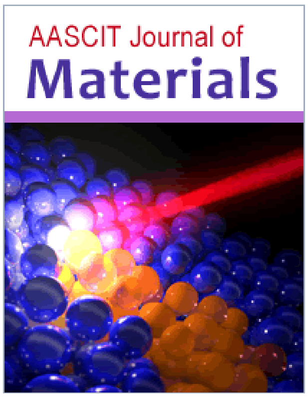
AASCIT Journal of Materials
2015; 1(2): 42-50

American Association for
Science and Technology



Radiation Degradation and Stability of Polymer

Wangtong He, Xuejia Ding

Beijing Laboratory of Biomedical Materials, Beijing University of Chemical Technology, Beijing, China

Email address

dingxj2011@126.com (Xuejia Ding)

Citation

Wangtong He, Xuejia Ding. Radiation Degradation and Stability of Polymer. *AASCIT Journal of Materials.* Vol. 1, No. 2, 2015, pp. 42-50.

Keywords

Radiation Resistant Polymer Materials,
Plasticizer,
Stabilizers,
Antioxidants,
Ligh Stabilizers,
Hindered Amine Light Stabilizer

Received: June 16, 2015
Revised: June 24, 2015
Accepted: June 25, 2015

Abstract

In recent years, because of the advantage of radiation technology-low energy, clean, environmental protection, etc., so that the use of radiation technology for polymer synthesis or processing research continues to heat up; however polymer materials irradiated via high-energy radiation prone to produce free group or to react with atomic oxygen in the air, resulting in the material cracking, crosslinking, branch, etc., it affects the performance of the materials. In this paper, we focus on the need for the research of radiation resistance of polymer material, It highlights the basic mechanism of polymer materials irradiation discoloration and the formulation of radiation resistant materials, which includes plasticizers, stabilizers, antioxidants and light stabilizers, the most representative is the study of a hindered amine light stabilizer and the latest irradiated materials research.

1. Introduction

It is well-known that the century of polymer materials paly a huge role. As polymer materials are widely used in medical and space technology, the development of research on radiation resistance of common polymer materials and space high-energy radiation and radiation resistance of high performance polymer materials gradually give rise to the attention of the countries all over the world. However, the vast majority of polymeric materials will change color-yellow, brown or black after undergoing high energy ray irradiation. In its radiation curing and radiation crosslinking process, due to the existence of radiation-induced discoloration affected its in processing performance (such as irradiation disinfection and sterilization) in many applications. Whereas radiation-induced changes in mechanical properties (and the chemistry which underlies these changes) have been extensively studied during the past four decades, radiation-induced changes in optical absorption have received little attention until quite recently and consequently this area has not been well explored.[1] Until recently, people realize the question for a more comprehensive and systematic exploration and research on the problem.

2. The Mechanism of Irradiation Discoloration

The radiation degradation of polymer is the fracture of the main chain、the lower molecular weight under the action of ionizing radiation, which turns out the solubility of polymer increase in the solvent, the corresponding the thermal stability and mechnical performance decrease. Because of the series of results producing by radiation degradation, so for the study of radiation degradation is far less attention than radiation crosslinking. In the process of polymer radiation degradation, the Oxidative degradation reaction will occur.

2.1. Radiation Degradation of Oxidation Reaction

Polymer irradiation discoloration whose products mainly include water, CO and CO_2 gas, alcohol, ketone, carboxylic acid and peroxide is the result of a series of reactions. For most of the polymer, It is thought to be caused by radiation energy automatic oxidation process, the process is as follows:

Initiation Reaction of Chain:

$$RH \rightarrow RH\cdot \rightarrow R\cdot + H\cdot$$

$$R\cdot + O_2 \rightarrow ROO\cdot$$

Propagation Reaction of Chain:

$$ROOH \rightarrow RO\cdot + HO\cdot$$

$$ROOH \rightarrow R\cdot + HOO\cdot$$

$$HO\cdot + RH \rightarrow R\cdot + H_2O$$

$$ROO\cdot + RH \rightarrow ROOH + R\cdot$$

$$RO\cdot + RH \rightarrow ROH + R\cdot$$

Termination Reaction:

$$R\cdot + R\cdot \rightarrow R\text{-}R$$

$$ROO\cdot + R\cdot \rightarrow ROOR$$

$$ROO\cdot + ROO\cdot \rightarrow ROOR + O_2$$

$$ROO\cdot + RO\cdot \rightarrow ROR + O_2$$

Polymer materials fracture produce R· after high energy ray irradiation intermolecular; R· can react with oxygen to generate ROO· in the air; ROO· can also capture the hydrogen atoms in polymer that produce ROOH and R·. From the above chemical reaction equations, we can perceive that the formation of R· is the direct cause of polymer materials radiation photodegradation, Once produced alkyl oxygen free radicals ROO·, it will take the hydrogen atoms of polymer molecular chain to form the hydroperoxides. At room temperature, hydrogen peroxide can be broken down slowly again to generate new free radical. there is no doubt that this will lead to further degradation of polymer materials. It is simultaneity that chain rupture and crosslinking in the process of polymer radiation degradation of oxidation. Chain fracture make polymer relative molecular weight reduce while brittleness reticular molecule generate by crosslinking, it leads to the decreased of physical properties of the material. As a result of the formation of the attraction of the conjugate group and the fall of free radicals or ion make the polymer show the color change. Such as the macroscopic expression of Polypropylene materials is yellow after high energy ray irradiation. On this basis, we can improve the performance of irradiation discoloration by enhancing the light stability of the material performance: strengthen the shielding and absorption of radiation ray; reinforce the free radicals decomposition of hydrogen peroxide; quench excited state molecules; capture free radicals. In other words, we can add plasticizer、antioxidants of inhibition radiation oxidative degradation、all kinds of light stabilizer and so on.

2.2. The Methods Irradiation Resistant

We have already understood the mechanism of irradiation discoloration, based on the mechanism of it, we have a lot of research methods to prevent the color change of the polymer materials.There is no doubt that the problem of the study will be very difficult, but I think that the study of this problem will have great significance. It will be further deepen for antioxidant, heat stabilizer and light stabilizers research. Radiation-resistant polymer materials will better applied to humans.

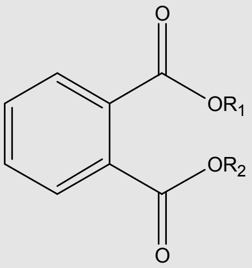
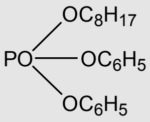
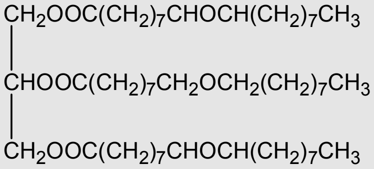
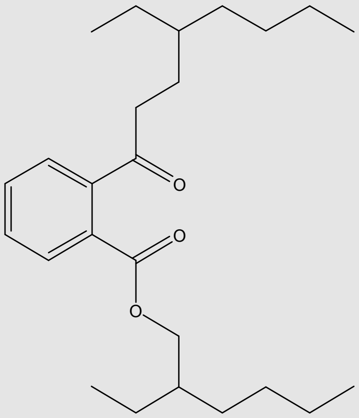
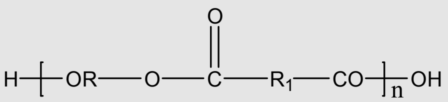
3. The Basic Formula of Polymer Materials

3.1. Plasticizer

There is a large number of polar groups in the polymer molecular and the intermolecular forces is strong. Not only making polymer processing performance deteriorate, but also causing polymer materials products stiffen, lacking of elasticity and suppleness, which reflectes in physical and mechanical properties. There is some changes between the interaction force and the role of the intermolecular hydrogen bond force in polymer-plasticizer system after adding into a certain amount of plasticizer. It makes polymer materials be easily processed and significantly increase of the elasticity and flexibility in the products. That is to say, plasticizer is a substance that adds into the material (usually plastic, resin or elastomer) to improve their processability、flexibility and stretchability. Plasticizer can reduce system melt viscosity and glass transition temperature and product elastic modulus, and will not change the basic chemical properties of the plasticized materials. Polymer materials commonly used plasticizer is phthalate octyl lipid (DOP). Because of poisonousness of the DOP, there is some restrictions on the use of many countries. The current main non-toxic plasticizer have citric acid esters, 1, 2-disubstituted cyclohexane dicarboxylic acid diisopropyl ester type, Estman168 plasticizers, polyester plasticizer, degradable biomaterials with plasticizer, epoxy plasticizer, etc.

Citrate esters plasticizers are more easily moving out than phthalate esters. It can be used in food packaging, medical appliances, children's toys and personal hygiene items, etc. 1, 2-disubstituted cyclohexane dicarboxylic acid diisopropyl ester transparent and precipitate harderly, it has good compatibility with polyvinyl chloride (PVC), so it can be used for the preparation of transparent PVC. Eastman168 plasticizer which developed by the United States is a kind of environment-friendly plasticizers, it is characterized by the security of higher and not cause harmful to human body. Polyester plasticizer is one main type of polymeric plasticizer, it has the feature of the relatively high molecular weight and can not easily move out, it can be used in high temperature insulation materials. Biodegradable plasticizer uses in biodegradable materials, such as polylactic acid (PLA), it can reduce itself hardness. Epoxy plasticizer is compounds containing three of epoxy group, it is the widely application of plasticizer. More representative of the plasticizers is epoxy soybean oil, which has good compatibility with PVC, the advantage of it is high temperature resistant, and can not easily moved out, it also can make the active chlorine atoms of PVC chain more stability, and absorbe quickly HCl decomposing by heat and light degradation. Epoxy plasticizer can use cooperatively with phthalic acid esters plasticizer and can be suitable for transparent PVC.

