The Trend of Additives for Poly(vinyl chloride) as Photostabilizers: Review Article

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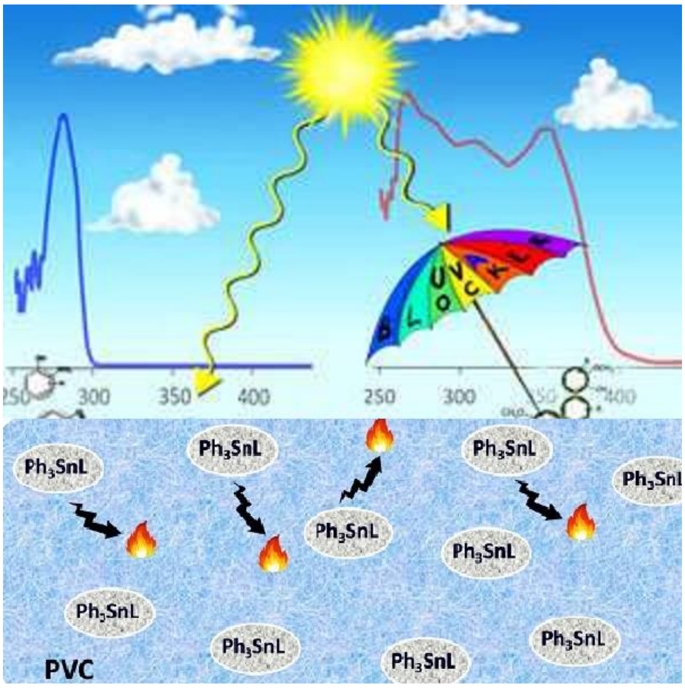
Abstract

Conservation of poly(vinyl chloride) from the ultraviolet light that causes degradation, have very attention in recent decades. PVC formularizations have a large number of additives playing fundamental functions during their conversion and adjusting the behavior properties of final products. In this review, various types of additives are briefly discussed to show their important properties and reasons for addition to their essential mechanisms that cause retardation of photo-degradation. The additives including organotin(IV), UV screeners, organic UV absorber and free-radical scavengers. [DOI: 10.22401/ANJS.22.4.06]



Keywords: PVC, Photo-stabilizers, organotin(IV), TiO_2, organic UV absorber, HALS.

Introduction

Poly(vinyl chloride) is the generality commonly applied in the synthesis of plastic that came after polyethylene and polypropylene [1]. PVC has different important properties such as ascendant chemical resistance, mechanical properties, non-flammability, stability, and low cost [2]. PVC is one of the most important plastic materials used worldwide in various phases of the construction industry, such as pipes, fittings and gutters, window profiles and doors, ceiling tiles, various furniture and upholstery applications, coatings for electrical cables, etc., mainly because of its economy, in addition to its durability and ease of assembly [3]. However, PVC gradually degradation when exposed to the ultraviolet (UV) light that leads to reduces of mechanical performance. Can see the degradation of PVC in discoloration, loss of ductility and micro-cracking [4].

PVC undergoes degradation when exposure to UV-light neither in the absence of oxygen nor in presence. PVC consists of C-C, C-H, and C-Cl bonds that expected does not absorb at wavelength of the light longer than 190-220 nm. The low poly(vinyl chloride) stability toward light due to the photo-absorbing structures, that inserted to the polymer through the polymerization manufacturing [5]. The main processes occurring in the photo- and photo-oxidative degradation of poly(vinyl chloride) polymers are [6]:

1. De-hydro-chlorination that proceeds and yields polyene structures with release HCI. This reaction may be controlled by decrease the surface region of the specimen and decrease the temperature. De-hydro-chlorination reduces with crosslinking processes. The participation of gaseous HCl speed up the photo-oxidation process of poly(vinyl chloride) in two ways [7]:
   - HCl serves as a chain-transfer factor, which interacting with different radicals like POO·to give very interactive chlorine radicals.
   - HCl dissolves metallic impurities and gives metallic salts that have a catalytic effect in oxidation reactions.
2. In the case of presence of oxygen, formation of carbonyl and hydro-peroxide group through crosslinking and chain scission reactions.

