ADDITIVES FOR PHOTODEGRADABLE POLYETHYLENE

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ABSTRACT

ADDITIVES FOR PHOTODEGRADABLE POLYETHYLENE

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Polyethylene (PE) is one of the most popular polymers used in daily life. However, saturated hydrocarbons cannot absorb the energy of light reaching to earth, so degradation process is rather slow which in return cause disposal problems. On the other hand, it was observed that in presence of oxygen and impurities in the polymer matrix, degradation can be rendered to shorter time intervals. This study covers investigation of effect of three different additives in UV induced oxidative degradation of polyethylene.

In this work vanadium (III) acetylacetonate, serpentine and Cloisite 30B were used as additives both together and alone to follow photodegradation of polyethylene. Amount of vanadium (III) acetylacetonate was kept constant at 0.2 wt%, while serpentine and Cloisite 30B were used between 1 and 4 wt%.

All compositions were prepared by using Brabender Torque Rheometer, and shaped as thin films by compression molding. Samples were irradiated by UV light up to 500 hours. Mechanical and spectroscopic measurements were carried out in certain time intervals to monitor the degradation.

It can be concluded that all combinations of three additives showed the fastest degradation behavior compared to pure PE. In the absence of vanadium (III) acetylacetonate the degradation was slowed and fluctuations were observed in the residual percentage strain at break values. There was not a significant change in tensile strength of all samples. Carbonyl index values followed by FTIR were always in increasing manner. Thermal properties were also investigated by DSC Thermograms and they did not change significantly.

Keywords: Polyethylene, photodegradation, clay nanocomposites, vanadium (III) acetylacetonate.

FOTOBOZUNABİLİR POLİETİLEN İÇİN KATKI MADDELERİ

Oluz, Zehra Yüksek Lisans, Polimer Bilim ve Teknolojisi Bölümü Tez Yöneticisi: Prof. Dr. Teoman Tinçer

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Polietilen günlük hayatta kullanılan en popüler polimerlerin biridir. Ancak doymuş hidrokarbonlar yeryüzüne ulaşan ışık enerjisini soğuramadığından bozunma süreci oldukça yavaştır ve sonuçta da doğada atık problemine sebep olmaktadır. Diğer yandan, oksijen ve polimer matrisi içerisinde yabancı maddelerin varlığında, bozunmanın daha kısa bir zaman aralığında gerçekleştiği gözlenmiştir. Bu çalışma, polietilenin UV oksidatif bozunmasında üç farklı katkı maddesinin etkisinin incelenmesi kapsar.

Bu çalışmada, polietilenin ışıkla bozunmasını takip etmek için vanadyum (III) asetilasetonat, serpentin ve Cloisite 30B ışıkla hem birlikte hem de tek başına katkı maddesi olarak kullanılmıştır. Vanadyum (III) asetilasetonat miktarı ağırlıkça % 0,2 'de sabit tutulurken, serpentin ve Cloisite 30B sırasıyla ağırlıkça % 1 ve 4 arası kullanılmıştır.

Tüm bileşimler Brabender Tork Reometre kullanılarak hazırlanmış ve sıkıştırma kalıplama ile ince filmler olarak şekillendirilmiştir. Numuneler 500 saate kadar UV ışığı ile ışınlandı. Bozunmayı izlemek için belirli bir zaman aralıklarında mekanik ve spektroskopik ölçümler gerçekleştirilmiştir.

Her üç katkı maddesinin kombinasyonunun saf polietilene göre en hızlı bozunma davranışı gösterdiği sonucuna ulaşılmıştır. Vanadyum (III) asetilasetonat yokluğunda bozunma yavaşlamış ve uzama miktarlarında dalgalanmalar gözlenmiştir. Numunelerin çekme mukavemetinde önemli bir değişiklik olmamıştır. FTIR ile takip edilen karbonil indeks değerleri sürekli artmıştır. Isıl özellikler DSC termogramları aracılığıyla incelenmiştir ve önemli bir değişiklik olmadığı gözlenmiştir.

Anahtar Kelimeler: Polietilen, fotobozunma, kil nanokompozitleri, vanadyum (III) asetilasetonat.

To my sister and my mother

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ABBREVIATIONS

Low Density Polethylene	
Polyethylene	
Cloisite 30B	
Serpentine	
Vanadium(III) acetylacetonate	

CHAPTER 1

INTRODUCTION

Products made from polyolefins, especially polyethylene, have increased significantly in recent decades largely due to their low cost and good mechanical properties. This increase in use leads to disposal problems which later guide to a much extended area of research in both academic and industrial aspects. Different types of degradation procedures such as oxidative, thermal and biodegradation, and their mechanisms were already examined. The degradation term is defined to entitle physical changes in the structure of the polymers due to chemical reactions caused by various factors such as heat, light, solvent, etc [1].

It has been estimated that due to being exposed to outdoor conditions, premature failing can be obtained in the structure of polyolefins. The degradation of polymers are affected by both intrinsic properties like molecular weight, molecular weight distribution, structure and external effects like rain, wind, moisture, UV portion of sunlight (although it forms just 5-6 % of total energy reaching from sun to earth), temperature and its variations. A large quantity of polymers are found to absorb energy in 280-350 nm range which is responsible for discoloration of polymers as well as the decline of mechanical properties of them [2]. As a result of subjecting polymers to air or simulated sunlight, the formation of carbonyl, vinyl, hydroxyl groups, and the evolution of acetone, acetaldehyde, water and

oxides of carbon are the cases most probable to be observed besides formation of crosslinks and increase in brittleness.

The extent of the degradation depends on how it interacts with the environment surrounding it. By controlling the parameters it is possible to have preferential conditions during and after degradation. This can be achieved with the help of using kinds of additives which lead to desirable condition. As one of the famous additives, starch is used to obtain biodegradable polymers while diketones such as iron acetylacetonate are effective in thermal degradation. Metal 2,4-pentanedione complexes, transition metal stearates or combination of these types of additives in different amounts lead to photo-degradation of polymers [3].

1.1. POLYETHYLENE

Polyethylene is one of the most commonly produced and used plastic due to its low cost and high performance. It has wide range of application areas such as biomedical applications, cable insulation and food packaging as well as many others.

A thermoplastic polymer, polyethylene, has a repeating unit of $-(-CH_2-CH_2-)_n$ with 28.05 g/mol and a melting of 105 to 115°C and a T_g of -125°C. The observation of melting and glass transition temperatures of it depends on the crystallinity and molecular weight of examined polyethylene sample.

Polyethylene shows resistivity to attacks by strong acids and bases, oxidants and reducing agents. It is a flammable polymer and after removal of flame source it continues burning while showing dripping behavior. It can be dissolved in hot aromatic hydrocarbon solvents like toluene or xylene and in chlorinated solvents such as dichlorobenzene. There are different types of polyethylene distinguished upon different molecular weight, crosslinking and branching of the polymer such as high density polyethylene (HDPE), ultra high molecular weight polyethylene (UHMWPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), cross-linked polyethylene (PEX), etc [4].

1.2. DEGRADATION

1.2.1. DEFINITIONS

<u>Degradation</u>: Degradation of a polymer means the detrimental change in physical properties hence appearance of plastics due to the change in chemical structure.

<u>Degradable Plastic</u>: Plastics which are designed to degrade under defined active environmental conditions as a result of biological, chemical and physical interactions resulting in losing some properties of it. But in this type of plastics it is considered neither the degradation process that the polymer exposed to nor the time scale of the degradation.

<u>Controlled Degradable Plastic</u>: In these type of polymers, the degradation process of the polymer is known and the degradation rate of the polymer is predictable.

<u>Biodegradable Plastic</u>: Plastics that are supposed to be degradable because of the effective actions and interactions of micro-organisms with the polymer.