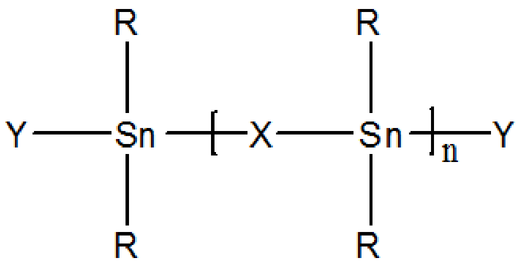
Table 1. *Structure of some plasticizers.*

Plasticizers	Structures
phthalic acid ester	
DPOP	
ESO	 $\begin{array}{l} CH_2OOC(CH_2)_7CHOCH(CH_2)_7CH_3 \\ \vert \\ CHOOC(CH_2)_7CH_2OCH_2(CH_2)_7CH_3 \\ \vert \\ CH_2OOC(CH_2)_7CHOCH(CH_2)_7CH_3 \end{array}$
Estman168	
Polyester	 $H\left[OR-O-\overset{\overset{O}{\Vert}}{C}-R_1-CO\right]_n OH$

3.2. Stabilizer

It can prevent or delay the thermal aging of polymer materials like PVC by adding suitable amount of stabilizers, which eliminates the materials that all had catalytic activity for the thermal degradation reaction of chain (hydrogen chloride and conjugated polyene).There are some kinds of lead salt, metal soap, organic stannum, rare earth and compound stabilizer we used commonly.

The type of lead salt stabilizer mainly refers to the basicity of lead the inorganic and organic acids, such as three basicity lead sulfate, dibasic lead phosphite and so on. Lead-based stabilizers that the first discovered and used in PVC is alkaline in itself. It also absorbes a certain amount of hydrogen chloride gas to form lead chlorid. Lead salt stabilizers have good thermal stability and dielectric properties and lubricating effect. Today, While lead soaps are the must efficient stabilizers, they are not used any more since they are poisonous[2]. Metal soap stabilizers are the collective of metal salts of higher fatty acids, most commonly using are lead, barium, calcium, cadmium, zinc, and magnesium, lithium, aluminum, rare earth metal soap ect. The thermal stability of this class stabilizer is in general, but the transparency, lubricity ability is better than lead salt, moreover it often used in conjunction with lead salts or organic tin stabilizer. There is some different from the performance of metal soap stabilizer according to the types of metal and the kinds of acid radical, respectively. The early stages of the cadmium and zinc soap has good thermal stability, while barium, calcium, magnesium, aluminum has good long-term heat stability, lead is roughly in the middle. In addition, the weatherability of cadmium, zinc and tin soap is great, but the toxicity of cadmium soap is bigger and uses less. Organic tin stabilizers are derivatives that contain carbon-tin keys alkyl compounds and have better stability and weatherability. We can adapt high temperature processing to ensure the transparency of the products. This class of stabilizers can be used for outdoor products and support transparent,colorful of products. Besides, part of the organic tin has some toxicity, DOTL stabilizers and methyl tin stabilizer have no toxicity, hence it can be applied in the food packaging, but expensive. What the structural general formula of organic tin stabilizer is



$$Y-\underset{R}{\overset{R}{Sn}}-\left[X-\underset{R}{\overset{R}{Sn}}\right]_n-Y$$

(R is methyl, butyl octyl and other alkyl; Y is fatty root; X is oxygen, sulfur, maleic acid, etc)

Figure 1. *The Structure of Organic Tin Stabilizer.*

Antimony-containing stabilizer is good momentum of development of the stabilizer now. its toxicity are lower than those of organic tin and the thermal stability is better than that of organic tin in low dosage. The current main containing antimony stabilizers have laurate antimony, three antimony (thioglycolic acid ethyl ester), 3 (lauryl mercaptan antimony), 1(thioglycolic acid, diisooctyl)2(lauric acid mercaptan) antimony, double (2 lauryl mercaptan antimony sulfide), five mercaptan antimony, etc. Rare earth heat stabilizer is a non-toxic heat stabilizer. It can improve the toughness of PVC by adding the type of stabilizers into PVC and it has better processability, transparency and weatherability, and often uses in conjunction with other stabilizers. In addition to the above several, it has developed hydrotalcite, graphite, montmorillonite and other inorganic stabilizers. Hydrotalcite whose alkaline of the surface can absorb hydrogen chloride gas is a kind of laminated material and the existence of anion can replace chlorine atoms in vinyl chloride in the hydrotalcite. Radka Kalouskova[3]and other researchers have drawn a conclusion that we would obtain great thermal stability effect when used hydrotalcite with zinc stearate together. Furthermore, people also began to study organic stabilizer. Fahmy[4] and other investigators studied N-benzoyl-4-(N-maleimido)-phenylhydrazine (BMPH), which is a biologically active thermal stabilizers, and it usually as rigid PVC heat stabilizer and auxiliary heat stabilizer, which showed excellent stability and antimicrobial resistance. Mohamed, N. A.[5] and other researchists have studied used poly (N'-acryloyl benzene hydrazide) (PABH) as heat stabilizer of PVC and used alkali type lead carbonate cooperatively. In recent years, calcium zinc stabilizers which are different from the stabilizers composing by organic group are paid more and more attention to people gradually. When use calcium zinc stabilizers, we need to add auxiliary stabilizing agent. N. Stipanelov Vrandecic[6] and other researchers have investigated the effect of Ca/Zn stabiliser on thermal degradation of poly(vinyl chloride)/chlorinated polyethylene blends, and they found that there is different from the mechanism of calcium zinc stabilizer for the polyvinyl chloride and chlorinated polyethylene.