The photo-degradation of PVC takes place by the hydrogen abstraction process Fig.(1). Hydrogen abstraction carries out from the PVC backbone via the free radicals ($R^{\bullet}$ or $P^{\bullet}$) that might be the formation of two kinds of polymer alkyl radicals [8]. In the oxygen presence, these radicals of polymer alkyl are extremely interactive toward oxygen molecules and form peroxy radicals ($PO^{\bullet}$) of the polymer. The peroxy radicals of the polymer could extract hydrogen from other neighboring macromolecule and form polymer hydro-peroxides [9]. The photodecomposition of hydro-peroxy groups could be the formalization of ketone, aldehyde, acid and other groups [10], that can be controlled by FTIR spectroscopy technique. The hydro-peroxide and ketone groups that formed may take part in the initiation step of photo-degradation; however, they do not perform an important part in this reaction.

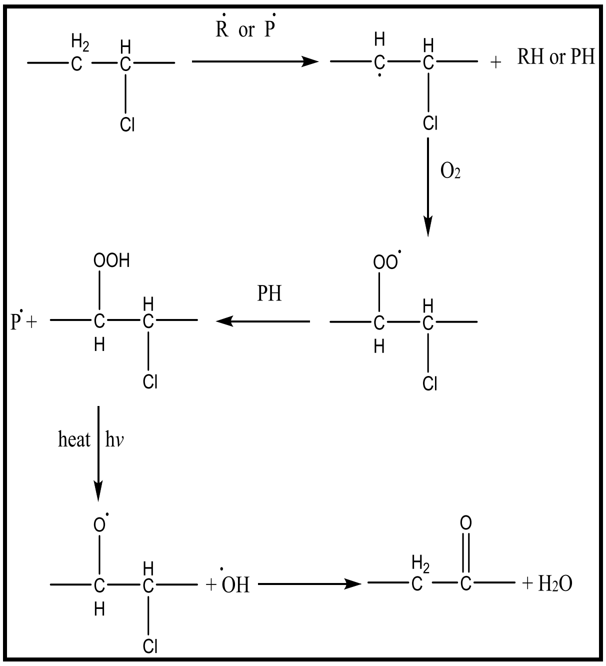


Fig.(1): Mechanism of poly(vinyl chloride) photo-degradation.

Therefore, different photo-stabilizer systems have been used to retardation the degradation of PVC.

Organotin(IV) Complexes

The main use of organotin (IV) compounds is to stabilize PVC against UV light [11]. Several di-organotin (IV) and tri-organotin complexes were syntheses by the reaction of Ph_3SnCl, Ph_2SnCl_2, Bu_3SnCl, Me_3SnCl and Me_2SnCl_2 with different ligands such as benzamidoleucine [12], ciprofloxacin [13,14], benzamidoacetic acid [15], benzamidoglycin [16], furosemide [17], naproxen [32] and telmisartan [33].

