B, C and D were supplied by ARÇELİK A.Ş Bulaşık Makinası, ANKARA.

2.1.2 Stabilizers

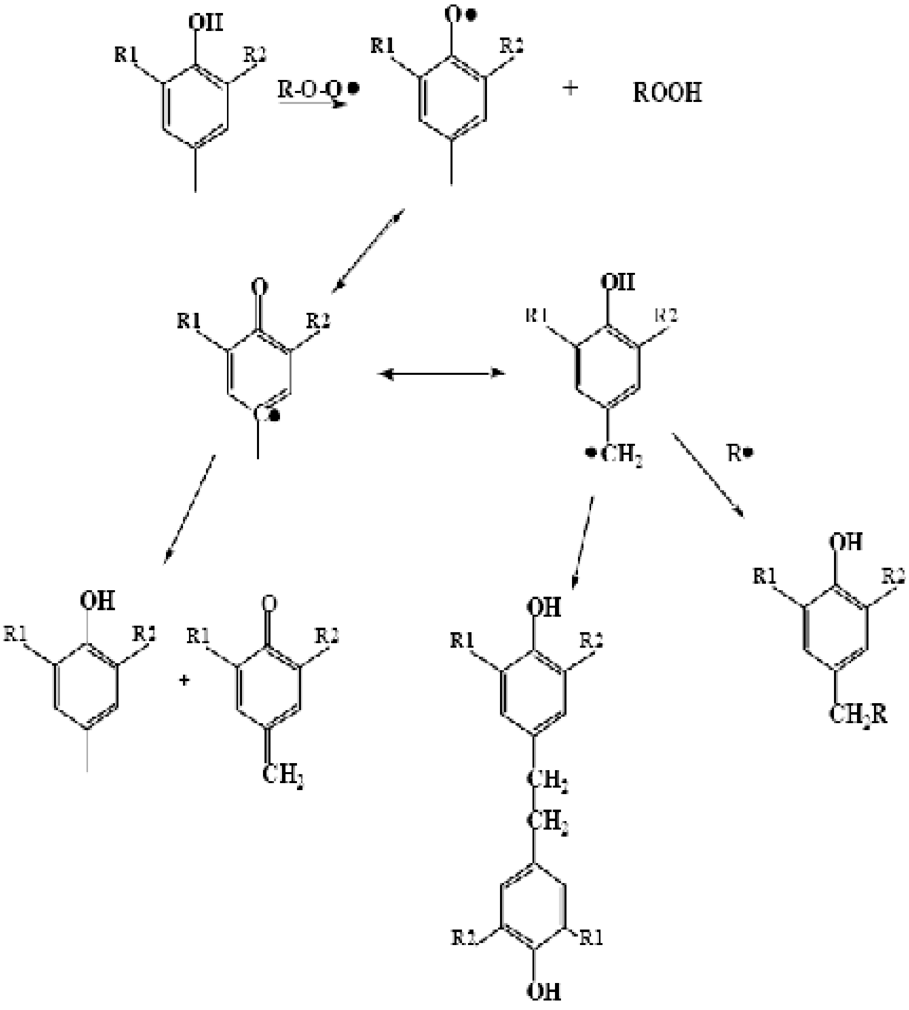
Three different types of UV stabilizer were supplied kindly by CIBA Specialty Chemicals Company, İstanbul.

These stabilizers are;

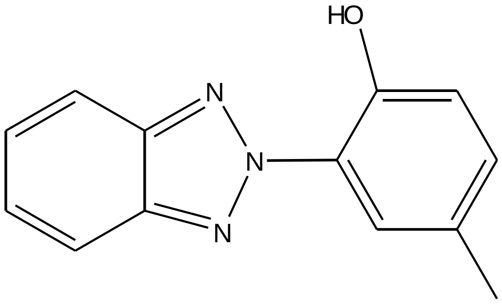
- *IRGANOX 1076 (Octadecyl-3-(3,5-di-tert.butyl-4hydroxyphenyl) propionate)*



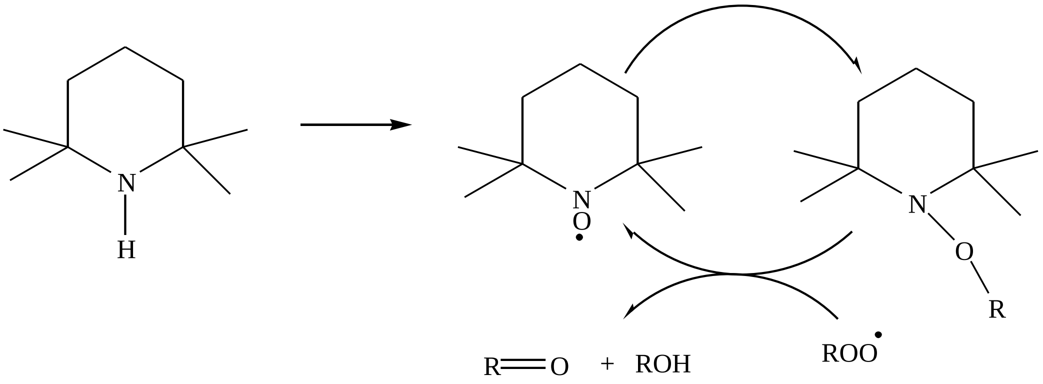
IRGANOX 1076 is a phenolic stabilizer. By the use of IRGANOX 1076 the easily abstractable hydrogen reacts with the free radical to yield inactive products. After donating a hydrogen atom, the resulting phenoxyl radical could be localized in the ring and also its sterically hindered side groups. Partially hindered phenols are a good choice As they are able to react further and thereby inhibit autoxidation in several steps [6].



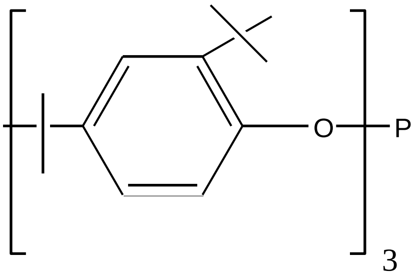
- *TINUVIN P (2-(2H-benzotriazol-2yl)-p-cresol)*



TINUVIN P (Hindered Amine Stabilizer) produces nitroxides which can intercept alkyl radicals to yield amino ethers that can react with peroxy radicals. Therefore TINUVIN P can destroy to species that could lead to polymer degradation and creates species which protect the polymer against degradation [6].



- *IRGAFOS 168 (Tris(2,4-ditert-butylphenly)phosphite)*



IRGAFOS 168 (Phosphate Containing Stabilizers) decomposes the hydroperoxide and suppresses the formation of radicals. Aromatic phosphates also preserve the hindered phenols. They react with unsaturated vinyl groups in the polymer and prevent discoloration by reacting with colored conversion products of the hindered phenol [6].

$$P(OAr)_3 \quad + \quad ROOH \quad \rightarrow \quad O=P(OAr)_3 \quad + \quad ROH$$

2.2 Preparation of Samples

ABS samples with different composition of stabilizers were prepared in order to determine the efficiency of the stabilizer and to compare with pure ABS.

500 g (for each sample) pure ABS was dried in the oven at 80-90 °C about 24 h. Stabilizers were dissolved in chloroform separately. This solution was poured onto granular ABS samples with mechanical mixing done for every 30 min for 8-10 h until all chloroform evaporated at room temperature. Mechanical mixing was necessary since chloroform dissolves ABS and the granules starts to adhere each other and prevents the uniform distribution of stabilizer into ABS. Weight percentages of stabilizers for each sample are given in Table 2.

Table 2: Amounts of stabilizer added to ABS Copolymer

SAMPLE	IRGANOX 1076 (wt%)	IRGAFOS 168 (wt%)	TINUVIN P (wt%)
Sample 1	**0.3**	X	X
Sample 2	X	**0.3**	X
Sample 3	X	X	**0.3**
Sample 4	**0.2**	**0.2**	X
Sample 5	**0.2**	X	**0.2**
Sample 6	**0.2**	**0.1**	**0.1**

Afterwards, samples were let dry at room temperature for 4 days. For better mixing ABS with stabilizers, samples extruded by Thermoprism TSE 16 TC, co-rotating, intermeshing twin-screw extruder. All samples were dried under vacuum to remove humidity before extrusion. Parameters of extrusion process are given in Table 3.

Table 3: Parameters of extruder machine

Temperature profile	160-170-190-220 °C
Torque	87 rpm
L/D ratio	24
Flow rate of feed	20 gr/min

Granules obtained from extrusion process were then dried in the vacuum oven about 24 h to get dry samples for compression molding. The thin (~1.0 mm) films of ABS samples were produced by compression molding in hot press at 215-220 °C. After compression molding, whiteness of each ABS plate were measured by Coloreye XTH Spectrometer.

2.3 UV Irradiations of ABS

Sylvanıa Par 38 medium pressure mercury lamb with 100 W power was used in UV radiation. All samples were irradiated from 20 cm distance at room temperature in a ventilated hood.

Pure ABS samples irradiated at three different UV intensities (2800 $\mu W/cm^2$, 1400 $\mu W/cm^2$ and 800 $\mu W/cm^2$) about 500 h. Variation in the b values which is the measure of yellowness were measured every 50 h. Later on all samples were irradiated at the same power of 2800 $\mu W/cm^2$.

All ABS samples were exposed to UV light (~2800 $\mu W/cm^2$) about 500 h. Discoloration of surfaces of all samples were analyzed every 50 h by Coloreye XTH Spectrometer.

A thin film of vegetable oil was applied on the ABS set of similar composition and this set was aged for 700 h to follow the yellowing. Variation in the b value were measured every 50 h.

Different types of commercial samples named as K, L, A, B, C and D were aged under UV light at about 500 h and degradation of these samples were followed and compared.

After completion of these four sets of experiments, the samples that showed the best resistance against photo-oxidative degradation were chosen and these samples were irradiated with the commercial K, L and pure ABS (Arçelik ABS and Lab ABS) samples for 900 h for comparison. In this set of samples, every sample was divided into small rectangular parts in which these parts were taken at various times of UV irradiation for spectroscopic analysis. The extent of the photochemical degradation on these small rectangular samples was carried by FTIR spectroscopy.

2.4 Sample Analysis

2.4.1 Surface Analysis of Samples By Coloreye XTH Spectrometer

Coloreye XTH spectrometer uses a three dimensional color space arrangement for representing all colors. This color space is defined by the color scale L^*, a^* and b^*, where L^* scale is a measure of lightness, a^* is a measure of redness ($+a^*$) or greenness ($-a^*$), b^* is a measure of yellowness ($+b^*$) or blueness ($-b^*$). Coloreye XTH Spectrometer was used to measure color of the samples.

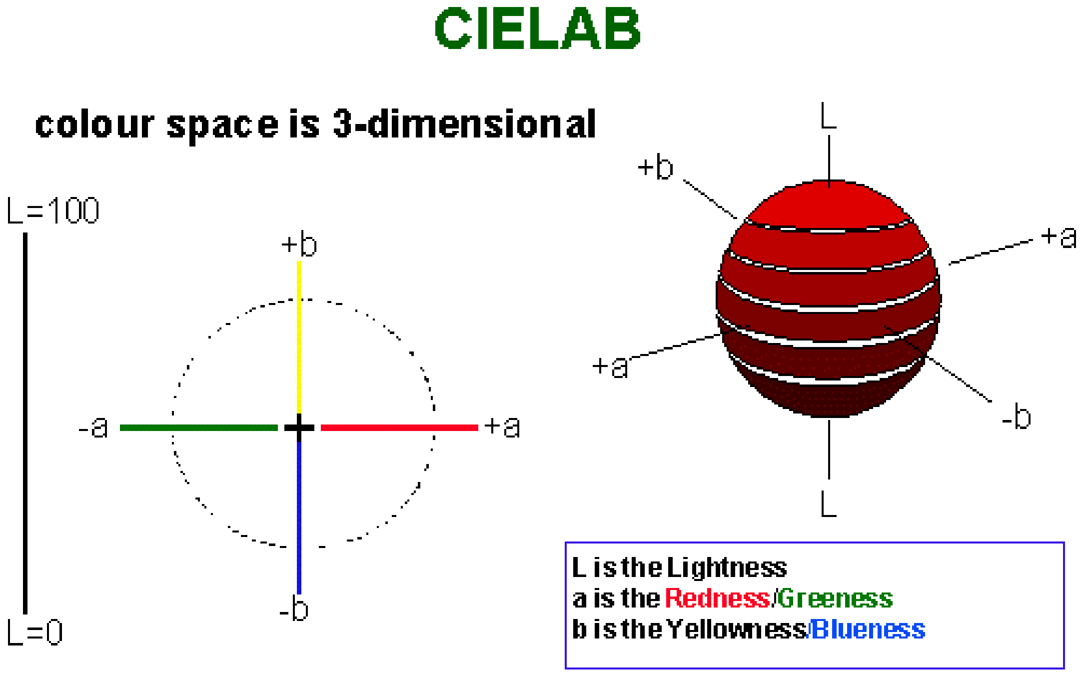


Figure 2.1: Coloreye XTH Spectrometer color space in 3-dimensionel

2.4.2 FTIR Analysis

In every 50 h small rectangular samples were cut from UV irradiated samples. Surface of these small rectangular samples were removed by using chloroform. This chloroform solution poured onto clean and flat surface. After evaporation of the chloroform, very thin films formed around 100 μm were analyzed in FTIR. Photo-oxidative degradation products that formed under UV irradiation were quantitatively measured by FTIR. Effect of the photo-oxidative degradation was followed by measuring the area under carbonyl peak (1721 cm^{-1}) in every 50 h.