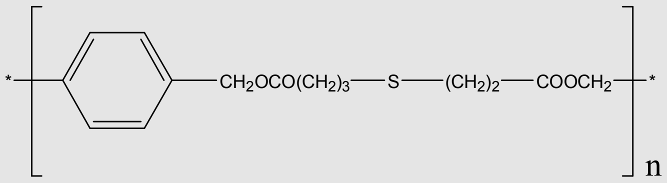
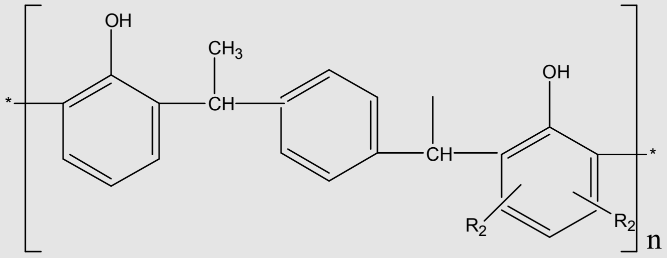
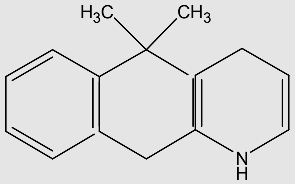
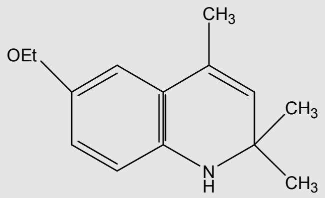
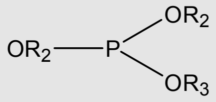
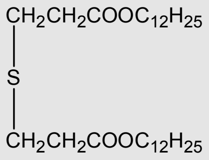
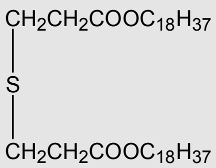
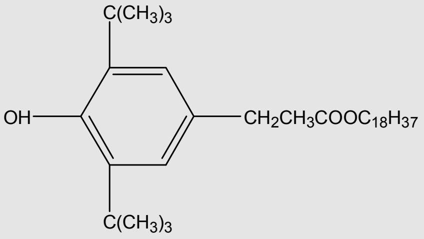
3.3. Antioxidants

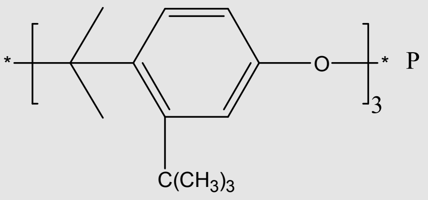
Antioxidant is a kind of polymer that can delay or inhibit oxidation degradation of the material to some extent. During the processing of polymers, because of high temperature in a short period of time, meanwhile, polymers subject to the very strong mechanical shearing action, that causes the chain of polymer molecules part fracture to generate free radicals, and polymers have long been oxygen, water, acid, alkali and other chemicals during the use of them, then polymers begin aging. Antioxidants are thought to be a free radical scavengers, it can prevent the growth of the chain and avoid the further degradation of polymers; the auxiliary antioxidants can clear the root of the form of free radicals, thus reduces fundamentally the formation of free radicals, and improves the thermal stability of the polymers.

We often use the main antioxidant which is divideded into amine antioxidants and phenolic antioxidant; Auxiliary antioxidants include sulphur and phosphite ester, etc. Main mechanism of hindered phenolic antioxidants is reactivity with free radical R· and ROO· and interrupt the growth of chain in the process of oxidation. Hindered phenolic antioxidants have single phenol, bisphenol, polyphenols, nitrogen heterocyclic polyphenols and other categories. The molecular weight of single and double phenolic antioxidants is low, but there is some deficiency in the properties of volatile and migration. Polyphenol antioxidants is the current leading products that have high molecular weight and wonderful compatibility with plastic, and excellent antioxidant performance. Phosphite ester antioxidants and antioxidant sulfur decompose hydroperoxide to low reactive molecules through the variation of the valence phosphorus and sulfur atom in itselves. If classified by molecular structure, it mainly includes thioester antioxidants and thiobisphenol antioxidants type phenol sulfide and so on. Compound Antioxidants are different primary and secondary antioxidants used in combination, or a combination of different types of antioxidants antioxidant use. They have the characteristics of taking advantage of each other, synergistic, interworking and achieve great antioxidant effects.