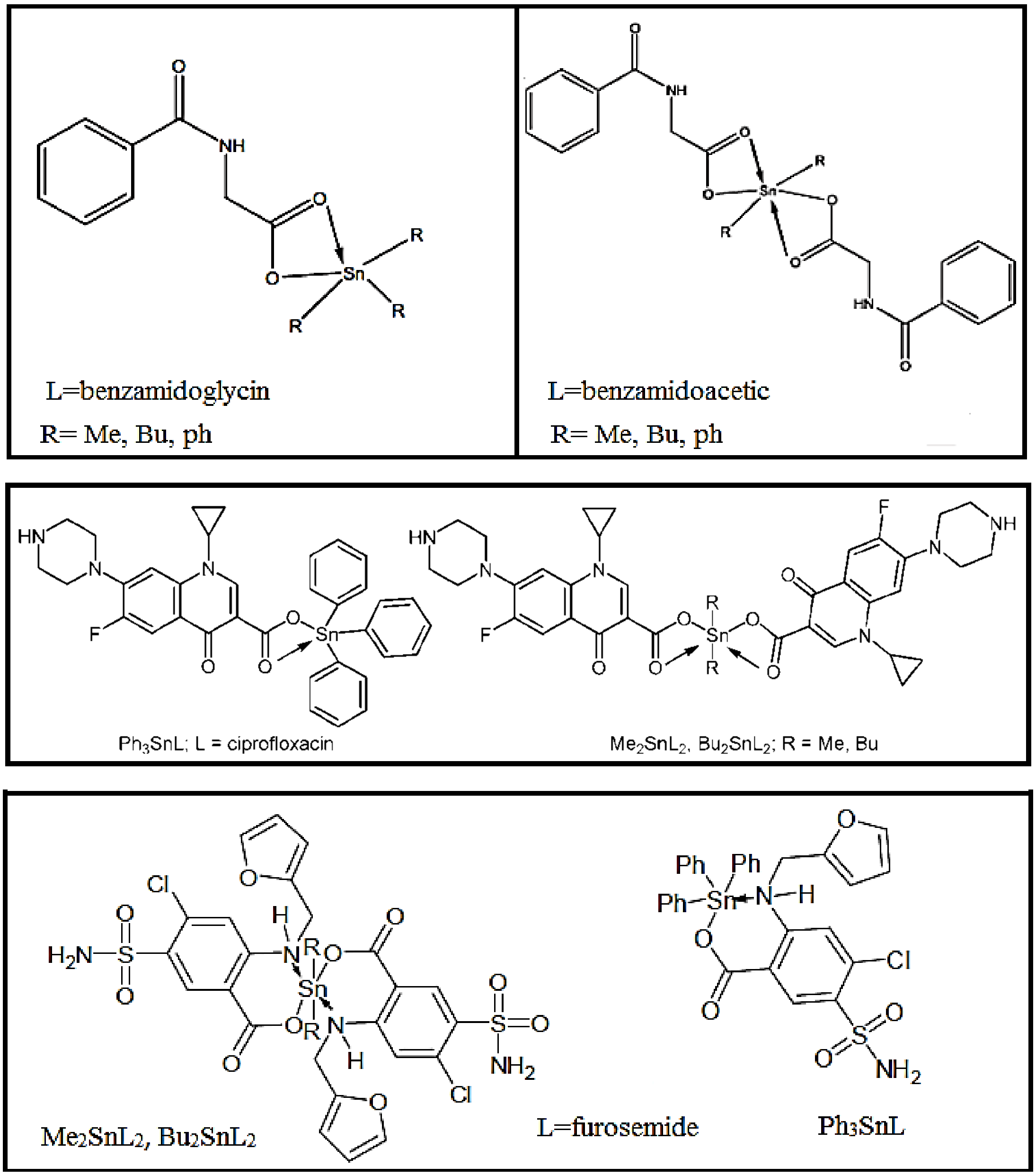


Fig.(2): Structures of organotin(IV) complexes with different ligands.

The PVC films containing a different concentration of several complexes 0.5% via weight were generated by the casting method by using tetrahydrofuran (THF) solvent. The photo-stabilization actions of these complexes were established by observing the polyene, carbonyl, and hydroxyl indices at a different time of irradiation of PVC films using FTIR Spectrophotometer (400–4000) cm^{-1} as display in Fig.(3).