CHAPTER III

RESULTS AND DISCUSSION

By changing the microstructure of ABS copolymer UV oxidation can induce photo-oxidative degradation of the copolymer. The butadiene phase is the main responsible phase that induces the photo-oxidative degradation in ABS degradation.

Photo-oxidative degradation of ABS copolymer begins, like all polymers, at the surface which is directly subjected to UV light. The surface of the ABS copolymer, however, shows more damage when compared to interior part and other polymers.

Photo-oxidative degradation of ABS leads to color development (yellowing) on the surface of the UV aged samples. Surface yellowing is one of the measures of the extent of photo-oxidative degradation. This means that as the UV irradiation time and energy of UV light increase, yellowness at the surface of ABS samples becomes more.

3.1. UV Aging at Different UV Powers

In order to determine effect of the UV radiation on photo-oxidative degradation, pure ABS samples were aged under different UV powers. Discoloration at the surfaces of these samples was analyzed by Coloreye XTH spectrometer at certain time intervals.

Pure ABS samples were aged with 2800 $\mu W/cm^2$, 1400 $\mu W/cm^2$ and 800 $\mu W/cm^2$ UV powers. Variations in the b value which is the measure of the yellowness were given in Fig.3.1, 3.2 and 3.3. As b value approaches to zero and positive value (+b: yellowness, -b: blueness) means that yellowness at surface of the aged sample increases.

Pure ABS* sample which was aged under 2800 μW/cm^2 UV light showed a rapid degradation between 100 h and 150 h, and yellowing rate of pure ABS* slowed between 150 h to 400h. After 400 h of UV radiation time, b value of this sample increased very fast from -0.53 to 1.45 (Figure 3.1). Linear line in the graph was drawn to determine the degradation rate and equation of this line was also provided in the figures.

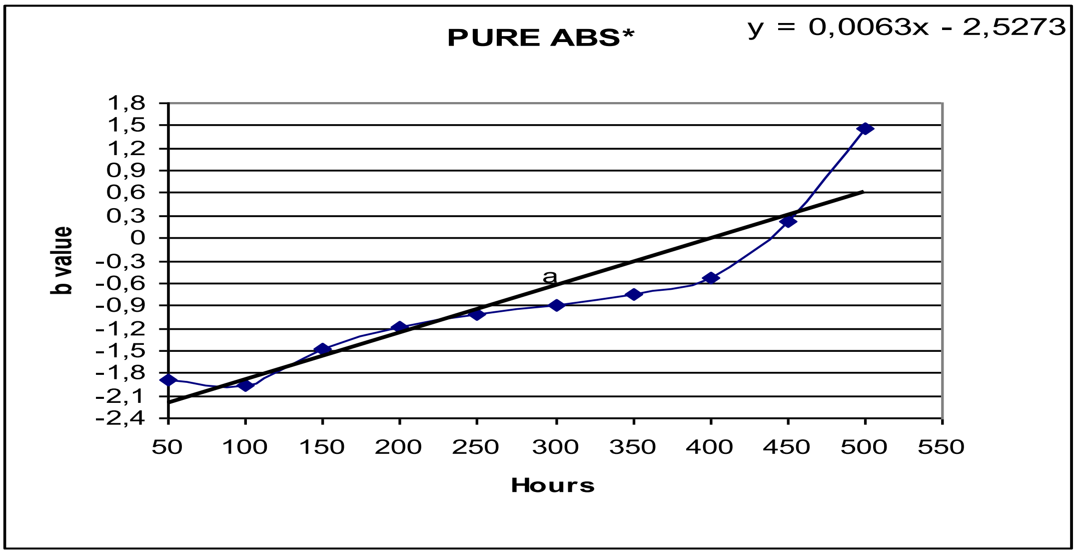


Figure 3.1: Pure ABS* sample aged under 2800 μW /cm^2 UV light; the variation of b value with respect to time

Pure ABS** (1400 μW/cm^2 UV energy) showed a similar degradation profile with that of the previous ABS* (Figure 3.2). There is a big difference between the final b values (at 500 h) of these samples. Pure ABS*'s b value at 500 h is 1.45 where as the b value of the pure ABS** was 1.1.

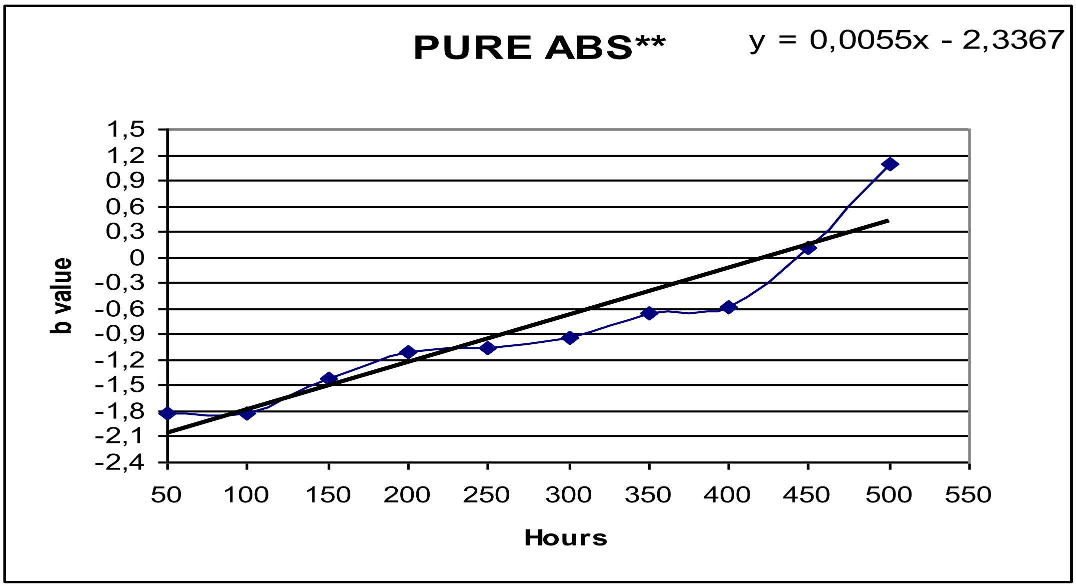


Figure 3.2: Pure ABS** sample aged under 1400 μW/cm^2 UV light; the variation of b value with respect to time

Lastly pure ABS, ABS***, was aged under 800 μW/cm^2 UV energy and therefore degradation of this last sample was expected to be slower than the other two. Yellowing profile of this sample was also similar to other two samples (Figure 3.3).

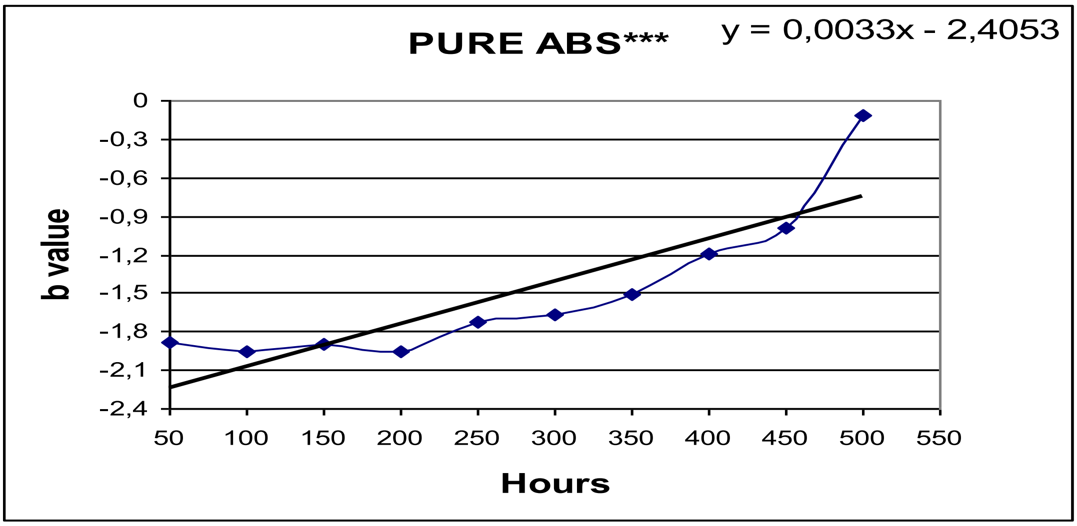


Figure 3.3: Pure ABS*** sample aged under 800 µW/cm^2 UV light; the variation of b value with respect to time

When the yellowing, in other words degradation, of these three samples is compared, it is clear that yellowing rate of pure ABS* sample (2800 µW/cm^2) is much more than the others (Figure 3.4). Indeed, the slope of the ABS* is higher than ABS**, which is higher than ABS***. This shows that higher the power faster the yellowing. Therefore, yellowing and the photo-oxidative degradation of samples increase with the power of the UV light.

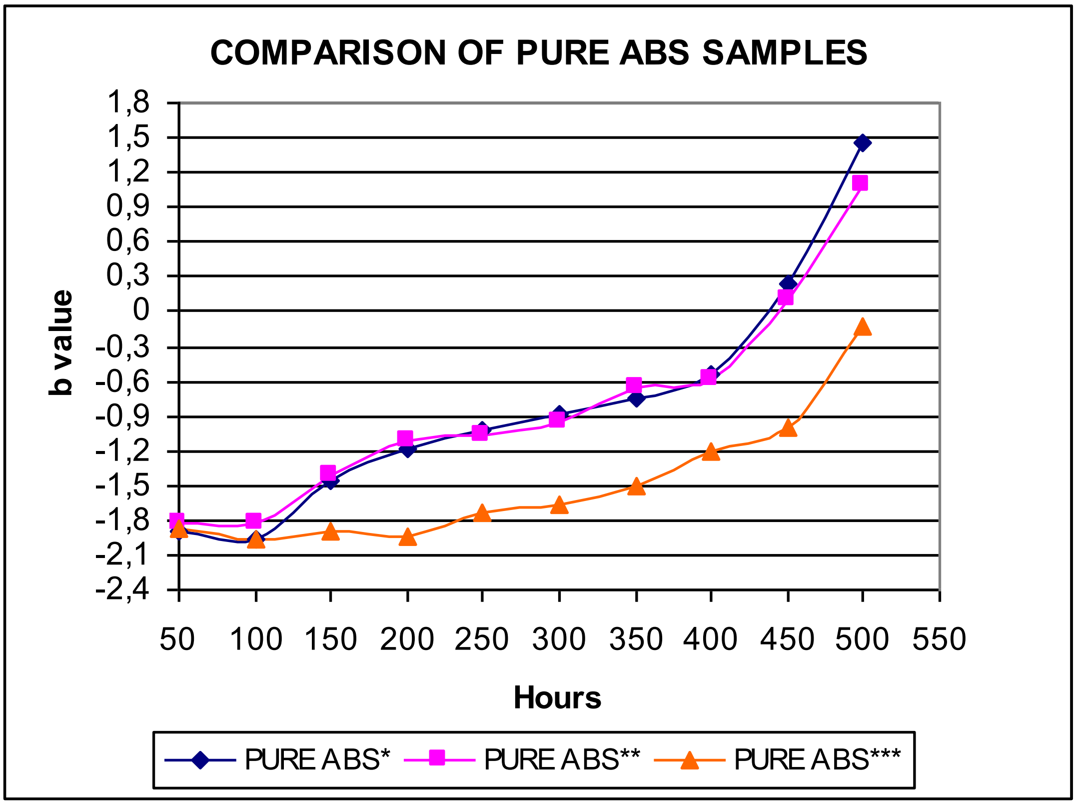


Figure 3.4: Comparison of pure ABS samples with respect to their b values

During UV degradation, cross-linking is assumed to occur at the surface of the polymer [9]. This cross-linking increases the density of the polymer at the surface and prevents the further penetration of the UV light and oxygen in the bulk phase [9]. Therefore, this initial crosslinking protects the material to a certain extent. After this initial crosslinking, as the irradiation time increases the crosslinking is destroyed and a sudden and faster increase is observed in yellowing.