Beijing Institute of Petrochemical Technology in China had developed the antioxidant called MODANOX2600, the thermal stability of this type of antioxidant is better than antioxidant1010 and antioxidant300. W. M. Heiserman[7] and his teamwork had researched on the two-dimensional phase behavior and vibrational structure of antioxidant1010 and 1076 monomolecular film at the air / water interface formation. The molecular structure of the antioxidant1010 and 1076 contains both hydrophilic group and hydrophobic groups at the same time, as a result, these two kinds of antioxidants tend to surface enrichment in order to reduce the surface energy. There is can be further study of antioxidants in polymer materials frost on the surface of the problem through a series of conclusions. Ciba Specialty Chemicals Holding Company[8]would combinate phenolic antioxidant with a new crystal modifier-Pentaerythritol-four [3-(3,5-2,4-hydroxy-tert-butyl-benzene)-propionate], as well as aqueous dispersions to form a new crystal system, this will facilitate the preparation of an antioxidant to a more environmentally friendly direction. Ciba Specialty Chemicals Holding Company[9] has announced one for polypropylene antioxidants called IrgastabFS533, the antioxidant can effectively reduce the oxidation reaction of polypropylene during processing. Yachigo[10] get antioxidant GM through antioxidant 2246 reacting with acryloyl chloride, its name is 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methyl methyl)-4-methyl phenol acrylate, By the late 1980s, Yachigo[11,12] made an intensive study of antioxidantGM and has drawn conclusion that antioxidant GM obtains excellent thermal stability in the absence of oxygen or hypoxic conditions, what is more, it can significantly improve the processing stability of the type of polybutadiene resins.

Table 2. *Structure of some antioxidants.*

Antioxidants	Structures
Poly TDP-2000	
Poly-Ao-TM-79	
BLE	
AW	
Phosphite Ester	
DLTP	 $\begin{array}{l}CH_2CH_2COOC_{12}H_{25}\\ \vert \\ S \\ \vert \\ CH_2CH_2COOC_{12}H_{25}\end{array}$
DSTP	 $\begin{array}{l}CH_2CH_2COOC_{18}H_{37}\\ \vert \\ S \\ \vert \\ CH_2CH_2COOC_{18}H_{37}\end{array}$
1076	

Antioxidants	Structures
168	

3.4. Light Stabilizers

Polymer material long-term or short-term exposure to sunlight placed under strong fluorescence, due to absorption of UV energy, auto-oxidation reaction occurs, resulting in degradation of the polymer, making the products the color, crisp, performance degradation, that they can not re-use, this process refers to as polymer light oxygen aging or photoaging. We can prevent the polymer to photoaging, greatly extending the service life of polymer materials by adding the light stabilizers. The main mechanism of this stabilizers are shielding and absorption of UV light, quenching of the excited state molecules, the capture of free radicals. The light stabilizer can be divided into light-shielding agent, UV absorbers, quenchers, radical scavengers four categories according to the stabilization mechanism.

UV absorbing light stabilizer absorbs light energy and heat energy by using its own molecular structure to avoid material absorbs light energy occurs photoxidation reaction, there are two major UV absorber-benzophenone and benzotriazole, etc. Quenching agent and UV absorber are similar, all of them avoid material light oxidation by transferring light energy, what the different is that the quenching agent interacts with the excited state functional groups, the groups are high energy and high chemical reactivity substance which produced due to the absorption of light energy, to transfer the energy of the functional groups, in industry, quenching agent is bivalent nickel complex containing heavy metal nickel, gradually people are reducing the usage in recent years because it have certain harm to human body. Light shielding agents achieves the effect of preventing oxidation by the reflection and shielding of the light energy include carbon black, titanium dioxide, zinc oxide, etc. the existence of it like the establishment of a barrier between the polymer and the light source, so that light is absorbed or reflected when it reaches the surface of the polymer, hinder the high-energy radiation deep inside the polymer, so as to curb effectively the aging of the polymer. Three types of light stabilizers-light shielding agents, UV absorbers, quenchers get industrial applications in the 1960s. Hindered amine light stabilizer began industrial production until the mid-1970s, but the number of its varieties, developing faster than other light stabilizers, Hindered amine light stabilizer is the main categories of light stabilizers.

Hindered amine light stabilizer is an organic amine compound having steric hindrance to 2,2,6,6-tetramethyl-4-piperidinyl to the parent structure. Under the effect of light energy, plastic chain reaction occurs, a hindered amine light stabilizer transforms the nitroxide because of the peroxide and oxide which are produced by the chain reaction, HALS may react with hydroperoxide and radical in the process of the reaction to generate the inactive product, thereby eliminates the free radicals in the material. Moreover, nitroxide produced polymer itself also has ability to capture active radical R·, RO·, ROO·, converting into a relatively stable RR, ROR, R-OO-R, etc., on the secondary radicals capture. Nitroxides capture a second later, would go back to the original state of nitrogen radicals, it can capture again, so the cycle can continue to capture the reaction of free radicals. Meanwhile, HALS have the ability to quench singlet oxygen and make transition from the excited to the ground state, intervene the light oxidation reaction before the chain initiator.