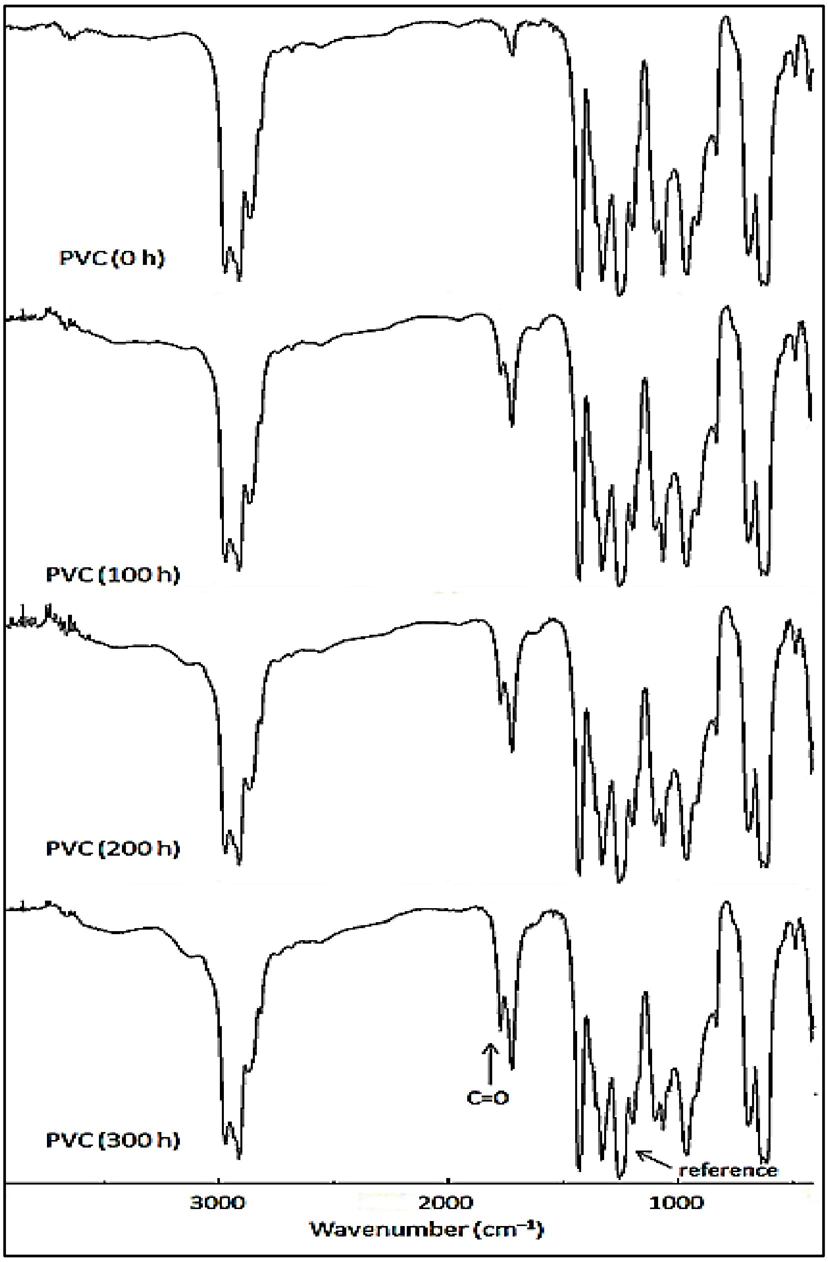


Fig.(3): Changes in FTIR spectra of PVC upon irradiation [18].

The bands of absorption for carbonyl, polyene, and hydroxyl groups represented at (1604, 1722 and 3500) cm^{-1}, respectively. The growth rate of functional groups will be reduced when organotin complexes added to PVC paralleled to PVC without complexes.

The morphologies of PVC films surface that containing complexes were tested by using an atomic force microscope (AFM) and a scanning electron microscope (SEM).

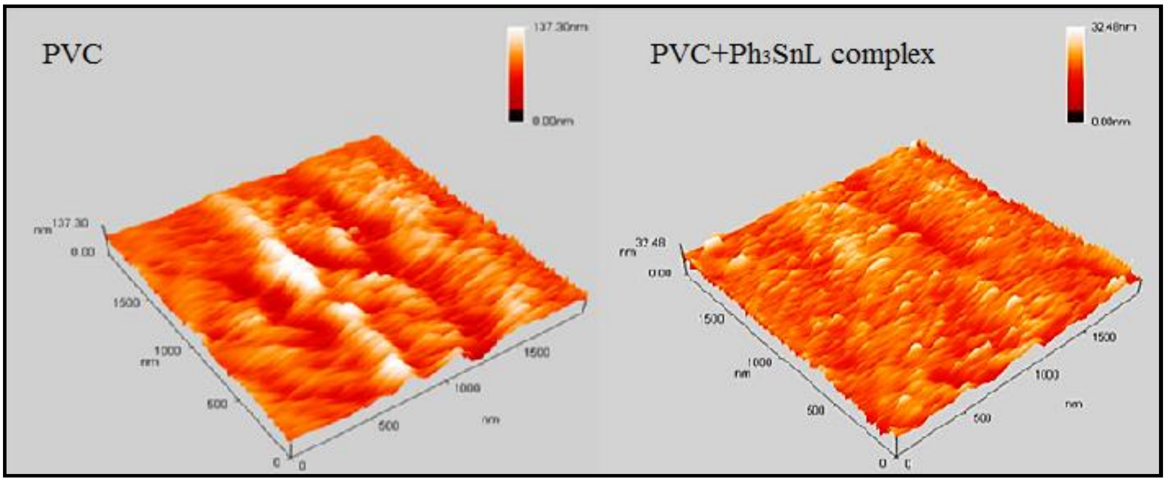


Fig.(4): Images of AFM for PVC film in the absence and presence of Ph_3SnL (L= furosemide) complex at 300h of irradiation [17].