As a result, rate of degradation at the surface decreased over a period of time of crosslinking and then we observe a sudden increase in yellowing. For pure ABS* and pure ABS** samples this behavior of the copolymer easily observed. However, the UV power exposed on pure ABS*** was much lower than the other two, degradation was slowly propagated and it was retarded.

3.2. UV Aging of Samples Containing Stabilizer

The effects of stabilizer addition on the yellowing of the ABS copolymer were investigated. Yellowing tendency of the pure ABS samples and the yellowing tendency of samples containing stabilizer were compared by aging all these samples under the same UV power (~2800 μW/cm^2). Through the Figures 3.5 to 3.10 the variation of b value with respect to UV irradiation times were given for the samples contained UV-light stabilizers. The Table 3 given in the experimental section described the composition of these six samples.

Sample 1 containing 0.3 wt% IRGANOX 1076 (phenolic stabilizer) showed a rapid degradation between 50 h and 150 h and nearly no observable degradation between 150 h to 250 h and degradation rate enhanced from 250 h to 400 h but after 400 h very rapid degradation was observed (Figure 3.5).

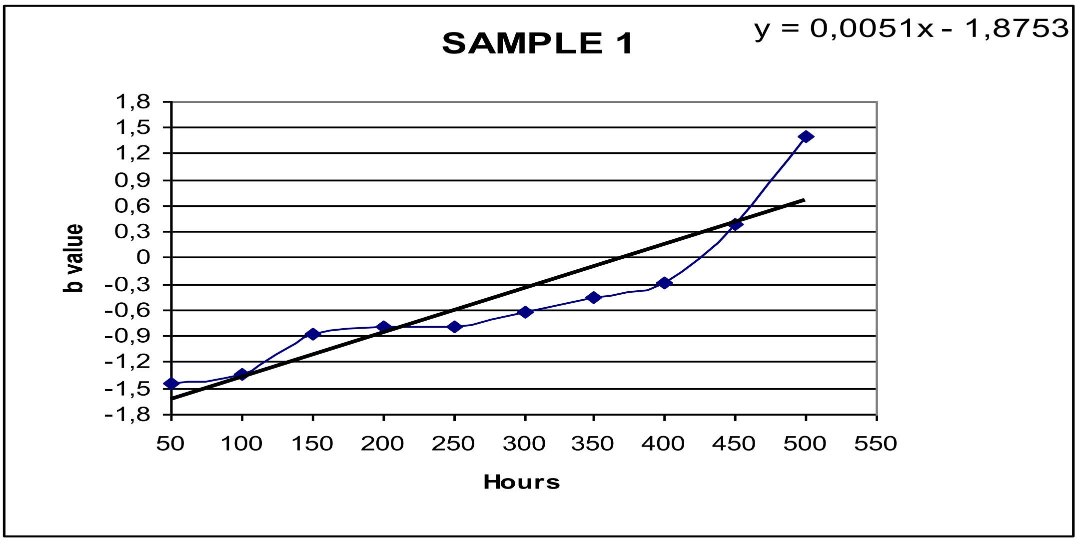


Figure 3.5: Sample 1 containing 0.3 wt% IRGANOX 1076; the variation of b value with respect to time

Sample 2 contained 0.3 wt% IRGAFOS 168 (phosphite containing stabilizer) showed a steeper degradation between 100 h and 150 h and than slowed down between 150 h and 400 h. The yellowing become faster after 400 h (Figure 3.6).

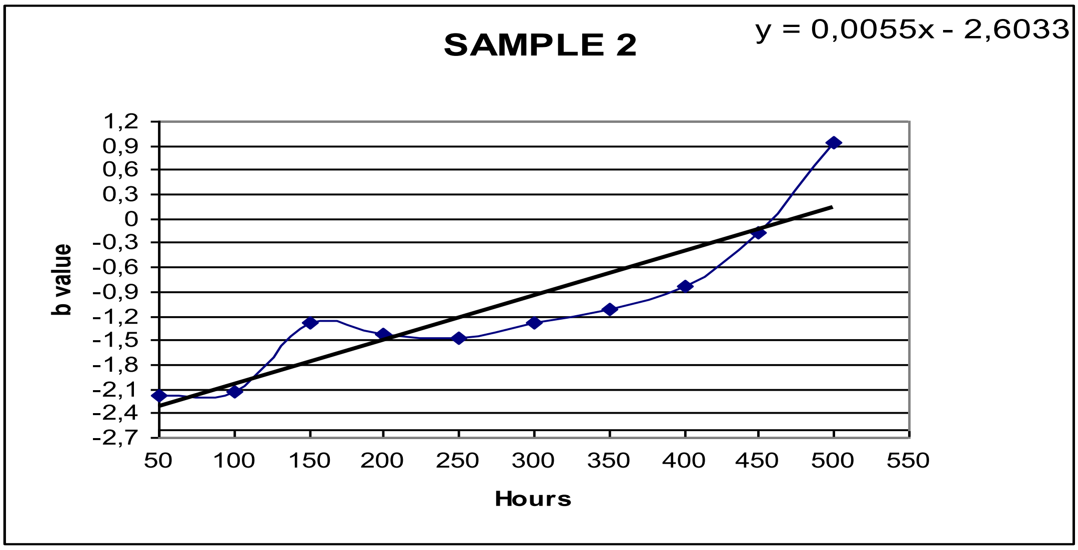


Figure 3.6: Sample 2 containing 0.3 wt% IRGAFOS 168; the variation of b value with respect to time

Sample 3 containing 0.3 wt% TUNIVIN P (hindered amine light stabilizer) like the previous two samples this sample showed a rapid degradation initially and then a stable yellowing profile was observed. Afterwards the yellowing increased faster especially after 350 h (Figure 3.7). Yellowing profile of this sample was similar to other two samples but degradation rate was very fast when compared to Sample 1 and Sample 2.

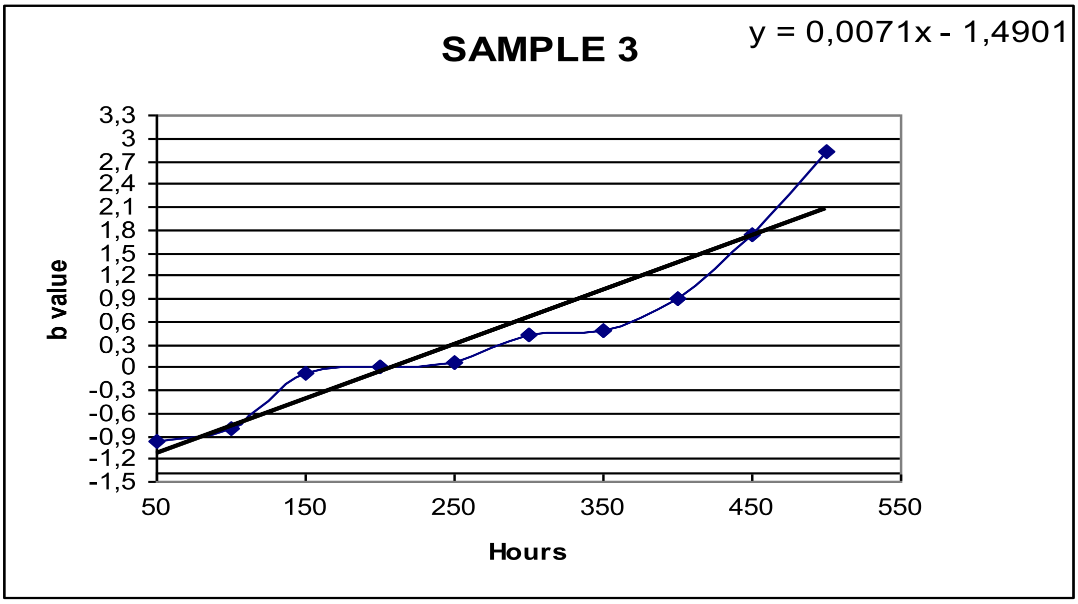


Figure 3.7: Sample 3 containing 0.3 wt% TUNIVIN P; the variation of b value with respect to time

Sample 4 containing equal amounts of, 0.2 wt% IRGANOX 1076 and 0.2 wt% IRGAFOS 168 showed very slow increase in yellowing up to 400 h, then a very steep increase was observed in yellowing in Figure 3.8. However, yellowing rate of this sample was lower than that of the three samples (Sample 1, 2 and3) mentioned previously.

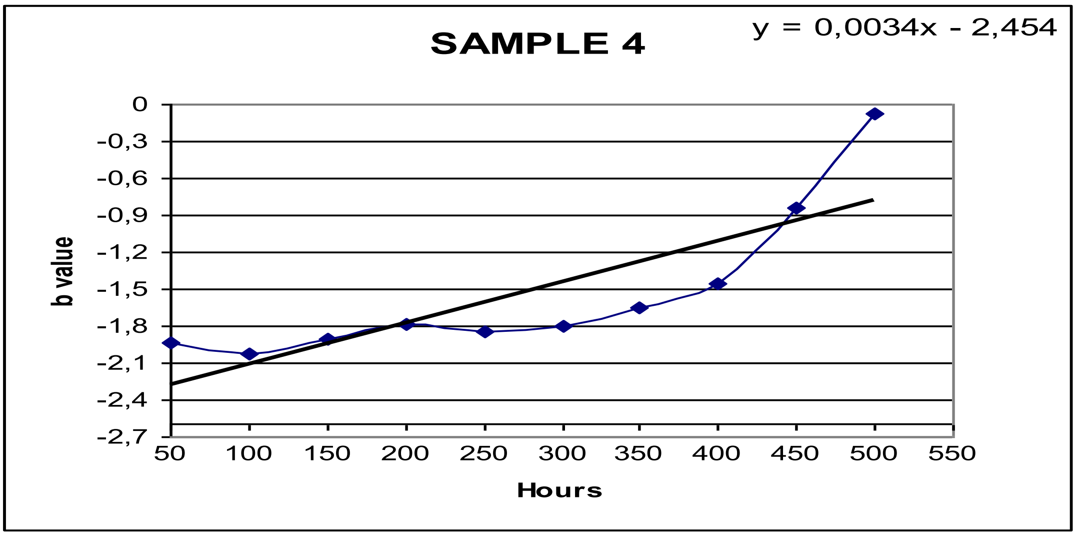


Figure 3.8: Sample 4 containing 0.2 wt% IRGANOX 1076 and 0.2 wt% IRGAFOS 168; the variation of b value with respect to time

Sample 5 contains mixture of 0.2 wt% IRGANOX 1076 and 0.2 wt% TUNIVIN P, (Figure. 3.9) showed almost no yellowing when compared to others. Then, after 400 h it showed a faster yellowing but still lower than any other samples.

