ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

EFFECT OF VARIOUS STABILIZER MIXTURES ON MECHANICAL AND PHYSICAL PROPERTIES OF $CaCO_3$ FILLED POLYPROPYLENE COMPOSITE IN DIFFERENT ENVIRONMENTAL CONDITIONS

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ÇEŞİTLİ STABİLİZATÖR KARIŞIMLARININ FARKLI ÇEVRESEL KOŞULLARA MARUZ BIRAKILMIŞ $CaCO_3$ DOLGULU POLİPROPİLEN KOMPOZİTİNİN MEKANİK VE FİZİKSEL ÖZELLİKLERE ETKİSİ

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ABBREVIATIONS

$CaCl_2$	: Calcium Chloride
$CaCO_3$	: Calcium Carbonate
CaSt	: Calcium Stearate
Ch	: Chromophore
(Ch)*	: Chromophore in excited state
CIE	: Commission Internationale de l'éclairage, French title of the International Commision on Illumination
CIELAB	: Color difference calculated by using the CIE 1976 L*a*b* opponent-color scales
DMDBS	: Diparamethyldibenzylidene sorbitol
DSC	: Differential Scanning Calorimetry
DTA	: Differential Thermal Analysis
ESR	: Electron Spin Resonance
HAS	: Hindered Amine Stabilizer
HALS	: Hindered Amine Light Stabilizer
HD	: Hydroperoxide Decomposer
LTTS	: Long-term Thermal Stability
MFI	: Melt Flow Index
MW	: Molecular Weight
MWD	: Molecular Weight Distribution
OIT	: Oxygen Induction Time
PP	: Polypropylene
Q	: Quencher
Q*	:Quencher in excited state
QM	: Quinone Methide
TGA	: Thermo-gravimetric Analysis
YI	: Yellowness Index

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a^*, b^*	: chromaticity values
A_k	: impact energy
b	: width of specimen
Δ	: heat
E_b	: modulus of elasticity
E_y	: tensile strain
ΔE^*_{ab}	: size of color difference
F	: applied load
F_{wl}	: weld-line factor
h	: thickness of specimen
$h\upsilon$	: light energy
L	: span lenght
L^*	: lightness
L_o	: gauge length
M	: average mass of cut-offs
m_{bf}	: weight of crucible filled with sample before putting into oven
m_{af}	: weight of filled crucible after getting out of the oven
m_{cr}	: weight of crucible
$R^\bullet$	: Free Radical
S	: reference time in seconds
σ_f	: flexural stress
σ_y	: tensile stress
t	: cut-off time interval
X	: thickness of impact test specimen
$X_{CIE}, Y_{CIE}, Z_{CIE}$	: tristimulus values of a specimen
X_n, Y_n, Z_n	: tristimulus values of a perfect reflecting diffuser
Y	: deflection
Y_k	: difference of width and notch depth

EFFECT OF VARIOUS STABILIZER MIXTURES ON MECHANICAL AND PHYSICAL PROPERTIES OF $CaCO_3$ FILLED POLYPROPYLENE COMPOSITE IN DIFFERENT ENVIRONMENTAL CONDITIONS

SUMMARY

As a result of their low cost, ease of processing, and wide range of properties, polymers have found their way into many applications and replaced conventional materials such as metals and wood. Along many others, polymers are widely used in commercial appliance goods, such as refrigerators, dishwashers and washing machines, gardening accessories such as tables and chairs, as insulators in wire coatings and in many other fields. During their lifetime polymeric materials are exposed to various environmental conditions such as; heat, light, chemicals and water. Exposure to these conditions may cause changes in physical or chemical properties of the polymer. Therefore, in contrast to these conventional materials, the addition of some special chemicals is necessary to ensure the long-term properties of polymers and maintain its already present properties.

The reason why the lifetime of plastic materials are shorter than expected is mainly the reactions with oxygen by means of radicalic mechanism, which leads to degradation. Since degradation results in failures in mechanical and esthetical properties of the plastic article, the polymer must be protected against degradation, which can be accomplished by the addition of stabilizers. In the choice of stabilizers, the structure of the polymer, chemical structures of the other additives present in the polymer matrix and the environmental conditions the end product will be exposed to must be considered.

The aim of this thesis is to stabilize a mineral filled composite, which is based on homopolymer polypropylene against oxidation and the effects of various environmental conditions. Inhibition of thermal, chemical and mechanical degradation is also the goals of this work. Synergistic interactions of the stabilizers with each other and with the filler found in the polymer matrix are another concern of this thesis.

The first and second parts of the thesis consist of a literature survey about degradation and stabilization to be able to decide which stabilizers would be appropriate for the stabilization of polypropylene subjected to detergent and bleach solutions, water vapor and heat. Investigated works in the literature mostly deal with synergistic effects of stabilizers that would improve their efficiency. Therefore in the experimental work of this thesis, the stabilizer mixture consisting of various possibly synergistic stabilizers was chosen by considering the environmental conditions. This stabilizer package was expected to protect the polymer against the effects of oxidation and mechanical degradation.

Third part of the thesis deals with the investigation of any synergistic interactions between the stabilizer mixture and two different nucleating agents. The stabilizer mixture consisted of an acid scavenger, a sterically hindered phenolic antioxidant, a phosphate based process stabilizer and a radical scavenger. To be able to determine any synergistic effects several formulations were prepared. The stabilized polymer mixture was considered as a base formulation. Four different formulations were prepared by the addition of different nucleating agents varying in both chemistry and amount. Similarly, different formulations containing only these nucleation agents in two loading levels (0,1 and 0,3% w/w) were also prepared to be able to determine the effects of nucleating agents in the absence of the stabilizer package. Processing techniques, such as extrusion and injection molding and the testing methods such as, yellowness measurements, tensile, flexural and impact tests were also performed to identify synergistic effects.

In the last part results of all the mechanical tests and color measurements are given and investigated in detail. Considering all the data gathered from these experiments, a suitable formulation among nine different formulations was chosen to be appropriate to be used in a plastic article that would be exposed to conditions like detergent, bleach solutions, elevated heat and water vapor. It was seen that nucleating agents show synergistic interactions with the stabilizer package used in this work.

ÇEŞİTLİ STABİLİZATÖR KARIŞIMLARININ FARKLI ÇEVRESEL KOŞULLARA MARUZ BIRAKILMIŞ $CaCO_3$ DOLGULU POLİPROPİLEN KOMPOZİTİNİN MEKANİK VE FİZİKSEL ÖZELLİKLERİNE ETKİSİ

ÖZET

Düşük maliyet, işleme kolaylığı ve sahip oldukları özelliklerin çeşitlilik aralığının geniş olmasının bir sonucu olarak polimerler, pek çok kullanım alanı bulmuş ve metal, tahta gibi bilinen malzemelerin yerine geçmiştir. Polimerler, metal tel kaplamalarında yalıtkan olarak; masa, sandalye gibi bahçe aksesuarlarında; buzdolabı, bulaşık makinesi ve çamaşır makinesi gibi ticari ev ürünlerinde ve daha pek çok farklı alanda kullanım alanı bulurlar. Kullanım süreleri boyunca polimerler ısı, ışık, kimyasallar ve su gibi çeşitli çevresel koşullara maruz kalırlar. Bunun sonucunda polimerin fiziksel ve kimyasal özelliklerinde değişiklikler olabilir.Dolayısıyla bilinen bu malzemelerin aksine, polimerilerin özelliklerinin uzun vadeli olmasının sağlanması ve hali hazırda sahip oldukları özelliklerin korunması için özel kimyasalların eklenmesi gereklidir.

Plastik malzemelerin yaşam süresinin beklenenden daha kısa olmasının başlıca nedeni, polimerin oksijenle radikalik mekanizmayla yürüyen ve bozunmaya neden olan reaksiyonlarıdır. Bozunma, plastik parçanın mekanik ve estetik özelliklerinin kötüleşmesine neden olacağından polimer, stabilizatörlerin eklenmesi vasıtasıyla bozunmaya karşı korunmalıdır. Stabilizatörlerin seçiminde; polimerin yapısı, polimer matrisinde bulunan diğer katkı maddelerinin kimyasal yapısı ve son ürünün maruz kalacağı çevresel faktörler göz önünde bulundurulmalıdır.

Bu tezin amacı, homopolimer polipropilen bazlı mineral dolgulu bir kompozitin oksidasyon ve çeşitli çevresel koşullara karşı stabilizasyonudur. Termal, kimyasal ve mekanik bozunmaların(degradasyonların) yavaşlatılması da bu çalışmanın amaçlarındandır. Stabilizatörlerin birbirleriyle ve polimer matrisinde bulunan dolgu maddesiyle sinerjik etkileşimleri çalışmanın bir diğer ilgi konusunu oluşturmaktadır.

Bu tezin ilk ve ikinci kısımları, deterjan, çamaşır suyu çözeltileri, su buharı ve ısıya maruz kalacak polipropilen için uygun stabilizatörlerin seçilebilmesi için degradasyon ve stabilizasyon hakkında yapılmış literatür araştırmasından oluşmaktadır. Literatürde karşılaşılan çalışmaların daha çok stabilizatörlerin etkilerini arttıracak sinerjik etkileşimlerle ilgili olduğu görülmüştür. Bu nedenle tezin deneysel çalışma kısmında, çevre koşulları da göz önünde bulundurularak olası sinerjik etkileşim gösterebilecek çeşitli stabilizatörlerin bir karışımı seçilmiştir. Bu stabilizatör paketinin polimeri oksidasyon ve mekanik degradasyondan koruyacağı öngörülmüştür.

Tezin üçüncü kısmı, stabilizatör karışımı ile iki farklı nükleasyon ajanı arasındaki olası sinerjik etkileşimlerin incelenmesiyle ilgilidir. Stabilizatör karışımı; bir asit yakalayıcı, sterik engelli fenolik antioksidant, fosfat bazlı proses stabilizatörü ve radikal yakalayıcıdan oluşmaktadır. Sinerjik etkilerin gözlenebilmesi için çeşitli

formulasyonlar geliştirilmiştir. Stabilize edilmiş polipropilen karışımı temel formulasyonu oluşturmaktadır. Bu temel formulasyona değişen miktarlarda iki farklı nükleasyon ajanının eklenmesiyle dört değişik formulasyon oluşturulmuştur. Stabilizatör karışımının yokluğunda nükleasyon ajanlarının etkilerini görebilmek için stabilize edilmemiş polimer karışımına değişen miktarlarda (0.1 ve 0.3 w/w) iki farklı nükleasyon ajanlarının eklendiği dört formulasyon daha geliştirilmiştir. Ekstrüzyon ve enjeksiyonla kalıplama gibi işleme teknikleri; çekme, eğme ve darbe testleri, sararma indeksi gibi test metotları da sinerjik etkileşimlerin varlıklarının tanımlanabilmesi için gerçekleştirilmiştir.

Son kısımda ise mekanik testler ve renk ölçümlerinin sonuçları detaylı bir biçimde verilmiş ve incelenmiştir. Bu deneylerden elde edilen bütün verilen göz önünde bulundurularak; deterjan ve çamaşır suyu çözeltileri, yüksek ısı ve su buharına maruz kalacak bir plastik parçanın yapılmasında dokuz farklı formulasyon arasından en uygun olacak bir formulasyon seçilmiştir. Bu çalışmada kullanılan stabilizatör karışımı ile seçilen nükleasyon ajanlarının sinerjik etkileşime girdikleri görülmüştür.

1. INTRODUCTION

As a result of their low cost, ease of processing, and wide range of properties, polymers have found their way into many applications and replaced conventional materials such as metals and wood. Along many others, polymers are widely used in commercial appliance goods, such as refrigerators, dishwashers and washing machines, gardening accessories such as tables and chairs, as insulators in wire coatings and in many other fields. However, in contrast to these conventional materials, several additives are necessary to ensure the long-term properties of polymers to prevent discoloration, mechanical failures, as well as protecting the chemical, physical and esthetical properties.

All organic materials (consisting essentially of carbon, hydrogen, oxygen and nitrogen) readily undergo reactions with oxygen. If the organic material is a polymer, such oxidation reactions are much of a concern because important properties of the polymer often change. When polymers oxidize, they lose mechanical properties such as, tensile strength and impact resistance. Spoiled surface appearance and discoloration of the plastic material may also result. Oxidation may occur in every stage of the lifetime of a polymer; not only during manufacturing and storage of the polymer in granule form, but also during processing and service life of the end article produced.

Presence of oxygen is not the only cause of poorer mechanical and esthetical properties. Mechanical shear forces that the polymer is exposed to during processing, heat and light may also cause the polymer to degrade, by means of generating free radicals. The formation of these radicals result in some chemical reactions in the polymer, which further on cause the polymer to degrade. The whole process of radical formation, radical propagation and termination via abstracting molecules from the polymer itself and from the surrounding compounds in a polymer mixture is called degradation. To protect the polymeric material during processing, storage and through the service lifetime from these reactions some special chemicals, which are called additives or more specifically stabilizers are used.

Additives are important for the success of most thermoplastics, because they optimize and control the properties of polymers for specific applications. According to their mode of action these chemicals either scavenge the free radicals or deactivate them by reacting with these active species instead of the polymer itself. Here, it may be said that the protection lifetime of an additive is related to its consumption rate, which therefore will be directly connected to the environmental conditions the polymer faces during its whole lifetime.

The interactions of the additives with the polymer are as important as the interactions of the additives along with the others in the polymer compound. The total effect of additives may be greater than the effect they show individually. Then these two are concerned as synergists.

In this thesis, different polymeric mixtures including inorganic filler material and various additives were prepared. All these polymeric mixtures were extruded, injection molded to be given shape and put into different aging environments (detergent and bleach solutions, oven, water vapor and UV) to determine the differences in mechanical and color properties. Any synergistic interactions between the additives and unexpected improvements or failures were also investigated.

The aim of performing such experiments was to stabilize a polypropylene compound subjected to detergent, bleach solutions; elevated heat and water vapor and to determine any synergistic interactions between the additives present in the polymer matrix. Several formulations were prepared and the changes of their properties under aging environments were observed by means of mechanical tests and color measurements. After the evaluation of the experimental results, compounds of poorer properties were eliminated. Considering the performance on tensile, flexural, impact properties and less coloration under various aging environments, which is thought to be the effects of synergistic interactions, the most appropriate polymeric compound stabilized against the mentioned conditions was chosen.

2. THEORETICAL PART & LITERATURE SURVEY

2.1. Polypropylene

Polymers of propylene in crystalline form, were first described by G. Natta with the introduction of heterogeneous, stereospecific catalysts discovered by K. Ziegler for the low-pressure polymerization of ethylene **(Hanna, 1990)**. Natta classified the three geometric forms of polypropylene as:

- Isotactic

  Methyl groups all aligned on one side of the chain

- Syndiotactic

  Methyl groups alternating

- Atactic

  Randomly positioned methyl groups

The geometrical structures of these three types of polypropylene are shown in Figure 2.1.

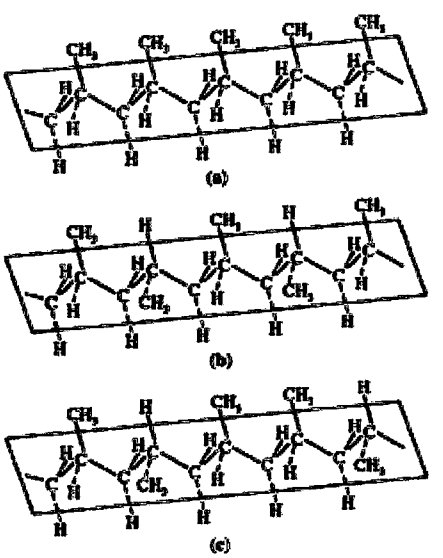


Figure 2.1 Three forms of polypropylene, (a) Isotactic, (b) Syndiotactic, (c) Atactic. **(Hanna, 1990)**

Both isotactic and syndiotactic forms crystallize when they are cooled from molten state; however, commercial injection molding and extrusion grade polypropylenes are 94-97% isotactic.

PP is commonly produced either as a homopolymer or a copolymer where in that case the co-monomer is ethylene. In both forms, PP is resistant to moisture and has good resistance to chemicals like weak acids, alkalies and solvents; and can be easily processed with injection molding and extrusion. The advantages of copolymerization with ethylene are the improvements in toughness and flexibility, but a slight decrease in heat resistance can be included as a disadvantage **(DeBoest, 1988)**.

The non-polar structure of PP is the cause why it has high resistance to most solvents and chemicals, as well as to moisture. PP, because of its nature, is less stable to heat, light and strong oxidizing acids and chlorinated solvents, presumably because of the presence of tertiary hydrogens, which is also the reason why polypropylene degrades preferentially by chain scission **(Canevarolo, 2000)**. Therefore it must be stabilized with special chemicals mainly as, antioxidants, light stabilizers and process stabilizers and many more according to the end-use of the plastic product. In Figure 2.2, by the abstraction of the tertiary hydrogen the formation of the tertiary alkoxy radical and β- scission reaction leading to chain breakage can be seen.

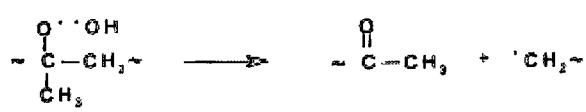


Figure 2.2 β-scission reaction involving tertiary alkoxy radicals **(Schwarzenbach et al., 2001)**

Its high crystallinity, gives PP good tensile strength and stiffness as well as surface hardness. Its brittleness can be overcame by the addition of copolymers of ethylene in the form of random or block copolymers.

PP has a high crystalline melting point; therefore it can keep its mechanical properties at elevated temperatures. The melting point of pure isotactic polypropylene is 176°C **(Hanson, 1989)**, but since the commercial products may

contain some amounts of non-isotactic polypropylene or may be copolymerized with ethylene the melting point of PP ranges between 165°C to 176°C.