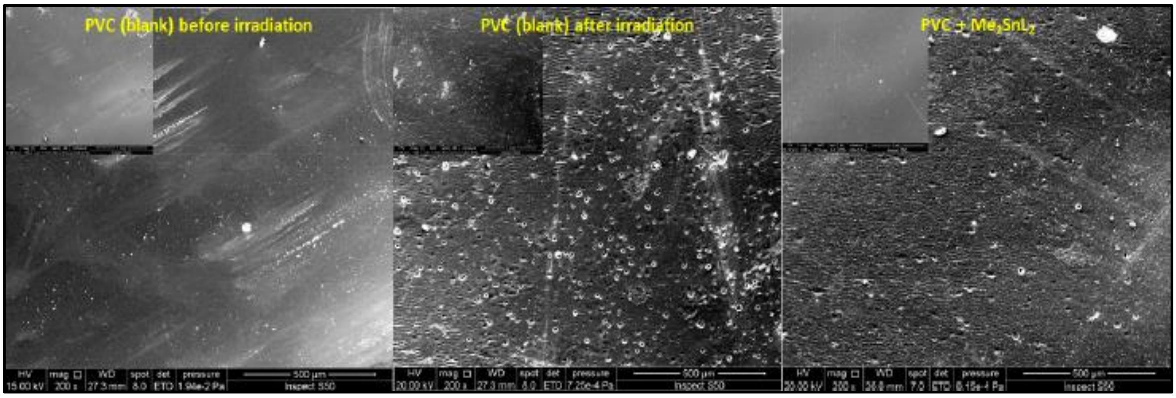


Fig.(5): SEM images of PVC films [13].

Fig.(4) shows the AFM images, the surface of PVC film containing organotin(IV) complex after irradiation was very smooth with low roughness factor (Rq) compared with blank PVC film has a high roughness factor. Figure 5 shows the SEM images, the PVC film with organotin(IV) complex after irradiation exhibit fewer cracks compared with blank PVC film it was clear damage.

Various suggested mechanisms (figure 6) that elucidated the role of complexes for photo-stability of PVC films:

1. Complexes serve as HCl scavengers: Tin behaves as strong Lewis acid, therefore act as HCl scavenger, which is also known as a secondary stabilizer of PVC.
2. Complexes perform as peroxide decomposers: organotin(IV) complexes might be decomposing peroxides and inhibit photo-degradation of PVC.
3. Complexes act as radical scavengers: occurs by the complexation of additives and peroxide radicals and forms unreactive charge transfer complexes (especially containing conjugated π-system ligands).
4. Complexes act as UV Absorbers: when the ligands have conjugated or non-conjugated π-system, and heteroatoms, the organotin(IV) complexes will absorb UV light and dissipated this energy as heat (less harm).

$$R_3SnL + UV \longrightarrow R_3SnL^* \longrightarrow R_3SnL + heat$$

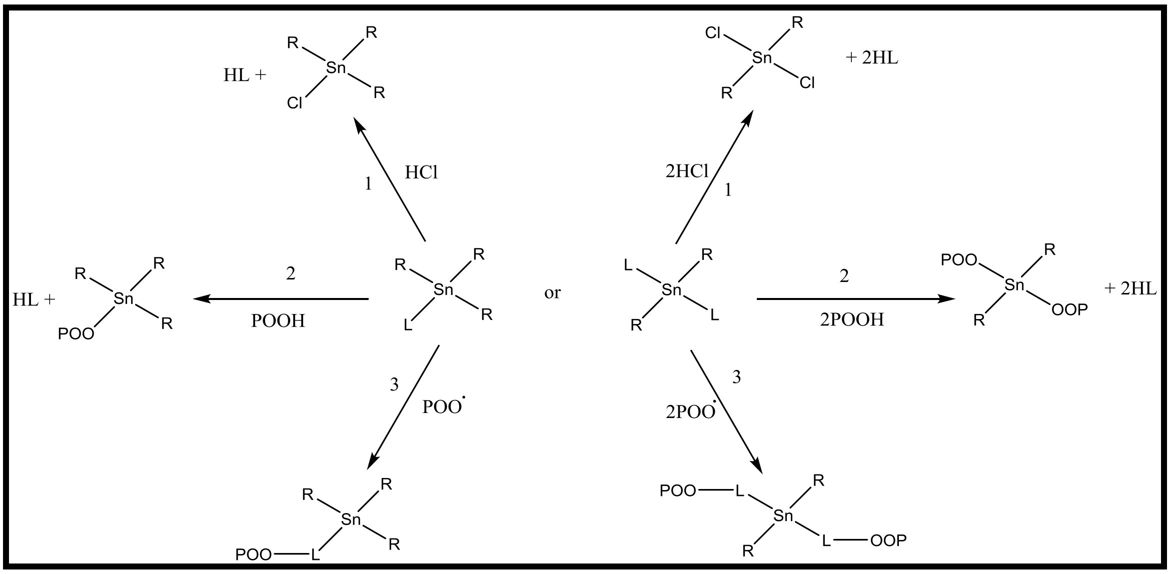


Fig. (6): Suggested mechanism of organotin(IV) complexes.