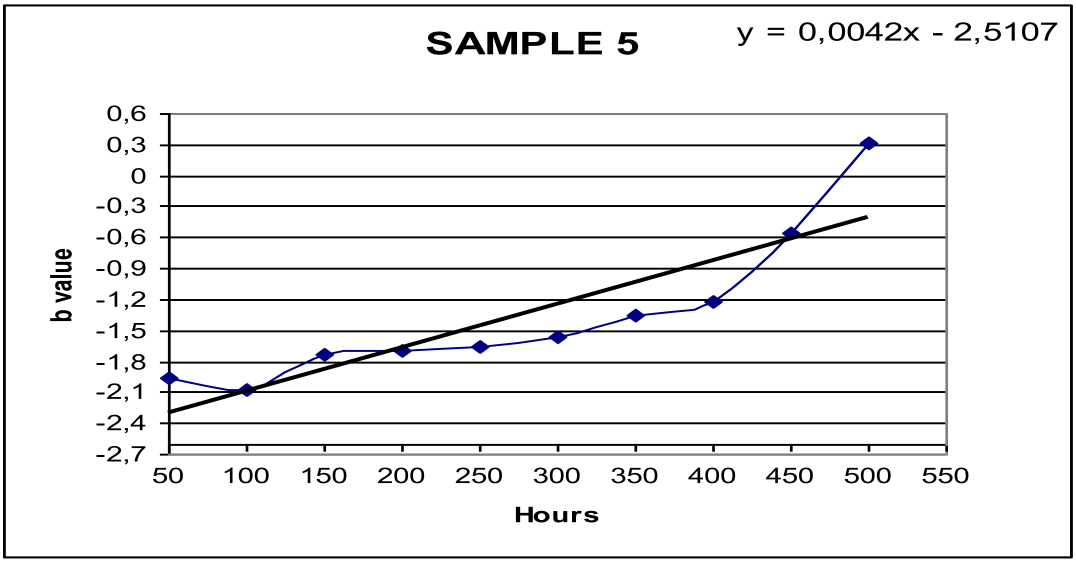


Figure 3.9: Sample 5 containing 0.2 wt% IRGANOX 1076 and 0.2 wt% TUNIVIN P; the variation of b value with respect to time

The composition 0.2 wt% IRGANOX 1076, 0.1 wt% TUNIVIN P and 0.1 wt% IRFAGOS 168 showed an initial rapid degradation, then rate of yellowing was slowed down and showed a low yellowing profile (Figure 3.10). Yellowing profile and yellowing rate of Sample 6 was similar to that of Sample 1.

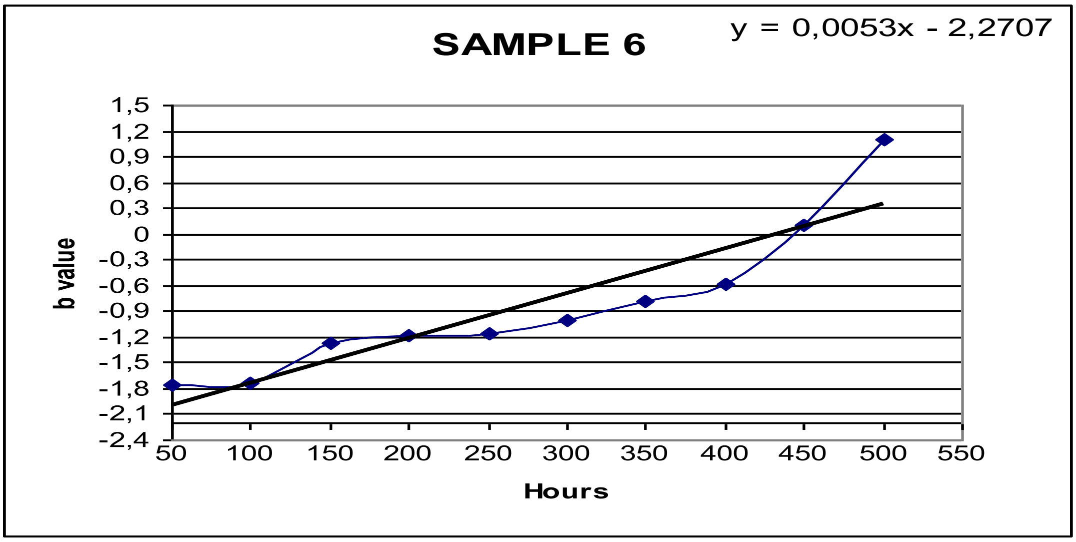


Figure 3.10: Sample 6 containing 0.2 wt% IRGANOX 1076, 0.1 wt% TUNIVIN P and 0.1 wt% IRGAFOS 168; the variation of b value with respect to time

Two samples of commercial ABS named as K and L were also aged under the same conditions. Yellowing of K was very rapid and it showed almost the similar yellowing profile with pure ABS samples (Figure 3.11). Therefore, K appears to contain no stabilizers.

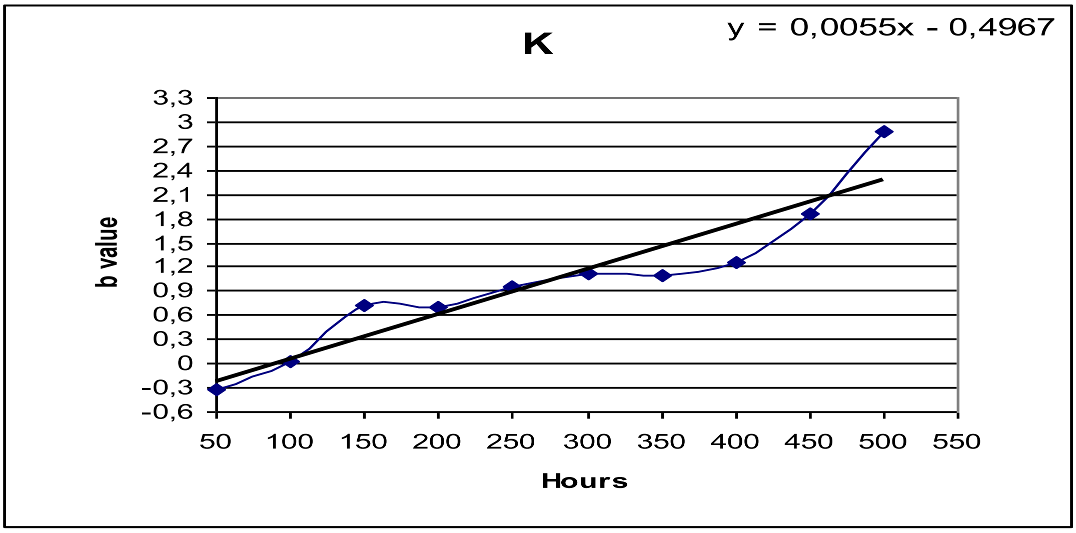


Figure 3.11: K commercial ABS sample; the variation of b value with respect to time

The sample L showed, however, a very high resistance to photo-oxidative degradation and yellowing. As it is seen from the Figure 3.12 almost no change in b value was seen up to 400 h then b value increased fast but still remained in negative values. This sample showed the same photo-oxidative degradation profile with the other samples and therefore this sample is said to be well stabilized.

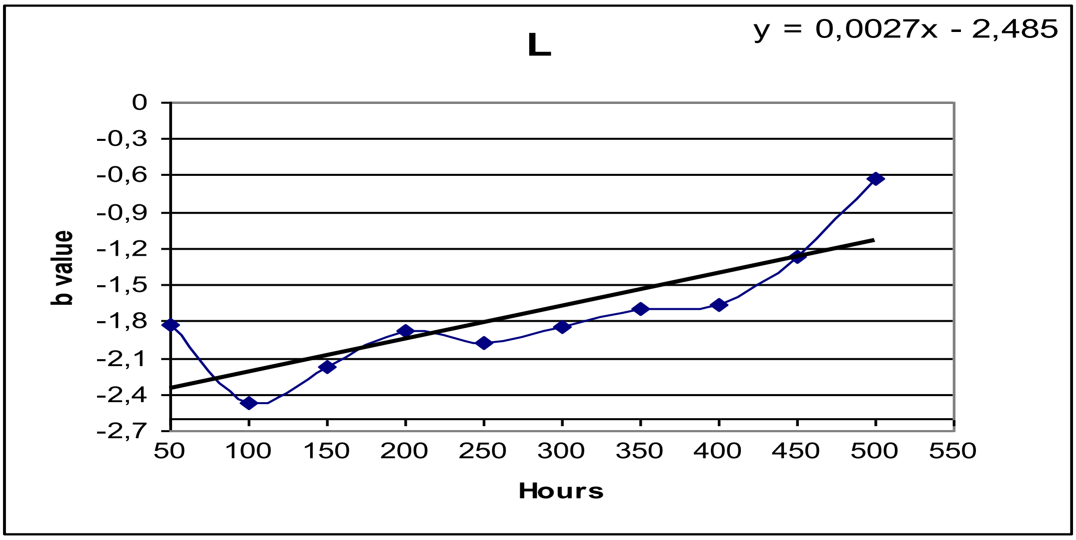


Figure 3.12: L commercial ABS sample; the variation of b value with respect to time

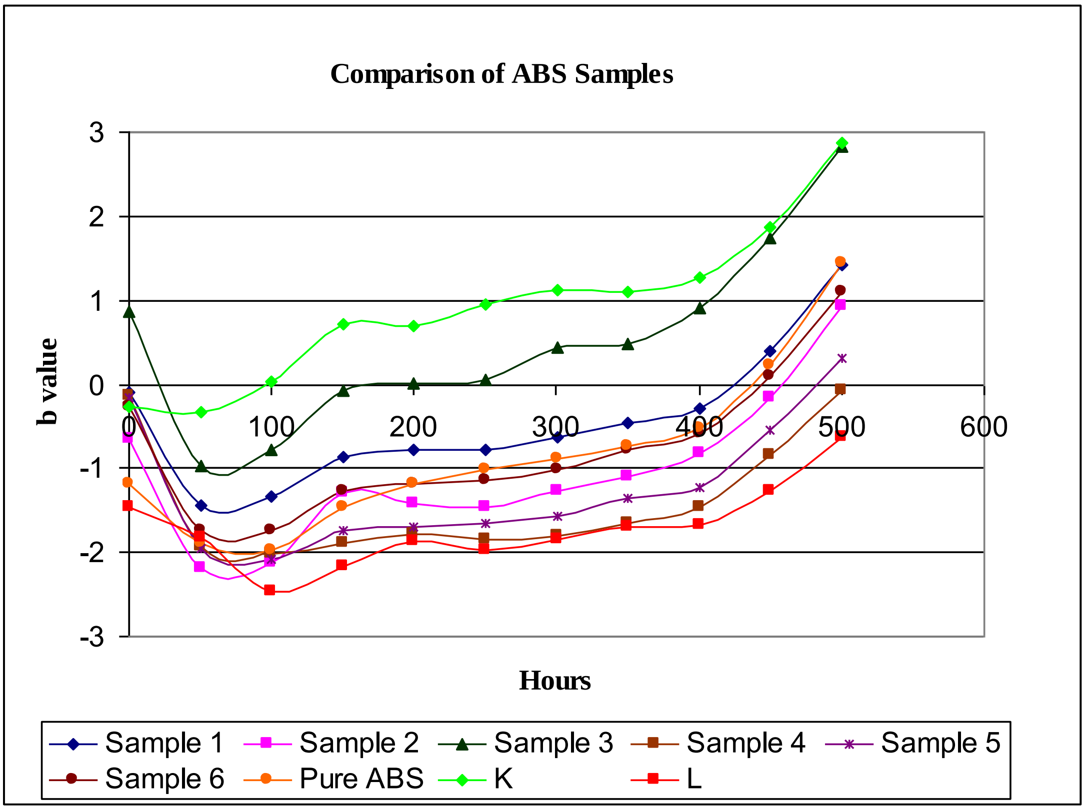


Figure 3.13: Comparison of ABS samples with respect to their b value

When all ABS samples (pure, stabilizer containing, commercial ones) were compared (Fig. 3.13), it was seen that sample L (commercial UV stabilized) showed the best resistance against yellowing. Sample 4 which contains 0.2 wt% IRGANOX 1076 and 0.2 wt% IRGAFOS 168 show very high resistance to UV light. The light resistance of this sample is close to that of the sample L. After L and Sample 4, Sample 5 comes next for the good resistance. Sample 1, Sample 2 and Sample 6 has almost similar photo-oxidation rate or yellowing. Sample 3 was the fastest yellowing when compared with the stabilizers containing samples. Sample K (other commercial sample) yellowing rate was slightly less then that of pure ABS*.

The slope of the lines in these graphs clearly reveals the order of yellowing in these samples. The smallest slope is 0.0027 (sample L) and then Sample 4 with 0.0034. The third most resistive is sample 5 (0.0042). It appears that TINUVIN P (Sample 3) has no strong contribution for stabilization even it makes worse. This sample has a slope of 0.0071 while the rest has the almost similar slope around 0.0051-0.0055 or extent of yellowing.

When three stabilizers efficiencies on photo-oxidative degradation of ABS copolymer are compared separately it is seen that IRGANOZ 1076 produced the best effect for the protection of polymer against UV light and then IRGAFOS 168 comes the second and then TINUVIN P. In conclusion, hindered phenol containing stabilizer, IRGANOX 1076, is more suitable stabilizer for ABS copolymer. However, TINUVIN P, which is a hindered amine light stabilizer, has a very negligible effect on the light stability of ABS.