Addition of fillers such as calcium carbonate to PP generally improves some characteristics of the composite. Because of its spherical form, calcium carbonate increases flexural modulus. On the other hand, because of its alkaline surface, organic acids can easily attack $CaCO_3$. Calcium carbonate might also cause the reduction of tensile strength and elongation.

2.2. Degradation

The effects of free radical generation is termed as degradation that can be simply defined as changes in physical properties, chemical structure or appearance of a plastic caused by chemical reactions involving bond scissions in the backbone of the macromolecule. During processing and service time, polymeric material is exposed to conditions, which initiate and accelerate the degradation process. These conditions affecting the polymer are given below:

- Shear forces
- Presence of oxygen
- Influence of chemicals
- Heat
- Light
- Water

Exposure to one or more of these effects, cause the formation of free radicals, which are highly reactive species. As a result of the reactions of these radicals with the polymer, changes in the chemical structure occur leading to mechanical and esthetical failures. A diagram showing the changes in properties of polymers versus time can be seen in Figure 2.3.

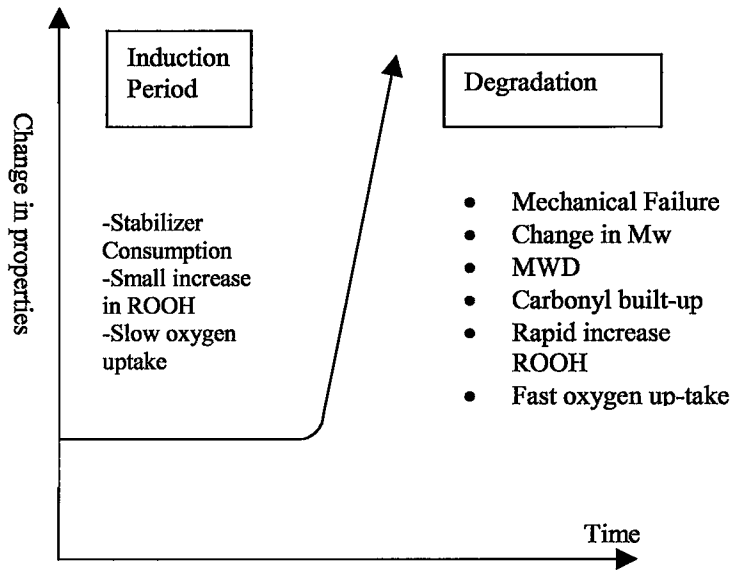


Figure 2.3 Changes in properties during aging of polymers **(Schwarzenbach et al., 2001)**

The induction period is a time space where little or no difference in the properties of the polymer is observed because stabilizers inhibit degradation during this period. Thus, reactions with oxygen are inhibited, too. This period ends with the consumption of stabilizers. After this induction period, degradation rate increases, reactions with oxygen speed up and finally mechanical and esthetical failures are observed. Therefore the efficiency of stabilizers is measured by the length of this induction period.

Degradation reactions are classified into two main groups, as single step reactions or chain reactions because of kinetic differences, as can be seen in Table 2.1. In single step reactions, the reaction rate is directly proportional to the rate of initiation. Single step reactions are seen in photochemical degradation mechanisms. On the other hand, chain reactions are characterized by the self-propagation of the process once initiated **(Schnabel, 1992)**. Initiation reaction products, themselves, are capable of reacting spontaneously with intact molecules in the polymer matrix.

Table 2.1 Degradation reaction types

TYPE OF REACTION	PROCESS	MODE OF INITIATION
Single Step Reaction	Norrish II type reaction in ketone polymers	Photochemical
Chain Reaction	Auto-oxidation	Thermal, photochemical, mechanical, chemical

Whether the degradation process is random or specific; is one of the major concerns. In linear homopolymers, the chain scission is generally random but in some cases specific scission is maintained. Non-random chain scissions are observed when the polymer is subjected to mechanical forces. Generally the central regions are more likely to undergo scissions when exposed to mechanical shear. Also in block copolymers, where long A-blocks are connected to short B-blocks, the specific site of attack is the short B-block fragments **(Schnabel, 1992)**.

2.3. Types of Degradation

No matter how the degradation process initiates in a polymer matrix, the main degradation process is uniform. The free radical formation advances the degradation reactions even up to chain scissions. According to various modes of initiation degradation can be classified in five groups:

- Oxidative degradation
- Thermal degradation
- Chemical degradation
- Mechanical degradation
- Light-induced polymer degradation

2.3.1. Oxidative Degradation

The processing of thermoplastic polymers, result in commercial end products. During processing, the polymer is exposed to heat and mechanical shear. Finished particles are designed to be used for many years with minimal changes in chemical,

physical and mechanical properties as well as esthetical aspects. Oxidation refers to the reactions with oxygen proceeding under mild conditions; e.g., at ambient or slightly increased temperatures.

The initiation of oxidation in polyolefins, are considered to involve metal ions from the catalysts used for polymerization comprising of transition metals and iron particles from the processing equipments **(Livanova and Zaikov, 1997)**. However, oxygen, heat, light and water are present throughout the whole lifetime of the plastic particle. Under these conditions, polymer chains undergo scissions, chain branching, and/or cross-linking. Another study investigating the Ziegler-Natta catalyst residue effects on heterogeneous oxidation performed by **Goss et al. (2003)** relates the loss of toughness as a result of degradation of the oxidative chain scissions. They add that oxidative chain scissions in the amorphous region of the polymer involve tie molecule scissions; recrystallization of low molecular mass polymer chains followed by those scissions and increased polarity; which produces densification. They also claim that the zones where oxidation is first initiated are the sites where Ziegler-Natta catalyst residues are accumulated. They conclude that oxidation, generates species that are able to increase the volume of the oxidizing zones and gradually consume the polymer.

In the degradation of polypropylene chain scission mechanism is dominant, because of the presence of tertiary hydrogens. On the other hand, polyethylene tends to form cross-links **(Waldman and De Paoli, 1998)**. Therefore understanding oxidative degradation, its prevention and inhibition is fundamental for plastics industry.

2.3.1.1. Auto-oxidation

The reactions of organic compounds with molecular oxygen, is referred to as auto-oxidation, because such reactions often proceed automatically. Auto-oxidation reaction is considered as a free radical initiated chain reaction, and as other radical reactions, it proceeds by three types of reactions: chain initiation, propagation and termination. Radical reaction taking place in auto-oxidation reactions are shown below, in Figure 2.4.

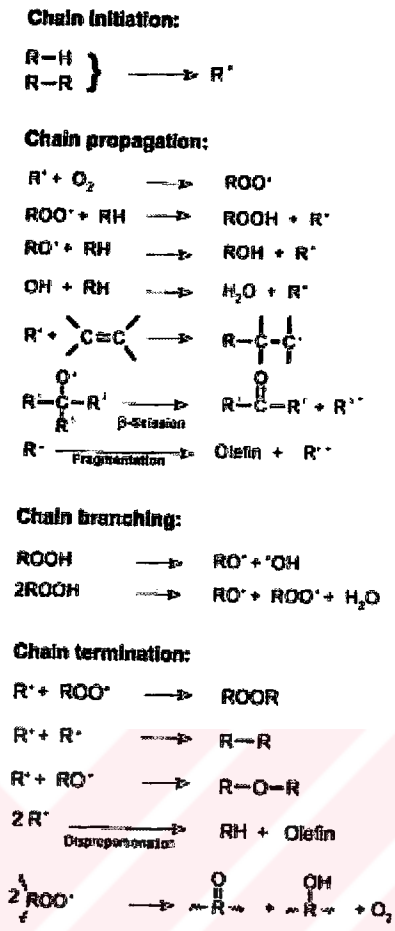


Figure 2.4 Typical reactions taking place in auto-oxidation. (Polymer backbone is denoted as R) **(Schwarzenbach et al., 2001)**

The origin of the primary alkyl radical $R^{\bullet}$ as the initiating species is not yet fully understood. Direct reaction of molecular oxygen with the polymer is not favored because of thermodynamic and kinetic considerations. One explanation for the formation of free radicals is that, during polymerization, catalysts such as transition metals or impurities in the monomers react with oxygen to form peroxy $ROO^{\bullet}$ radicals **(Livanova and Zaikov, 1997; Schwarzenbach et al., 2001)**. These radicals abstract hydrogen from the polymer backbone thus form alkyl radicals. A reaction mechanism of alkyl radical formation is suggested by **Waldman and De Paoli (1998)**. The formation of alkyl radicals, and the oxidative degradation of polyolefins under the effect of temperature (thermo-oxidative degradation) are shown in Figure 2.5. In this figure the pendant groups, which are denoted as X, can either be hydrogen or methyl groups.

In step 1, under the influence of heat or light the pre-formed free radicals abstract hydrogen from the polymer backbone. Step 2 shows the reaction between this macroalkyl radical and the molecular oxygen, which yields in the formation of the macroperoxy radical. The peroxy radical abstracts another hydrogen from the polymer chain thus, forming another macro radical and a hydroperoxide in step 3, while in step 4 the formation of another macroperoxy radical from the reaction of macroalkyl radical formed in Step 3 with molecular oxygen is shown. Step 5 shows the formation of the alkoxy radical by the hemolytic scission of O-O bonds of hydroperoxides. Steps 6 and 7 are the possible reactions of the macroalkoxy radical with the polymer itself and another macroalkyl radical. In step 6 the abstraction of hydrogen from the polymer chain yields in the formation of macroalkyl radical and once again it reacts with molecular oxygen forming peroxy radicals, which is shown in step 8. On the other hand the alkoxy radical formed in step 5 may react with alkyl radical, which is shown in step 7 and the two chains may terminate forming cross-links.

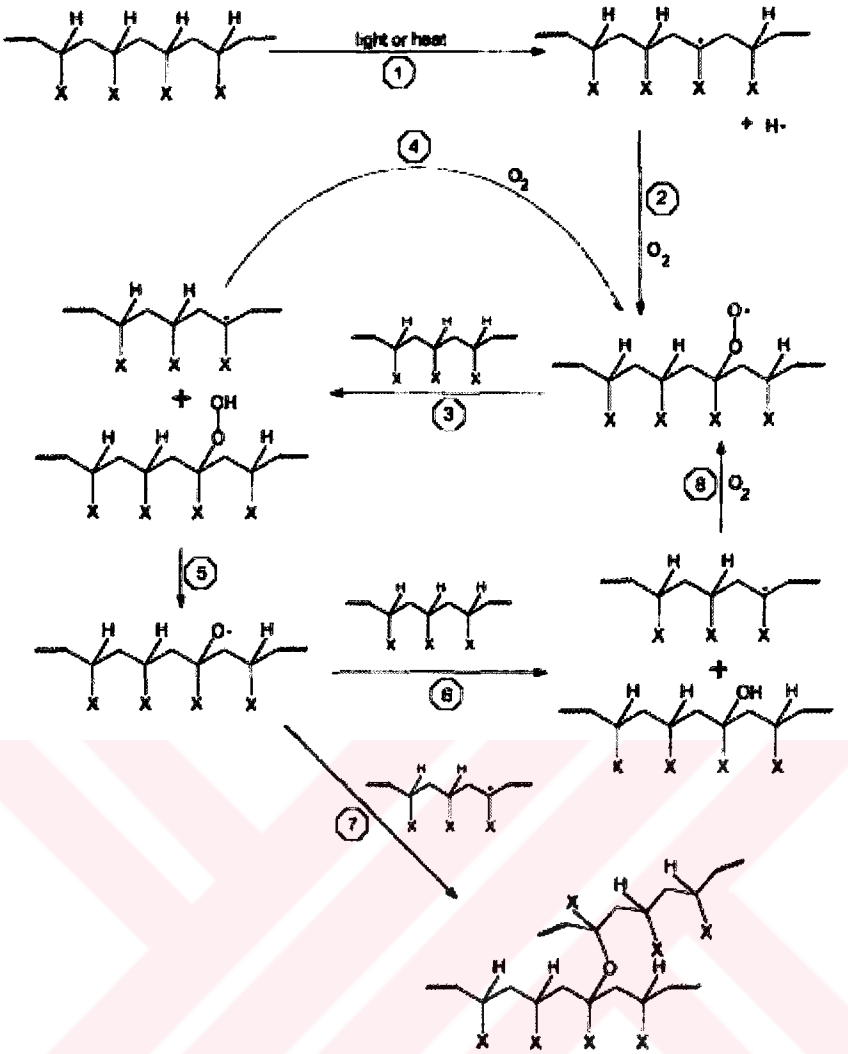


Figure 2.5 The formation of the alkyl radical and the thermo-oxidative degradation mechanism **(Waldman and De Paoli, 1998).**

One reason for the formation of weak sites against thermo-oxidative degradation is secondary crystallization (post-crystallization) **(Schwarzenbach et al., 2001).** It is the process in which crystals continue to grow after the polymer has been molded. Semi-crystalline polymers that are heated above their T_g (glass transition temperature) are the ones that face secondary crystallization. This process leads to localized densification, which then creates areas of stress in amorphous regions connecting adjacent spherulites. These localized areas of stress are attacked thermo-oxidatively, initiating the degradation.

Among the main products of auto-oxidation of linear saturated polymers are hydroperoxides and their decomposition products. For polypropylene formic acid, acetic acid and acetone were found as the major volatile products **(Schnabel, 1992; Commereuc et al., 1996).**

2.3.2. Thermal Degradation

If the temperature is high enough, impurities or additives present in the polymer matrix may react with the polymer itself, causing chemical changes. Therefore, thermal degradation refers to the situation where the polymer, at elevated temperatures, starts to undergo chemical changes not because of another compound but because of its own components. Once free radicals are formed, they readily react with molecular oxygen that is found in the surrounding or as in molten state in the polymer matrix, which is referred to as thermo-oxidation.

2.3.3. Chemical Degradation

This type of degradation refers to processes, which are induced under the influence of chemicals such as, acids, bases, solvents and reactive gases **(Schnabel, 1992)**. A significant conversion is only seen at elevated temperatures because the reaction activation energy for this process is high.

2.3.4. Mechanical Degradation

Polymer processing occurs at temperatures above the crystalline melting temperatures of polymers. Because of their macromolecular structure polymers have high melt viscosities. Therefore, processing these materials, conveying or shaping, requires the application of pressure. The resulted shear induces degradation especially at points of high flow resistance.

Polymer bond ruptures are frequently seen in stress-induced processes. The scission of bonds and alkyl radical formation by the effect of shear is shown below, in Figure 2.6.

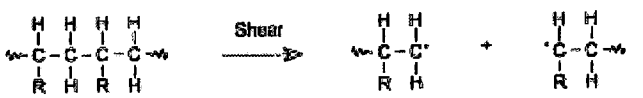


Figure 2.6 Formation of alkyl radicals during processing by the effect of shear forces **(Schwarzenbach et al., 2002)**

2.3.5. Light-induced Polymer Degradation

Light-induced polymer degradation (photo-oxidation), refers to the physical and chemical changes caused by the exposure of polymers to UV or visible light. For the initiation of photochemical reactions, the presence of chromophoric groups in the

polymer or in the additives is adequate. Photo-oxidation is in fact, a combined effect of both light and oxygen. The effect of sunlight in the presence of oxygen in air is the main concern in photo-oxidation. Because in the presence of oxygen, alkyl radicals formed on the polymer backbone are converted into peroxy radicals and then into hydroperoxides. This formation leads to chain scissions and molecular mass decreases.

The formation mechanism of hydroperoxides in polypropylene matrix is shown in Figure 2.7, where PH stands for the polymer itself.

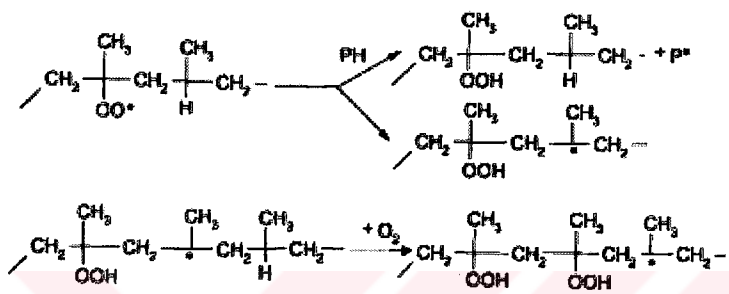


Figure 2.7 Formation mechanism of polypropylene hydroperoxides **(Gugumus, 2001)**

After a period of exposure to UV radiation, the chromophore groups become photo-chemically active. As a result of photo-oxidation macroalkoxy radicals and hydroxyl radicals are formed.

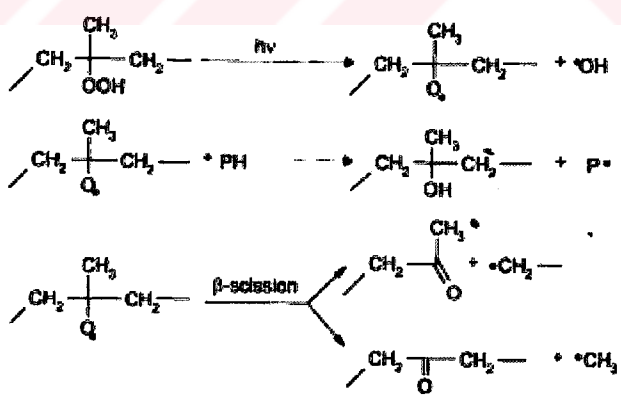


Figure 2.8 Photo-oxidation of polypropylene under the influence of oxygen **(Gugumus, 2001)**

Therefore, UV stabilization of a polymer is mandatory when there is outdoor application. But two major problems may arise in the usage of UV stabilizers. The first one is related to the impurities possibly contained in the filler. They may act as sensitizers for photo-oxidation. This is particularly true for transition metals.