UV Screeners

Such as pigments including titanium dioxide using as UV screeners for different PVC. Titanium dioxide is an inorganic UV absorber and a very substantial pigment for PVC materials produced for outdoor uses. Regular concentrations of titanium dioxide that use for UV preservation in rang of (4-10) wt%. The role of the titanium dioxide by absorbing or screen almost of the UV light and switch the energy of absorbed radiation into minimal hurtful thermal energy, that way departing little of energy absorbed by PVC [19].

The role of titanium dioxide is summarized in reflect of UV light and reduce the discoloration. The TiO_2 must be used with different light stabilizers, however, TiO_2 can delay the discolouration of irradiated PVC films efficiently, however, the surface undergoes oxidation and form the caverns Fig.(7) that bring by both the bad protection to surface of specimen and the photo-catalysis that is stimulated by UV light, water, and oxygen that accelerates deterioration [20].

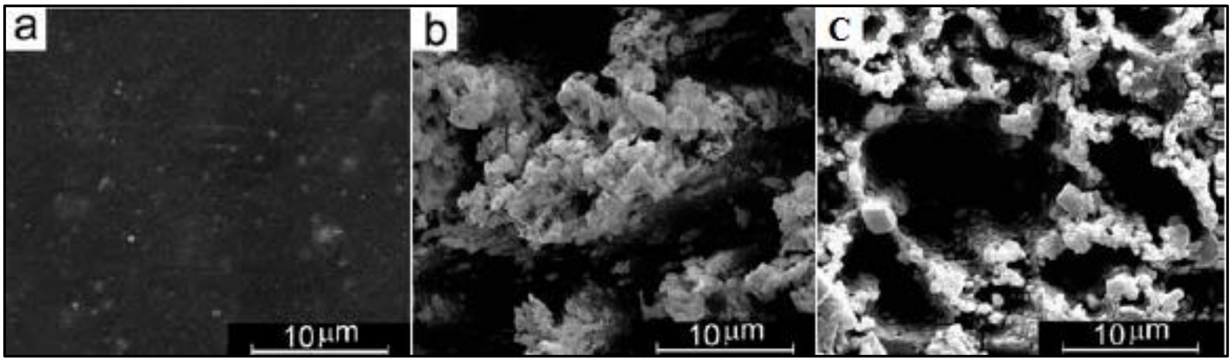


Fig.(7): SEM images of a- PVC blank before irradiation, b- PVC blank after 480 h irradiation, c- PVC with TiO_2 after 480 h irradiation.

In another study, investigated the influence of TiO_2 on the changes of molecular and chemical that occur in PVC surface through accelerated weathering. The outcomes present that polyene and carbonyl groups were produced on the surface of the blank (PVC without TiO_2) after 480 hours of accelerated weathering. However, in the presence of TiO_2, the intensity of functional groups will decrease. Furthermore, a remarkable decrease in the number of average molecular weight (Mn) and the consistency of an unsolvable clot was watched for blank after accelerated weathering, while the time desired for the Mn to come down increased in the participation of TiO_2, and no unsolvable clot has appeared through weathering. These outcomes prove that two types of reactions (crosslinking and chain scission) occurred simultaneously in PVC without TiO_2, whereas in the presence of TiO_2, only the chain scission takes place. However, the presence of TiO_2 has initiated the chain scission comparison to PVC in absence of TiO_2 [21].

The role of TiO_2 in PVC degradation [22]:

- Scatters visible light and to mask discoloration.
- Screens ultraviolet light and conserves the polymer by preventing immediate UV-degradation.
- TiO_2 photo-catalytically converts the surface of PVC from harmful to smooth which leads to color faint.

Organic UV Absorber

The role of organic UV absorbers summarized by absorbing harmful UV radiation. These additives can absorb UV radiation more than the polymers (PVC) and exit. The excited states of these compounds will be relaxing to the ground state rapidly and efficiently re-emitted this radiation in longer wavelength (less harmful), which leads to high stabilization efficiency and excellent photo-stability [23].

It can be categorized as UV absorbers based on chemical class, such as benzophenones, benzotriazole, Schiff bases, etc. [24].

Mixtures of the 4-hydroxybenzophenone, 2,4-dihydroxybenzophenone and phenyl salicylate with their identical glucosides have been studied as photo-stabilizers for hard PVC. Benzophenones have a hydroxyl group and ether, that absorbs UV radiation efficiently, and would be absorbed and dissipate this harmful energy to the polymer as heat.