If the stabilities of two or more types of stabilizer containing samples are compared, it is seen that combination of IRGANOX 1076 and IRGAFOS 168 shows the best performance against the photo-oxidative degradation of the copolymer in this work. Sample 4 containing 0.2 wt% IRGANOX 1076 and 0.2 wt% IRGAFOS 168 showed the best resistance against the yellowing. Sample 5 containing 0.2 wt% IRGANOX 1076 and 0.2wt% TINUVIN P comes second and the last one is the Sample 6 containing 0.2wt% IRGANOX 1076, 0.1wt% IRGAFOS 168 and 0.1 TINUVIN P.

Normally phenolic stabilizers (IRGANOX 1076 or similar type) alone imparts improved but limited resistance to discoloration upon the UV light exposure and also phosphite containing stabilizers (IRGAFOS 168 or similar type) does not noticeably improve the resistance of ABS copolymer to discoloration [7, 23]. However, the combination of these two stabilizers phosphite containing stabilizers enhances the stabilizer effectiveness of the phenolic stabilizers and also reduces the color production in the polymer as a consequence of the stabilizing action of the phenolic stabilizer [8, 19]. This claim was also confirmed with results of htis study.

In addition, when the samples that contain only one type of stabilizer are compared with the samples containing combination of phenolic stabilizer (IRGANOX 1076) and hindered amine light stabilizer (TINUVIN P), the combined stabilization showed better resistance against degradation. However, the combination of three stabilizers shows antagonistic effect on copolymer degradation. The reason behind of this result is that the third stabilizer disturbs the synergistic effect of other two.

3.3. UV Aging of Oil Applied Samples

Vegetable oil was applied to the surface of a new set of ABS samples and these samples were UV aged during 700 h and surface analysis of these samples were done at certain time interval. Yellowing profiles without oil and with oil were compared for each sample.

For Sample 1, in Figure 3.14 the yellowing was apparently slowed down as a result of protective layer of oil.

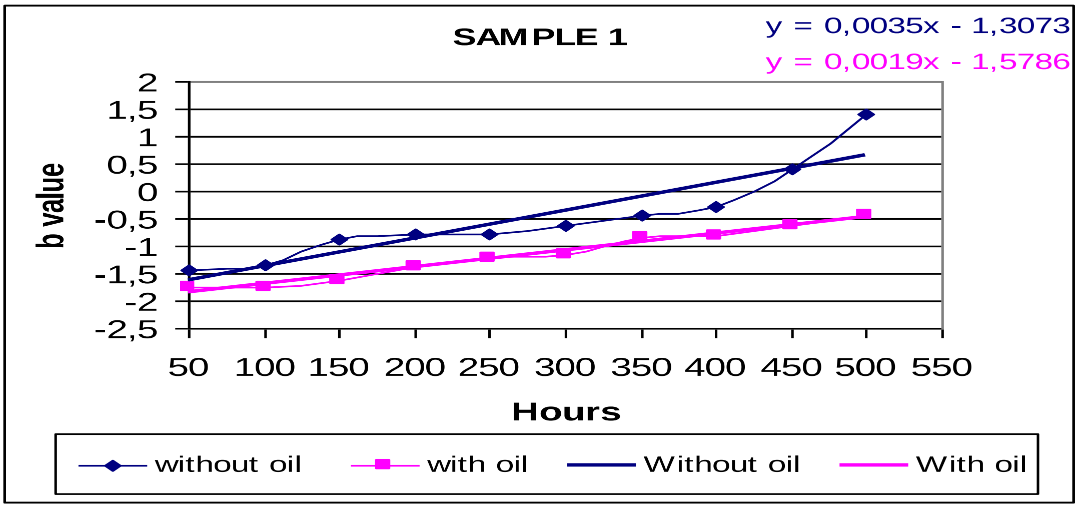


Figure 3.14: Sample 1 containing 0.3 wt% IRGANOX 1076; the variation of b value with respect to time

For Sample 2 copolymer yellowing profile was similar to each other and also degradation rate of two cases were close to each other (Figure 3.15).

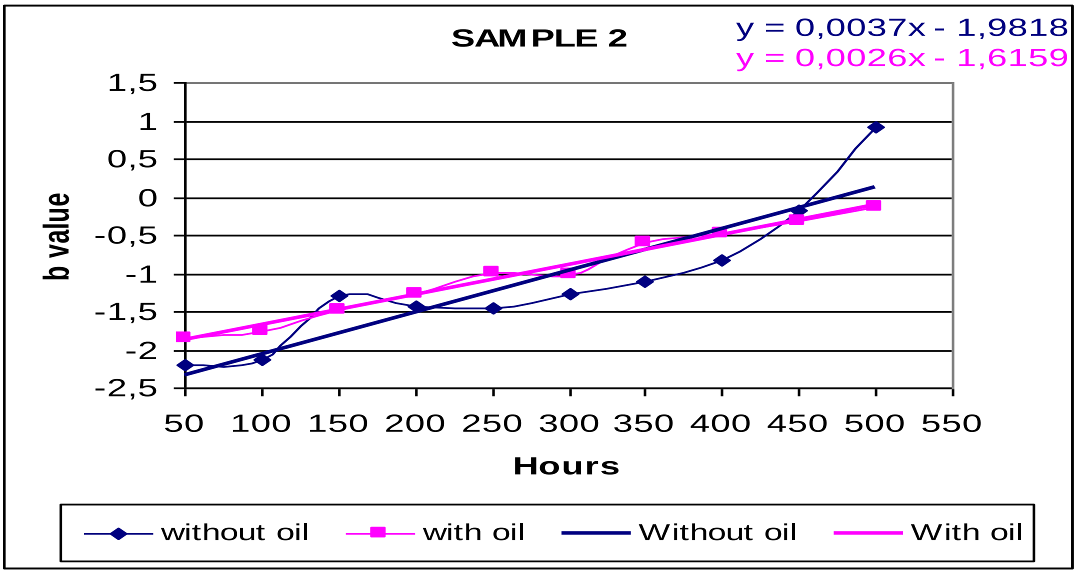


Figure 3.15: Sample 2 containing 0.3 wt% IRGAFOS 168; the variation of b value with respect to time

Sample 3 showed almost similar behavior to Sample 1 and yellowing without oil situation was twice of yellowing with oil (Figure 3.16).

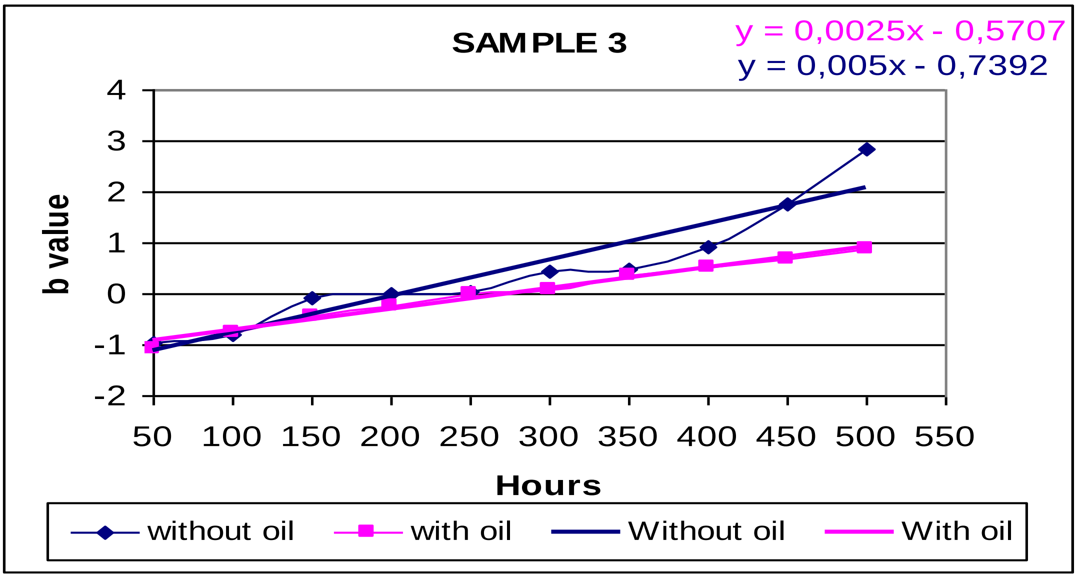


Figure 3.16: Sample 3 containing 0.3 wt% TUNIVIN P; the variation of b value with respect to time

For Sample 4 yellowing without oil situation was much higher than with oil coating at any time but a big difference was observed after 400 h (Figure 3.17).

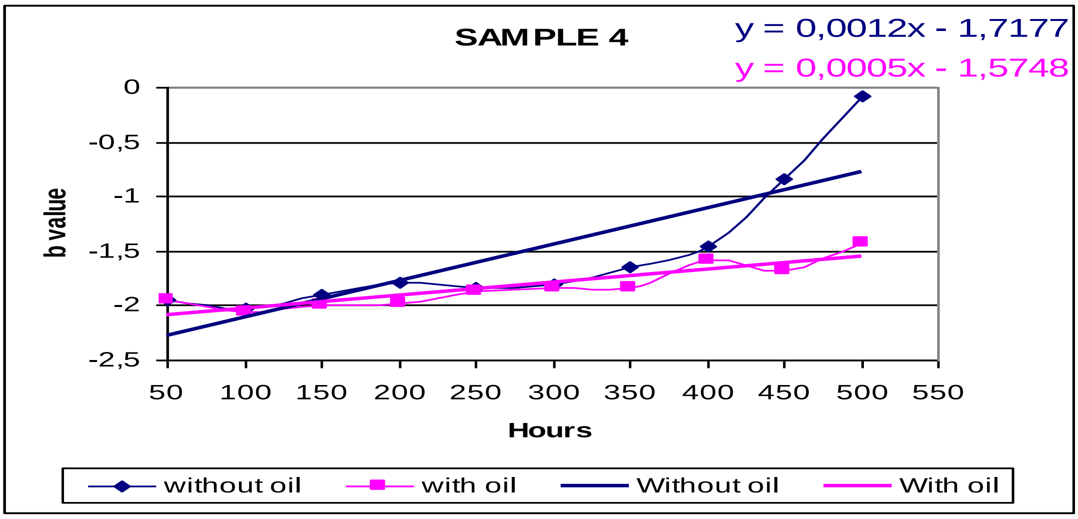


Figure 3.17: Sample 4 containing 0.2wt% IRGANOX 1076 and 0.2wt% IRGAFOS 168; the variation of b value with respect to time

Sample 5 had an unusual behavior for oil case. The yellowing with oil and without oil were close to each other and therefore degradation profiles were expected to be very similar; but the unusual point was yellowing with oil was higher than without oil in early UV irradiation times (Fig. 3.18), and the order reverses as expected.

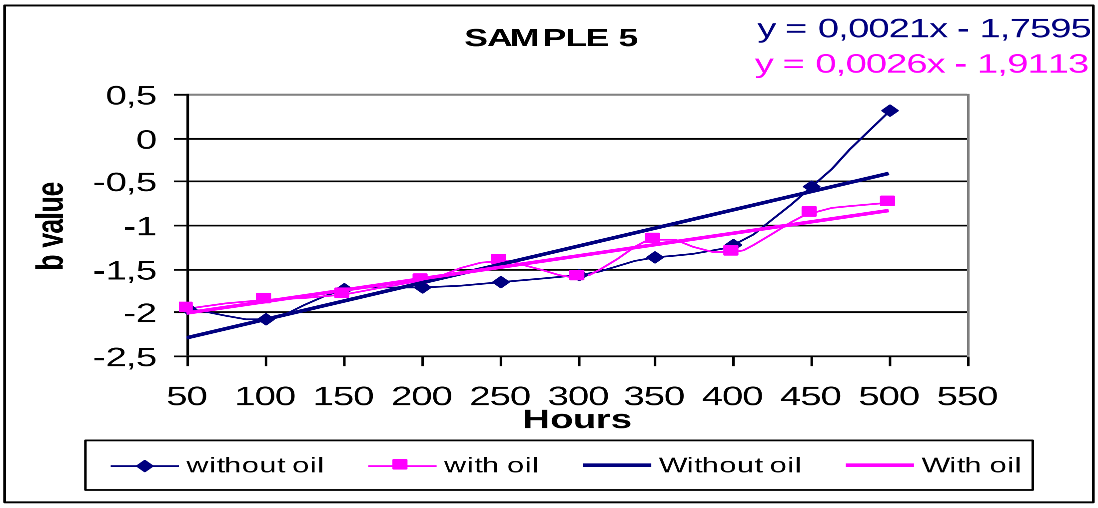


Figure 3.18: Sample 5 containing 0.2 wt% IRGANOX 1076 and 0.2 wt% TUNIVIN P; the variation of b value with respect to time

For Sample 6, yellowing rate with oil was again slower than yellowing rate without oil (Figure 3.19).