<u>Photo-degradable Plastic</u>: In this kind of polymers, the reason of degradation is the interaction of sunlight with polymer and its ability to break the covalent bonds in the structure of the polymer [5].

1.2.2. DEGRADATION OF POLYMERS

More or less all of the polymers are exposed to the factors that cause degradation at nearly all stages of the life of the macromolecule. These stages are namely production, storage, transportation and finally end use. Because of different kinds of effects like light, thermal, and mechanical impacts, structure of the polymer is affected in a deteriorating way. It causes the polymer chain to be in smaller pieces via bond scission in the backbone of the polymer which cause the fragments unable to take part in mechanical properties leading the brittleness and short life of the polymer [1,6]. But it is reported that changes which are visible on the surface such as discoloration or transparency loss are obvious before an important change in physical properties such as tensile strength or elongation at break can be observed.

Polymers are the materials which have a great variety of usage areas, including outdoor applications. Under these circumstances, it has been reported that sunlight is one of the most effective factor in the degradation of polymers which cause the photo-degradation of polymers. Therefore it should be examined carefully and continuously. But also the combination of photo-degradation with the other factors leading such as thermal and biodegradation has to be regarded as well [6]. These effects are so integrated that the degradation seems to be very similar especially in thermal degradation. The products obtained via thermal degradation are nearly same with the photo-degradation; the only difference is not obtaining vinyl groups and ketone products as a result of thermal degradation [3].

The temperature range that the macromolecules are exposed to in the outdoor conditions in fact cannot supply the enough energy to break the chemical bonds. On the other hand, stress due to the expansion and contraction because of thermal gradients in the polymer lead to thermomechanical degradation. In addition to this, heat can be a rate controlling parameter in other degradation mechanisms since all rate constants are temperature dependent according to Arrhenius equation [7].

Considering the biodegradation, the best combination is theorized as the kind of degradation in which firstly photo-degradation occurs and then the products of degradation such as carbonyl groups are attacked by microorganism in the environment leading to shorter polymer chains and finally carbon dioxide and water [8]. Why this has been a theory until recent years is there was a popular thought that hydrocarbon polymers with molar mass higher than 5000 do not degrade in biological environment. But with the help of two international workshops [9, 10], it has been declared that there is no strict and obvious distinction between the order and duration of the two degradation process when combined effects are applied. Also, it has been proved that degradation processes that begin with photo-oxidative degradation mechanism can last in the absence of light but presence of oxygen. So the going on degradation leads to so small molecular weights that the macromolecule becomes wettable by water, but the most effective biodegradation starts at 5000 and below molecular weight though it can be observed in higher molar masses with less effect [5].

1.2.3. PHOTO-DEGRADATION OF POLYMERS

The use and exposure to environmental conditions of polymers can cause changes in chemical and physical properties ending up brittleness and complete failure at the latest stage. It is believed that the key role in this phenomena belongs to the UV portion of the sunlight [6, 12]. When the photons interact with the polymer chains numerous complicated reactions start and it is estimated that these reactions continue even in the dark [5, 11]. The interactions of photons can be directly with the polymer chain or this process can be with the help of some additives, catalyst residues or

photosensitive impurities in the polymer matrix either on purpose or accidentally placed [6].

A polymer sample of which degradation process has started with the help of UV light, lies in an oxygen supplied conditions, after a particular time which is called as induction period, it starts to absorb oxygen leading to production of peroxide groups. The rate of the oxygen absorption is directly proportional to the surface area of the polymer where it is inversely proportional with the thickness of the polymer film because of the problem in oxygen diffusivity [6, 13]. These foundings make it clear that polymer degradation starts at the surface of the polymer but then after sufficient time it can be observed throughout the bulk [14, 15]. Also it is specified that ozone has a very remarkable role in the oxidation degradation of macromolecules as well [3].

The mechanism of photo-oxidation of polymers is quite similar to the mechanism of thermal degradation. The mechanism is as follows:

 Initiation Reaction: The reaction may be initiated many kinds of initiation factors such as light, heat, oxygen, etc. Polymer radicals (P·) are needed for rapid degradation and oxidation.

$$\mathsf{PH} \rightarrow \mathsf{P} \cdot + \mathsf{H} \cdot$$

2. <u>Formation of Polymer Hydroperoxides</u>: Previously formed macro radicals are able to combine by addition reaction with oxygen to form peroxy radicals of polymers.

$$P \cdot + O_2 \rightarrow POO \cdot$$

The formed peroxy radicals can abstract a hydrogen atom from other polymer chains to produce polymer hydroperoxides.

 $POO \cdot + PH \rightarrow P \cdot + POOH$

3. <u>Decomposition of Polymer Hydroperoxides</u>: Produced polymer hydroperoxides can decompose due to being exposed to light as in the following equations [16,17,18,19].

 $POOH \rightarrow P \cdot + \cdot OOH$

 $POOH \rightarrow PO \cdot + \cdot OH$

The energy of light with the wavelength above 300nm is enough to break the two bonds above of which bond energies are 175 and 290 kJ/mol, respectively. Cleavage PO-OH bond predominates, but breaking of POO-H bond is not very favorable with this amount of energy. To break that bond shorter wavelengths are needed since the bond energy of it is 375 kJ/mol [7].

The previously formed radicals can take part in radical induced decomposition of hydroperoxides as follows:

 $POOH + RO \rightarrow PO + ROOH$

 $POOH + HO \rightarrow POO + H_2O$

4. <u>Intramolecular Propagation of Peroxy Radicals</u>: In this stage of the degradation, intermolecular regrouping of the hydrogen atoms occurs.



- 5. <u>Formation of Ketone and Aldehyde Groups</u>: Different paths through which ketone and aldehyde groups are formed are shown below:
 - (i) Beta scission of alkoxy radicals is very important because of its part in backbone scission.



(ii) The reaction of reactive hydroxyl radical groups with labile atoms such as tertiary hydrogen in case of cage effect.



(iii) The decomposition of hydroperoxy radicals via biradical formation as intermediate.



(iv) Reaction of two polymers both having alkoxy radicals leading to hydroxyl and carbonyl groups by disproportionation.



6. <u>The Termination Reaction</u>: In this reaction two active radicals are combined with each other to form inactive products.

 $POO \cdot + POO \cdot \rightarrow$ inactive product

 $POO \cdot + P \cdot \rightarrow inactive product$

 $P \cdot + P \cdot \rightarrow$ inactive product

1.2.4. CHARACTERIZATION OF POLYMER DEGRADATION

The degradation of polymers can be analyzed with the help of many kinds of techniques in both qualitative and quantitative manner. Since changes in molecular structure occur because of degradation, characterization technique aiming at examining the change in molecular composition and studying the course of obtained polymer composition should be appropriate. FTIR

Spectroscopy is one of the most important techniques used for this purpose due to the formed groups such as vinyl, carbonyl and hydroxyl during degradation. As for following thermal behavior and properties of the degraded polymer the most common method is Differential Scanning Calorimetry. So with the help of obtained data such as crystalline melting temperature (T_m), heat of fusion (H_f), and percent crystallinity the effects of degradation on thermal properties can be examined. Also mechanical properties are very important properties of polymers that must be followed definitely, since the use of polymers mostly depend on the mechanical properties. The mechanical properties like tensile strength and percent elongation are reported not to change with the same rate of chemical reaction occurring in the structure of the polymer.

In the degradation process depending on the initiative effect, different kinds of changes can be observed such as in morphology which is a change at molecular level but the polymer is examined by the experiments in macroscopic level like mechanical or optical properties [6].

1.2.5. PHOTO-DEGRADATION AND PHOTO-OXIDATION OF POLYETHYLENE

Polyethylene, one of the most widely produced and used plastics, is studied to observe the degradation behavior of the polymer. It is found that in the absence of oxygen, polyethylene with no additive is a relatively stable material. Degradation via chain scission and hydrogen abstraction can occur after being exposed to UV light for a very long time.