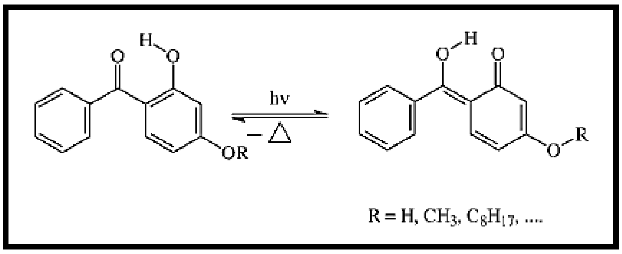


Fig.(8): Absorption of UV light process by benzophenones.

The PVC films prepared by molding method having a concentration of 2% by weight of UV-absorbers or glucosides in the solvent of tetrahydrofuran. The mixtures exhibited photo-stabilizing effects by decreased rates of de-hydro-chlorination and decreased weight loss [25].

The {5,5´-disulfide-bis[2-(2-hydroxy-3,5-di-tert-butylphenyl)-2Hbenzotriazole]} synthesized and applied as an efficient UV absorber (the maximum of absorption for DSBHTBB at 364 nm) in order to prevent the photo-degradation of polymeric. The results revealed DSBHTBB be able to prevent the discolouration that results from treatment by irradiation of PVC [26].

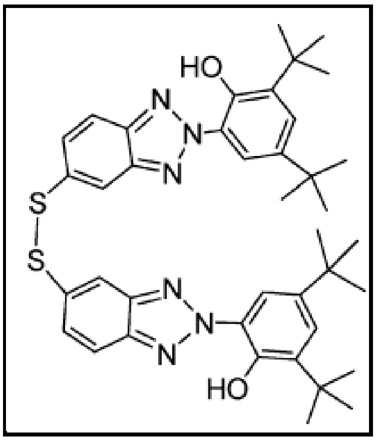


Fig.(9): Structure of DSBHTBB.

Schiff bases (2N-salicylidene-5-(substituted)-1,3,4-thiadiazole) have been used as photo-stabilizer of polyvinyl chloride (PVC) films. The films of PVC having 0.5 wt % of Schiff bases prepared by the molding method in tetrahydrofuran (THF) solvent. According to the experimental results, the stabilization may occur due to the absorption of UV light by the Schiff bases that lead to dissipate the energy as heat [27].

The suggested mechanism of the activity of Schiff bases involves direct absorption of

UV light, the change in energy of photons that absorbed is due to the intramolecular proton transfer and then through an "internal conversion process to the ground state" where the energy dissipated as heat Fig.(10).

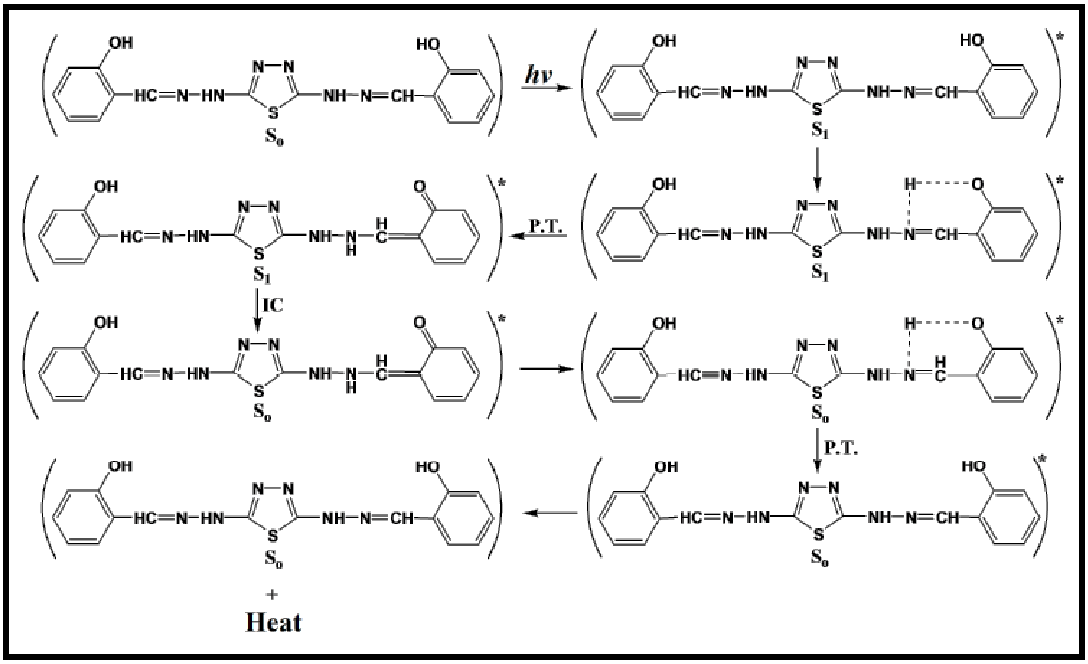


Fig. (10): The mechanism of the photo-stabilization of 2,5-di(arylhydrazones)-1,3,4-thiadiazole compounds as UV-absorber. Where "" and "•" perform excited state and free radical, respectively [27].*

Free-radical Scavenger

Hindered amine light stabilizers (HALS) produced in the 1970s, act mostly as free radical scavengers, quenchers or peroxide decomposers, in another meaning, it dominates the market for light stabilizers. Hindered amines are originated from the tetra-methyl piperidine structure Fig. (11) [28].