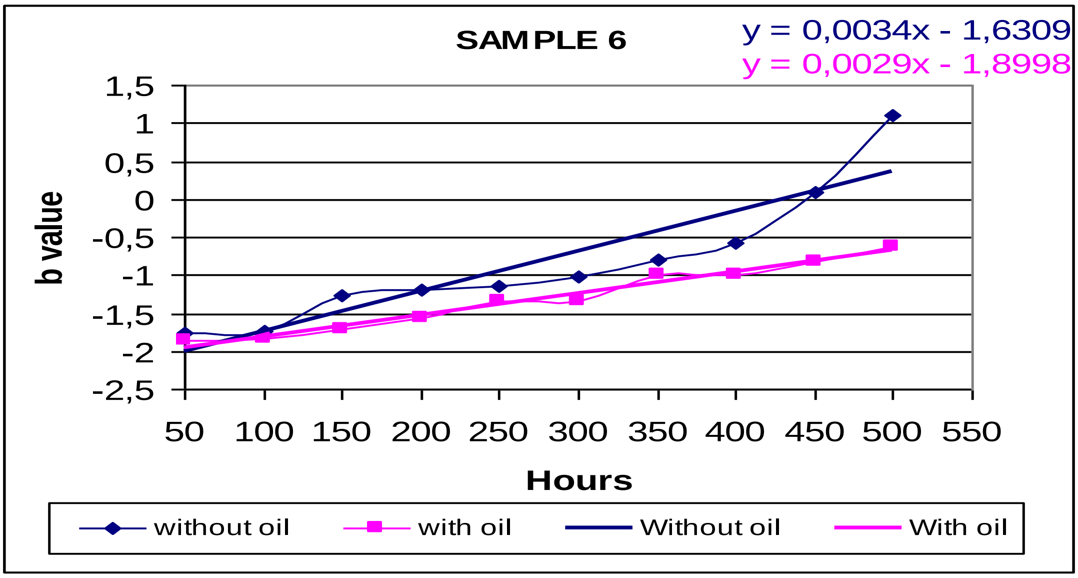


Figure 3.19: Sample 6 containing 0.2wt% IRGANOX 1076, 0.1wt% TUNIVIN P and 0.1wt% IRGAFOS 168; the variation of b value with respect to time

Application of oil to the surface of the K retarded the yellowing of this commercial ABS copolymer noticeably. As it is seen from the Figure 3.20, yellowing rate with oil was nearly one third of yellowing rate without oil case.

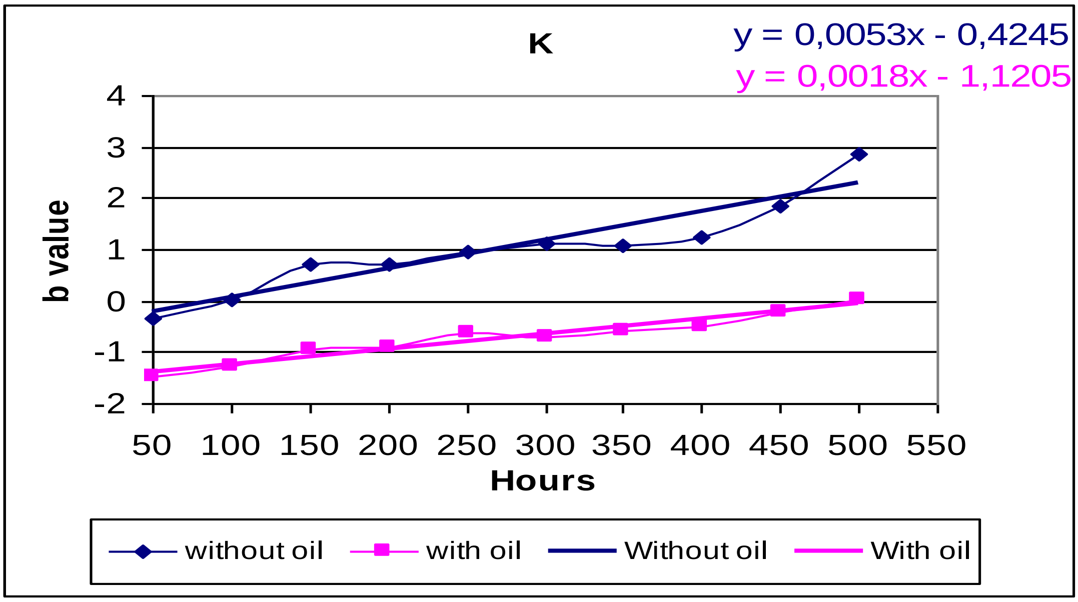


Figure 3.20: K (commercial ABS sample); the variation of b value with respect to time

L the other commercial ABS sample showed an unusual and opposite behavior similar to Sample 5, yellowing rate of the sample with oil was higher than without oil case (Figure 3.21).

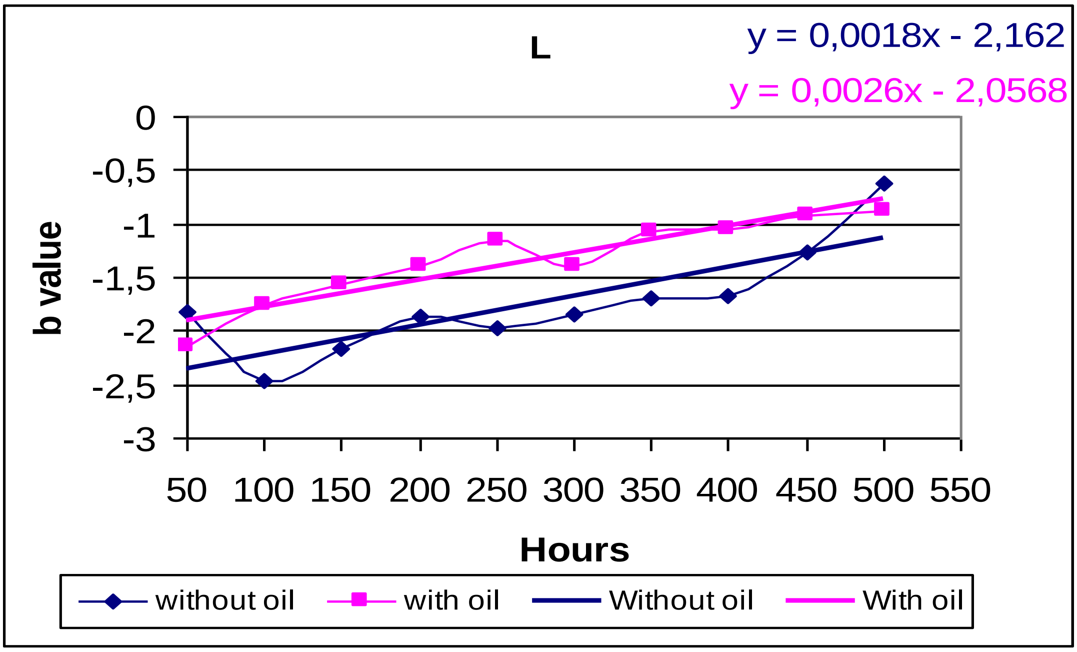


Figure 3.21: L (commercial ABS sample); the variation of b value with respect to time

As a result, as it is seen from the graphs above, yellowing of oil applied samples are much slower than that of the untreated samples with some exceptions like Sample 5 and commercial L. Oil acts as a layer that limits the oxygen diffusion through the polymer and this action of oil inhibits and slows down the photo-oxidative degradation rate of samples.

The slope of the linear lines, here again, indicates the rate of the yellowing in these samples.

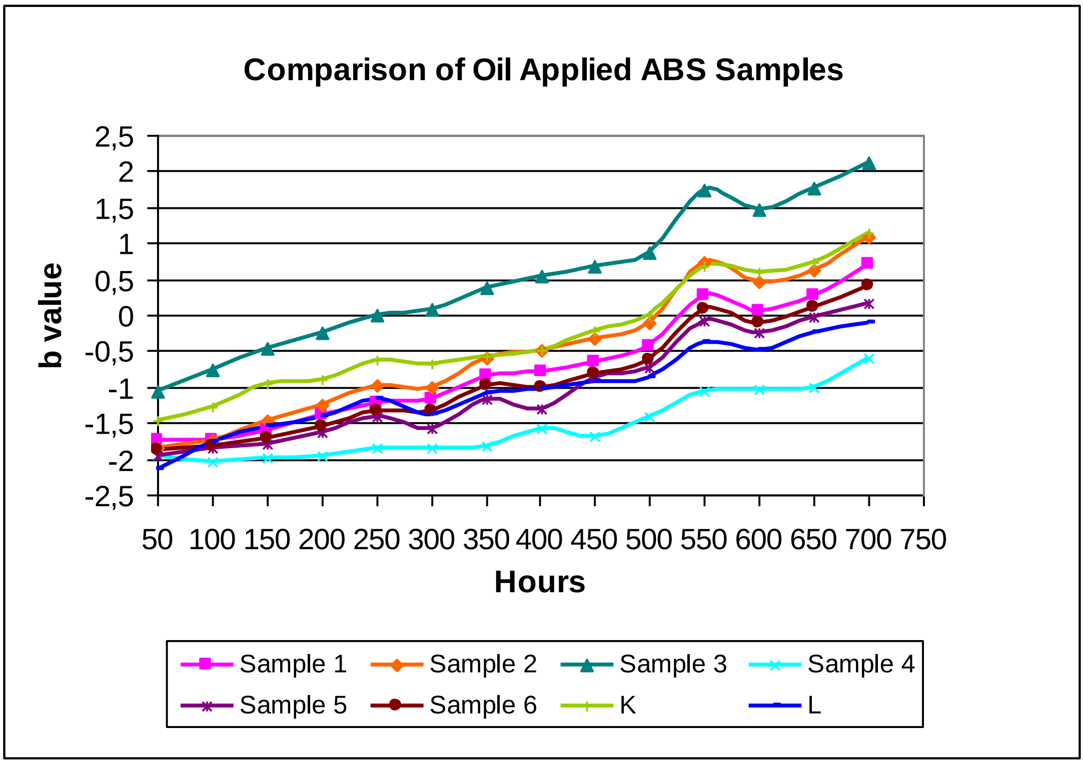


Figure 3.22: Comparison of the oil applied ABS Samples with respect to their b value

As it is seen from the graph above (Fig. 3.22), Sample 4's resistance against UV degradation is higher than commercial sample L. Also, Sample 3 shows a very rapid degradation with respect to all other samples.

3.4. UV Aging of Commercial ABS Samples

Additionally, commercial ABS samples that were coded as K, L, A, B, C and D were aged under UV light and compared with each other.

As it is seen from the Figure 3.23 Sample K, D and B showed a very rapid degradation under UV light and degradation rates of these samples were nearly linear. Sample B revealed the same degradation profile with sample K and D, but lower degradation rate. Sample C and Sample L showed a good resistance against the photo-oxidative degradation.