In many studies it is reported that after being liable to UV light, oxygen uptake is observed in the samples as well as formation of many groups such as carbonyl, hydroxyl and vinyl with evolution of acetone, acetaldehyde, water, carbon dioxide, etc. During degradation of polyethylene there is a competition between crosslinking and chain scission. The mechanical properties of the polymer sample vary depending on this competition. If the crosslinking predominates, then modulus increases which is named as stiffening effect. It has also been reported that, crosslinking in polyethylene chains increases if the crystallinity and the thickness of the polymer film decrease which means amorphous parts of polymer readily degrades. So the diffusion of oxygen is higher in the more amorphous polymers [7].

1.3. TRANSITION METALS AS PHOTO-OXIDATIVE AGENTS

It has been estimated that some transition metals that exist in polymer matrix by coincidence or on purpose act as degradation accelerator when exposed to UV light while some others show just the opposite of this effect. For example, nickel and cobalt complexes cause the polymer become more stable to UV light, whereas ferric and copper complexes favor the photodegradation. The excited ions of the latter metals behave as catalytic activators and they cause the radicalic degradation reactions to occur.

As mentioned above, metallic compounds can be categorized in two groups as retarders and accelerators and their role in polymer degradation can be varied with some factors which are as follows [6]:

- \diamond The physical state and the type of polymer
- The conditions that the polymers are subjected such as chemicals, pollutants, microorganisms, light, heat, etc.
- ♦ Valency of the metal
- \diamond Kind of the metal
- ♦ Metallic, ligand or anion compounds

Also with the variation in the amount of nickel and iron compounds used in polymer, the time of use and the duration of degradation can be established according to the usage area of the polymer [20].

1.4. POLYMER NANOCOMPOSITES

Polymers are used in a great variety of areas in daily life; therefore different applications are in concern, latest of which is the polymer nanocomposites. It has been estimated that composites of polymers with nano-sized fillers like organo-modified montmorillonite or bentonite, can make the thermal and mechanical properties of the polymer to improve significantly even at very low concentrations because of the interaction of fillers in nano-level scale with polymer matrix [21].

The methods that are used to obtain the polymer nanocomposites can be named as follows:

- Solution Blending Method: In a polar organic solvent, both polymer and organo-modified clay are dissolved. The polymer generally does not coil and stay extended, so after removal of solvent an intercalated nanocomposite can be obtained.
- In Situ Method: Monomer is in the polar solution, and clay is spread in the polar solvent. At the end generally nanocomposites with exfoliated structure are obtained after addition of curing agent to the latest solution.
- Melt Intercalation Method: In this method the melted polymer is stirred with the filler to optimize interaction. During the process, the temperature should not be higher than the decomposition temperature of both polymer and the modifier used.

Fillers used in the polymer matrix must be dispersed in the medium well which makes the preparation of nanocomposites be a both technical and scientific challenge. It is started to be believed that, the size and shape of the particle as well as surface morphology and the distribution in the matrix polymer is more important than the chemical nature of the filler [1].

The type of method used to obtain the polymer nanocomposite has an important role on the properties of product since it affects the structure of the nanocomposite. If the interaction between the layers can be conserved, then the obtained product is named as an intercalated nanocomposite. But when the interaction cannot be stabilized, then the layers of clay distributed randomly in the polymer matrix, then the final product is an exfoliated nanocomposite. If the clay does not have any interaction with the polymer matrix, then the polymer matrix.

By now, there have been numerous researches on the degradation of polymers, but the effect of nanocomposites on these polymers, especially polyethylene, have not been studied in detail yet. The superficial works on degradability of polymer nanocomposites carried out with the help of UV radiation in biotic environment [22]. Finally it has been estimated that polymer nanocomposites show higher degradability than pure samples since once the oxygen is in the polymer matrix, it is captured there enough to initiate the degradation of the polymer. So the acceleration of the degradation is due to the reduction in oxidation induction period, but not due to the change in the kinetic or mechanism of the degradation process [23].

1.5. SERPENTINE

Serpentine is a type of phyllosilicates which differs from the others like mica or chlorite groups because of its distribution and formation. It is a really cheap and plentiful mineral in the nature [24]. It can be light or dark green and it is a translucent material which can be used as a flux in steel production, as filler in road pavement, as floor material for construction as well as decorative stones [25]. It is found along the mountains and island arcs such as New South Wales, Austria, from Alps to Asia Minor and the East Indies with the Philippines.

The chemical formula of serpentine groups is $Mg_3Si_2O_5$ (OH)₄ and the distance between repeating units are observed to be 0.7 nm (7 Å) [26,27]. Instead of magnesium and silicon nickel, cobalt, aluminum, ferric or ferrous ions can be replaced [28]. There are mainly three types of serpentine which are namely antigonite, chrysotile and lizardite. The one which has slightly different composition when compared to other two is antigonite. Though it is not indicated in the formula, the Mg:Si ratio is a bit smaller than one [29] but it has a larger dimension which is nearly 40 Å. The rest, lizardites and chryosotiles, are generally found together in nature. Lizardites are the most abundant serpentine type in the nature and its layers lie straight while layers of chrysotiles have curved structure. [30,31].

1.6. AIM OF THE STUDY

The aim of this study was to prepare environmentally friendly polyethylene films that can degrade when exposed to UV light for a certain period of time. In order to achieve this, three different additives were added to polyethylene in different concentrations and alone, then the change in both chemical and physical properties hence degradation were followed. The reason why polyethylene was chosen as matrix polymer is the common use of this polymer in many different kinds of application in industrial aspect.

The additives used were vanadium (III) acetylacetonate, serpentine and Cloisite 30B. Transition metal complexes are known to be very affective in photo-degradation, and vanadium (III) acetylacetonate is one of the transition metal complexes of which efficiency in UV induced degradation has never been examined before. Cloisite 30B is generally used in plastics and rubbers as to improve their physical properties. It is a modified montmorillonite with a quaternary ammonium salt. The aim of using Cloisite 30B in this study is to obtain composite of polyethylene and this nanoclay. Serpentine is an abundant clay like rock, and used in this study to obtain composite that accelerate the photo-degradation. Prepared film samples were exposed to artificial UV light and the change in chemical and mechanical properties were assessed in different time intervals. FTIR, DSC, and mechanical testing were used to follow the extent of degradation by analyzing both degraded samples and non-degraded ones as initial conditions.

CHAPTER 2

EXPERIMENTAL

2.1. MATERIALS

2.1.1. POLYETHYLENE

As matrix polymer, polyethylene is used in this study. Polyethylene used in this study is the product of ExxonMobil LDPE (Belgium). Its density is 0.925 g/cm³ and melt flow index of the polymer is 2 g/10 min. The melting temperature of the polymer is 111° C.

2.1.2. ADDITIVES

2.1.2.1. VANADIUM (III) ACETYLACETONATE



Figure 1: Chemical structure of vanadium (III) acetylacetonate

Vanadium (III) acetylacetonate was supplied by Sigma-Aldrich. Physical state of the compound at room temperature is a fine powder solid and its melting point is 181-184 °C. Its color is dark brown and its molecular weight is 348.27 g/mol.

The amount of the vanadium (III) acetylacetonate used in compositions was 0.2 % by weight, and kept constant in all samples.

2.1.2.2. CLOISITE 30B

The supplier of Cloisite 30B is Southern Clay Products, USA. The physical state of the compound at room temperature is solid and its deflection temperature is 96° C. It is a white powder and typical dry particle size is 2 µm if less than 10% by volume.

The amounts of Cloisite 30B used in the samples were 1, 2 and 3 % by weight.