Because of this, the fillers chosen should be as pure as possible. The second problem is the deactivation of the stabilizers by the filler. This is caused by the adsorption of the polar stabilizers on the filler surface. This physical effect can be reduced considerably by addition of a certain amount of polar substances into the polymer matrix **(Gugumus, 2001)**.

2.4. Detection of Degradation

Degradation in polymers can be detected by observing the changes in the molecular size, physical appearance, chemical and mechanical properties. Being able to detect degradation is an important parameter for checking the stabilizer efficiency and understanding the mechanism of action of radicalic species formed.

2.4.1. Changes in Molecular Size and Structure

In the detection of degradation, determination of molecular size plays an important role in linear soluble polymers. Molecular weight (MW) and molecular weight distribution (MWD) are important properties that characterize a polymer. Mechanical properties depend on molecular weight, too. A decrease in polymer molecular weight causes a gradual reduction of mechanical properties. Melt flow index (MFI) or a gel permeation (GPC) chromatogram can easily show the changes in MW. Other mostly used analytical techniques are differential thermal analysis (DTA), and differential scanning calorimetry (DSC). Using DSC instrument oxygen induction time (OIT) can be measured which is considered as a major parameter for detecting degradation.

2.4.2. Changes in Physical Appearance

Due to thermal-oxidation, polymeric material may show discoloration from yellow to brown stains. Even when a stabilizer is used some discoloration can be seen because as well as the polymer itself, the stabilizer can be oxidized, too **(Pospisil et al., 2002)**.

2.4.3. Changes in Chemical Properties

Under the influence of solvent, reactive gases or radiation chemical properties of polymers might change. These changes are observed with spectroscopic methods such as, infrared (IR) and ultraviolet (UV), especially to detect the formation or

disappearance of chromophoric groups. Nuclear magnetic resonance (NMR), and electron spin spectroscopy (ESR) are also helpful methods for analyzing polymers **(Schnabel, 1992)**. ESR measurements allow the detection and identification of free radicals, such as peroxyl radicals in polypropylene, which have lifetime estimation of 10^{-2}s, but owing to their short lifetime less than 10^{-8}s alkoxyl radicals cannot be detected. But as a whole ESR is very useful in detecting the mechanism of action of degradation and degradation products.

2.4.4. Changes in Mechanical Properties

Degradation of polymers cause some decrease in the mechanical properties. Resistances to stress and strain values are decreased because the bonds get weaker after degradation. The polymeric material becomes more brittle.

2.5. Inhibition of Autoxidation

The oxidative degradation of polymers can be inhibited by the use of suitable stabilizers called antioxidants. They are added to the polymer in amounts of up to 2% w/w during processing. One from many ways of inhibiting oxidation is to use radical scavengers, which trap carbon centered radicals. But the attack of molecular oxygen to the carbon-centered radicals is a fast reaction (10^7 to 10^9 $mol^{-1}s^{-1}$), **Schwarzenbach et al. (2001)**, thus this reaction cannot be completely avoided. On the other hand peroxy radicals, $ROO^{\bullet}$, react with hydrogen donating antioxidants forming the relatively stable hydroperoxides (ROOH).

$ROO^{\bullet} + RH \xrightarrow{k_3} ROOH + R^{\bullet}$ (Reaction Step1)

$ROO^{\bullet} + InH \xrightarrow{k_2} ROOH + In^{\bullet}$ (Reaction Step2)

$In^{\bullet} + RH \xrightarrow{k_1} InH + R^{\bullet}$ (Reaction Step3)

Figure 2.9 Inhibition reactions of H-donors **(Schwarzenbach et al., 2001)**
(For detailed explanation about k_1, k_2 and k_3; see Section 2.6.1.1.)

In the coarse of degradation, to avoid any chain branching resulting from the formation of alkoxy $R^{\bullet}$ and hydroxyl $HO^{\bullet}$ radicals, hydroperoxide decomposers are used.

2.6. Stabilization & Stabilizers

Stabilization is mandatory to protect the polymeric material from the attack of free radicals. Stabilization process is the addition of special chemicals (additives), which are referred to as stabilizers that help to inhibit degradation.

Stabilizers are used to protect polymeric materials mainly against the attack of free radicals formed thus, inhibit degradation. Stabilizers are generally added to the polymer during processing, i.e., extrusion, injection molding. But some amounts of primary stabilizers such as antioxidants can also be added at the polymerization stage. Stabilizers are classified into three main groups according to their modes of action. These groups are listed below:

Antioxidants:

- Primary antioxidants:
    - Hydrogen Donors (H-donors)
    - Alkyl Radical Scavengers
- Secondary antioxidants:
    - Hydroperoxide Decomposers (HD)
- Metal Deactivators

Light Stabilizers:

- Light screeners
- UV absorbers
- Quenchers

Acid Scavengers

A table of selected commercial stabilizers consisting of some types of the additives mentioned above is shown in Table 2.2. Their chemical as well as commercial names, properties, and application guides are included, too.

Table 2.2 List of properties of some selected commercial stabilizers

Chemical Name	Comercial Name	Properties	Guidelines for use
Dioctadecyl 3,3'-thiodipropionate	**Irganox PS 802** **Ciba Spec. Chem.**	Thiosynergist heat stabilizer used in combination with a primary phenolic antioxidant provides longterm heat stabilization. Low volatility- relatively low odor.	In general Irganox PS 802 can be used to improve the long-term heat stability of polymers at recommended levels of 0.005-1%
1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione	**Irganox 3114** **Ciba Spec. Chem.**	Phenolic primary antioxidant for processing and long-term thermal stabilization. (3 functional phenolic groups). Blends with Irgafos 168 or with Irgafos 168 and HP-136 are noteworthy.	In polyolefins, levels range btw. 0.05-0.3% depending on substrate, processing conditions, stability requirements. Optimum level is application specific.
Pentaerythriol Tetrakis(3-/3,5-di-tert-butyl-4-hydrophenyl)-propionate)	**Irganox 1010** **Ciba Spec. Chem.**	Phenolic primary antioxidant for processing and long-term thermal stabilization. Prevents thermo-oxidative degradation during service life. (4 functional phenolic groups). Blends with Irgafos 168 or with Irgafos 168 and HP-136 are noteworthy.	In polyolefins, concentration levels range between 0.05-0.4% depending on, substrate, processing conditions, stability requirements. Optimum level is application specific.
Tris(2,4-ditert-butylphenyl)-phosphite	**Irgafos 168** **Ciba Spec. Chem.**	Hydrolytically stable phosphate processing stabilizer. As a secondary antioxidant it reacts with hydroperoxides formed by autooxidation. Prevents discoloration. Performs best when combined with other antioxidants. Blends of Irgafos with Irganox range and Lactone H136 type are particularly effective.	Typically 500-2000 ppm is combined with appropriate levels of other additives. Optimum level is application specific.
50% Irgafos 168 ; 50% Irganox 1010	**Irganox B225** **Ciba Spec. Chem.**	A processing and long-term stabilizer system – is a synergistic blend. Addresses applications requiring more long-term thermal stability. Effectively used in polyolefins-PP,PE. Advantages are; maintanance of original melt flow, low color formation, improvement of long-term thermal stability	In polyolefins, the concentration levels range typically between 0.1-0.25% depending on substrate and processing conditions. Optimum level is application specific.
57%Irgafos 168 ; 28%Irganox 1010, 15% HP-136	**Irganox HP2215** **Ciba Spec. Chem.**	High performance melt processing stabilizer system. Lactone HP-136 acts as a C-centered radical scavenger.	In recommended applications concentration levels range btw. 0.05-0.15%
1,3,5-Triazine-2,4,6-triamine,N,N'''-[1,2-ethane-diyl-bis[[[4,6-bis-[butyl(1,2,2,6,6-pentamethy-4-piperidinyl)amino]-1,3,5-triazine-2-yl]-3,1-propanediyl]]bis[N',N''-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-	**Chimassorb119FL** **Ciba Spec. Chem.**	Monomeric Hindered Amine Light Stabilizer(HALS). It's also effective as antioxidant and contributes significantly to the long term heat stability of polyolefins. Particularly effective in PP, PE. Benefits are, improved melt flow control, low initial color& maintanence, superior effectiveness at high processing temperatures, lower use levels leading improved additive compatibility.	**Thick sections :** 0.15-0.5% **Fibers:** 0.05-1.0.%

2.6.1. Antioxidants

These types of stabilizers protect the polymer by scavenging or inhibiting the free radicals. The two types of antioxidants are primary and secondary antioxidants. Hydrogen donors and carbon centered radical scavengers are denoted as primary antioxidants while hydroperoxide decomposers are referred to as secondary antioxidants. Antioxidants must satisfy some requirements so as to provide efficient protection. The physical loss of stabilizers from the polymer matrix must be minimal; also antioxidants used must have molecular weights greater than 700g/mol so as to avoid the migration to the polymer surface **(Schwarzenbach et al., 2001)**. The properties of an efficient antioxidant studied further by **Schwarzenbach et al. (2001)** can be listed as shown below:

- Ability to reach polymer's attacked sites through diffusion in viscous melt.
- Compatibility in the polymer.
- Solubility in solid polymer.
- Low volatility.
- Resistance to extraction into the environment.

2.6.1.1. Hydrogen Donors (H-donors)

Once the peroxy radicals are formed, they abstract hydrogen from the polymer backbone, which is the rate-determining step in the auto-oxidative degradation **(Schwarzenbach et al., 2001)**. As a result of this reaction they form relatively stable, polymer-bound hydroperoxide as shown in reaction step 1 in section 2.5. What H-donors do is to offer the peroxy radical a more abstractable hydrogen, which is denoted as lnH in reaction step 2. By this way the abstraction of hydrogen from the polymer backbone can be avoided up to a large extent. The reaction rates calculated for reaction steps 1 and 2 do have a relationship of $k_2 >> k_3$. A suitable H-donor doesn't react further by the abstraction of hydrogen from the polymer backbone. This is because of the $k_1 << k_2$ relationship between the reaction rates of steps 1 and 3.

Among the H-donors lie sterically hindered phenols, alkyl amines and aromatic amines. However, aromatic amines are preferred to alkyl amines because of steric hindrance.

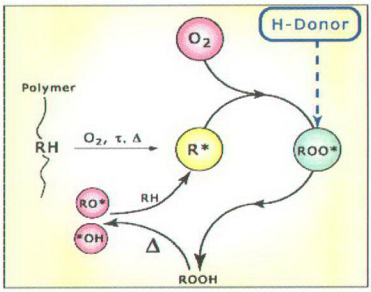


Figure 2.10 The schematic diagram showing the utility of H-donor in degradation cycle. **(www. specialchem4polymers.com/tc/Antioxidants)**

The figure 2.10 describes the action mechanism of H-donors after the alkyl radical is formed. The presence of molecular oxygen, heat and light cause the formation of the first free radical. In the presence of oxygen alkyl radical turns into peroxy radical and this is where H-donors give their phenolic hydrogen to obtain hydroperoxides. Exposure to elevated temperature may cause this compound to decompose into $RO^{\bullet}$ and $HO^{\bullet}$ radicals, which provide this degradation cycle to move further on.

a) Aromatic Amines:

Secondary aromatic amines and diamines have been used as antioxidants for a long time. But they discolor and stain the end product; therefore their application in the plastic industry is rather limited **(Schwarzenbach et al., 2001)**. The chemical structure of an aromatic amine is given below.

Figure 2.11 An aromatic amine donating a peroxy radical with hydrogen **(Schwarzenbach et al., 2001)**

b) Phenols:

Phenolic antioxidants are the most widely used type of stabilizers. The phenoxy radical is quite stable because of the steric hindrance of the substituents in the 2,6-position. Phenolic antioxidants are used for long term heat protection throughout the

service lifetime of the plastics as well as the stabilization of polymer melts during processing **(Schwarzenbach et al., 2001)**. They interfere in the primary oxidation but they are consumed in the stabilization process. A hindered phenolic structure is shown below:

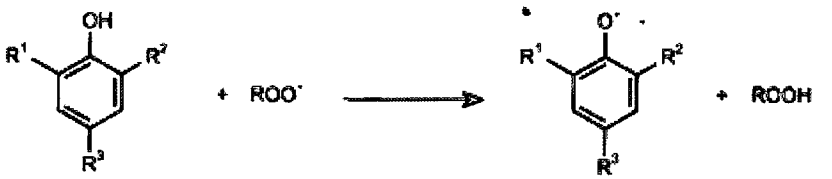


Figure 2.12 A sterically hindered phenol donating peroxy radical with hydrogen **(Schwarzenbach et al., 2001)**

The degradation shows itself in many ways, such as the weakening of mechanical properties and discoloration. Some antioxidants contribute to this effect. Not only the degraded polymer itself, but also the degradation products of phenolic antioxidants may cause this color formation.

Quinone structures, which are the degradation products of phenolic antioxidants, are mainly responsible for the color formation in a polymer article. It is assumed that for sterically hindered phenols, the first step is the donation of the phenolic hydrogen to a radical species. The second step is the donation of an α- or benzylic-hydrogen, leading to the formation of quinone **(Barret et al, 2002)**. In Figure 2.13 the donation of the phenolic hydrogen and resonance structures of the sterically hindered phenolic antioxidant are shown.

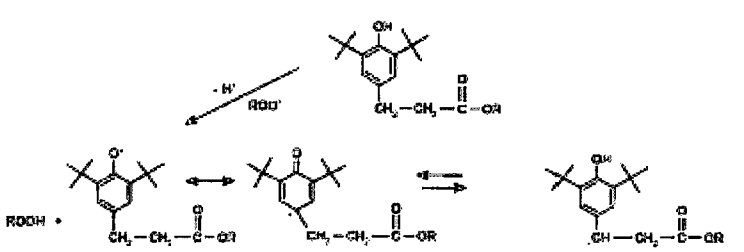


Figure 2.13 Donation of a phenolic hydrogen and the proceeding resonance structures **(Schwarzenbach et al., 2001)**

The reactions of the phenoxyls do not end up here. Phenoxy radicals with a H-atom on the C-atom vicinal to the phenyl group in 4-position can undergo a disproportionation reaction, resulting in the formation of a initial phenol and a quinine methide. Quinone methides (QM) also react with alkyl, alkoxy and peroxy

radicals. But far from inhibiting auto-oxidation they are rather retardants for oxidation reactions **(Pospisil et al. 1996a), (Pospisil et al. 1996b)**. The reactions of phenoxy radicals with alkyl and peroxy radicals and the disproportionation reaction of two phenoxyls are shown in Figure 2.14.

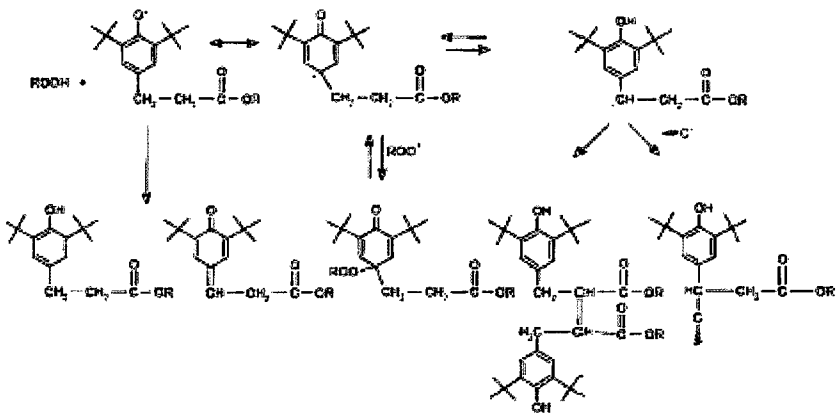


Figure 2.14 Reactions of phenoxy radicals **(Schwarzenbach et al., 2001)**

2.6.1.2. Hydroperoxide Decomposers (HD)

Hydroperoxides are transformed into non-radical and thermally stable products by hydroperoxide decomposers.

Hydroperoxides are generally used in combinations with hydrogen donors such as phenolic antioxidants. Among the widely used hydroperoxide decomposers lie compounds of trivalent phosphorus and sulfur.

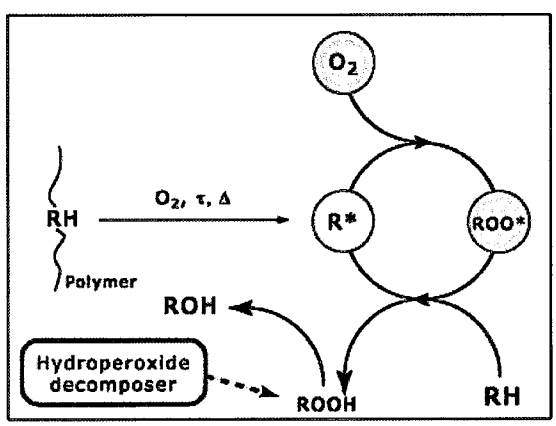


Figure 2.15 The schematic diagram showing the working mechanism of hydroperoxide decomposer in degradation cycle **(www. specialchem4polymers.com/tc/Antioxidants)**

In this figure the combined effect of hydroperoxide decomposers and H-donors are described. The degradation process proceeds as it is explained in Figure 2.10 but

instead of the decomposition reaction of hydroperoxide into $RO^{\bullet}$ and $HO^{\bullet}$ radicals, which will keep the degradation going, hydroperoxide is reduced to alcohol in the presence of hydroperoxide decomposers**(Schwarzenbach et al., 2001)**.

a) Phosphites/Phosphonites:

Phosphites or phosphonites are widely used in combinations with antioxidants as processing stabilizers, decomposing hydroperoxides. After polymerization, most plastics are pelletized and shipped to compounders, polymer converters and subsequently manufacturers of the final plastic article. During this process, the polymer undergoes several processing steps, which usually involve extrusion of molten polymer. Each processing step causes degradation, a result of the combined effect of shear, heat and oxygen. Processing stabilizers are antioxidants that are incorporated into the polymer to prevent degradation during processing. Degradation may show itself in two ways **(Schwarzenbach et al., 2001)**, which are shown below:

- Decrease in the molecular weight of the polymer (chain scission),
- Increase in the molecular weight of the polymer due to recombination reaction.