Japan's Asahi Denka Kogyo company[13] produced high molecular weight HALS light stabilizer by using propylene chloride to react with pipradrol and made it stabilized polyethylene with excellent weather resistance. Korea[14]would piperidinol and maleic anhydride grafted polyisobutylene rubber produce high molecular weight light stabilizers. Songwon Industrial Company of Japan[15,16] used allyl benzo triazole compound and maleic anhydride copolymers to make high molecular weight light stabilizers, its structure is:

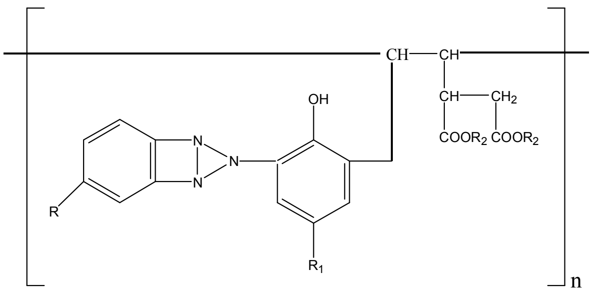


Figure 2. The Structure of the stabilizer.

Cytec company[17]introduced a new one HALS-CYASORB UV-3808PP5, this stabilizer allows the polymer product for long periods without fog, no smoke, no frost, and showed significant weather resistance, low cost,its structure is:

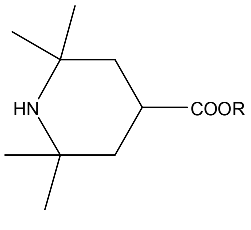
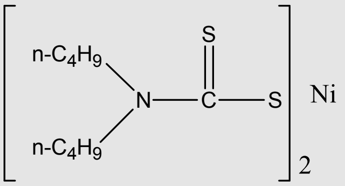
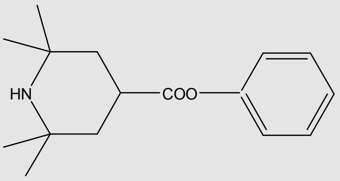
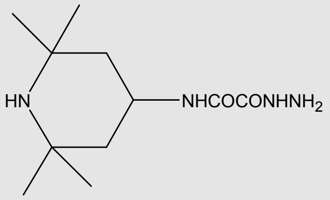
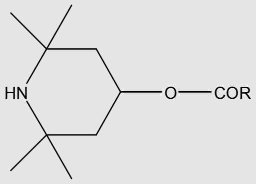
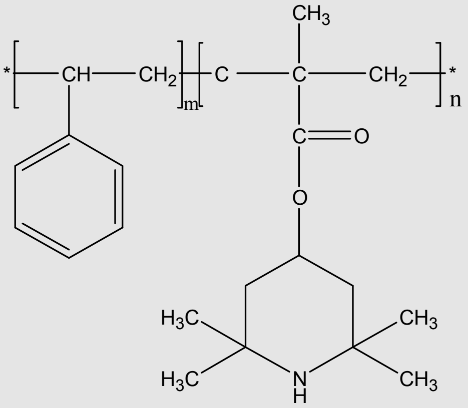
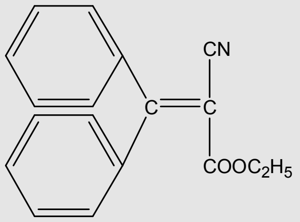


Figure 3. The Structure of UV-3808PP5.

DuPont company[18] produced a light stabilizer, its commodity brand is 210, which is nanoscale titanium dioxide. it is composed of tiny particles of titanium dioxide to absorb ultraviolet light and it is mainly used in sports products, outdoor equipment, textiles, etc., it can also be used in plastic molding and thin sheets. And this is not like a traditional light stabilizer, as migration from the polymer products, so it's action time to be more long-lasting effect. At present, hindered amine light stabilizer is moving low alkalized and molecular weight, multi-functional and reactive direction.

Table 3. *Structure of some light stabilizers.*

Light Stabilizers	Structures
NBC	
LS-744	
Luchem HA-R100	
UV-3808PP5	
P. D. S	
N-35	

4. Research Status

Currently there are a great many of the studies of polymer materials irradiation discoloration. Among them, the research of hindered amine light stabilizers are the most representative basing on the inhibition mechanism of oxidative degradation reaction.