Figure 2: Chemical structure of Cloisite 30B

2.1.2.3. SERPENTINE

Serpentine is clay like rock of which color is dark green. It is a type of phyllosilicates with chemical formula of Mg₃ Si₂O₅ (OH)₄. Typical dry particle size is 1.19 μ m if less than 10% by volume. The relevant properties of serpentine were given in detail in reference 32.

The amounts of fine powder serpentine used in the samples are 1, 2, 3 and 4 % by weight.

2.2. PREPARATION OF SAMPLES

The samples were prepared in Brabender Plasticorder Torque Rheometer at constant temperature at 180°C and the compositions shown in Table 1 were mixed at 45 rpm for 10 min. Obtained samples were then compression molded by ATS FAAR Pneumo Hydraulic Press at 190°C for 5 min. The compression molds were quenched into tap water in less than 2 minutes and cooled to room temperature. The final thickness of the films were 220+ 40 μ m.

Name of Sample	Vanadium (III)	Cloisite 30B	Serpentine
	acetylacetonate %	%	%
LDPE	-	-	-
А	0.2	-	-
В	-	1	-
С	-	2	-
D	-	-	1
Е	-	-	2
F	0.2	1	-
G	0.2	2	-
Н	0.2	-	1
I	0.2	-	2
J	-	1	3
К	-	2	2
L	-	3	1
М	-	1	4
Ν	-	2	3
0	0.2	1	3
Р	0.2	2	2
Q	0.2	3	1
R	0.2	1	4
S	0.2	2	3
Т	0.2	1	1

Table 1. The compositions of samples

2.3. UV EXPOSURE

Artificial UV exposure was carried out to follow photo-degradation. Two Sylvania PAR38 lamps were used nearly 30 cm away from the samples with a rate of 25000 μ W/cm² at 290 nm, which was measured by Black-Ray UV Meter. During the experiment, the temperature was measured to be 25°C. Standard dogbone shapes were cut for UV testing and kept under UV light, then removed after 0, 50, 100, 200, 300 and 500 hours of exposure to be characterized by IR and mechanical measurements.

2.4. SPECTROSCOPIC MEASUREMENTS

In order to follow the oxidative degradation in the structure of the polymer, IR measurements were carried out. The change in the spectra of the samples caused by UV induced oxidative degradation was followed by IR of the regions of carbonyl band at 1730 cm⁻¹ and crystalline CH₂ stretching band at 722 cm⁻¹. IR spectra of samples were obtained by FTIR- Nicolet iS10 Thermoscintific Smart Omni-Transmission. Since the samples were shaped as thin films they were directly placed in the instrument without any other preparation.

2.5. MECHANICAL TESTING

Dogbone shaped samples were exposed to UV light and mechanically tested before and after. Thickness of each sample was measured with micrometer before carrying out mechanical tests.

LLYOD LR5K Mechanical Tester was used for mechanical testing. Tests were carried out at room temperature and the speed of the test was 10 cm/min. The gage length of the samples was constant and 6.5 cm. At least four
measurements were carried out and the averages of these results were reported.

2.6. DSC STUDIES

Scinco DSC N-650 was used for DSC measurements and nearly 15 mg of each sample were analyzed. The temperature range was from 25 to 200° C, at a heating rate of 20° C/min.

CHAPTER 3

RESULTS AND DISCUSSION

To date, numerous researches on polyethylene degradation have been carried out. Different kinds of additives were used including transition metal complexes, and polymer layered silicates to obtain nanocomposites which are recently considered to be a good candidate. Though these are not studied in detail yet, it will be useful to overcome disposal problem of polyethylene due to extensive use [1, 7].

Exposure to UV light starts photo-oxidation process in the structure of the polymer since the energy of light is enough to initiate degradation via production of active macroradicals. With the help of special additives, the polymer becomes more vulnerable to UV light and the induction period of the degradation which means the interaction of polymer chains with oxygen is shortened thus the produced radicals have a significant role in autocatalytic degradation reactions [33].

There are several methods used to monitor the UV induced oxidation degradation of polymers. Since the degradation leads to formation of carbonyl compounds such as aldehydes and ketones, the increase in the carbonyl band at 1730 cm⁻¹ is a good measure of degradation. This increase in carbonyl band is then compared with a fixed crystalline CH_2 stretching band at 722 cm⁻¹ so that the degradation can be followed. The ratio of the

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former to latter is carbonyl index and a common way to indicate the degradation [37]. Also mechanical properties especially elongation at break are considered to follow the degradation, because the longer the polymer is exposed to UV light, the smaller the fragments become leading to a fail in mechanical properties [1].

3.1. CARBONYL INDEX MEASUREMENTS

In order to evaluate UV induced oxidative degradation of polyethylene, pure PE and twenty samples with different type and amount of additives were aged under UV light, carbonyl indexes of samples were then analyzed in certain time intervals.

Carbonyl indexes of the samples were calculated, results were then reported as difference in data of time 't' and '0' to be able to examine the increase in carbonyl index.

It is clearly observed in Figure 3 that, the slowest degradation was observed in pure LDPE as expected. In the absence of oxygen or impurities, polyethylene is a relatively stable material because pure saturated hydrocarbons cannot absorb the light reaching earth (above 300nm). So exposure to UV light does not cause a remarkable change in spectroscopic and mechanical properties of pure polyethylene in short time intervals [7, 36]. The increase in carbonyl index value of it could not go beyond 0.021 due to the very slow degradation nature of polyethylene at the end of 500 hours.

When compared to pure LDPE, sample A, containing vanadium (III) acetylacetonate (VAc) 0.2 % by weight, showed a significant increase in carbonyl index with irradiation time. Until 300 hours irradiation, the increase was very high when compared to others, but after 300 hours there was a sharp increase in carbonyl index up to 0.187. This increase could be due to

the some reversible photo-redox reactions of the transition metal that lead to a faster degradation of the polymer [7].

In the presence of metal complexes the initiation of the photo-redox reactions via UV light can follow two different paths which are as follows [6]:

 The transition metal complex is decomposed with absorption of the energy of UV light, where in our case M is vanadium and X acetylacetonate [38].

$$M^{3+}(X^{-})_{3} \xrightarrow{h \upsilon} M^{2+}(X^{-})_{2} + X \cdot$$

RH + X · \longrightarrow R · + HX

2. After excitation by UV the energy of the complex may be transferred to a molecule in the polymer chain, so following reactions occur:

$$M^{3+}(X^{-})_{3} \xrightarrow{h_{\mathcal{V}}} M^{3+}(X^{-})_{3}^{*}$$

$$M^{3+}(X^{-})_{3}^{*} + RH \longrightarrow M^{3+}(X^{-})_{3} + RH *$$

$$RH^{*} \longrightarrow R^{*} + H^{*}$$

After initiating the degradation with the help of both transition metal complex and UV light, oxygen takes place in the series of reactions [34]:

 $R \cdot + O_2 \longrightarrow ROO \cdot$ $ROO \cdot + RH \longrightarrow ROOH + R \cdot$

Then the degradation goes on with the produced active radical.



Figure 3: The variation of carbonyl index difference of sample A, B, C, D, E and pure LDPE with respect to time

Modified with a quaternary ammonium salt, Cloisite 30B (CL) is a natural montmorillonite. It has been estimated in the literature that when modified montmorillonite compounds are melt intercalated with a polymer, nanocomposites are obtained resulting in degradable products [1]. This is considered to be due to formation of active sites in the polymer matrix because of the influence of decomposition ammonium primarily. Sample B containing CL 1% by weight showed an initial increase after 200 hours irradiation. Then the degradation was found to be with a lower rate, though ending up with a significant increase in carbonyl index value than pure LDPE. Sample C containing CL 2% by weight obtained to be slower in degradation than B but again faster than pure LDPE. The decrease may be because of the difference in distribution of layers in the polymer matrix [33, 34].