Both types of reactions take place simultaneously, but one or the other will predominate depending on the processing conditions, the molecular structure and the polymerization technology used to initially manufacture the polymer. Optimal stabilization is achieved when the initial molecular weight of the polymer is maintained during processing.

As processing stabilizers, phosphates or phosphonites are widely used in combination with sterically hindered phenolic antioxidants. They contribute to stabilization by decomposing hydroperoxides into non-reactive, non-radicalic species, as well as, inhibiting the color formation in the polymer article because of the degradation of phenolic antioxidant itself.

The sensitivity of phosphites/phosphonites to hydrolysis causes some problems such as the corrosion of metallic processing equipment **(Schwarzenbach et al., 2001)**. Alkylated aromatic group possessing phosphites are preferred because they are more stable than the phosphates containing alkyl groups. The suggested mechanism of action of a phosphorus based hydroperoxide decomposer is shown in Figure 2.16.

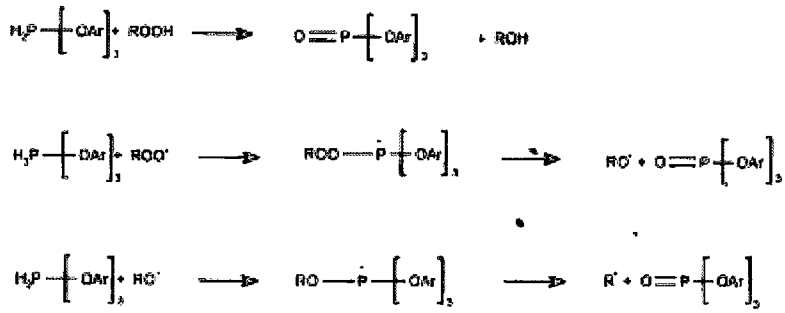


Figure 2.16 The decomposition reaction of a hydroperoxide decomposer of the trivalent phosphorus type **(Schwarzenbach et al., 2001)**

b) Thiosynergists:

These are sulfur based hydroperoxide decomposers. They do not improve the melt stability of polymers during processing. **(Drake et al, 1993)** But they are efficient for long-term thermal stability at temperatures of 100-150°C, in contrast to phosphorous-based hydroperoxide decomposers. Sulfur based hydroperoxide decomposers are generally used in combination with phenol antioxidants.

2.6.1.3. Alkyl Radical Scavengers

Alkyl radicals practically react with molecular oxygen without activation energy **(Schwarzenbach et al., 2001)**. The reaction occurs at approximately the same rate at any temperature forming peroxy radicals, which are the reasons for chain scissions in polymers during degradation. Therefore, scavenging alkyl radicals would immediately stop autoxidation. But because of the high reaction rate of alkyl radicals with molecular oxygen, it is hard to compete with this reaction using any kind of carbon-centered radical scavengers. Figure 2.17 shows how radical scavengers take part in inhibiting degradation process.

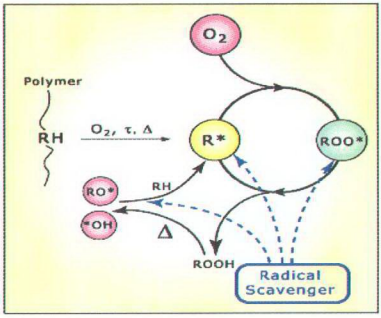


Figure 2.17 The schematic diagram showing the action mechanism of a radical scavenger **(www. specialchem4polymers.com/tc/Antioxidants)**

Hindered amine stabilizers (HAS); hydroxyl amines, benzofuranone derivatives and acryloyl-modified phenols, are not only effective in long-term thermal stability but they also act as radical scavengers **(Schwarzenbach et al., 2001; Schwetlick and Habicher, 2002)** . They are not consumed in the stabilization process, they are not capable of interfering in the primary oxidation but they are active in the secondary step in which they prevent the acceleration of oxidation. The chemical structure of a benzofuranone derivative alkyl radical scavenger is given below:

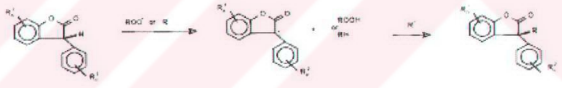


Figure 2.18 Scavenging of radicals by a benzofuranone derivative radical scavenger **(Schwarzenbach et al., 2001)**

Hydroxyl amines are in fact multifunctional. As well as decomposing hydroperoxides, they scavenge carbon-centered radicals, too **(Voigt and Todesco, 2002)**. Hydroxyl amines are especially used in color critical cases. To provide the polymer with long-term thermal stability they are used in combination with HALS: The mechanism of action of hydroxylamines, are shown in Figure 2.19.

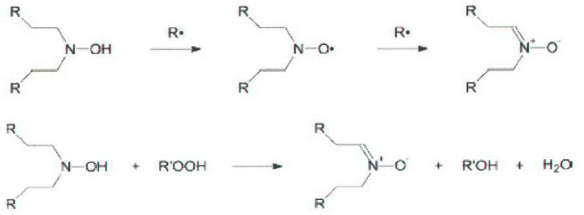


Figure 2.19 Free radical and hydroperoxide decomposition mechanisms of hydroxyl amines **(Voigt and Todesco, 2002)**

2.6.1.4. Metal Deactivators

Trace quantities of metal ions catalyze oxidation process in polymers. Metal ions that might come from impurities in the polymer matrix, mainly from the catalysts used during synthesis or from the processing equipments catalyze the decomposition of hydroperoxides. As a result, reactive radicals are formed as shown in Figure 2.20.

Figure 2.20 The decomposition of hydroperoxides in the presence of metal ions **(Schwarzenbach et al., 2001)**

To deactivate these metal ions, metal deactivators are used. These compounds form stable complexes with the metal ions, thus the stability of polymers is improved.

2.6.2. Light Stabilizers

Light-induced damage to polymer is up to a great extend due to free radical oxidative chain reactions. Therefore antioxidants, which are of the chain terminator type, act also as photo-stabilizers **(Gugumus, 2001)**. Luminescence techniques are in application for the detection of low concentrations of UV-light absorbing impurities in transparent polymers such as polypropylene. These impurities can be on the main chain or at side groups, as well as, being distributed randomly without being chemically bound to the polymer matrix. Owing to their ability to absorb

light, they play an important role as initiators for photochemical degradation processes.

Photo-stabilizers are usually classified according to their mode of action. There are listed below:

- Light screeners
- UV absorbers
- Excited state quenchers
- Antioxidants

2.6.2.1. Light Screeners

For protecting articles from light absorption painting is not applicable when the particle is a polymer. It is because of the incompatibility of most polymers with dyes. On the other hand, the use of pigments, perform quite well, because most pigments absorb not only visible light but also UV radiation **(Schnabel, 1992)**. What's more light absorption in pigmented polymers is only limited to a thin surface layer, leaving the layers beneath the surface unaffected. Pigments like, carbon black, ZnO, MgO, Fe_2O_3 are used as light screeners. But the application of pigments is limited because of the compatibility problems that might occur in many cases.

2.6.2.2. UV Absorbers

The mechanism of action of UV absorbers is based on the absorption of UV radiation and its dissipation in a way that doesn't lead to photosensitization, such as dissipation as heat. As well as having high absorption themselves, UV absorbers must be very stable to light, because if not they would be consumed very fast in the polymer matrix. The major disadvantage of these stabilizers is that they need a certain sample thickness (absorption depth) for optimal protection of a plastic article. In **Gugumus (2002a)** this relation between sample thickness and UV absorption, is explained by Lambert-Beer's law.

Turton and White (2001) also investigated the depth profiles in 3mm thick PP moldings containing stabilizer, pigment (TiO_2) and both. It was seen that the addition of pigment to the polymer caused degradation to fall to minimal levels in both stabilized and unstabilized polypropylene. They also speculate that, at the

beginning of UV exposure the predominating reaction is the chain scission at all depths. Reaction in the interior is due to the pre-existing concentration of oxygen. The oxygen diffusing through the polymer cannot reach the center because it is rapidly consumed at the surface and just below. They concluded that, in stabilized polypropylene samples the level of degradation is uniform at all depths. On the contrary, in unstabilized polypropylene the degradation is more severe at the surface than at the interior parts of the polymer sample. This is explained by the reduction of oxidation process in the presence of stabilizer. In this case, the consumption of oxygen at the surface will be lower; therefore oxygen can diffuse through the interior parts of the polymer making degradation more possible than that of unstabilized polypropylene.

Benzophenone and benzotriazole derivatives are mostly used as UV absorbers. The chemical structures are shown below in Figure 2.21 and 2.22.

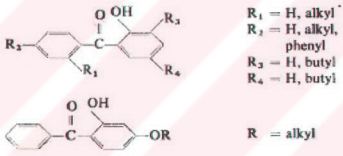


Figure 2.21 2-Hydroxy-benzophenones **(Schnabel, 1992)**

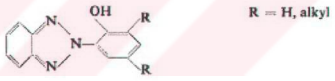


Figure 2.22 Benzotriazoles **(Schnabel, 1992)**

2.6.2.3. Quenchers

These light stabilizers take over the energy absorbed by the chromophore groups present in the polymer and dispose of it to prevent degradation as shown in Figure2.23.

$(Ch) + h\nu \longrightarrow (Ch)^*$ (reaction step 1)

$(Ch)^* + Q \longrightarrow (Ch) + Q^*$ (reaction step 2)

$Q^* \longrightarrow Q + \text{heat}$ (reaction step 3)

$Q^* \longrightarrow Q + h\nu'$ (reaction step 4)

Figure 2.23 The mechanism of quenching **(Schnabel, 1992)**

The energy can be dissipated in two ways: as heat or as fluorescent or phosphorescent radiation (Reaction Step 3 and 4).

The action of quenchers is independent of sample thickness. Thus, they can stabilize thin articles such as films. Quenchers currently in use are complexes or chelates of transition metals. Nickel chelates are the most commonly used quenchers. An example of a nickel chelate quencher is shown in Figure 2.24.

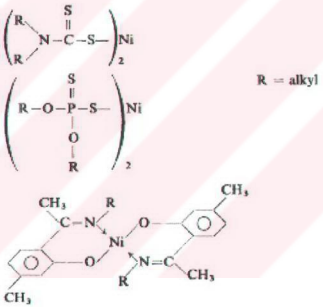


Figure 2.24 Examples of nickel chelates acting as quenchers **(Schnabel, 1992)**

2.6.2.4. Antioxidants

Hindered amine light stabilizers (HALS) are among the most commonly used light stabilizers that are of antioxidant origin. There are two approaches to the action mechanism of HALS. One is related to the nitroxyl radical and the other is related to kinetics of stabilization, stabilizer loss and degradation product formation **(Schwarzenbach et al., 2001)**.

2.7. Acid Scavengers

Acid scavengers are the third group of products added to polyolefins in addition to antioxidants and process stabilizers. Acid scavengers are also referred to as antacids or co-stabilizers. They contribute to the overall performance of polymers. There are several basic criteria that acid scavengers have to meet **(Holzner and Chmil, 2001)**:

- High purity
- Thermal stability
- Appropriate price-performance ratio
- Compatibility with the polymer matrix
- Melting point below polymer processing temperatures
- Particle size that enable optimum dispersability

During polymerization of polyolefins, the use of catalysts, such as Ziegler-Natta catalysts present a problem in that acidic products remain in the polymer. Polyolefins polymerized by Ziegler-Natta catalysts contain halogen components in the low ppm range. These catalyst residues remaining in the polymer matrix may cause problems due to their acidity. Therefore, co-stabilizers, usually acid acceptors such as metal stearates (calcium stearate, zinc stearate); inorganic oxides (CaO, MgO), carbonates ($CaCO_3$) and lactates are used to neutralize these acidic residues **(Holzner and Chmil, 2001)**. When stearates are used, their fatty properties modify the polymer with water repellency and lubricity, as well as, the scavenging of acids. Therefore, stearates give resins a certain amount of lubricity, leading to some mold release and slip properties. Inhibiting the increasing level of acidity in the matrix protects the polymer from discoloration as well as preventing mold corrosions. Acid scavengers do not improve the processing stability in polyolefins. The effects of acid scavengers on discoloration do not follow uniform rules, so for every application experimental study is needed.

2.8. Fillers

Fillers are relatively cheap, solid substances that are added in rather high percentages to plastics, to adjust volume, weight, cost and technical performance. They must interact with the base material, in other words the filler surface has to come more or less in close contact with the polymer matrix.

Fillers for plastics are divided basically into two groups: inactive or extender fillers and active fillers which are also referred to as functional fillers. Inactive fillers are used mainly to reduce cost, while functional fillers modify special properties of the polymer, such as surface, color, density, shrinkage, expansion coefficient, conductivity, permeability, mechanical and thermal properties; supplying it with the necessary requirements demanded of the polymeric article. Most fillers increase the modulus and the tensile yield strength and decrease the elongation at break. However, increased stiffness causes decreased toughness, which is determined by impact tests. These results have also been confirmed in the studies of **Silva et al., (2002)**. They also conclude that, at low filler concentrations because of the good dispersion in PP matrix, a better interaction of the filler thus, better mechanical properties are achieved. On the contrary, at high filler concentrations, by the tendency to form agglomerates, resulting in poor interaction causes a decrease especially in impact strength.

However it is here noteworthy to say that, there's no filler that is completely inactive and reduces only cost. The effectiveness of a filler material depends on its type (particle size, particle size distribution and particle shape), loading and surface treatment. Some examples to fillers are calcium carbonate, talc, silica and kaolin.

Among the widely used fillers (approximately 70% of the world filler consumption, **(Walter, 2001)** lies natural calcium carbonate, $CaCO_3$, which is an extender filler. Many different forms are recognized, such as limestone, marble, calcite, chalk, aragonite and dolomite (calcium-magnesium carbonate). Among these calcite and chalk are the most commercially used forms. Some grades, surface treated with stearic acid are also obtainable. Calcite, the most stable type of calcium carbonate, might occur in different crystalline forms.

Both polypropylene homopolymer and copolymer accept $CaCO_3$ at loadings of 20 to 50% by weight **(Baker et al., 1987)**.

2.9. Nucleating Agents

Nucleating agents reduce cycle time during melt processing of semi-crystalline polymers, affect their physical properties and may increase the clarity of these materials. When they are used to improve the optical properties such as clarity and transmittance they are referred to as clarifying agents.

The semi-crystalline polymer molecules are arranged in a way that the polymer structure consists of both crystalline and amorphous parts. In semi-crystalline polymers, the crystalline phase consists of spherulitic segments, which are radially oriented crystalline lamellae. In between these lamellae there are molecules that connect adjacent lamellae, which are tie molecules. These molecules are considered to be the part of the amorphous region of the semi-crystalline polymer. Crystalline structure can be changed by various ways such as, heating of the polymer above its glass transition temperature and annealing. All changes in the crystalline structure affect the end properties of the polymer.

What nucleating agents do is to change the spherulite size to improve physical and optical properties. They also increase the rate of crystallization, therefore making the reduction of process cycle time possible.

Nucleating agents cannot affect the crystallization rate of all polymers because for a polymer to be sensitive towards nucleation, the rate of crystal growth shouldn't be too high or too low. Taking the crystallization rate into consideration PP is one of the easiest polymers to nucleate with an intermediate crystallization rate of 0,63 **(Kurja and Mehl, 2001)**.

There are some important properties ensuring an optimal performance of the nucleating agents. General features, which are indicatives of good nucleating agents, are listed below:

- Occupying both an inorganic and a polar group
- Good dispersion in the polymer
- Insolubility or ability to become insoluble in the polymer

On the other hand, a nucleating agent can be an impurity, an organic compound like benzoic acid or an inorganic compound like talc or pigments, a foreign polymer crystal or a diluent **(Kurja and Mehl, 2001)**.

Upon the addition of nucleating agent to a semi-crystalline polymer two effects are observed. Firstly, the overall rate of crystallization increases, thus a faster solidification of the molten polymer upon cooling is gained. This leads to shorter cycle times during injection molding.

Second, the average spherulite size decreases and this alters the mechanical and optical properties of the nucleated against non-nucleated material. Mechanical properties such as tensile strength, heat distortion temperature and hardness are increased, while the Izod impact strength may increase or decrease slightly. Because of the decreased spherulite size, the optical properties such as haze and clarity are also improved.

The method of evaluating the nucleating agent efficiency is to determine the crystallization temperature peak using DSC. Crystallization temperature is defined as the temperature at peak minimum during crystallization exotherm. The comparison of the crystallization temperature peaks of nucleated and non-nucleated PP is shown in Figure 2.25.

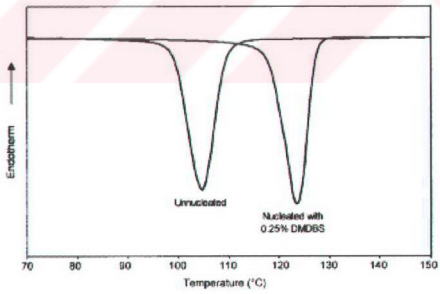


Figure 2.25 The comparison of crystallization peak temperatures of a nucleated and a non-nucleated polymer by DSC **(Kurja and Mehl, 2001)**

The abbreviation DMDBS in the figure stands for the initial letters of the chemical structure: diparamethyldibenzylidene sorbitol, which is also a commercial and widely used product.