Drahomir Vyprachticky[19] have researched the system of hindered amine light stabilizer and hindered phenolic antioxidant, they discovered that the two substances showed antagonistic effect in the whole system, that is to say, the two substances can not be applied to the polymer and significantly improve radiation resistance of the polymer by a series of conclusions. Hiroshi Yamashita[20] have already investigated that in the presence of acidic compounds, it will accelerate HALS decomposition of hydrogen peroxide, at the same time, the decomposition process is cracked. Even with weak acid such as phenolic antioxidants combination it can also cause antagonistic effect. Chirino-Padron[21]have discussed that the interaction between three kinds of HALS (Tinuvin144, CyasorbUV3346, Tinuvin622) and two kinds of phenolic antioxidants (Hostanox03, Cyanox1790) in the natural aging process of PP films, when used it together, both also appeared antagonistic effect and synergistic effect, these effects attributed to the physical and chemical interaction. Cristina Luengo[22] have considered that the effect of ultraviolet light degradation of styrene-ethylene-butadiene-styrene (SEBE) when combinated phenolic antioxidants with difunctional HALS or low polymerization HALS, they drawn a conclusion that there was synergistic effect obviously, the synergistic effect of difunction HALS was more significant, while the synergistic of the low polymerization HALS was slightly poor, this may be due to the migration or diffusion of the low polymerization in polymer. Kazumi Kikkawa[23]have examinated that the antagonism between hindered amine light stabilizers and sulfur-containing compound by using electron spin resonance and UV spectrum, the results showed that nitroxyl formed by HALS or the disappearance of nitroxyl were not affected by the influence of sulfur-containing compounds itself, but affected by the acidity of the intermediate product. antagonism between HALS and sulfur-containing antioxidants can explained that HALS and intermediate products (nitroxyl, hydroxylamine and hydroxylamine ether) react with acid products formed by sulfur-containing antioxidant or salt formation. F. Gugumus[24] have studied the possibilities and limits of synergism with light stabilizers (Tinuvin770, Tinuvin622, Chimassorb944 and Chimassorb119 and so on) in polyolefins, it was found that generally does not produce a synergistic effect but additive effect when two kinds of low molecular weight HALS combinated, there was also antagonistic effect for some special compound. It generally exhibited a synergistic effect when combinated low molecular HALS with high molecular HALS; from the experimental resulting we can infer that it is based on different mechanisms together to protect the polyolefin at least, these mechanisms included Tinuvin622 made the main active center like the oxygen atoms lose activity and Chimassorb944 caused catalyst remained in polymer to lost activity. Norman S. Allen[25] have already examinated the reaction between two new phosphite stabilizers and universal polymeric hindered piperidine ultraviolet light stabilizers in the heat and light degradation of PP and PE film by fo urier transform infrared spectrometer (FTIR). There was always synergistic effect in the heat and light degradation of PP and PE film no matter what the proportion or the concentration of hindered piperidine phosphorous (phosphate amine) and UV stabilizers, this because the phosphoramide could destroy hydroperoxide and remove oxygen by 4-amino groups, thus to protect the Chimassorb944. There was antagonistic effect when used it with Chimassorb944 together, because of the poor compatibility in PE. For other stabilizers present application mainly have Wang Huiliang[26] studied show that hindered amine light stabilizer 2,2,6,6- tetramethyl piperidinol-4-methacrylate or 1,2,2,6,6- pentamethyl piperidine alcohol-4-methacrylate added into PP could improved the radiation resistance of PP. L. C. Burnea[27] have discovered that the radiation stability of polypropylene/lead zirconate composites by isothermal and nonisothermal chemiluminescence and FI-IR spectroscopy afterγ-irradiation at 20,50,100 and 250kGy relative to neat material, The two investigation methods proved the favorable effect of $PbZrO_3$ filler especially for samples containing 5wt% lead zirconate. Even if polypropylene is degraed during γ-exposure in air, lead zirconate significantly delays and inhibits oxidation by surface bonding of free radical which restrains the reactions of hydrocarbon radical with diffused oxygen. Minoru Iwata[28]have researched that the recovery of radiation-induced coloration on various polyimides-Kapton (Du-pont), Upilex (Ube) and Pixeo TP-T(Kaneka), he had draw a conclusion that the behavior of color fading depended on the uniformity of degradation. If the coloration immediately after irradiation is needed to evaluate the degradation, it is necessary to understand the recovery behavior on each type and the thickness of polymer because the order of radiation resistance varies depending upon the length of time that has elapsed since air exposure of irradiated sample.

5. Summary

As people on the improvement of product quality, performance requirements, and the strengthening of global environmental protection consciousness, development of efficient, environmentally sound versatility plastic stabilizer has become the dominant direction of the 21st century, many large companies and research institutions are continuing to strengthen research. A large number of antioxidants, light stabilizers have a synergistic effect of emerging. The future development trend is still reflected in the efficient, special effects, non-toxic, pollution-free, multi-functional complex.

Currently, irradiation discoloration of the polymer is still in the primary stage of the study, Once these the issues of the radiation resistant polymers are resolved, Irradiation-resistant polymer materials prospects in all fields will be broader.

References

[1] R. L. Clough, K. T. Gillen, G. M. Malone, J. S. Wallace. Color formation in irradiated polymers [J]. Radiat. Phys. Chem, 1996, 48(5):583-589.

[2] H. Ismet Gokcel, Devrim Balkose, Ugur Kokturk. Effects of mixed metal stearates on thermal stability of rigid PVC[J]. European Polymer Journal, 1999, 35:1501-1508.

[3] Radka Kalouskova, Miroslava Novotna, Zdenek Vymazal. Investigation of thermal stabilization of poly (vinyl chloride) by lead stearate and its combination with synthetic hydrotalcite[J]. Polymer Degragation and Stability. 2004, 903-909.

[4] Fahmy, M. M, Mohamed, R. R, Mohamed, N.A. Novel antimicrobial organic thermal stabilizer and co-stabilizer for rigid PVC[J]. Molecules. 2007(7):7927-7940.