Sample D which contains Serpentine (SE) 1% by weight and sample E comprised of SE 2% by weight. UV induced oxidative degradation observed to be faster than pure LPDE. From Figure 3, it can be concluded that the increase in amount of serpentine leaded to an increase in degradation rate. Serpentine has clay like structure, so its role in degradation is expected to be similar to CL, though the mechanism has not been clarified yet.

When B (CL 1%) and D (SE 1%) revealed similar profile in increase of carbonyl index, the increase in additive amount leaded to decrease in carbonyl index value in the case of C (CL 2%) but increase in the case of E (SE 2%). This difference could most likely be the result of different distribution of the fillers in the polymer matrix. Consequently VAc, without any doubt, is the most effective agent for faster photo-oxidative degradation in this set of samples.



Figure 4: The variation of carbonyl index difference of sample F, G, H and I with respect to time

In Figure 4, all four samples which contained combination of 0.2% VAc and either 1 and 2% SE or 1 and 2% CL, occurred to show more or less the same trend of increasing in carbonyl index after 300 hour of UV irradiation. Also pure LDPE and sample A containing 0.2 wt% VAc were fitted in this figure to examine the effect of clay additives and transition metal complexes better. It was obtained that I (0.2 wt% VAc and 2 wt% SE) had the fastest carbonyl index increase, 0.334, which means UV induced oxidative degradation was observed very effectively in this composition. The order of decreasing in carbonyl index values of the rest of the samples were as follows: H (0.2 wt% VAc and 1 wt% SE), G (0.2 wt% VAc and 2 wt% CL) and F (0.2 wt% and 1 wt% CL). Because the samples showed the similar behavior in increasing of

carbonyl index, it could be concluded that the degradation became faster with the combination of two additives, since the lowest increase in this group of samples, 0.211, was higher than the fastest degrading sample with only VAc as additive 0.187.

Nanocomposites which are obtained by using clay products are observed to enhance mechanical properties of the polymer due to being distributed finely in the matrix. These new class of materials promotes the degradation of polymer higher than pristine polymer, even used in very small amount up to 5 wt% [1]. It is stated that, this effect is due to the capture of oxygen in the polymer matrix long enough to shorten the induction period of UV induced oxidative degradation, but no change was observed in the kinetics of the degradation [33, 34].

The dispersion and distribution of the clay layers inside the polymer matrix is said to have influence on the degradation rate [33]. There are three possibilities for composite structure. First one is the intercalated composite which is the case that layers retain nearly the same with a bit more distance in between having polymer chains around. In the second case the layers are homogenously distributed in the matrix chains, and it is named as exfoliated nanocomposite. If the polymer chains fail to interact with clay layers effectively, then the resulting structure is not a nanocomposite but microcomposite that the degradation is obtained to promote most effectively is the exfoliated type. The way to synthesize that type of nanocomposites, in-situ polymerization is followed. When melt intercalation method is used, the final product is generally obtained be intercalated nanocomposites [1, 33, 34].





Samples reported in Figure 5 were prepared by melt intercalation method, and the amount of filler was kept between 4-5 wt% to achieve UV induced oxidation degradation. The highest increase in carbonyl index was achieved by sample N containing 2 wt% CL and 3 wt% SE ending up to 0.105. This value was not as high as the carbonyl index increase in the case of VAc, but still effective enough to accelerate the degradation. The following sample was M with 1 wt% CL and 4 wt% SE having nearly the same value with N, 0,102.

When the amount of clays dispersed in the polyethylene matrix was lowered to 4 wt% in total, the increase in carbonyl index was also decreased slightly. Sample K containing 2 wt% CL and 2 wt% SE showed 0.085 increase in carbonyl index, and sample L with 3 wt% CL and 1 wt% SE followed K. The final sample was obtained to be J containing 1 wt% CL and 3 wt% SE ending with a 0.072 increase.



Figure 6: The variation of carbonyl index difference of sample O, P, Q, R, S and T with respect to time

In the set of data reported in Figure 6, sample Q containing 0.2 wt% VAc, 3 wt% CL and 1 wt% SE showed a fast increase in carbonyl index measurements, 0.206. Up to 300 hour of UV irradiation the increase was slow, but after that time a high extent of carbonyl index increase was achieved. Then sample R with 0.2 wt% VAc, 1 wt% CL and 4 wt% SE followed sample Q. The carbonyl index increase observed in this sample was 0.190. As in the case of Q, the increase was effective after 300 hour of irradiation time. The third sample was S containing 0.2 wt% VAc, 2 wt% CL and 3 wt% SE, again having a sharper slope beginning at 300 hour of irradiation. Sample P with 0.2 wt% VAc, 2 wt% CL and 2 wt% SE showed an increase close to the previous samples, 0.152.

Samples T and O followed the others in carbonyl index increase. Sample T with 0.2 wt% VAc, 1 wt% CL and 1 wt% SE showed 0.102 increase, while sample O containing 0.2 wt% VAc, 1 wt% CL and 3 wt% SE was up to 0,070. Although these increases are lower than the previous samples, they are enough to be effective in UV induced oxidation degradation.

Considering the last set of samples, again it was observed that containing total 5 wt% clay samples obtained to be more effective in carbonyl index increase, though the best result was sample Q with 4 wt% of total clay. In this group, general behavior of the carbonyl index was increasing with the increase in the percentage of total clay, also the addition of VAc leaded to better results. The combination of VAc and clays was observed to be more effective in carbonyl index increase thus photo-oxidative degradation than they were used alone.

Comparing all samples and their results, it was found out that samples in which VAc and either CL or SE added together showed the highest increase in carbonyl index. SE used up to 2 wt% had better results than CL used up to 2 wt% when 0.2 wt% VAc were used in each, all promoting the carbonyl increase thus the fastest photodegradation. The following samples were the ones that in addition to 0.2 wt% VAc, 5 wt% of SE and CL used total together showing carbonyl index increase between 0.200 and 0.070. Then samples with 5 wt% of SE and CL used total showed from 0.072 to 0.187 increase. The slowest degradation was obtained in compositions that contained SE and CL in 2 and 1 wt% alone, though compared to pristine polyethylene matrix increase in carbonyl index was achieved in all samples.

3.2. MECHANICAL PROPERTIES MEASUREMENTS

Any kind of degradation process leads to cleavage of bonds in the structure of polymer. In light (i.e. UV) induced oxidative degradation of polyethylene, bonds are broken because of applied UV light and then the process continues even in dark [5, 11], when the oxygen amount is sufficient, with the help of active macroradicals formed at first stage of the degradation. The more the polymer degrades, the more the chains split in smaller pieces, so a remarkable change in mechanical properties of the polymer is achieved. With the increase in irradiation time, more weakened material is obtained since the chains are no longer strong enough to distribute the applied stress and the fragments fail to take part effectively in mechanical processes.

In this study, mechanical properties of the degraded polyethylene samples were monitored by examining elongation at break and tensile strength results of the polymer as a function of UV irradiation time.

3.2.1. ELONGATION AT BREAK OF SAMPLES

The more the polymer degrades, the shorten the chains are, so a remarkable decrease in elongation at break value of polymer is seen. It is worth noting that elongation at break of the examined species is a parameter that is affected most by the variations in structure and molecular level [33].

It is estimated that there are two process in the degradation of polymers; namely 'chain scission' and 'crosslinking'. These processes are considered to be competitive during degradation. The order of obtaining the processes is effective in the type of mechanical behavior of the polymer [35].