2.10. Synergism of Stabilizers

In the coarse of degradation many reactions involving free radicals have to be dealt with. Therefore, different kinds of stabilizers like, antioxidants, hydroperoxide decomposers, process stabilizers and radical scavengers are used. As it might well be understood, one individual stabilizer is not enough to overcome all these reactions. Blends of additives containing two or three types of stabilizers are favored because the interactions between themselves as well as the polymer itself result in higher performance than expected.

If the effect of two combined stabilizers is more than the sum of the effects of each individual stabilizer, then this is referred to as synergism. The opposite of this situation is called antagonism, where the effect of the two combined stabilizers is less than the sum of the effects of each individual stabilizer. When the total effect of stabilizers is equal to the sum of the separate effects of stabilizers, then this is only the additive effect. These concepts related to the interactions of more than one stabilizers used in polymer compounds can be seen in Figure 2.26.

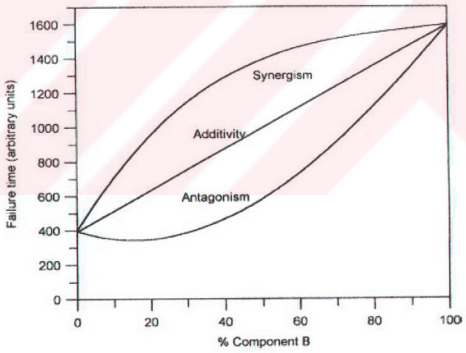


Figure 2.26 The synergistic, antagonistic and additive effects of two components A and B **(Gugumus, 2002a)**

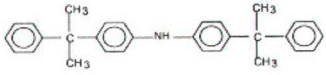
Synergism of stabilizers in polymer matrices is a widely studied subject. Nevertheless, general conclusions cannot be made because synergistic effects vary according to the polymer grade used and process conditions. Therefore, for each stabilizer system any effect of synergism is decided after the test results.

Gugumus (2002a) investigated the synergism or antagonism between two hindered amine light stabilizers (HALS) by examining one single combination of the two HALS. He claimed that 1:1 combination of the two components give the most reliable results and the results obtained in one PP type were valid with all the PP types so far available and polyolefins in general. He concluded that the combinations of high and low molecular mass HALS give synergism more often than combinations of two low molecular mass HALS. This has been explained by the complementary effects resulting from diffusion of the low molecular mass HALS to the surface layers while the high molecular mass HALS resists to migration and extraction, remaining deep in the polymer matrix.

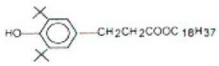
Gugumus (2002b) investigated the synergism between light stabilizers, especially UV absorbers in polyolefins. He claimed that the effects depend on the particular combination and the particular polyolefin. He concluded that the combinations of two UV absorbers could be synergistic or antagonistic or just shows additive effects depending on the particular PP used. One broad conclusion is that when one of the components is an oxanilide strong synergism in PP is seen. However, the combinations between benzophenone and benzotriazole do not show synergism in PP but in PE depending on the particular polyethylene used.

Ohkatsu et al. (2003) investigated the chemical structure of phenolic antioxidants capable of trapping peroxy radicals. Due to new ortho-substituent effect, to enhance the number of trapped peroxy radicals, o-allylphenols were molecularly designed. They explored that some o-allylphenols can trap both alkyl and peroxy radicals, depending on the oxygen concentration of the surrounding atmosphere. They claimed that this structure is superior to other phenolics because of the fact that on the surface of the polymer peroxy radicals dominate for oxygen is abundant near the surface. On the contrary, alkyl radical formation proceeds on the inside where there is oxygen deficiency. They also discussed the alkyl radical trapping mechanism of phenols.

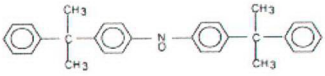
Shanina et al. (1999) investigated the synergistic effects of binary and ternary stabilizer systems used in polypropylene. Three different kinds of additives were studied, which were, an amine (1), a phenol (2), and a nitroxyl radical (3). The chemical structures of the stabilizers are shown in Figure 2.27.



1



2



3

Figure 2.27 The chemical structures of stabilizers used in this study. **(Shanina et al. 1999)**

The most important finding of this study is that the ternary system of these kinds of stabilizers can not give much better results than a binary one because the amine-nitroxyl radical has no synergistic effect. The phenol and nitroxyl radical seem to show the most synergistic effect. The 1:1 mixture of these stabilizers, show the maximum synergy effect regardless of the concentration. This is explained by the formation of some 1:1 complex of stabilizers, which is more effective to radicals.

Voigt and Todesco (2002) investigated new synergistic stabilizers systems for the better maintenance of melt flow rates, lower initial color and better color maintenance, increased long term thermal stability and light stability, enhanced additive compatibility and resistance to interactions with other additives. In this study phosphites-binary systems (phenolic antioxidant and phosphate) and lactone-ternary systems (phenolic antioxidant, phosphate and carbon centered lactone radical scavenger) are compared. They concluded that lactone systems are capable of trapping carbon-centered radicals; therefore auto-oxidation can be interrupted as soon as it starts. They also claim that phenol free lactone ternary systems with hindered amine light stabilizers are resistant against discoloration due to the absence of phenols.

Yamashita and Ohkatsu (2003) investigated the antagonism between hindered amine light stabilizers and acidic compounds including phenolic antioxidants. It was found that the hydroperoxide decomposition reaction by HALS is accelerated in the

presence of an acidic compound. It is also inspected that the decomposition reaction proceeds homolytically. Since processing of polymers is achieved under high temperatures, it is important to decompose hydroperoxides heterotycally as efficiently as possible. They concluded that the salts of HALS with an acidic, phenolic antioxidant might produce free radicals, which accelerate the decomposition of polymers. The role of HALS nitroxides in the decomposition of hydroperoxides is also discussed.

2.11. Melt Processing Stability

Polymers are converted into finished articles by various processing techniques, such as extrusion, injection molding and mixing. Three main factors affect rates of degradation in these processes: high temperature, shear forces and the unavoidable presence of oxygen. Processing not only affects physical properties of the polymeric material but also has an influence on its stability. To minimize these effects, process stabilizers must be used.

The effectiveness of a stabilizer can be best confirmed by multiple extrusions. When the stabilization is not enough the molecular weight of polymer will decrease due to chain scissions as a result of degradation **(Schwarzenbach et al., 2001)**. This decrease in MW will cause an increase in melt flow index (MFI). The choice of stabilizer can therefore be given after the MFI values at the end of several extrusions. Yellowness index (YI) is also another parameter, too. The color change in polymers, occur from the oxidation products of both the polymer itself and the phenolic stabilizer. These oxidation products like quinone methides contain chromophoric groups that lead to discoloration. Stabilizers referred to as processing stabilizers are the combinations of sterically hindered phenolic antioxidants and phosphites or phosphonates. Phosphates prevent chemical reactions of phenol during processing, avoiding the formation of oxidation products of phenols. For applications involving high temperature processing, the use of benzofuranone stabilizer is beneficial. Because during processing e.g., extrusion, the oxygen dissolved in the polymer matrix is consumed so rapidly that the diffusion of oxygen is not possible. As a result, the concentration of alkyl radicals, $R^{\bullet}$, is greater than that of peroxy radicals, $ROO^{\bullet}$. Alkyl radical formation also results from high shear forces in the course of processing **(Schwarzenbach et al., 2001)**. The formation of

the alkyl radicals during processing makes the use alkyl radical scavengers e.g., benzofuranone derivatives, an important parameter.

2.12. Long Term Thermal Stability (LTTS)

During their service time, most plastic articles are exposed to elevated temperatures, light and moisture. By diffusion of air, oxygen entrance takes place all the time resulting in thermo-oxidation (auto-oxidation in an oxygen-rich environment under elevated heat). The most important stabilizers for long-term thermal stability are sterically hindered phenols. Hindered amine stabilizers (HAS) are also used as long-term thermal stabilizers. They are preferred to phenolic antioxidants in some cases where discoloration must be avoided **(Schwarzenbach et al., 2001)**. Sterically hindered phenols can be used alone or in combination with hydroperoxide decomposers (HD) or thiosynergists. When phosphite based hydroperoxide decomposers are used together with phenolic antioxidants, HD protect the phenol during processing thus, leaving it ready for LTTS. However, they do not contribute to LTTS, for phenol concentration is effective on long-term thermal stability in polyolefins. Aliphatic amines are also used as long-term heat stabilizers for polypropylene. In the presence of HAS or antioxidants, they increase the thermo-oxidative stability of PP, due to their ability to react with aldehydes thus, preventing the formation of peracids. Several investigations are made to clarify this topic.

Gijsman and Gitton-Chevalier (2003) investigated the differences between the types of hindered amine stabilizers (HAS), concerning the presence of different types of aliphatic amines in their backbones. A new perspective is brought to a generally accepted mechanism, which suggests that the acceleration of oxidation reaction is due to the formation of hydroperoxides. It's found that the rate of radical formation in the decomposition of hydroperoxides is too slow to explain the auto-acceleration of oxidation reaction. Therefore, the auto-acceleration is thought to be due to the decomposition of peracids formed by the oxidation of oxidation products. They concluded that, especially primary and secondary amines that are able to prevent the formation of peracids by scavenging aldehydes are important groups that increase the thermo-oxidative stability of PP.

2.12.1. Testing Long-term Thermal Stability

Oven aging is the most used and simple method for measuring antioxidant effectiveness and the effects of thermo-oxidative degradation at a selected temperature. Changes in visual appearance, mechanical properties (embrittlement on bending, elongation, tensile impact) as well as physical properties (crystallinity) and chemical decomposition are examined periodically. Prior to oxidative degradation during oven aging, physical aging occurs, which shows itself with the changes in the crystallinity of the polymer. The changes in the crystalline structure of the polymer, also yields in the changes in mechanical properties. The decrease in the molecular weight is in correlation with the loss of mechanical properties, too. A reason to the decrease in mass is explained in the study of **Czégény et al. (2000)**, as the migration of the oxidation products to the surface and then their evaporation.

Although oven-aging technique is simple in concept and easy to perform, it has some disadvantages. When forced-air ovens are used, antioxidant losses because of evaporation might be seen. Contamination of ovens with antioxidants and their decomposition products is also another disadvantage. As a result, transfer of stabilizers in different combinations might occur, which affects the test results. The variety of ovens, sample holders, sample preparation techniques and different shapes of sample are other parameters that affect the test results. Therefore, for oven aging of PP standards such as, **ASTM D 3012-84** and **ISO 4577** are proposed.

Methods of detecting thermo-oxidative degradation are not only the observation of mechanical properties. Analytical methods such as IR are also used. Measuring the intensity of C=O absorption provides information about the level of degradation. The oven lifetimes of particular specimens are a function of a number of variables, which are listed below **(Schwarzenbach et al., 2001)**:

- Stabilizer/stabilizer system
- Stabilizer concentration
- Specimen thickness
- Test temperature
- Processing of test specimen (processing temperature and methods such as extruded or injection molded samples, processing stabilizer used)

- Definition of the end point

Considering all the parameters, oven-aging tests are performed to determine the efficiency of the stabilizer system against thermo-oxidation.

2.13. Pyhsical Properties of Additives

No matter what the end use of the polymer, all the additives used must satisfy some conditions **(Billingham, 2001)**:

- They must be capable of performing their intended functions, both chemical and physical
- While some are phase-separated, some form homogeneous solutions; e.g., a plasticizer must be soluble in the polymer high enough to modify the free volume, and a nucleating agent must be insoluble remaining as particles.
- They must be able to survive the chemical conditions of processing and service. Phenolic antioxidants cannot act as light stabilizers because they are photo-chemically destroyed. Also phosphite stabilizers used as process stabilizers are hydrolytically unstable. Therefore the possibilities of chemical losses must be well considered while designing the stabilizer system.

The two main reasons of the chemical losses are the migration and the evaporation (volatility) of additives. Solubility in the polymer is also another important parameter. Some research by **Földes (1998)** showed that, additives dissolve in the amorphous parts of the polymer. This has been explained by the molar volume differences between the polymer and the additives. The molar volume of additives is greater than the volume of the crystal unit cell of a polymer. Inhibiting the entrance of additives to the polymer crystal. This is considered to be an advantage because; oxygen doesn't enter the crystal phase. Thus, the stabilizers are accumulated at the regions where degradation occurs.

Solubility of additives is not only dependent on the structure of the polymer but also on its thermal history and density.

Diffusion of additives is critical to control the loss rates of additives. It controls how easily an additive can be extracted from polymer and dominates the loss by evaporation from thick samples. Diffusion of a polymer additive is the migration of

a molecule, which is many times larger than the polymer's repeating unit, through a matrix of polymer chains, whose motion is also restricted by the entanglements between chains. As being a kinetic parameter, diffusion is more complex than solubility and affected by many factors **(Billingham, 2001)** :

- Polymer morphology
- Temperature
- Polymer type
- Diffusant molecular weight

Crystallinity introduces twisted regions to the migration path through the polymer, and partly decreases the molecular mobility of the amorphous polymer. Filler particles, as well as, crystalline regions act as impermeable barriers to diffusion. Thus, in the presence of fillers diffusion slows down **(Billingham, 2001)**.

The temperature dependence of diffusion of additives in polymers is very complex. Up to an extent, the diffusion of phenolic antioxidants can be explained by the Arrhenius equation that is shown below.But the validity is rather limited.

$$D = D_o \exp(-E_d/RT) \qquad (2.1)$$

Diffusion is sensitive to both the motions of the polymer and the diffusant. The type of polymer is also effective in diffusion rate. It's particularly more rapid in the melt of a semi-crystalline polymer than below T_m and severely restricted below T_g.

One might conclude that, the main requirements for good retention of additives in a polymer are low volatility and high solubility **(Billingham, 2001)**. For thin samples, a low diffusion rate is favored. On the other hand, for thick samples a higher diffusion rate is better if the degradation takes place at the sample surface, or to prevent chemical or physical losses near the surface.

3. EXPERIMENTAL PROCEDURE

3.1. Materials

The polypropylene (PP) was HE125MO with the melt index of 12 g/10min. and the density of 908 kg/m^3, from Borealis, Austria.

Antioxidant mixture, (AO), which was a blend of a hydroperoxide decomposer, sterically hindered phenolic antioxidant and lactone based radical scavenger with the ratios of 57%, 28% and 15%, respectively, was supplied from Ciba Specialty Chemicals, Switzerland.

Two different types of nucleating agents were used in this study. One of them was of sodium salt origin, which is a nucleating agent for semi-crystalline polymers. The other one was of sorbitol origin, which is in fact a clarifying agent for polypropylene acting as a nucleating agent. These two nucleating agents were also supplied from Ciba Specialty Chemicals, Switzerland.

Calcium stearate VG-S, (CaSt), which was a vegetable grade stearate, was supplied from Ferro Corporation, Portugal, with a bulk density of 0,2-0,3g/cm^3 and with a fineness of 99% min. 325 mesh.

Calcium Carbonate ($CaCO_3$), non-surface-treated and with an equal spherical diameter of 5,5 microns, was supplied from OMYA Madencilik, Turkey.

3.2. Compounding Formulations

The filler percentage by weight was chosen according to the most appropriate price/performance ratio. A phenolic antioxidant and a phosphate based hydroperoxide decomposer was chosen because of their synergistic interaction and their relatively long term protection against oxidation. A radical scavenger was crucial for these formulations because of the conditions they were exposed during extrusion such as elevated heat and high shear. Two different types of nucleating agents were also thought to be appropriate to be included in any of the formulations

because of their ability to increase crystallization rate and crystallization temperature hence decrease the process cycle-time. Calcium stearate was used as the anti-acid to scavenge any acidic compounds that may generate because of the catalyst residues or any impurities in the polymer matrix.

To investigate the effects of two different nucleating agents and to determine any kinds of synergistic interactions, various formulations were prepared as shown in Table 3.1. To examine any synergistic effects between nucleating agents and the antioxidant mixture given in Section 3.1 in detail, a reference compound based on 40% $CaCO_3$ filled polypropylene, stabilized with the antioxidant mixture was selected. By the addition of the two types of nucleating agents one at a time to this reference compound with the ratios of 0,1 and 0,3%, four different formulations were also prepared. Nucleating agents with the same ratios were compounded with unstabilized polypropylene and filler at the same time. Any contributions of nucleating agents to the oxidation process of the polymeric material were aimed to be observed.The loading level of calcium carbonate filler was kept constant at 40% w/w in all formulations. As an acid scavenger calcium stearate was used in all formulations, at a level of 0,5% w/w.

In Table 3.1 following nomenclature is used: PP denotes the homopolymer polypropylene, HE125MO while; AO stands for the antioxidant mixture. S1 and S3 refer to the nucleating agent of sodium salt type with the ratios of 0,1 and 0,3% by weight, respectively. Similarly, C1 and C3 refer to the nucleating (clarifying) agent of sorbitol type with the ratios of 0,1 and 0,3% by weight, respectively. Acid scavenger calcium stearate is denoted as CaSt.

Table 3.1 Formulations

	Sample Name	PP (% by weight)	$CaCO_3$(% by weight)	CaSt(% by weight)	AO(% by weight)	N.A. of sodium type (% by weight)	N.A. of sorbitol type (% by weight)
Group 1	PPAO	59,2	40	0,5	0,3	-	-
	PPAOS1	59,1	40	0,5	0,3	0,1	-
	PPAOC1	59,1	40	0,5	0,3	-	0,1
	PP-S1	59,4	40	0,5	-	0,1	-
	PP-C1	59,4	40	0,5	-	-	0,1
Group 2	PPAOS3	58,9	40	0,5	0,3	0,3	-
	PPAOC3	58,9	40	0,5	0,3	-	0,3
	PP-S3	59,2	40	0,5	-	0,3	-
	PP-C3	59,2	40	0,5	-	-	0,3

3.3. Compounding Process in Twin-screw Extruder

3.3.1. Twin-screw Extruder

The extruder was a co-rotating (both screws turn in the same direction) twin-screw extruder; Leistritz MICRO 27, with a screw diameter of 27mm and with 44:1 L/D (shaft length/screw diameter). Twin-screw extruder machine data is given in Table 3.2.