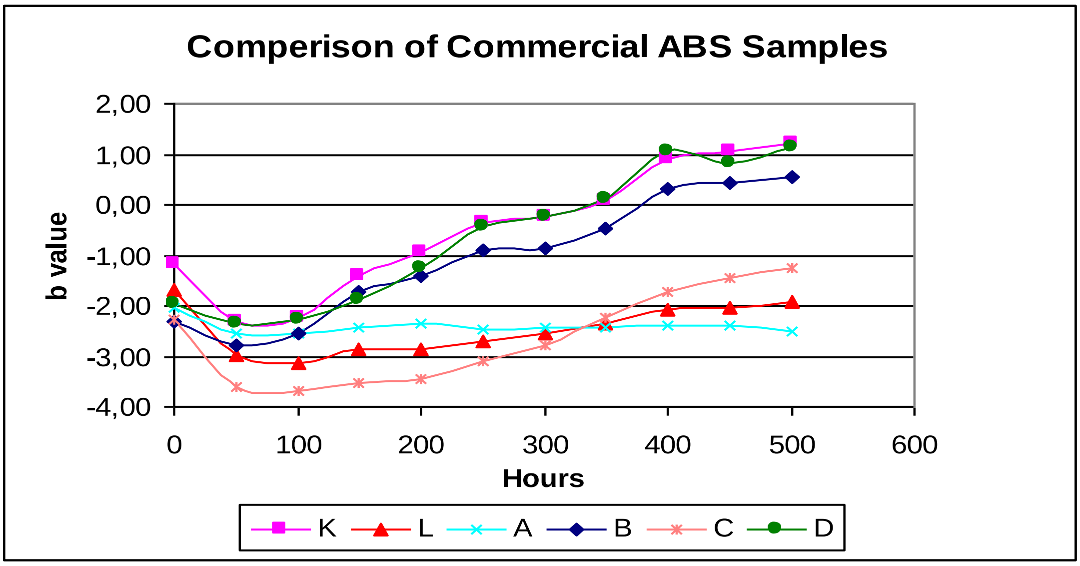


Figure 3.23: Commercial ABS samples; b value versus time

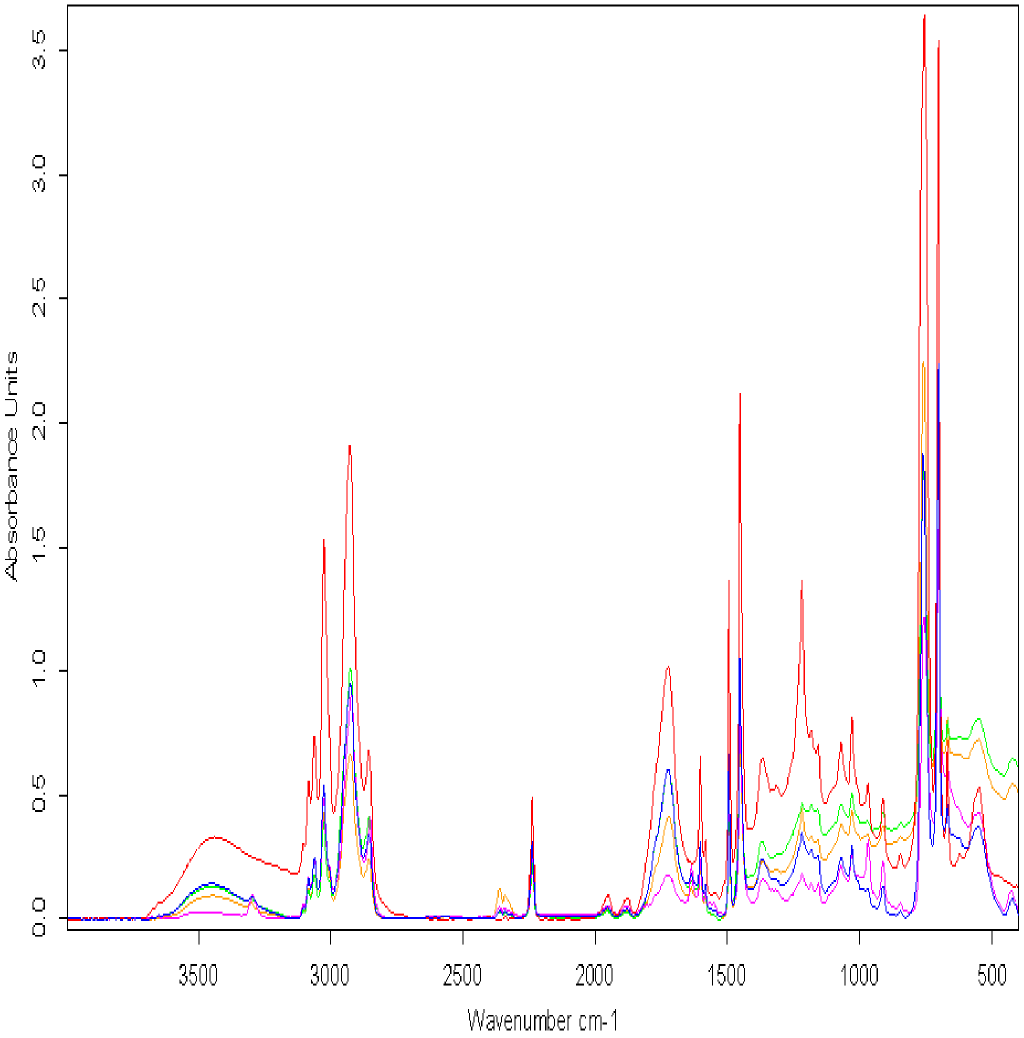
During the UV aging at surface of the Sample A yellowing was not observed. This sample showed the best resistance against degradation among the other commercial ABS samples. The best of all, these commercial ABS samples are Sample A, Sample C and Sample L whereas the others are apparently not well stabilized.

3.4 Comparison of Samples According the Their Carbonyl Region Absorbance

Photo-oxidative degradation of polymer is related to structure, morphology and oxygen diffusion coefficient of polymer. During the photo-oxidative degradation of ABS copolymer oxygen attacks the polybutadiene component and degradation of ABS copolymer mostly depends on polybuadiene content. In photo-oxidative degradation of ABS polymer, the density at the surface of samples increases and limits the diffusion of the oxygen through the ABS samples [24]. So that degradation rate of samples decreases through the samples at the initial stages. Furthermore, if a stabilizer is used, it is expected that stabilizer in the ABS copolymer firstly deplete at the surface.

Photo-oxidative degradation of ABS occurs in two stages. In the first stage, hydroperoxide and α,β-unsaturated carbonyl species formation occurs and then irradiation leads to saturation of carbonyl species that accumulates in polymer [18]. In the second stage, photo-oxidation products undergo photolysis reactions that results in carbonyl group formation. Oxygen containing groups such as aldehydes, ketones, peroxides were detected with FTIR analysis of UV irradiated polymers.

Representative stabilizer containing ABS samples, commercial L and Pure ABS samples (Arçelik ABS and Lab ABS) were aged under UV light about 900 h. Radicals that were formed during the UV degradation undergo several reaction that yield hydroperoxides, ketones and esters [5]. As a result of these reactions the absorbance intensities of hydroxyl and carbonyl peaks were increased. Figure 3.24 shows the formation of carbonyl (1800-1600cm^{-1}) and hydroxyl (3600-3200cm^{-1}) photo-products at 900 h of irradiation.



Absorbance at 900h:	Arçelik ABS (Pure ABS)
Absorbance at 900h:	LAB ABS (Pure ABS)
Absorbance at 900h:	L
Absorbance at 900h:	Sample 4
Absorbance at 900h:	Sample 5

Figure 3.24 FTIR spectra of samples at 900 h

The variation of hydroxyl, carbonyl and double bond in the Arçelik ABS at 966 cm^{-1} (vinylene group in polybutadiene part) is given with respect to time in Fig. 3.25.

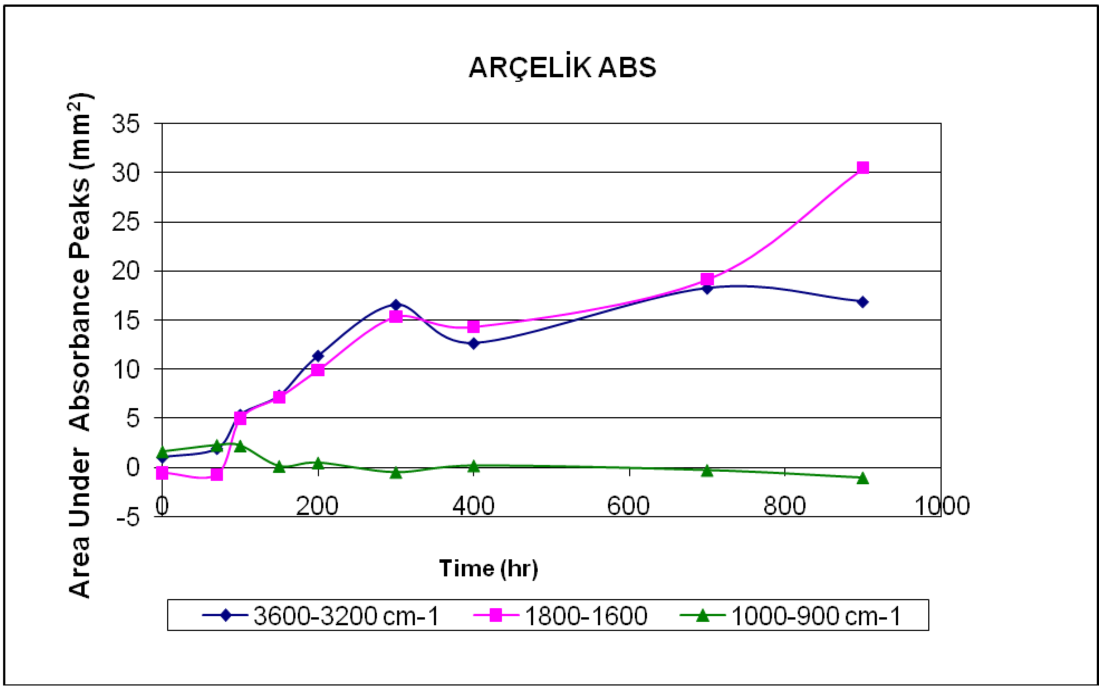


Figure 3.25: Area Under Absorbance Peaks for Arçelik ABS. ■ Carbonyl at 1721 cm^{-1}, ♦ Hydroxyl at 3400 cm^{-1}, ▲1-4 trans butadiene at 966 cm^{-1}

Formation of the hydroxyl and carbonyl groups are almost the same until 700 h, but we observed a sudden increase in carbonyl groups while the hydroxyl intensity remained the same. This means that extensive exposure of UV light chain breakage becomes predominant and carbonyl formation increases (β-chain scission and cage reaction) while the hydroxyl stays constant. Carbonyl absorbance intensities (1800-1600cm^{-1}) of the all samples were increased with UV-irradiation time, Figure 3.25 and Figure 3.26. When the carbonyl absorbance intensities of the samples were compared, pure ABS (lab ABS) had the highest carbonyl absorbance intensity whereas the sample L showed the lowest which means that Lab ABS had lowest resistance against UV irradiation and faster oxidation. Sample 4 and Sample 5 which contain stabilizer show good resistance against UV light until 400 h. Then, these samples showed a faster carbonyl increase indicating that the stabilizer become slowly ineffective.

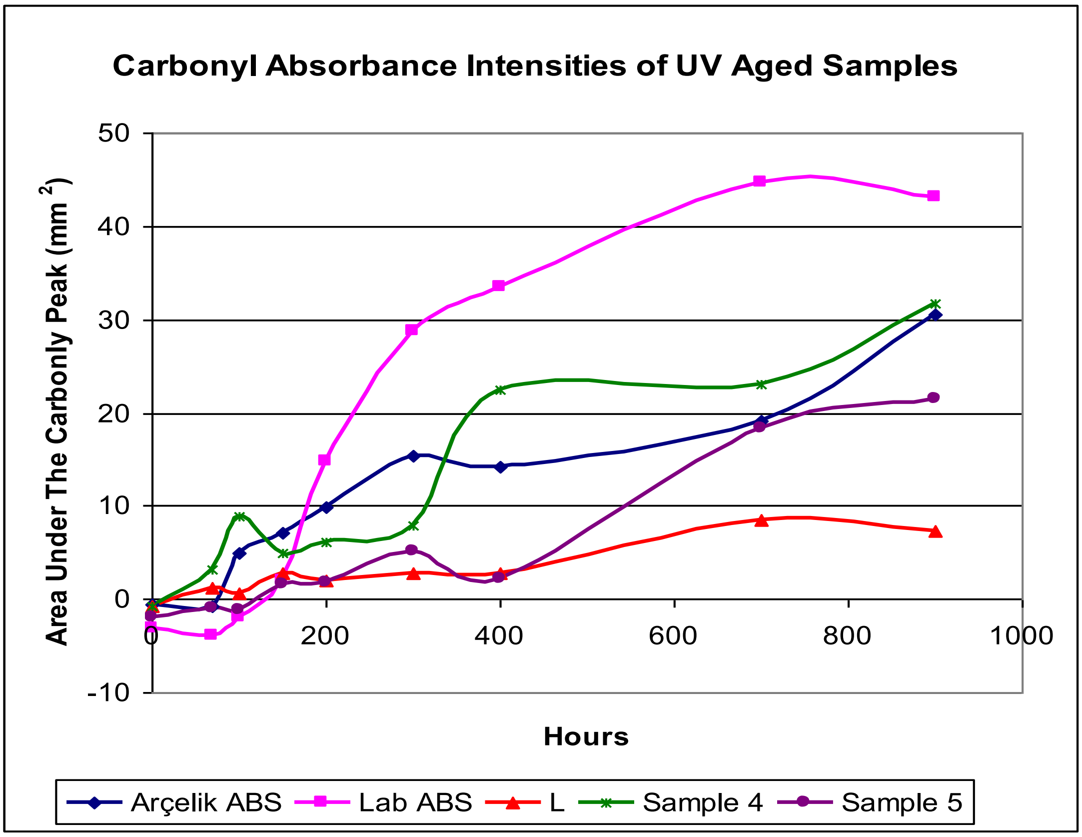


Figure 3.26: Carbonyl Absorbance Intensities of UV Aged Sample

As the yellowing is an indication of the degradation, yellowness and the variation carbonyl peaks of the aged samples come together in a single graph (Figure 3.27). b value, measure of yellowness, with respect to carbonyl absorbance for the corresponding times were drawn in Fig. 3.27.