Chain scission is the continuous breakage of the bonds of polymer backbone because of light, heat or molecular oxygen so decrease in elongation at break and polymer's average molecular weight is achieved. On contrary to chain scission, in the case of crosslinking there occurs increase in elongation at break value of polymer due to the formed crosslinking points that can handle the applied stress. The way that crosslinking occurs is the combination of macroradicals in a way that can create links which are able to resist well to stress applied. The sequence of chain scission and crosslinking depends on the type of polymer, and temperature and oxygen level of the medium [2, 4]. In this study, in order to achieve UV induced oxidative degradation, in different weight percentage and combinations VAc, CL and SE were used, all of which are known to be effective in degradation so decrease in mechanical properties during this process was followed. The results were shown as residual percentage strain at break which means the ratio of percentage strain at break at time 't' to time '0' to be able to follow degradation.



Figure 7: The variation of residual percentage strain at break values of sample A, B, C, D, E and pure LDPE with respect to time

Results reported in Figure 7 showed that the sample which had the least decrease in residual percentage strain at break was LDPE showing crosslinking as expected. A sudden decrease was observed at first 100 hour of irradiation but then the degradation seemed to be slowed. The following sample was D with 1 wt% SE. It showed crosslinking at 100 hour of UV irradiation but then degrading via chain scission observed. Until 400h, the rate of degradation of D was slower than LDPE but then it started to be faster ending up 0.51 of residual percentage strain at break. Having the same final value with D, B containing 1 wt% CL promoted crosslinking at 200 hour of irradiation time, but before and after chain scission was predominant so decrease in residual percentage strain at break was achieved.

C with 2 wt% CL and E with 2 wt% SE samples showed fast decrease in elongation at break compared to B and D, and similar to them C and E had close values to each other by showing crosslinking slightly at 200 hour of induction time for C while E obtained to have crosslinking at around 300 hours. The fastest degrading sample of this set of mixtures was A containing 0.2 wt% VAc which showed a significant and smooth decrease up to 0.06 in residual percentage strain at break.



Figure 8: The variation of residual percentage strain at break values of sample F, G, H and I with respect to time

In Figure 8, the results of samples that contain 0.2 wt% VAc and 1-2 wt% of CL or SE were reported, in addition to pure LDPE and composition A (0.2 wt% VAc) to be able to compare the effects of both transition metal complex and clay additives, and all of them showed a fast decrease at the end of 500 hour of UV irradiation. Sample F with 0.2 wt% VAc and 1 wt% CL, had 0,14 of residual percentage strain at break value. The following sample was G containing 0.2 wt% VAc and 2 wt% CL and it ended up the same value with H which was comprised of 0.2 wt% VAc and 1 wt% SE. The best result in these samples was achieved by sample I with 0.2 wt% VAc and 2 wt% SE, though the final data of the all samples are very close to each other. In this

set of samples effect of crosslinking is not obtained as clear as the previous ones.



Figure 9: The variation of residual percentage strain at break values of sample J, K, L, M and N with respect to time

The following set of samples included the combination of CL and SE 4-5% in total, and the results were reported in Figure 9. Sample K with 2 wt% CL and 2 wt% SE showed the least decrease in residual percentage strain at break, while at 100 and 300 hour of UV exposure crosslinking was observed, except those time intervals chain scission was also seen. J containing 1 wt% CL and 3 wt% SE found to follow and showed the same behavior with K.

Sample M with 1 wt% CL and 4 wt% SE had nearly same result, 0,32, with J showing crosslinking at 200 hour of irradiation time. Last two samples of this set of mixtures were L with 3 wt% CL and 1 wt% SE and N with 2 wt% CL and 3 wt% SE had close results to each other showing crosslinking at 100 and 300 hours of UV exposure, respectively.

All samples in this set of compositions containing the mixture of CL&SE showed fluctuations in percentage strain at break values during degradation. This may be due to unequal interaction of particles in PE matrix.



Figure 10: The variation of residual percentage strain at break values of sample O, P, Q, R and T with respect to time

In Figure 10, the set of samples which contained 0.2 wt% VAc in addition to 2,4 and 5 wt% total clay additives were reported. The composition of all six samples were as follows: O with 0.2 wt% VAc, 1 wt% CL and 3 wt% SE, P with 0.2 wt% VAc, 2 wt% CL and 2 wt% SE, Q with 0.2 wt% VAc, 3 wt% CL and 1 wt% SE, R with 0.2 wt% VAc, 1 wt% CL and 4 wt% SE, S 0.2 wt% VAc, 1 wt% CL and 3 wt% SE and T with 0.2 wt% VAc, 1 wt% CL and 1 wt% SE. In this set, every mixture had nearly the same residual percentage strain at break values, from 0.20 to 0.26, with no significant crosslinking stage.

The results were generally very consistent with carbonyl index measurements. When all results were considered, the fastest decrease in residual percentage strain at break was achieved in the samples that contained either CL or SE with VAc, from 0.04 to 0.14. Including 5 wt% of SE and CL total with 0.2 wt% VAc followed the first set of samples releasing results from 0.20 to 0.25. Samples with 5 wt% of SE and CL used total then gave good results between 0.18 and 0.42. CL used in 2 and 1 wt% alone samples showed decrease better than pure LPDE which is 0.61.

3.2.2. TENSILE STRENGTH OF SAMPLES

Tensile strength results were reported in Figure 11, 12, 13 and 14. Because tensile strength is a bulk property and there was not a significant change observed throughout all samples but results fluctuated between 8-14 MPa.



Figure 11: The variation of tensile strength values of sample A, B, C, D, E and pure LDPE with respect to time



Figure 12: The variation of tensile strength values of sample F, G, H and I with respect to time



Figure 13: The variation of tensile strength values of sample A, B, C, D, E and pure LDPE with respect to time



Figure 14: The variation of tensile strength values of sample A, B, C, D, E and pure LDPE with respect to time

3.3. THERMAL PROPERTIES MEASUREMENTS

In order to use polyethylene effectively in industry and daily life, and maintain the applicability of the polymer there should not be significant change in the thermal properties of the material [1]. DSC analysis was, therefore, carried out to monitor the variations in thermal properties i.e. melting temperature.

After following DSC thermograms it was found out that there was no significant change in thermal properties of the samples. Considering all samples general trend of melting temperature was in range of $\pm 2^{\circ}$ C temperature change which cannot be accepted as an important change. Melting point of LDPE was about 114.85°C. There were two exceptional case throughout all samples which did not fit in $\pm 2^{\circ}$ C temperature range, K with 2 wt% CL and 2 wt% SE and O with 0.2 wt% VAc, 1 wt% CL and 3 wt% SE.

Name	Tm (°C)	Area of	Mass of
of		Peak	Sample
Sample		(J/g)	(mg)
LDPE	114.85	99.59	12.50
А	114.19	98.96	10.00
В	115.47	105.63	18.60
С	116.30	81	14.70
D	115.13	92.41	10.10
E	115.93	89.43	14.80
F	114.87	99.59	14.00
G	114.67	101.19	12.30
Н	115.51	104.52	15.00
I	116.20	87.53	15.00
J	116.36	91.81	14.30
К	117.26	101.58	10.70
L	115.56	103.28	18.10
М	116.69	90.92	18.40
Ν	115.12	133.60	20.40
О	117.41	88.81	18.40
Р	114.43	104.00	13.50
Q	114.07	114.72	14.80
R	114.87	103.79	12.80
S	115.89	102.97	15.20
Т	118.11	105.87	23.20

Table 2. Table of melting point, area under melting peak and mass ofsamples

CHAPTER 4

CONCLUSION

In this study vanadium (III) acetylacetonate, serpentine and Cloisite 30B were used as additives to obtain photodegradable polyethylene. These three additives were added to pure polyethylene both alone and together. Samples were irradiated by UV light for 500 hours. Mechanical and spectroscopic measurements showed that UV induced oxidative degradation of polyethylene were obtained faster than pure polyethylene.