Table 3.2 The machine data of twin-screw Leistritz Micro 27 extruder **(Leistritz Micro 27 Extruder User's Manual)**

Model	convertible from co- to counter-rotating
Axle base of screws	23mm
Screw diameter	27,0mm
Diameter of kneading discs and -blocks	27,0mm
Material of screw	12.379
Barrel diameter	27,2HB
Material of barrel E, 1-5 and 9-10 6-8	1.8550 nitrided; nitrided layer 0,5-0,6mm 12.379
Screw functionary lenght	44 D
Screw torque max.	2 x 100Nm
Drive	DC-Motor
Drive pover	10,5 kW
Max. motor speed	2700 rpm
Total speed increasing ratio	i = 5,38
Max. screw rotation	500 rpm
Power transmission	Coupling
No. of heating zones	12
Heating power	10,2 kW
No. of cooling zones	10
Kind of cooling	ZIK (Zylinder Intensiv Kühlung = Barrel Intensive Cooling)
Kind of cooling of feeding zone	Water
Max. flow of feeding zone	30 l/h
Max. melt pressure	300 bar
Max. melt temperature	350 degree Celcius
Operating height	1050 mm
Approx. weight	950 kg

The extruder is equipped with three Brabender flex-wall, loss-in-weight, gravimetric feeders, operated by the Congrav RC4 unit; a degassing port connected to a vacuum pump, a water bath, a dryer and a pelletizer. The extruder barrel consists of seven heating zones. First zone (inlet zone) is cooled down. The reason why the inlet zone is cooled down is to prevent the messing-up of the polymer and the chemicals through the walls of the barrel and screws instead of being conveyed further into the barrel The polymer is conveyed to the first zone where melting starts by screw rotation. The die with a two-strand hole is positioned at the forward end of the extruder. In Figure 3.1 these parts of the barrel are shown. The polymer melted in the barrel by the help of heat and work supplied by the electic motor through the screws, the molten and mixed polymer compound leaves the die hot and viscous. In water bath the polymer is cooled down and solidified as shown in Figure 3.2.

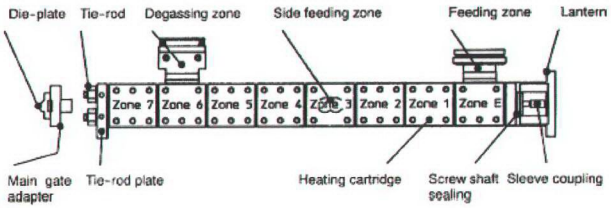


Figure 3.1 Description of parts of the twin-screw extruder barrel
(Leistritz Micro 27 Extruder User's Manual)

A pressure sensor is also connected to the barrel to measure the melt pressure generated by the rotating action of the screws.

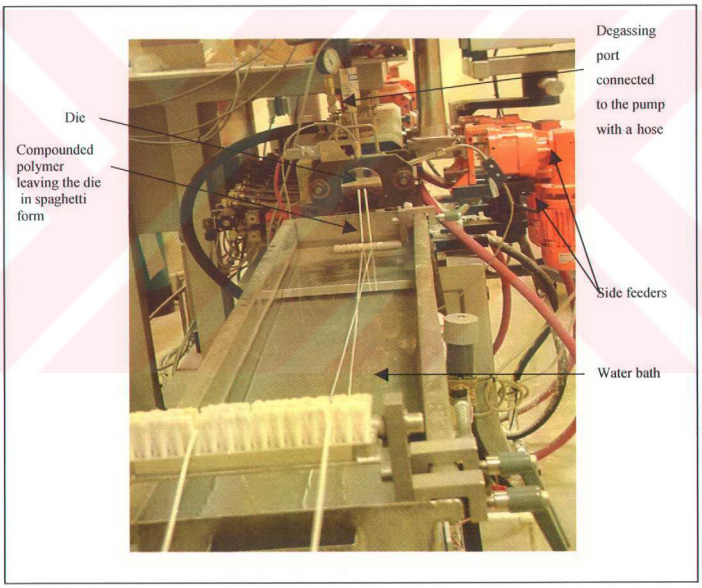


Figure 3.2 The molten polymer strands leaving the die and entering the water bath

3.3.2. Compounding Process

The homopolymer was fed to the extruder via the first feeder through the feeding zone. The additives and CaSt were pre-mixed and then were fed to the extruder via the second feeder, again through the first feeding zone. $CaCO_3$ were fed to the

extruder via side stuffer, accompanied by third feeder. Locations of the feeders are shown in Figure 3.3. The compounded material in molten state was taken out of the extruder through the two holes of the die and was immediately immersed into water bath to cool down, as can be seen in Figure 3.2. Solidified polymer strands were then pelletized.

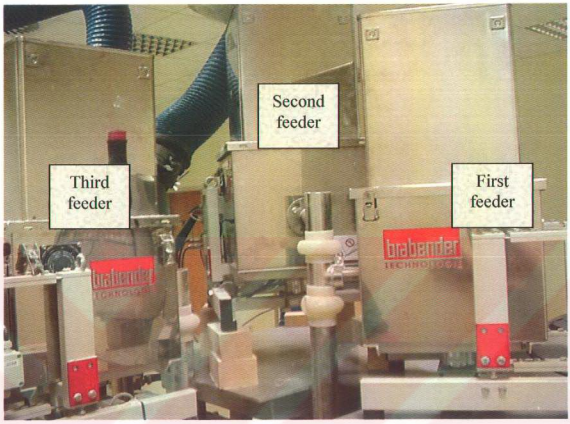


Figure 3.3 Locations of the gravimetric feeders of the twin-screw extruder

3.4. Injection Molding

Injection molding of thermoplastics is based upon the ability of thermoplastic materials to be softened by heat and to harden when cooled. As no chemical change takes place during heating and cooling, this cycle can be repeated for numerous times, within the limits of the effects of degradation caused by the exposure to heat and mechanical shear forces **(Farris et al., 1962)**.

Molding material in the form of granules is fed through the hopper from the beginning of the barrel. Inside the barrel the polymer is heated and softened. The softened polymer is melted and mixed with the help of the rotational motion of the screw. The molten polymer is pushed out at the other end of the barrel through a nozzle into a relatively cool closed mold, where it hardens. The finished article is then ejected by ejecting pins.

As an injection molding machine, Arburg Allrounder 320C was used to produce tensile, flexural specimens and plaques, according to ISO standards. The different types of molds and the injection molding machine itself is shown in Figures 3.4-3.7.

Figure 3.4 flexural specimen mold according to ISO178 standard

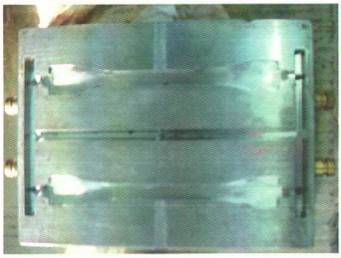


Figure 3.5 tensile specimen mold suitable to produce specimens with weld-line according to ISO R527 standard

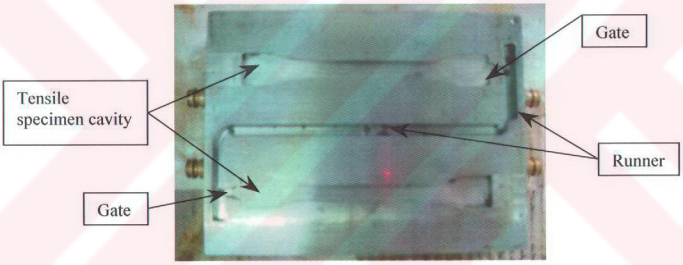


Figure 3.6 tensile specimen mold according to ISO R527

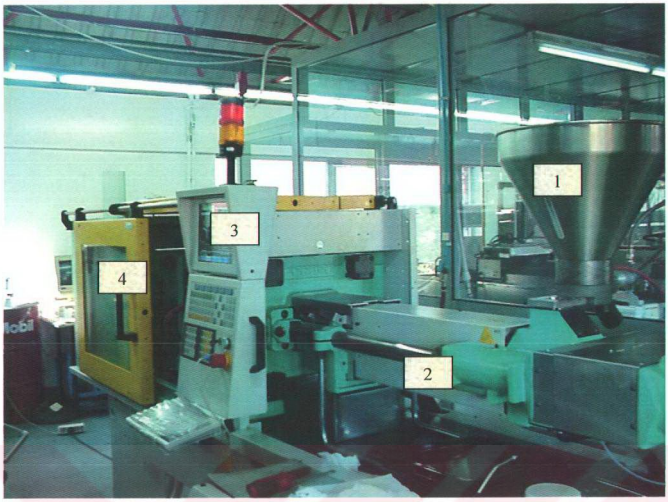


Figure 3.7 Arburg Allrounder 320C injection molding machine, 1)-hopper, 2)-heating cylinder, 3)-control panel, 4)-molding section

3.5. Injection Parameters

The five barrel zone temperatures from the hopper to the nozzle and the mold temperature were set to: 215, 220, 225, 230, 230°C and 31°C, respectively.

3.5.1. Tensile test specimens

Three stages of injection speed and pressure are used as shown in Table 3.3.

Table 3.3 Injection parameters for the three stages of injection speed and pressure for tensile test specimen production

	Step 1	**Step 2**	**Step 3**
Injection speed (cm^3/s)	100	120	100
Injection pressure (bar)	800	850	800

Four stages of holding pressures were applied: 0,3s, 900 bar, 6,50s, 900 bar, 2,30s, 700 bar, 0,30s, 25 bar.

The screw rotation speed was 20m/min, backpressure was 105 bar, shot volume was 36 cm^3.

The overall cycle time to obtain a tensile test specimen was 35,8s.

3.5.2. Tensile test specimens with weld-line

Three stages of injection speed and pressure are used as shown in Table 3.4.

Table 3.4 Injection parameters for the three stages of injection speed and pressure for tensile test specimens with weld-line production

	Step 1	Step 2	Step 3
Injection speed (cm^3/s)	100	120	100
Injection pressure (bar)	650	700	650

Four stages of holding pressures were applied: 0,3s, 575 bar, 6,50s, 575 bar, 2,30s, 500 bar, 0,30s, 25bar.

The screw rotation speed was 20m/min, backpressure was 105 bar, shot volume was 38 cm^3.

The overall cycle time was 35,71s.

3.5.3. Flexural test specimens

Three stages of injection speed and pressure are used as shown in Table 3.5.

Table 3.5 Injection parameters for the three stages of injection speed and pressure for flexural test specimen production

	Step 1	Step 2	Step 3
Injection speed (cm^3/s)	154	120	100
Injection pressure (bar)	800	850	800

Four stages of holding pressures were applied: 0,3s, 950 bar, 7,30, 950 bar, 3,10s, 850 bar, 0,30s, 25bar.

The screw rotation speed was 25,7m/min, backpressure was 130 bar, shot volume was 38 cm^3.

The overall cycle time was 42,24s.

3.5.4. Plaques

The injection speed and pressure for 80x80x2 mm plaques for color measurements is shown in Table 3.6.

Table 3.6 Injection parameters for the three stages of injection speed and pressure for plaque production

	Step 1	Step 2	Step 3
Injection speed (cm^3/s)	154	120	100
Injection pressure (bar)	800	850	800

Four stages of holding pressures were applied: 0,3s, 900 bar, 7,50, 900 bar, 2,30s, 700 bar, 0,30s, 25bar.

The screw rotation speed was 20m/min, backpressure was 105 bar, shot volume was 50 cm^3.

The overall cycle time was 35,82s.

3.6. Determination of Physical and Chemical Properties

3.6.1. Physical Properties

3.6.1.1. Determination of Ash Content

The level of inorganic filler in the organic polymer matrix is measured by a method of determining the ash content as described in **ISO 3451 Method A, (1981)**. The porcelain crucibles are weighed and then small amounts of the pellets obtained from the extrusion process are weighed and added to these empty crucibles. The filled crucibles are then put into the furnace, Heraeus K 1252 type that is heated to 600±25°C. This test temperature is chosen so as not to degrade $CaCO_3$. The crucibles are kept in the furnace at 600±25°C for an hour and after that they are placed in a desiccator and allowed to cool down for half an hour and then weighed. Ash content (filler level) in the composite is calculated as in Equation 3.1.

$$\text{Ash (\%)} = [(m_{bf}-m_{cr})/(m_{af}-m_{cr})] \times 100 \quad (3.1)$$

where m_{bf} is the weight of the crucible filled with sample before putting into furnace, m_{af} is the weight of the crucible filled with sample after taking out of the furnace and m_{cr} is the weight of the empty crucible.

Melt Flow Index: Since degradation is a process proceeding due to free radical mechanism, chain scissions are of high expectance. As the degree of degradation increases, short (low molecular weight) chains are expected. Shortening of the chains (decrease in molecular weight), results in a decrease in the viscosity of the polymer. As a consequence of this decrease in viscosity, an increase in melt flow index is observed. The result will be more reliable, when repeated after multiple extrusions.

3.6.1.2. Determination Of Melt Flow Index

Melt flow index (MFI) or melt flow rate (MFR) is measured by using Zwick 4106 testing machine according to **ISO 1133** test standard. The testing device is basically an extrusion plastometer operating at a fixed temperature. Temperature control equipment and heater is located around a vertical cylinder. At the bottom of the cylinder, a circular, straight and uniform die having 2.095±0.005 mm opening is located. Test weight is directly applied onto the piston which is concentric with the cylinder vertical axis and which can move downward within the cylinder. Test temperature and weight is set to 230°C and 2.16kg, respectively. After cleaning of the cylinder and piston, 6grams of test samples in pellet form is fed into the preheated cylinder. During the charging, the material is compressed by hand pressure to ensure the charge is free from air. For 4 minutes, 1 kg preload is applied via the piston and then 2.16 kg test weight is practiced. The molten material is extruded through the die. The rate of extrusion is measured by cutting off the extrudate at suitable time interval; e.g., 30 seconds. At least three cut-offs, are weighed with balance having 0,001g of accuracy. The melt flow rate expressed in grams per the reference time (10 minutes), is given by the equation:

$$\text{MFI (230°C, 2.16kg)} = (S*M)/t \quad (3.2)$$

Where S is the reference time in seconds, i.e., 600 seconds; m is the average mass of the cut-offs, in grams; and t is the cut-off time interval, i.e., 30 seconds.

3.6.1.3. Determination of Yellowness Index:

Yellowness index of specimens are measured with a Minolta CM 3600d Spectrophotometer, according to **ASTM-D 1925-70**. Yellowness index is defined as the magnitude of yellowness relative to magnesium oxide for CIE source C and expressed as follows:

$$YI = [100(1{,}28X_{CIE} - 1{,}06Z_{CIE})]/Y_{CIE} \quad (3.3)$$

X_{CIE}, Y_{CIE}, Z_{CIE} are tristimulus values of the specimens relative to source C. These values are required to match a color in the CIE system **(ASTM E284)**.

Before aging processes yellowness indices (YI) of previously injected plaques having 80x80x2mm dimensions are measured. These pre-measured values form a baseline for the other measurements after any aging process. Yellowness index is obtained by the subtraction of values measured after any aging process from the baseline.

Measurements in the Minolta CM 3600d Spectrophotometer are calculated according to the L*a*b* color space (also referred to as CIELAB). Color space is defined as the geometric space (a sphere), usually of three dimensions in which colors are arranged systematically. In L*a*b* color space, L* indicates lightness, a* and b* indicate the chromaticity coordinates. +a* to –a* is the coordinates from red to green; and +b* to –b* are the coordinated from yellow to blue. In thr Minolta spectrometer the tristimulus values are converted into L*, a* and b* values according to these equations given in **Minolta User's Manual**:

$$L^* = 116(Y/Y_n)^{1/3} - 16 \quad (3.4)$$

$$a^* = 500[(X/X_n)^{1/3} - (Y/Y_n)^{1/3}] \quad (3.5)$$

$$b^* = 200[(Y/Y_n)^{1/3} - (Z/Z_n)^{1/3}] \quad (3.6)$$

In these formulations the X, Y, Z are tristimulus values of the specimens and X_n, Y_n, Z_n values are tristimulus values of a perfect reflecting diffuser.

The color change ΔE*ab indicates only the size of the color difference but not in what way the colors are different. ΔE*ab is defined according to Equation 3.4 **(Minolta User's Manual; ASTM E308-85)**:

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (3.7)$$

The preparation of specimens for color measurements and the color measurement procedure were performed as it is told in this section. The plaques were measured always on the same side and attention was given to place the sample always in the same position so that the port from which light is send is at the center of each individual plaque. The spectrometer used to measure the yellowness indices of specimens aged in different aging environments, is shown in Figure 3.8.

Figure 3.8 Minolta spectrometer used in the measurements of yellowness index

3.6.2. Mechanical Properties

As mentioned, degradation affects the chemical and physical properties of polymeric materials thus, affecting their mechanical properties. The mechanical properties can be determined mostly by tensile, flexural and impact tests.

3.6.2.1. Measurement of Tensile Properties:

Tensile properties of the compositions are measured by using Instron 4505 universal tensile machine equipped with 5 KN load cell as load indicator and long stroke extensometer as extension indicator. Tensile test is performed at room temperature, i.e., 23°C with a relative humidity of 50%.

Tensile properties are examined by using injection molded tensile specimens described as test specimen type one according to **ISO / R 527**. Test specimens are awaited in a dessicator for at least 48 hours to get rid of post crystallization or physical aging and hydrolysis effect. Testing speed is set to 50 mm/min and gauge length (L_o) is set to 50 mm.