[5] Mohamed, N.A. Thermal degradation behavior of poly(vinyl chloride)in the presence of poly(N’acryloyl benzhydrazide)[J]. Polymer Degragation and Stability. 1994(4):540-543.

[6] N. Stipanelov Vrandečić, I. Klarić, U. Roje. Effect of Ca/Zn stabiliser on thermal degradation of poly(vinyl chloride)/chlorinated polyethylene blends[J]. Polymer Degradation and stability. 2001, 74(2):203-212.

[7] W. M. Heiserman, S. Z. Can, R. A. Walker. Tnterfacial behavior of common food contact polymer additives[J]. Jounral of Colloid and Interface Science. 2007, 311(2):587-594.

[8] Daniel Schafter, Johannes Van Der Schaaf, Paul Adriaan Guckel. Phenolic antioxidant in crystalline form[P]. USP7262319. 2008. 8.

[9] Ciba Launches Stabilizer for Polypropylene Fibre[J]. Additives for Polymer. 2005. 1:5.

[10] Shinichi Yachigo, Toyonaka, Tamaki Ishii. Stabilizer for polymeric substance and polymeric substance composition containing the same[P]. US Patent 4525514. 1985.

[11] Shinichi Yachigo, Manji Sasaki, Yukoh Takahashi. Studies on polymer stabilizers: Part I -A novel thermal stabilizer for butadiene polymers[J]. Polymer Degradation and Stability. 1988. 22(1):63-77.

[12] Shinichi Yachigo, Fumitoshi Kojima, Manji Sasaki. Studies on polymer stabilizers: Part IV Prevent of oxidative discoloration[J]. Polymer Degradation and Stability. 1992. 37(2):107-113.

[13] Ono Kaori. Resin composition containing UV-absorbing polymers and optiacal films, polarizing plates, and displays[P]. JP. 2002, 363, 420, 2002-11-18.

[14] Kim Haa Shik. Synthesis and properties of new polymeric photstabilizers containg HALS groups[J]. Polymer(kores). 2001. 25(5):625-634.

[15] Ozawa Akihiro. Ultraviolet-absorbing polyamide or polyester material compositions with improved durability[P]. JP. 88-172, 729. 1988-07-16.

[16] Kang Seoh Won. Copolymers of benzotriazol monomers with maleic or fumaric acid derivatives and polymeric material compositions[P]. U. S. P, 4,686,268. 1987-08-11.

[17] Asian plastics compounder improves product quality and meets auto specification with CYASORB light stabilizer[R]. Polymer Addivtives Casc Study. 2007 Cytec Industries Inc.

[18] DuPont Unveils TiO_2-based light stabilizer,extends antistat additives range[J]. Additives for Polymer. 2008(1):5-6.

[19] Vyprachticky D, Pospisil J, Sedlar J. Possibilities for cooperation in stabilizer systems containing a hindered piperidine and a phenolic antioxidant-A review[J]. Polymer Degradation and Stability. 1990. 27(3):227-255.

[20] Yamashita H, Ohkatsu Y.A new antagonism between hindered amine light stabilizers and acidic compounds including phenolic antioxidant[J]. Polymer Degradation and Stability. 2003. 80(3):421-426.

[21] Chrinos-Padron A J. A spectroscopic study of the interaction between hindered amines and high molecular weight phenols during the natural weathering of polypropylene fims[J]. Polymer Degradation and Stability. 1990. 29(1):49-64.

[22] Cristina L, Norman S A, Arthur W. Synergistic profiles of chain-breaking antioxidants with phosphites and hindered amine light stabilizers in styrene-ethylene-butadiene-styene(SEBS) block copolymer [J]. Journal of Vinyl and Additive Technology. 2006. 12(1):8-13.

[23] Kikkawa K, Nakahara Y, Ohkatsu Y. Antagonism between hindered amine light stabilizers and sulfur-containing compounds[J]. Polymer Degradation and Stability. 1987. 18(3):237-245.

[24] Gugumus F. Possibilities and limits of synergism with light stabilizers in polyolefins [J]. Polymer Degradation and Stability. 1985. 13(1):31-76.

[25] Allen N S, Ortiz R A, Anderson G J. Interaction in the thermal and light stabilizing action of novel aromatic phosphites with a 2-hydroxybenzophenone and hindered piperidine stabilizer in polyolefin film[J]. Polymer Degradation and Stability. 1998. 61(2):183-199.

[26] Wang H L, Chen W X. Effect of penta and tetramethyl HALS on the radiation resistance of polypropylene [J]. Appl Polym Sci. 1998. 69(13):2649-2656.

[27] L. C. Burnea, T. Zaharescu, A. Dumitru, I. Plesa, F. Ciuprina. Radiation stability of polypropylene /lead zirconate composites[J]. Radiation Physics and Chemistry. 2014. 94:156-160.

[28] Minoru Iwata. Recovery of radiation-induced coloration on various polyimides [J]. Science Direct. 2008. 266:3071-3074.