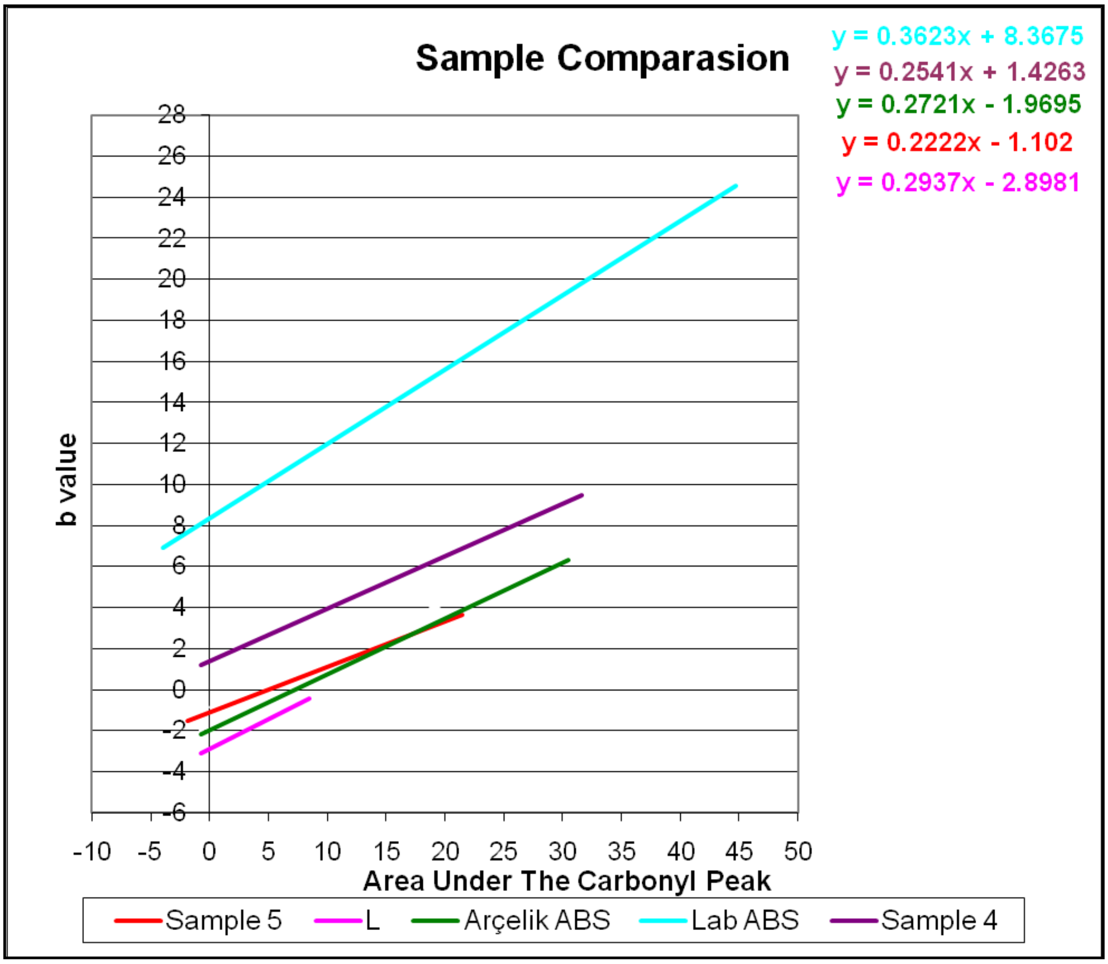


Figure 3.27: Yellowness and carbonyl absorbance of the samples

As it is seen from the Fig. 3.27 yellowness versus carbonyl absorbance gives a linear change. Therefore, the extent of photo-oxidative degradation can be easily estimated just measuring the yellowness by using simple spectrophotometric instruments. This way just gives a qualitative result for a period of light exposure of which can be used to understand the extent of photo degradation.

CHAPER IV

CONCLUSIONS

This study showed that as the UV power of the irradiation increases yellowness of the samples increase almost linearly. As the UV power increases from 800 $\mu W/cm^2$ to 2800 $\mu W/cm^2$, yellowing become faster.

Stabilizers were added to Pure ABS samples to increase their resistance against yellowing. In this study, IRGANOX 1076 (sterically hindered phenolic antioxidant), IRGAFOS 168 (hydrolycally stable phosphite stabilizer) and TINUVIN P (hydroxyphenol benzotriazole) were used alone or in combination with each other. The analysis showed that sample that contained 0.2 wt% IRGANOX 1076 and 0.2 wt% IRGAFOS 168 and commercial sample L resists strongly against yellowing. In conclusion, phosphite containing stabilizers enhances the stabilizer effectiveness of the phenolic stabilizers and also reduces the color production in the polymer.

Additionally oil was applied to the surface of a new set of ABS sample and these samples were aged under UV light about 700 h. Yellowing tendency of these samples were compared with the yellowing tendency of ABS samples that were aged under UV light without oil. Samples with oil smeared had more resistance to UV radiation with respect to ABS samples without oil. This indicates that oil limits the oxygen diffusion through the polymer and slows down the photo-oxidative degradation.

Commercial ABS samples were compared with each other. They were aged under UV lamp about 500 h. According to Coloreye XTH Spectrometer measurements sample A and then commercial sample L showed the best resistance to photo-oxidative degradation.

Samples that showed good resistance to UV light were retested and they were analyzed with FTIR to follow the chemical structure carbonyl, hydroxyl and unsaturated bonds at 966 cm^{-1}.

The carbonyl variation with respect to time increased depending on the type of sample, faster in unstabilized ABS, and slower in stabilized ABS.

Finally, yellowing is an indication of the photo-oxidative degradation and qualitative measurement of photo-oxidative degradation can be done by measuring the yellowness of the sample with a simple spectrophotometer.

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APPENDIX A

Table A.1: b Value of the Pure ABS Samples Aged Under Different UV Power

TIME	**50 h**	**100 h**	**150 h**	**200 h**	**250 h**	**300 h**	**350 h**	**400 h**	**450 h**	**500 h**	**UV Power (µW/cm^2)**
PURE ABS*	-1.9	-1.97	-1.47	-1.19	-1.02	-0.89	-0.74	-0.53	0.23	1.45	2800
PURE ABS**	-1.82	-1.83	-1.41	-1.11	-1.06	-0.95	-0.66	-0.58	0.11	1.1	1400
PURE ABS***	-1.88	-1.96	-1.89	-1.95	-1.73	-1.67	-1.51	-1.2	-0.99	-0.12	800

Table A.2: b Value of the Stabilizer Containing Samples Commercial ABS Samples

TIME	50 h	100 h	150 h	200 h	250 h	300 h	350 h	400 h	450 h	500 h	UV Power ($\mu W/cm^2$)
SAMPLE-1	-1.45	-1.33	-0.87	-0.79	-0.78	-0.63	-0.45	-0.29	0.4	1.41	2800
SAMPLE-2	-2.19	-2.13	-1.29	-1.43	-1.46	-1.27	-1.11	-0.83	-0.17	0.93	2800
SAMPLE-3	-0.97	-0.79	-0.073	0.02	0.06	0.43	0.48	0.91	1.75	2.83	2800
SAMPLE4	-1.94	-2.02	-1.9	-1.79	-1.84	-1.8	-1.65	-1.46	-0.84	-0.08	2800
SAMPLE-5	-1.96	-2.08	-1.73	-1.7	-1.65	-1.57	-1.36	-1.22	-0.55	0.31	2800
SAMPLE-6	-1.75	-1.73	-1.27	-1.19	-1.15	-1.01	-0.79	-0.58	0.1	1.11	2800
PURE ABS*	-1.9	-1.97	-1.47	-1.19	-1.02	-0.89	-0.74	-0.53	0.23	1.45	2800
PURE ABS**	-1.82	-1.83	-1.41	-1.11	-1.06	-0.95	-0.66	-0.58	0.11	1.1	1400
PURE ABS***	-1.88	-1.96	-1.89	-1.95	-1.73	-1.67	-1.51	-1.2	-0.99	-0.12	800
K	-0.33	0.03	0.72	0.7	0.95	1.12	1.1	1.26	1.86	2.88	2800
L	-1.82	-2.47	-2.17	-1.87	-1.98	-1.84	-1.7	-1.67	-1.27	-0.625	2800

Table A.3: b Value of the Oil Sprayed ABS Samples

TIME	50 h	100 h	150 h	200 h	250 h	300 h	350 h	400 h	450 h	500 h	550 h	600 h	650 h	700 h	UV Power (μW/cm^2)
ABS-1	-1.75	-1.74	-1.61	-1.39	-1.22	-1.16	-0.85	-0.8	-0.64	-0.43	0.27	0.05	0.26	0.7	2800
ABS-2	-1.84	-1.75	-1.48	-1.26	-0.99	-1.01	-0.59	-0.48	-0.32	-0.12	0.73	0.46	0.62	1.08	2800
ABS-3	-1.06	-0.75	-0.45	-0.24	0.01	0.085	0.38	0.53	0.67	0.88	1.75	1.47	1.77	2.12	2800
ABS-4	-1.95	-2.05	-1.99	-1.97	-1.86	-1.84	-1.83	-1.58	-1.68	-1.42	-1.05	-1.03	-1.01	-0.61	2800
ABS-5	-1.95	-1.86	-1.79	-1.63	-1.41	-1.58	-1.17	-1.3	-0.86	-0.74	-0.08	-0.25	-0.03	0.17	2800
ABS-6	-1.87	-1.83	-1.7	-1.56	-1.34	-1.33	-0.99	-1	-0.82	-0.62	0.08	-0.11	0.12	0.42	2800
K	-1.47	-1.29	-0.96	-0.9	-0.62	-0.69	-0.57	-0.5	-0.22	0.01	0.69	0.59	0.74	1.13	2800
L	-2.15	-1.76	-1.56	-1.4	-1.16	-1.39	-1.08	-1.04	-0.93	-0.87	-0.37	-0.48	-0.24	-0.12	2800

Table A.4: b Vaule of the Commercial ABS Samples

TIME	50 h	100 h	150 h	200 h	250 h	300 h	350 h	400 h	450 h	500 h	UV Power (μW/cm^2)
A	-2.53	-2.55	-2.44	-2.35	-2.49	-2.43	-2.43	-2.38	-2.41	-2.51	2800
B	-2.77	-2.53	-1.73	-1.42	-0.89	-0.85	-0.46	0.32	0.42	0.54	2800
C	-3.60	-3.69	-3.53	-3.46	-3.08	-2.79	-2.25	-1.71	-1.44	-1.25	2800
D	-2.36	-2.29	-1.87	-1.24	-0.44	-0.23	0.11	1.06	0.84	1.12	2800
K	-2.33	-2.23	-1.42	-0.96	-0.34	-0.22	0.09	0.89	1.04	1.23	2800
L	-2.97	-3.15	-2.88	-2.86	-2.71	-2.56	-2.36	-2.06	-2.03	-1.94	2800