The thickness and width within the parallel portion of specimens are measured by screw micrometer reading at least 0.02mm. Then, the specimen is fixed to self-aligning grips of the tensile test machine. The extensometer is attached to the specimen over the parallel portion of it and the machine is started. The loads and corresponding deformations are recorded at a time interval of 0.2 seconds. Following tensile properties are measured:

a) Tensile stress or yield stress designated as σ_y (tensile load per unit area of original cross section within the narrow parallel portion). Tensile stress expressed in Newton per square millimeter (N/mm^2) is the first point on the load/extension curve at which an increase occurs without an increase in load.

b) Tensile strain or percentage elongation at yield designated as εy (percent increase in the distance of reference lines on the narrow parallel portion of the test specimen or extensometer arm). Tensile strain is the percentage elongation corresponding to yield stress point.

c) Elastic modulus or Young modulus is calculated from initial linear portion of the load extension curve by dividing the difference in stress corresponding to a section of the straight line by the corresponding difference in strain.

d) Energy up to break or toughness is the area under the stress-strain curve up to the point of break.

e) Energy up to yield point is the area under the stress curve up to the yield point.

3.6.2.2. Determination of Weld Line Factor

Weld line is the junction line, visible in the molded article, caused because of the meeting of two flow fronts in the mold.

For the ease of comparing the effect of weld line on mechanical properties of molded material, the weld line factor (F_{wl}) defined in **Nadkarni and Ayodhya (1993), Kim and Suh (1986) , Ersoy (2003)** as it is shown below:

$$F_{wl} = \frac{\text{Property value of specimen with weld line}}{\text{Property value of specimen without weld line}} \quad (3.8)$$

Weld line factor is calculated for tensile yield strength, yield elongation, tensile modulus, flexural strength and flexural modulus.

3.6.2.3. Determination of Izod Impact Strength

According to **ISO 180** standard Izod impact strength is determined. Similar to tensile test specimens, injection molded test bars having dimensions of 4±0.2, 10±0.2, 80±0.2 are waited within a dessicator for at least 48 hours to get rid of post crystallization or physical aging and any hydrolysis effect. The thickness and width are measured by screw micrometer reading at least 0.02mm. Then, 2mm notch with notch base radius 0.25±0.05 is machined at mid-span of specimen. The test specimen and the notch are defined in the ISO standard as type 1A. The testing machine is Ceast equipped with 2.75 J impact capacity pendulum. Blank test (i.e., without any specimen in place) is carried out to ensure the total friction losses. The specimen is placed into test machine grips in such a way that the notched surface is faced to the impact point. The pendulum is then released and the impact energy is recorded after making correction for frictional losses. The Izod impact strength, in kilojoules per square meter (Kj/m^2), is calculated as follows:

$$\text{Izod impact Strength} = A_k/(XxY_k)x10^3 \quad (3.9)$$

Where A_k is the impact energy, in joules absorbed by the test specimens and it is corrected for frictional losses. X is the thickness, in millimeters, of specimens. Y_k is the difference of width and notch depth, in millimeters.

3.6.2.4. Determination of Flexural Properties:

Flexural properties of the compositions are measured by using Instron 4505 universal testing machine equipped with 5 KN load cell as load indicator and three point bending fixture. The test is performed at room temperature, e.g., 23°C.

Flexural properties are determined according to **ISO 178**. Similar to tensile test specimens, injection molded test bars having dimensions of 4±0.2, 10±0.5, 80±0.5 are waited within dessicator for at least 48 hours to get rid of post crystallization or

physical aging and any hydrolysis effect. Span of two lower arms of bending fixture is set to 60 mm. Testing speed is set to 50 mm/min and the extrusion from travel of traverse of testing machine.

The thickness and width are measured by screw micrometer reading at least 0.02 mm. Then, the specimen is laid to lower arms of the fixture fixed to stationary testing machine base. The third arm of the fixture, which is the movable traverse of testing machine, is slowly contacted with test piece at mid-span and the machine is started. The loads and corresponding deformations are recorded at the time interval of 0.2 seconds. Following tensile properties are measured:

- Flexural stress or flexural yield stress designated as σ_f is calculated as follows:

$$\sigma_f = (3 \times F \times L) / (2 \times b \times h^2) \quad (3.10)$$

where, F is applied load in mega-newtons, L is the span length in meters, b is the width and h is the thickness of specimen. Flexural stress is expressed in mega-pascal (MPa) or newton per square millimeter (N/mm^2).

- Flexural deflection:

It is the distance over which the top of specimen surface at mid-span has deviated during flexure from its original position and is designated as σ_{fy}

- Flexural modulus or apparent modulus of elasticity (E_b):

It is calculated from initial linear portion of the load extension curve by using at least five values of the deflection and load. E_b is calculated as follows:

$$E_b = (L^3 \times F) / (4 \times b \times h^3 \times Y) \quad (3.11)$$

Where L is span length, b and h are the width and thickness of the specimen respectively, F is the load at a chosen point on the initial linear portion of the load versus deflection curve, Y is the deflection corresponding to load F. L, b, h and Y are in millimeter and F is in newtons, then E_b is in N/mm^2.

- Energy up to break or toughness is the area under the stress strain curve up to the point of break.

- Energy up to yield point is the area under the stress strain curve up to yield point.

3.6.3. Aging Properties

3.6.3.1. Oven Aging

Test specimens (tensile, flexural testing specimens and plaques) are immersed into an oven at elevated temperatures. The effects of relatively long exposure to high temperature on mechanical properties, due to the changes in the chemical properties, are tried to be investigated.

The test temperature in the oven is kept constant at 95°C. Under the exposure to this temperature, test specimens were kept in the oven for 7, 15 and 30 days. For every mechanical test, six specimens were taken out of the oven on these periods and changes in tensile, flexural and impact properties were observed. For the determination of color changes three plaques were taken out to be able to perform the measurements and then put back because color measurements should be performed with the same sample for every measurement period.

3.6.4. Detergent Aging

Test specimens (tensile, flexural testing specimens and plaques) are immersed into a 1% detergent solution at 95°C. The effects of relatively long exposure to detergent solution and high temperature on mechanical properties and discoloration are tried to be investigated.

Test specimens were kept in the 1% detergent solution at 95°C for 7, 15 and 30 days. For every mechanical test, six specimens were taken out of the oven on these periods and changes in tensile, flexural and impact properties were observed. For the determination of color changes three plaques were taken out to be able to perform the measurements and then put back because color measurements should be performed with the same sample for every measurement period.

3.6.5. Bleach Aging

Test specimens (tensile, flexural testing specimens and plaques) are immersed into a 1% bleach solution at 40°C. The effects of relatively long exposure to bleach

solution and high temperature on mechanical properties and discoloration are tried to be investigated.

Test specimens were kept in the 1% bleach solution at 40°C for 7, 15 and 30 days. For every mechanical test, six specimens were taken out of the oven on these periods and changes in tensile, flexural and impact properties were observed. For the determination of color changes three plaques were taken out to be able to perform the measurements and then put back because color measurements should be performed with the same sample for every measurement period.

3.6.6. Water Vapor Aging

Test specimens (tensile, flexural testing specimens and plaques) are subjected to water vapor at 100°C. The effects of relatively long exposure to water vapor on mechanical properties and discoloration are tried to be investigated.

Test specimens are subjected to water vapor at 100°C for 7, 15 and 30 days. For every mechanical test, six specimens were taken out of the oven on these periods and changes in tensile, flexural and impact properties were observed. For the determination of color changes three plaques were taken out to be able to perform the measurements and then put back because color measurements should be performed with the same sample for every measurement period

3.6.7. UV Aging

Plaques are exposed to UV light at room temperature. The effects of exposure to UV discoloration is tried to be investigated.

Test specimens are exposed to UV light for 7, 15 and 30 days. For the determination of color changes three plaques were taken out to be able to perform the measurements and then put back because color measurements should be performed with the same sample for every measurement period

4. RESULTS AND DISCUSSION

In this thesis, the behaviors of different formulations, containing inorganic filler material (calcium carbonate), acid scavenger (calcium stearate), antioxidants and two types of nucleating agents, on the chemical and physical properties of polymeric material as well as their mechanical and esthetical (such as discoloration) properties were observed. In the meantime any synergistic interactions between any of these additives and nucleating agents, which may nourish the properties of the non-additive included polymeric material were also investigated.

4.1. Color Measurements

Collecting the yellowness index data on 7^{th}, 15^{th} and 30^{th} days measured by the spectrometer shown in Section 3.6.1.3. YI versus time graphs were drawn to be easily able to detect which specimens showed better results than others. The five graphs of yellowness indices of specimens aged in different aging environments are shown, respectively.

The measured yellowness index values of specimens aged in detergent solution are shown in Figure 4.1.

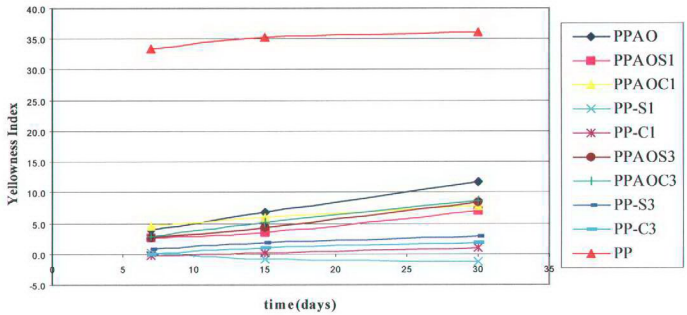


Figure 4.1 Yellowness index of formulations aged in detergent solution

Yellowness index-time graph of specimens aged in detergent solution shows clearly that the addition of antioxidants (PPAO) decreases yellowing nearly one third compared to the unstabilized, filled polypropylene (PP). Looking at the overall picture one important observation made is that all the formulations containing only nucleating agents show less yellowness indices than the formulations containing both antioxidants and nucleating agents. The reason why formulations without stabilizers show less discoloration may be because of the well organization of crystalline structures. The stacking of crystals would lower gas penetration and therefore the reaction with oxygen, which results in oxidative degradation, would be inhibited. Among the formulations that doesn't contain any antioxidants but nucleating agents, PP-S1, which is the formulation with 0,1% by weight nucleating agent of sodium salt origin shows less discoloration. Compared to PPAO, PPS1-3 and PPC1-3 show less yellowness index most probably, due to the crystallization effect mentioned above. In adition to this, as stated by **Barret et al. (2002)** another reason can be the lack of the oxidation products of the stabilizers themselves. For example, the relatively colorful oxidation product of phenolic antioxidant, quinone methide, causes a probable increase in yellowness index.

When both antioxidants and nucleating agents are used together, yellowness indices after 30 days of aging in detergent solution are found between PPAO and PPS1-3, PPC1-3. PPAOS1 formulation containing 0,1% by weight nucleating agent of sodium salt origin shows the less discoloration among the formulations that contain

antioxidants. Addition of nucleating agents may overcome the negative effect of oxidation products of phenolic antioxidant, which may cause a rise in yellowness index.

The measured yellowness index values of specimens aged in the oven are shown in Figure 4.2.

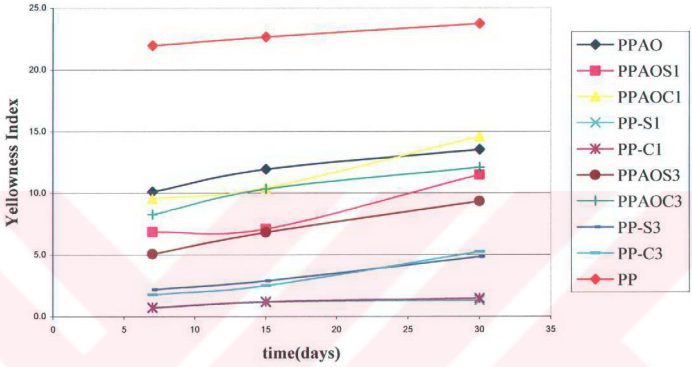


Figure 4.2 Yellowness index of formulations aged in oven

As it was the case with detergent aged specimens, in the yellowness index-time graph of oven-aged specimens the addition of antioxidants (PPAO) decreases yellowing compared to the unstabilized (PP) polymeric mixture, too. In oven-aged specimens among the formulations that doesn't contain any antioxidants but nucleating agents, PP-S1 and PP-C1, show less discoloration. Again looking at the overall picture, the observation made beforehand still counts and the formulations containing only nucleating agents show less yellowness indices than the formulations containing both antioxidants and nucleating agents. The reason can be explained as the same as in the case of detergent aged specimens. Also the absence of oxidation products of stabilizers themselves is effective, too.

In oven aged samples, the formulation PPAOS3, showed the least yellowness among the stabilized and nucleated samples. But again the performance of PPAOS1 formulation is also noteworthy. The highest yellowness index was seen in the formulation containing 0,1% by weight nucleating agent of sorbitol type. Then

PPAO and PPAOC3 followed respectively. Therefore it can be claimed that under elevated heats in the absence of water, sorbitol has a negative effect on yellowing.

The measured yellowness index values of specimens aged in water vapor are shown in Figure 4.3.

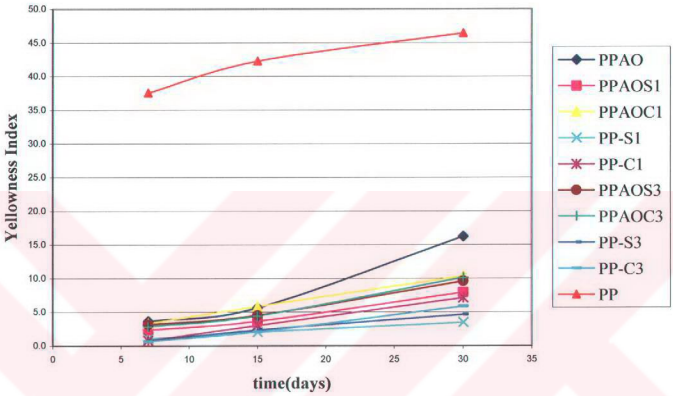


Figure 4.3 Yellowness index of formulations aged under water vapor

The same tendency in the decreasing of YI when antioxidants are added to the polymer mixture is observed in water vapor aged specimens, too. The positive effect of antioxidant-nucleating agent combination can be seen clearly from the yellowness index values, which are all less than the PPAO formulation. Among the stabilized and nucleating agent-included formulations, PPAOS1 shows the least yellowing under water vapor, as it was the case with the other environments discussed previously. In addition to this, among the un-stabilized but nucleated formulations, PP-S1, showed the least yellowing, as similar to results obtained in detergent solution and in the oven. The positive synergistic effect of nucleating agent of Na-salt type with the antioxidants used in the formulations and other additives can be observed.

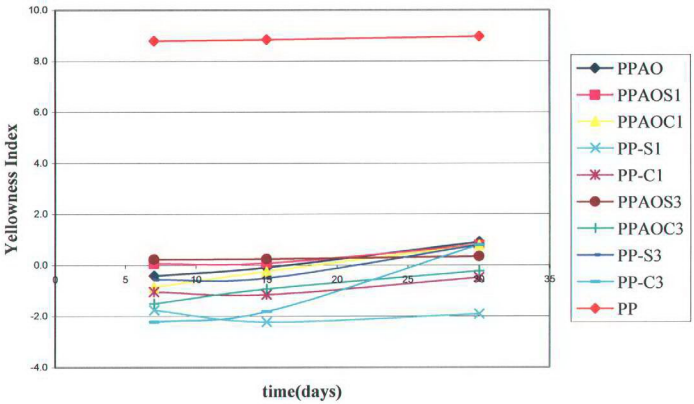


Figure 4.4 Yellowness index of formulations aged under UV

As shown in Figure 4.4, unstabilized PP exhibit the highest yellowness index as the specimens are exposed to UV light. But the effect of antioxidants and nucleating agents are not so clearly detected for specimens exposed to UV as the specimens aged in the pther environments. For some samples, even whitening is observed. The highest value (YI=1) was obtained with the only stabilized formulation and this yellowing was not naked eye detectable. Nevertheless the greatest ΔYI was recorded in the formulation PP-C3 after the 15th day.

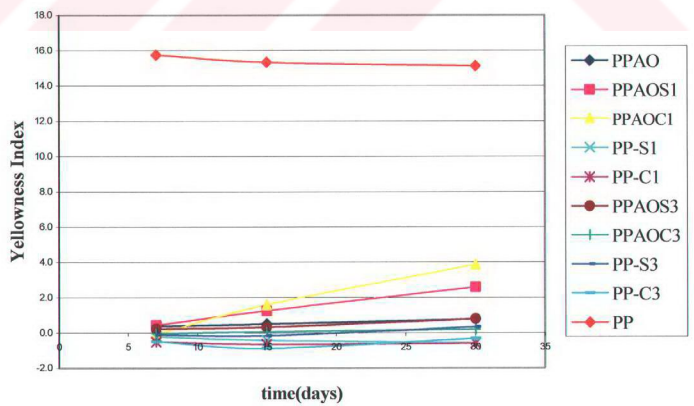


Figure 4.5 Yellowness index of formulations aged in bleach solution at 40°C

As shown in Figure 4.5, the un-stabilized and non-nucleated polymer mixture showed the greatest yellowness index in bleach solution, like in all other aging environments. The unexpected results were obtained with the PPAOS-1 and PPAOC-1 formulations. They showed the two highest YI values among all the other formulations. Even the YI values were high for the stabilized and 0,1% by weight nucleating agent-included formulations, the yellowness index of PPAOS1 was less than PPAOC1.