Carbonyl index measurements showed that addition of all additives either alone or in combination with each other leaded to higher carbonyl index increase than pristine polyethylene. The fastest increase in carbonyl index values was obtained in the composition of serpentine with 0.2 wt% vanadium (III) acetylacetonate due to the acceleration effect of transition metal in photo induced oxidative degradation. Cloisite 30B in presence of 0.2 wt% vanadium (III) acetylacetonate was the second composition in degradation. Though the mechanism of nanocomposites are not clarified yet, it was observed that higher amount of clay additives leaded to faster increase in carbonyl index when only one of clay products used. In combination of two clay additives, it is thought that there were unequal interactions; however compositions showed faster degradation, though the increase was not as high as in the previous composition.

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Residual percentage strain at break values were evaluated and results were obtained to be consistent with spectroscopic measurements. In lower residual percentage strain at break values, higher carbonyl index increase was obtained. Considering tensile strength of the samples there was not a significant change but fluctuations during 500 hours of irradiation, because tensile strength is a bulk property.

Thermal properties were investigated by DSC thermograms examining melting points of samples. There occurred no significant change, because the difference in melting points was in ± 2 ^oC range. There were three exceptions not fitting in this range, which can be explained by some experimental errors.

In conclusion, the fastest degradation was obtained in the samples which contained 1 or 2 wt% serpentine or Cloisite 30B in addition to 0.2 wt% vanadium (III) acetylacetonate. In the case of combination of three additives it was observed that the increase in weight percentage of serpentine leaded to faster degradation, however, the interactions and the mechanism of degradation due to clay additives are not clarified yet.

REFERENCES

- [1] Pandey, J. K.; Reddy, R.; Kumar, A. P.; Singh, R. P. *Polymer Degradation and Stability* 2005, 88: 234-250
- [2] Miltz, J.; Narkis, M. Journal of Applied Polymer Science 1976, 20: 1627-1633
- [3] Heacock, F. J.; Mallory, F. B.; Gay, F. P. *Journal of Applied Polymer Science* 1968, 6: 2921-2934
- [4] Peacock, A. J.; Calhoun A. *Polymer Chemistry Properties and Applications* 2006, Hanser Gardner Publishers, Munich, 1-56990-397-2
- [5] Scott, G.; Gilead, D. *Degradable Polymers Principles and Applications* 1995, Chapmen and Hall, London, 0 412 59010 7
- [6] Hamid, S. H.; Amin, M. B.; Maadhah, A. G. *Handbook of Polymer Degradation* 1992, Marcel Dekker, New York, 0 8247 8671 8
- [7] Rabek, J. B. and Ranbey, B., *Photodegradation, Photo-oxidation and Photostabilization of Polymers* 1975, Wiley-Interscience Publication, London, 0471 70788 0
- [8] Geuskens, G. *Degradation and Stabilization of Polymers* 1975, Applied Science Publishers, London, 0853346399
- [9] Wellfair, S.T. *The Plymouth Student Scientist* 2008, 2: 243-301

- [10] http://www.cpcb.nic.in/upload/NewItems/NewItem_150_PlasticsWaste.pdf, (28.02.2012)
- [11] Raab, M.; Kotulak, L.; Kolarik, J.; Pospisil, J. *Journal of Applied Polymer Science* 1982, 27: 2457-2466
- [12] Feldman, D. *Journal of Polymers and the Environment* 2002, 10: 163-173
- [13] http://www-pub.iaea.org/MTCD/publications/PDF/te_1062_prn.pdf, (28.02.2012)
- [14] Emanuel, N. M.; Buchachenko, A. L. *Chemical Physics of Polymer Degradation and Stabilization* 1987, VNU Science Press, Netherlands, 9067640921
- [15] Grassie, N.; Scott, G. *Polymer Degradation and Stabilization* 1985, Cambridge University Press, New York, 0521357977
- [16] Peterson, J.D.; Vyazovkin, S.; Wight, C.A. *Macromolecular Chemistry* and Physics 2001, 202, 775–784
- [17] Gugumus, F. Polymer Degradation and Stability 2000, 69: 23-34
- [18] Gugumus, F. Polymer Degradation and Stability 2001, 74: 327–339
- [19] Gugumus, F. Polymer Degradation and Stability 2000, 69: 23-34
- [20] Kaczmarek, H.; Sionkowska, A.; Kaminska, A.; Kowalonek, J.; Swicatek,
 M.; Szalla, A. *Polymer Degradation and Stability* 2001, 73: 437–441
- [21] Tidjani, A.; Wilkie, C. A. *Polymer Degradation and Stability* 2001, 74: 33-37

- [22] Therias, M. S.; Mailhot B.; Gardette J. L.; Da Silva C.; Haidar B.; Vidal A. *Polymer Degradation and Stability* 2005, 90: 78–85.
- [23] La Mantia F. P.; Dintcheva N. Tz.; Malatesta V.; Pagani F. *Polymer* Degradation and Stability 2006, 91:3208–3213.
- [24] Tan, S.; Tinçer, T. Journal of Applied Polymer Science 2011, 121: 846-854
- [25] Klein, C.; Hurlbut, C. S. *Manuel of Mineralogy* 1993, Wiley Interscience Publication, New York, 047157452X
- [26] Wenk H. R.; Bulakh A.; *Minerals-Their Constitution and Origin* 2004, Cambridge University Press, Cambridge, 0521529581.
- [27] Nesse W.D., *Introduction to Mineralogy* 2000, Oxford University Press Inc., New York, 0195106911.
- [28] Tartaj P.; Cerpa A.; Garcia-Gonzalaz M. T.; Serna C. J.; *Journal of Colloid and Interface Science* 2000, 231: 176-181.
- [29] Ernst W. G.; Serpentine and Serpentinites: Mineralogy, Petrology, Geochemistry, Ecology, Geophysics, and Tectonics 2004, Bellwhether Publishing Ltd., Columbia, 0966586980.
- [30] Deer W. A.; Howie R. A.; Zussman J.; *An Introduction to the Rock Forming Minerals* 1966, Longman, New York, 9780582300941.
- [31] Auzende A. L.; Daniel I.; Reynard B.; Lemaire C.; Guyot F.; *Phys. Chem. Minerals* 2004, 31: 269-277.
- [32] Tan S., "*Characterization of Serpentine Filled Polypropylene*", The Degree of Doctor of Philosophy in Polymer Science and Technology,

The Graduate School of Natural and Applied Sciences of Middle East Technical University, Ankara, 2008.

- [33] Dintcheva, N.Tz.; La Mantia, F. P.; Malatesta, V. Polymer Degradation and Stability 2009, 94: 162–170
- [34] Qin, H.; Zhang, Z.; Feng, M.; Gong, F.; Zhang, S.; Yang, M. *Journal of Polymer Science*: Part B: Polymer Physics 2004, 42: 3006-3012
- [35] Alexandre, M.; Dubois, P. *Materials Science and Engineering* 2000, 28:1-63
- [36] Scott, G., *Mechanism of Polymer Degradation and Stabilization 1990,* Elsevier Science Publishers, England, 1-85166-505-6
- [37] Akay, G.; Tinçer, T.; Ergöz, H. E. *European Polymer Journal* 1980, 16: 601-605
- [38] Ferguson, G.; Hood, M. Polymer International 1992, 28: 35-40

