A Review: Thermal Degradation and Stabilization of Poly (Vinyl Chloride)

Bibi Effat Tahira[1*], M I Khan[1], Rumana Saeed[1,] Shomaila Akhwan[1]

[1] Department of Chemistry, Kohat University of Science & Technology (KUST), Kohat, 26000, Khyber Pakhtunkhwa, Pakistan

ABSTRACT

Polyvinyl chloride is used as a third-most widely produced plastic formed by the polymerization of vinyl chloride and has tremendous applications all around. It is thermally degraded by dehydrochlorination, in the absence of oxygen and evolves HCl. Thermogravimetry (TG/DTG) coupled with evolved gas analysis (MS detection) of volatiles was used to characterize the thermal behavior of commercial PVC cable insulation material during heating in the range 20-800°C in air and nitrogen, respectively. In addition, simultaneous TG/FTIR was used to elucidate chemical processes that caused the thermal degradation of the sample. There are two general approaches to the stabilization of polymers by modification of molecular structure and the use of additives. This degradation must be controlled by the addition of stabilizers. The mainly used stabilizers are Schiff bases, Alkyltin Stabilizers, Mixed Metal Stabilizers, Alkyl Phosphites Stabilizers, β -Diketones Stabilizers, Epoxidized Fatty Acid Esters Stabilizers, Hydrotalcites Stabilizers, Tin Stabilizers, Organotin Mercaptides and Organotin Sulfide Organotin Carboxylates. The heat stabilizer must prevent the dehydrochlorination reaction. Among these Schiff bases were find best regarding environmental effects.

Keywords: PVC, Thermogravimetry, Degradation, FT-IR

Introduction:

Poly (vinyl chloride) is commonly abbreviated as PVC, It is the third-most widely produced plastic, after polyethylene and polypropylene.[1] PVC

is used in construction because it is more effective than traditional materials such as copper, iron or wood in pipe and profile applications. It can be made softer and more flexible by the addition of plasticizers, the most widely used being phthalates. In this form, it is also used in clothing and upholstery, electrical cable insulation, inflatable products and many applications in which it replaces rubber. [2]

Pure polyvinyl chloride is a white, brittle solid. It is insoluble in alcohol, but slightly soluble in tetrahydrofuran. [3] PVC is useful because it resists two things that hate each other: fire and water. Because of its water resistance it's used to make rain coats and shower curtains, and of course, water pipes. It has flame resistance, too, because it contains chlorine. When you try to burn PVC, chlorine atoms are released, and chlorine atoms inhibit combustion.

Structurally, PVC is a vinyl polymer. It's similar to polyethylene, but on every other carbon in the backbone chain, one of the hydrogen atoms is replaced with a chlorine atom. It's produced by the free radical polymerization of vinyl chloride. PVC can also be prepared by treating acetylene with hydrochloric acid (HCl). [5] (Figure 1)
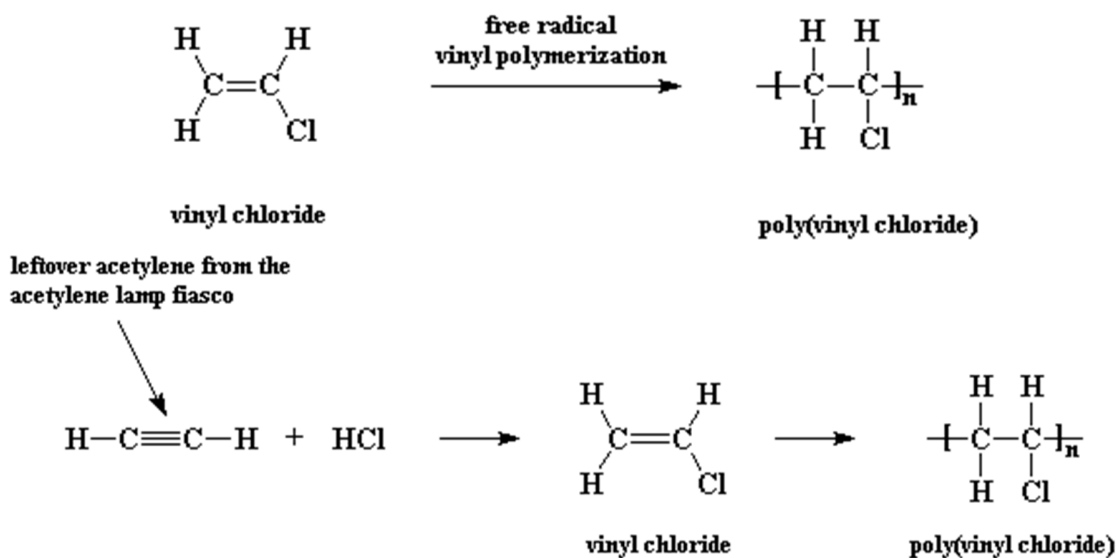