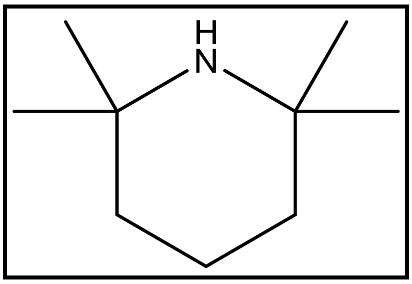


Fig. (11): 2,2,6,6-tetramethylpiperidine.

HALS has a large difference in structures that variation in molecular weights, with minimal evaporation and perfect stabilization at rising temperatures. They can be used in the presence or absence of UV absorbers and quenchers, which provide surface preservation. It is at low concentrations (0.1%), with high efficiency [29].

Two types of piperidine derivatives with low-molecular-weight and a high molecular weight hindered amine light stabilizers (HALS) that used with and without ultraviolet absorbers [(2-(2-hydroxy-3-tert-butyl-5-methylphenyl)-5-chlorobenzotriazole) and (2-hydroxy-4-(octyloxy) benzophenone)] inset to plasticized PVC specimens. PVC samples with HALS and UVA revealed excellent results (differences of color, mechanical properties, and FTIR) and show avoid discolouring and photo-oxidation due to irradiation [30].

The accurate mechanism of stabilization for hindered amines efficiency suggested that they scavenge free radicals by a mechanism demonstration in Fig.(12). Initially, oxidation of hindered amine and forming nitroxyl radical that interacts with free radicals to compose an alkoxyamine, which interacts with a peroxy radical to reproduce the main hindered amine, that starts the circle again [31].

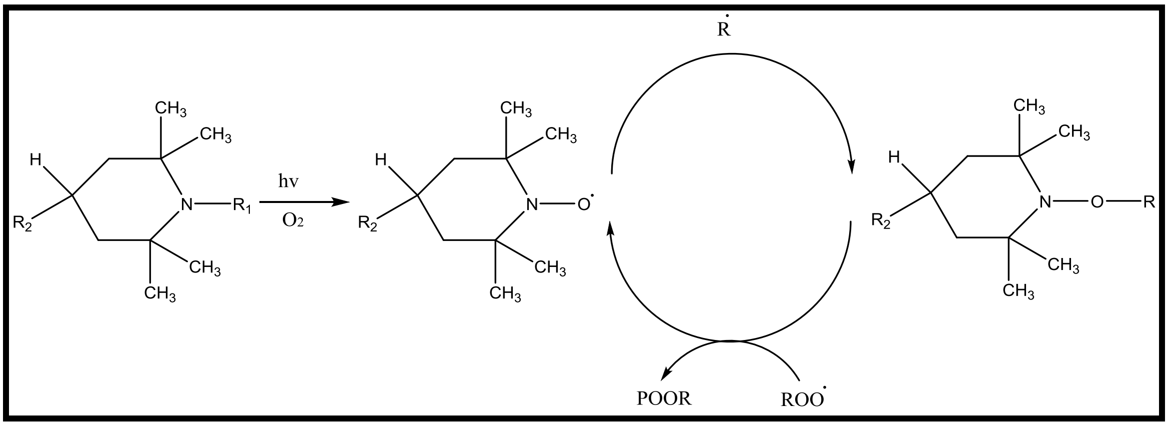


Fig.(12): Stabilization mechanism of HALS.

Conclusion

Due to the photo-degradation that occurs for PVC when exposing to the UV light, we need to use additives to retardation of this degradation, while maintaining the properties of PVC. Such additives are organotin (IV) complexes, TiO_2 pigments, benzophenones, benzotriazole, Schiff bases and hindered amine light stabilizers. By comparing among the researches that discuss in this review, HALS and TiO_2 could be used with other UV absorbers as photo-stabilizer systems for PVC, while organotin(IV) complexes and organic UV absorber more efficient and can be used without other photo-stabilizer systems.

Acknowledgments

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