APPENDIX A

DSC Thermograms of Pure LDPE, A, F, G, H, I





Figure A.2: DSC thermogram of 0.2 wt% VAc in LDPE



Figure A.3: DSC thermogram of 1 wt% CL and 0.2 wt% VAc in LDPE



Figure A.4: DSC thermogram of 2 wt% CL and 0.2 wt% VAc in LDPE







APPENDIX B

FTIR Spectra of pure LDPE, A, F, G, H, I



Figure B.1: FTIR spectrum of pure LDPE



Figure B.2: FTIR spectrum of 0.2 wt% VAc in LDPE



Figure B.3: FTIR spectrum of 1 wt% CL and 0.2 wt% VAc in LDPE



Figure B.4: FTIR spectrum of 2 wt% CL and 0.2 wt% VAc in LDPE



Figure B.5: FTIR spectrum of 1 wt% SE and 0.2 wt% VAc in LDPE



Figure B.6: FTIR spectrum of 2 wt% SE and 0.2 wt% VAc in LDPE

APPENDIX C

Stress-Strain Curves of Pure LDPE, A, F, G, H, I



Figure C.1: Stress-strain curve of pure LDPE


Figure C.2: Stress-strain curve of 0.2 wt% VAc in LDPE



Figure C.3: Stress-strain curve of 1 wt% CL and 0.2 wt% VAc in LDPE



Figure C.4: Stress-strain curve of 2 wt% CL and 0.2 wt% VAc in LDPE



Figure C.5: Stress-strain curve of 1 wt% SE and 0.2 wt% VAc in LDPE



Figure C.6: Stress-strain curve of 2 wt% SE and 0.2 wt% VAc in LDPE

APPENDIX D

Data Tables

		,			
0h	50h	100h	200h	300h	500
0.054	0.059	0.062	0.067	0.070	0.075
0.076	0.085	0.097	0.106	0.124	0.287
0.080	0.089	0.091	0.098	0.130	0.143
0.083	0.087	0.089	0.094	0.098	0.115
0.083	0.084	0.086	0.092	0.102	0.150
0.060	0.062	0.063	0.073	0.078	0.152
0.076	0.085	0.097	0.106	0.124	0.287
0.075	0.091	0.106	0.114	0.167	0.290
0.077	0.080	0.085	0.088	0.138	0.316
0.083	0.090	0.094	0.120	0.152	0.417
0.070	0.110	0.121	0.119	0.147	0.142
0.066	0.103	0.109	0.116	0.172	0.151
0.063	0.086	0.095	0.102	0.130	0.145
0.067	0.082	0.095	0.102	0.141	0.169
0.065	0.083	0.101	0.104	0.104	0.170
0.076	0.091	0.115	0.125	0.113	0.146
0.069	0.093	0.110	0.114	0.122	0.221
0.082	0.083	0.090	0.094	0.120	0.288
0.073	0.073	0.115	0.120	0.127	0.263
0.079	0.096	0.107	0.125	0.142	0.250
0.076	0.093	0.103	0.110	0.094	0.178
	0h 0.054 0.076 0.080 0.083 0.083 0.060 0.075 0.075 0.077 0.083 0.070 0.065 0.065 0.065 0.065 0.065 0.065 0.065 0.065 0.076	Oh 50h 0.054 0.059 0.076 0.085 0.080 0.089 0.080 0.089 0.083 0.087 0.083 0.087 0.060 0.062 0.075 0.091 0.075 0.091 0.077 0.080 0.073 0.090 0.070 0.110 0.066 0.103 0.067 0.082 0.063 0.082 0.065 0.083 0.076 0.091 0.065 0.083 0.065 0.083 0.076 0.091 0.069 0.093 0.076 0.083 0.076 0.083 0.073 0.073 0.074 0.093 0.075 0.093 0.076 0.093 0.077 0.096 0.076 0.093	Oh 50h 100h 0.054 0.059 0.062 0.076 0.085 0.097 0.080 0.089 0.091 0.080 0.089 0.091 0.083 0.087 0.089 0.083 0.087 0.089 0.060 0.062 0.063 0.076 0.085 0.097 0.076 0.085 0.097 0.076 0.085 0.097 0.076 0.085 0.097 0.075 0.091 0.106 0.077 0.080 0.085 0.083 0.090 0.094 0.070 0.110 0.121 0.066 0.103 0.109 0.063 0.086 0.095 0.065 0.082 0.095 0.065 0.083 0.101 0.076 0.093 0.110 0.076 0.083 0.090 0.073 0.073 0.115 0.079	Oh50h100h200h0.0540.0590.0620.0670.0760.0850.0970.1060.0800.0890.0910.0980.0830.0870.0890.0940.0830.0870.0860.0920.0600.0620.0630.0730.0760.0850.0970.1060.0750.0910.1060.1140.0770.0800.0850.0880.0830.0900.0940.1200.0660.1030.1090.1160.0630.0860.0950.1020.0650.0830.1010.1040.0760.0910.1150.1250.0690.0930.1100.1140.0730.0730.1150.1200.0790.0960.1070.1250.0790.0930.1030.110	Oh50h100h200h300h0.0540.0590.0620.0670.0700.0760.0850.0970.1060.1240.0800.0890.0910.0980.1300.0830.0870.0890.0940.0980.0600.0620.0630.0730.0780.0760.0850.0970.1060.1240.0760.0850.0970.1060.1240.0760.0850.0970.1060.1240.0760.0850.0970.1060.1240.0770.0800.8550.0880.1380.0700.1100.1210.1140.1670.0660.1030.1090.1160.1720.0630.0860.0950.1020.1300.0650.0830.1010.1040.1040.0650.0830.1010.1140.1220.0690.0930.1100.1140.1220.0820.0830.0900.0940.1200.0730.0730.1150.1200.1270.0790.0960.1070.1250.1420.0760.0930.1030.1100.094

Table D.1: Variations in carbonyl index results of samples

Name of	0h	50h	100h	200h	300h	500
Sample						
LDPE	326	318	239	219	206	200
А	325	190	122	118	75	21
В	127	115	89	104	86	64
С	327	274	142	158	155	119
D	123	93	100	97	92	63
E	190	152	140	101	112	69
F	251	142	130	106	77	36
G	226	178	137	70	42	23
Н	268	203	183	143	95	27
Ι	46	188	168	122	111	16
J	150	68	87	55	124	48
К	210	110	155	154	174	86
L	240	120	185	94	64	48
М	201	200	173	195	160	63
Ν	147	140	102	64	92	27
0	247	123	119	101	95	57
Р	137	118	102	92	69	34
Q	237	117	105	98	86	51
R	173	120	105	96	87	44
S	256	169	126	104	95	50
Т	151	117	187	88	70	40

Table D.2: Variations in percentage strain at break results of samples

Name of	0h	50h	100h	200h	300h	500
Sample						
LDPE	10.4	12.1	10.1	10.4	10.7	10.3
А	11.4	10.2	9.4	9.9	11.6	9.0
В	9.6	9.7	8.9	9.7	9.5	9.6
С	11.5	9.0	11.8	10.3	9.1	11.0
D	10.8	8.0	8.9	9.3	8.5	9.2
Е	10.7	10.3	10.9	10.3	9.2	9.3
F	12.5	11.0	10.8	10.8	11.3	9.1
G	10.2	11.0	14.6	11.0	10.5	8.9
Н	9.7	10.5	10.0	11.3	9.6	8.9
I	14.2	14.6	10.3	9.9	11.6	10.9
J	11.6	11.6	11.1	11.7	11.3	10.8
К	13.3	12.6	11.7	11.8	11.8	11.5
L	11.1	10.5	10.2	10.9	10.7	10.2
М	10.2	11.4	11.7	12.1	12.1	12.1
Ν	10.8	9.9	9.7	10.6	11.0	10.0
0	10.9	10.7	11.2	10.8	9.2	10.6
Р	10.3	11.4	10.9	10.4	9.6	10.6
Q	11.1	11.5	11.4	11.0	9.7	11.5
R	11.5	11.9	11.9	11.2	9.4	10.6
S	10.4	11.3	11.1	11.9	9.3	10.5
Т	10.3	10.3	11.6	11.6	10.4	10.5

Table D.3: Tensile strength results of samples