Figure 1: Synthesis of poly (vinyl chloride)

1. **Thermal Degradation of PVC**

1.1. Mechanism of PVC Degradation

When PVC is processed at high temperatures, it is degraded by dehydrochlorination, chain scission, and cross linking of macro-

molecules. Free hydrogen chloride (HCl) evolves and discoloration of the resin occurs along with important changes in physical and chemical properties.

The evolution of HCl takes place by elimination from the polymer backbone; discoloration results from the formation of conjugated polyene sequences of 5 to 30 double bonds (primary reactions). Subsequent reactions of highly reactive conjugated polyene crosslink or cleave the polymer chain, and form benzene and condensed and/or alkylated benzenes in trace amounts depending on temperature and available oxygen (secondary reactions). [6] There are two general approaches to the stabilization of polymers by;

(1) Modification of molecular structure

(2) The use of additives.

Dependent on the mode of degradation, either or both of these techniques may be employed. When the initiation rate is low, additives can be effective and radical traps[1] or chain terminators[1] may be used under these conditions. At high initiation rates, additives are less effective, and stabilization by structure modification may be the only practical approach. Additives would be overwhelmed by the large number of radicals formed during initiation. [7]

1.1.1. <u>Dehydrochlorination of PVC in the Absence of Air (Primary Degradation)</u>

Any mechanism of degradation has to explain a series of experimental facts. Structural irregularities, such as tertiary or allylic chlorine atoms, increase the degradation rates measurably at the beginning of the process by a rapid dehydrochlorination that starts the degradation process. Initial rates of degradation are proportional to the content of these irregularities. However, PVC degrades even if these irregularities are eliminated by special polymerization conditions or treatments because of the dehydrochlorination of normal monomer units (random elimination).

It is estimated that after allowing for the differences in concentrations and reaction rates, the rate of random degradation in commercial PVC because of normal chain secondary chlorine atoms has the same order of magnitude as does degradation that results from structural ir-

regularities. *Cis*-ketoallylic structures, although very reactive in dehydrochlorination, are not present in commercial PVC but can be generated by thermal oxidative processes. After the reactive irregularities initially present are exhausted, degradation continues because of the elimination initiated from normal monomer units. These findings indicate that thermal degradation in PVC is an intrinsic property of this polymer and that change in synthesis conditions or special treatments that eliminate structural irregularities improve the stability of PVC, but cannot completely eliminate its degradation. Stabilizers must be used.