4.1.1. Overall results of yellowness index tests

- Addition of antioxidants lowers the yellowness index severely, for all specimens aged under all environments.
- Formulations containing only nucleation agents show less discoloration than the both stabilized and nucleated formulations.
- Among the stabilized and nucleated formulations, PPAOS1 show the best results (least discoloration) in almost every aging environment.
- Among the nucleated formulations, PP-S1 show the best results in almost every aging environment.
- The addition of nucleating agent of sodium salt type to the stabilized filled PP compound decreases discoloration almost in all environments, especially where the aging environment contained both heat and water.

This may be explained by the synergistic interactions of sodium salt type nucleating agent with the antioxidants and calcium stearate. Acid scavenger CaSt captures any acidic species that might occur because of the catalyst residues. A reason why acidic species are not wanted in the polymer matrix apart from corrosion is that they catalyze hydroperoxide decomposition, which would lead to the consumption of antioxidant. While reacting with these acidic species CaSt forms $CaCl_2$ salt. Since $CaCl_2$ can dissolve in water the Cl^{-1} ion may also react with any hydrogen to produce acidic species. But in the presence of nucleating agent of sodium salt type this Cl^{-1} ion may also react with Na^{+1} ion found in the structure of the compound forming a salt, therefore inhibiting the acid formation. Because of that, when sodium salt type nucleating agents are used together with the antioxidants and CaSt while compounding PP with $CaCO_3$, it is observed that, for the end product the increasing

trend of YI slows down. That can be claimed as an evidence of the validity of salt formation and interactions with the ions.

4.2. Mechanical Properties

Testing of mechanical properties consisted of impact, flexural and tensile tests. Tensile tests were performed for both normal and with weld-line specimens. All the procedures followed and testing equipment were described in section 3.6.2.

4.2.1. Impact Properties

Izod impact strength tests were performed with test specimens according to the ISO180 standard. The procedure of this test is explained in section 3.6.2.3. in detail. In table 4.1 the impact strengths of both the un-aged and aged specimens in various environments are shown. Specimens were subjected to Izod impact strength test on 7^{th}, 15^{th} and 30^{th} days but Table 4.1 only shows the results of impact strengths after one month of aging.

Table 4.1 The Izod impact strengths of un-aged and aged specimens in various aging environments.

Sample Name	Un-aged specimens	Specimens aged in detergent solution	Specimens aged in bleach solution	Specimens aged in oven	Specimens aged under water vapor
PPAO	2,69	4,06	3,12	3,71	2,81
PPAOS1	3,26	3,70	3,48	4,02	3,63
PPAOC1	2,83	3,19	3,11	3,16	2,92
PP-S1	3,10	3,43	2,80	3,49	3,35
PP-C1	2,86	3,17	2,72	3,14	3,20
PPAOS3	2,62	3,71	2,77	3,62	3,27
PPAOC3	2,67	2,49	2,17	2,69	2,61
PP-S3	3,10	3,77	3,26	3,70	3,49
PP-C3	2,86	3,11	2,96	3,10	2,99

For the un-aged specimens containing only nucleating agents, the impact strength doesn't change when the nucleating agent amount is increased as it is in the cases of PP-S1, PP-C1, PP-S3 and PP-C3. The addition of 0,3% by weight of nucleating agents regardless of their type doesn't improve impact properties.

The best results in Izod impact strength measurements are obtained with the formulation containing both antioxidants and 0,1% by weight of nucleating agent of Na-salt type (PPAOS1). Considering the overall data, another result obtained is that when there is elevated heat in the aging environment the impact properties increase. This may be explained by the annealing effect of the test temperatures.

The poorest results were obtained with the formulation containing antioxidant and 0,3% by weight of nucleating agent of sorbitol type. This can be explained by the antagonistic effect of the nucleating agent with the antioxidants when used in 0,3% amount.

Comparing the two formulations containing antioxidants but different kinds of nucleating agents, specimens with the 0,1% nucleating agent of Na-salt type showed higher impact strength than the 0,1% sorbitol type nucleating agent containing specimens. This observation is also valid in specimens formulated with 0,3% nucleating agents, too.

When the two formulations PPAOS1 and PPAOS3 are compared, the impact properties even get poorer when 0,3% nucleating agent is used. Therefore for the nucleating agent of sodium salt type, 0,1% seems to be a better amount than 0,3%.

4.2.1.1. The overall results of Izod impact tests

- For both nucleating agents, when used with antioxidants, considering the impact strength values, the optimum amount was seen to be the 0,1% amount.
- When there is elevated heat in the aging environment the impact properties increase no matter which nucleating agent is added. This effect can be explained by the annealing effect at the test temperatures.

4.2.2. Tensile Properties

In table 4.2 the tensile properties of nine different formulations and calcite filled polypropylene is shown. A noteworthy result is that the addition of antioxidants increases the modulus of the polymeric article.

Table 4.2 Tensile properties of un-aged specimens

Sample name	Stress at max. load (MPa)	Strain at max. load (%)	Young's modulus (MPa)	Stress at max. load (MPa)	Strain at max. load (%)	Young's modulus (MPa)
	Normal	Specimens		Weld-line	Specimens	
PPAO	20,79	4,73	3314,35	18,52	2,79	3073,62
PPAOS1	21,13	4,71	2920,08	18,66	2,58	2838,36
PPAOC1	21,17	4,54	3095,91	19,05	2,51	3312,84
PP-S1	21,52	3,98	2925,64	18,58	2,21	3248,19
PP-C1	22,45	3,80	3582,08	19,42	2,44	3381,39
PPAOS3	21,65	3,90	3381,96	19,03	2,03	4015,56
PPAOC3	22,35	4,32	3900,41	19,72	2,26	3447,03
PP-S3	22,18	4,10	2890,08	19,82	2,37	2870,30
PP-C3	21,71	3,42	3281,23	19,40	2,17	3322,54

Comparing the two formulations both stabilized but nucleated with different nucleating agents, PPAOS1 and PPAOC1, there are no important differences in tensile properties. When 0,3% by weight of Na-salt type nucleating agent is added to the formulation, the stress values decrease. For the 0,1% by weight nucleating agent containing specimens, the Young's modulus values are observed to increase. In the PP-C1 specimens when the nucleating agent amount is increased to 0,3% by weight the impact properties get poorer. 0,3% may not be the optimum amount for

non-stabilized specimens. On the other hand, when the nucleating agent amount is increased in the formulation containing Na-salt type nucleating agent only the Young's modulus value decrease.

Looking at the overall values, stabilized and 0,3% by weight nucleating agent of sorbitol type added formulation, PPAOC3, shows the best tensile properties for both normal and weld-line specimens.

To determine the changes in tensile properties of these specimens, they were exposed to different aging environments and their mechanical properties were again measured after aging on 7^{th}, 15^{th} and 30^{th} days. Table 4.3 shows the tensile properties of aged for one month, hence degraded specimens.

Four formulations were inspected in detail because they showed noteworthy results both after aging and beforehand. PPAOS1 formulation was chosen because it showed superior properties on the inhibition of discoloration and good impact strength. Also PPAOC3 was again observed in detail because it was the formulation with the best tensile properties among the un-aged specimens. Since PPAOS1 showed good properties, to be able to identify the antioxidant effect, the un-stabilized formulation PP-S1 was observed in detail. In the un-aged samples when the nucleating agent amount of PP-C1 formulation was increased a decrease in tensile properties was observed. To be able to see if this behavior still counts after aging under different formulations PP-C1 formulation was kept among the closely observed results. Also it made a good indication of which nucleating agent performed better in the absence of antioxidants.

Table 4.3 Tensile properties of both normal and weld-line specimens

		un-aged samples			detergent aged			bleach aged			oven aged			water vapor aged		
		Stress at max. load (MPa)	Strain at max. load (%)	Young's Modulus (MPa)	Stress at max. load (MPa)	Strain at max. load (%)	Young's Modulus (MPa	Stress at max. load (MPa)	Strain at max. load (%)	Young's Modulus (MPa)	Stress at max. load (MPa)	Strain at max. load (%)	Young's Modulus (MPa)Mod.	Stress at max. load (MPa)	Strain at max. load (%)	Young's Modulus (MPa)
Normal Specimens	PPAO	20,79	4,73	3314,35	22,73	5,39	2888,56	21,77	4,12	3068,51	22,79	5,28	3169,93	22,94	4,85	3027,21
	PPAOS1	21,13	4,71	2920,08	23,33	5,42	3618,79	24,54	4,79	4424,34	23,80	4,83	3511,00	25,13	4,58	4617,00
	PPAOC1	21,17	4,54	3095,91	23,72	5,41	4008,87	25,13	4,45	4422,65	23,83	4,82	3704,52	25,47	4,48	4244,03
	PP-S1	21,52	3,98	2925,64	23,08	4,18	3190,83	22,75	3,39	3953,34	23,34	4,07	3304,72	25,10	4,12	3561,44
	PP-C1	22,45	3,80	3582,08	22,44	3,60	3500,41	24,56	3,31	3683,04	24,19	3,86	3525,03	25,06	3,98	3714,03
	PPAOS3	21,65	3,90	3381,96	23,24	4,41	3573,27	23,11	3,20	3713,67	24,12	4,35	3505,95	23,93	4,15	4329,06
	PPAOC3	22,35	4,32	3900,41	24,87	4,57	3660,66	24,79	3,27	3985,46	24,58	4,48	3909,36	25,13	4,31	3709,50
	PP-S3	22,18	4,10	2890,08	24,15	4,98	3788,69	25,69	3,68	4080,81	24,18	4,44	3378,74	25,67	4,29	3760,04
	PP-C3	21,71	3,42	3281,23	23,61	4,42	4212,81	24,71	3,53	4135,54	23,89	3,71	3683,39	24,21	3,75	3930,28
Weld-line Specimens	PPAO	18,52	2,79	3073,62	19,95	3,21	2884,84	19,33	2,41	2989,63	20,14	3,10	2981,44	20,37	3,03	3004,75
	PPAOS1	18,66	2,58	2838,36	20,50	2,96	4143,54	21,49	2,36	4238,12	20,95	2,56	3375,20	20,44	2,49	3627,75
	PPAOC1	19,05	2,51	3312,84	20,71	2,93	3901,06	22,00	2,42	4677,58	20,65	2,66	3554,91	20,37	2,53	3486,70
	PP-S1	18,58	2,21	3248,19	20,10	2,17	3532,24	19,06	1,97	3161,86	21,20	2,27	4065,95	19,86	2,32	3249,74
	PP-C1	19,42	2,44	3381,39	19,68	1,94	3727,78	21,04	2,03	3553,97	21,36	2,36	3270,89	21,73	2,45	3265,37
	PPAOS3	19,03	2,03	4015,56	19,92	2,41	3124,06	19,49	1,81	3313,27	20,17	2,20	3354,78	20,19	2,19	3476,34
	PPAOC3	19,72	2,26	3447,03	20,72	2,72	3134,19	20,06	2,08	3183,12	21,02	2,53	3354,89	21,03	2,42	3319,11
	PP-S3	19,82	2,37	2870,30	21,40	2,65	3970,03	20,85	2,20	2076,43	21,82	2,32	3357,95	21,64	2,33	3271,58
	PP-C3	19,40	2,17	3322,54	20,57	2,82	3668,13	20,61	2,29	3756,38	20,99	2,35	3652,69	20,40	2,21	3881,02

As shown in Table 4.3, as a result of aging and thus degradation, failures in mechanical properties would be expected. But on the contrary, after aging in different environments mechanical properties of specimens improved. This may be explained again by the positive annealing effect of the test temperatures, overwhelming the negative effect of degradation on tensile properties. It is also claimed that, the testing time was not enough to degrade the specimens so severely that their properties would not be worsened.

Both stabilized and nucleated formulations showed better tensile properties than the others. This positive result of stabilization on tensile properties was expected.

4.2.2.1. The overall results of tensile tests

- Although it is not the case in un-aged specimens, among the aged formulations PPAOS1, both stabilized and nucleated with 0,1% w/w nucleating agent of sodium salt origin showed the best tensile properties.
- When PP-S1 and PP-S3 are compared, there is no noteworthy increase in the tensile properties by the addition of 0,3% w/w nucleating agent.
- On the other hand, PP-C3 showed slightly better results than PP-C1. Yet again a noteworthy result is that, PPAOC3 showed poorer properties than PPAOC1. Therefore it can be said that, for nucleating agents of sorbitol type the optimum amount is 0,1% w/w.
- In aged specimens, the addition of nucleating agent independent from the type of nucleating agent, Young's modulus increases. None or slight improvements are observed in stress and strain values.

4.2.3. Flexural Properties

The determination of flexural properties and the test procedure were explained in Section 3.6.2.4. In Table 4.4 the flexural properties of both un-aged and aged specimens are shown.

In un-aged samples, by the addition of nucleating agents to the stabilized polymer mixture with a loading level of 0,1% w/w, increase in Young's modulus and σ_f are observed. When the loading level is increased to 0,3% w/w, Young's modulus and σ_f values increase, too. However, these values are less than the ones obtained with a

0,1% w/w loading level of nucleating agents. When nucleating agents are used with antioxidants 0,1% w/w loading level may be the optimum amount.

In formulations containing only nucleating agents, better stress and Young's modulus values are obtained when 0,3% w/w loading level is used. Another noteworthy result obtained by the increasing of nucleating agent amount is that, a higher increase in σ_f and Young's modulus is observed with the nucleating agent of sodium salt origin.

4.2.3.1. The overall results of flexural tests

- Considering all the results of flexural tests for both aged and un-aged specimens, the formulation, stabilized and nucleated with 0,1% w/w nucleating agent of sodium salt origin show satisfactory results.

Table 4.4 Flexural properties of both un-aged and aged specimens

	un-aged samples			detergent aged			bleach aged			oven aged			water vapor aged		
	Stress at yield (MPa)	Strain at yield (%)	Young's Modulus (MPa)	Stress at yield (MPa)	Strain at yield (%)	Young's Modulus (MPa)	Stress at yield (MPa)	Strain at yield (%)	Young's Modulus (MPa)	Stress at yield (MPa)	Strain at yield (%)	Young's Modulus (MPa)	Stress at yield (MPa)	Strain at yield (%)	Young's Modulus (MPa)
PPAO	35,92	5,97	1678,80	41,09	5,92	2153,01	39,13	5,15	2367,53	41,48	5,79	2347,19	39,	5,72	2377,44
PPAOS1	40,94	4,96	2593,44	43,49	5,75	2325,66	41,75	5,38	2508,07	45,15	5,17	2603,26	39,35	5,51	2518,28
PPAOC1	40,60	5,03	2607,26	42,05	5,89	2349,75	41,37	5,61	2653,61	44,37	5,83	2560,43	40,39	5,47	2634,86
PP-S1	37,35	5,13	2306,26	38,65	5,65	2464,81	40,57	5,41	2566,67	41,08	5,58	2512,84	42,29	5,59	2496,24
PP-C1	39,05	5,10	2410,13	40,16	5,67	2657,73	40,57	5,40	2558,58	43,09	5,55	2786,54	42,89	5,54	2769,15
PPAOS3	38,70	5,16	2030,70	43,07	5,56	2387,15	40,98	4,71	2757,11	44,00	5,44	2679,03	42,47	5,35	2804,16
PPAOC3	38,84	5,48	2068,03	43,45	5,70	2475,16	41,66	5,22	2807,83	44,04	5,69	2673,40	42,87	5,53	2779,38
PP-S3	43,18	6,39	2555,88	44,39	5,70	2317,67	43,37	4,99	2673,34	47,19	5,54	2633,93	42,56	5,05	2819,25
PP-C3	41,67	4,97	2766,21	42,81	5,71	2595,19	41,20	4,92	2949,35	46,27	5,59	2809,43	40,97	5,22	2899,00

5. CONCLUSION

In this study, the possible synergistic interactions of antioxidant mixture and two different types of nucleating agents were investigated. The selected antioxidant mixture consisted of an acid scavenger, a sterically hindered antioxidant, a phosphate based hydroperoxide decomposer and a radical scavenger. Along with the investigation of any synergistic interactions between these chemicals, the inhibition of degradation in polypropylene subjected to detergent and bleach solutions, elevated heat and water vapor was also observed. The physical and mechanical changes during exposure to these environments were recorded.

From the yellowness index measurements it was seen that the addition of the antioxidant mixture reduced discoloration. Better results were obtained with the formulations consisting of both antioxidants and 0,1% w/w amount of nucleating agents. Among these formulations the best performance was observed in the formulation containing nucleating agent of sodium salt type (PPAOS1). This formulation was recorded to give outstanding results in aging environments containing both water and heat. This may be explained by the synergistic interactions of sodium salt type nucleating agent with the antioxidants especially, calcium stearate. Acid scavenger CaSt captures acidic species, which are not wanted in the polymer matrix because apart from corrosion, they catalyze hydroperoxide decomposition, which would lead to the consumption of antioxidants. While reacting with these acidic species CaSt forms $CaCl_2$ salt. Since $CaCl_2$ can dissolve in water, the Cl^{-1} ion may also react with any hydrogen to produce acidic species. But in the presence of nucleating agent of sodium salt type this Cl^{-1} ion may also react with Na^{+1} ion found in the structure of the compound forming a salt, therefore inhibiting the acid formation. Since discoloration starts from the surface the theory of salt formation and interactions with the ions may prove to be true.

Results of the mechanical tests showed that the tensile and impact properties of the formulations improve after aging for 30 days. This observation may be explained by the predomination of the annealing effect of the test temperatures, overwhelming the

negative effect of degradation. In addition to this, it is considered that 30 days of aging time might not be sufficient enough to emphasize the negative degradation effect. The best performance both in tensile and impact strength tests was obtained with the formulations containing antioxidants and 0,1% w/w nucleating agent of sodium salt type (PPAOS1).

Similar results were observed for both impact and flexural tests.

Therefore, after the evaluation of mechanical tests and color measurement results, the formulation PPAOS1 seemed to be promising to be used in a plastic article subjected to detergent, bleach solutions, heat and water vapor.

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