Figure 2: Dehydrochlorination of structural irregularities
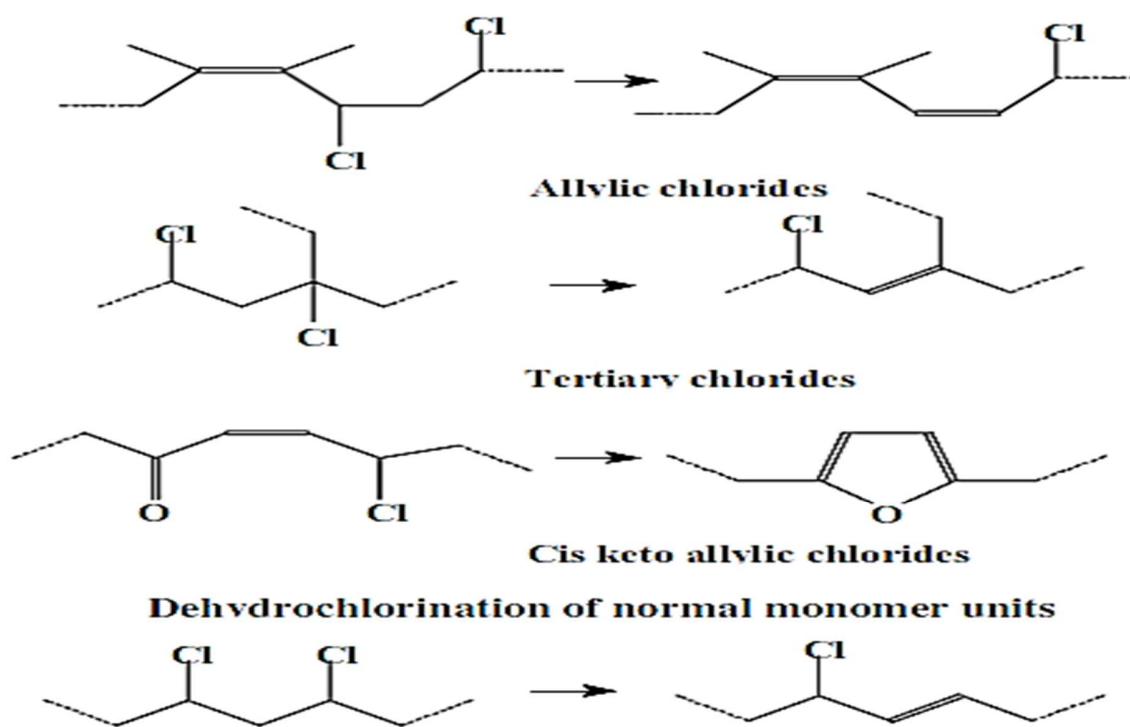
Not all allylic chlorine atoms preexisting and/or formed in the degradation process accelerate degradation. Single double bonds can be identified in degraded PVC by NMR spectroscopy. Double bond sequences, once formed, do not increase by continuation of degradation. There are allylic chlorides with some forms of alkenic double

bonds that are stable under degradation conditions.

The dehydrochlorination of PVC is a very specific chemical process because of the existence of a long series of alternating CH-Cl and CH_2 groups in the polymer backbone that makes possible a chain of multiple consecutive eliminations. However, the parallel formation of conjugated polyene sequences containing 1 to 30 double bonds cannot be explained by a simple consecutive elimination. The chain reaction model explains this apparent contradiction. [6] (Figure 3)
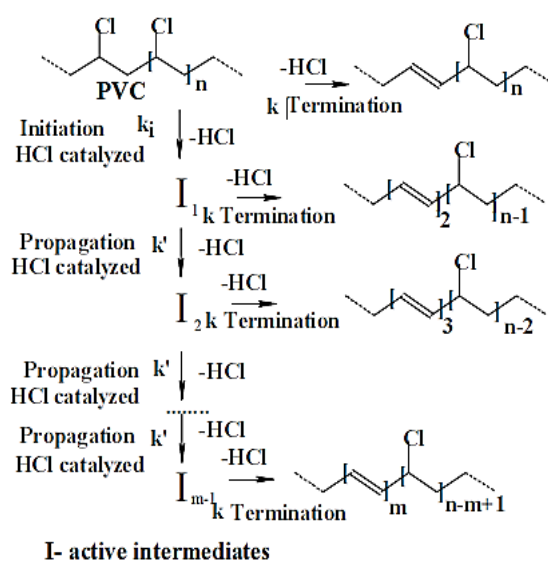

Figure 3: Dehydrochlorination of PVC

There is a general consensus that the intermediates in the degradation process are allylic sequences with progressively increased numbers of conjugated double bonds. However, the mechanism of initiation, propagation, and termination steps is controversial. An early mechanism hypothesized that the intermediates were allylic radicals.[8, 9] (Figure 4)
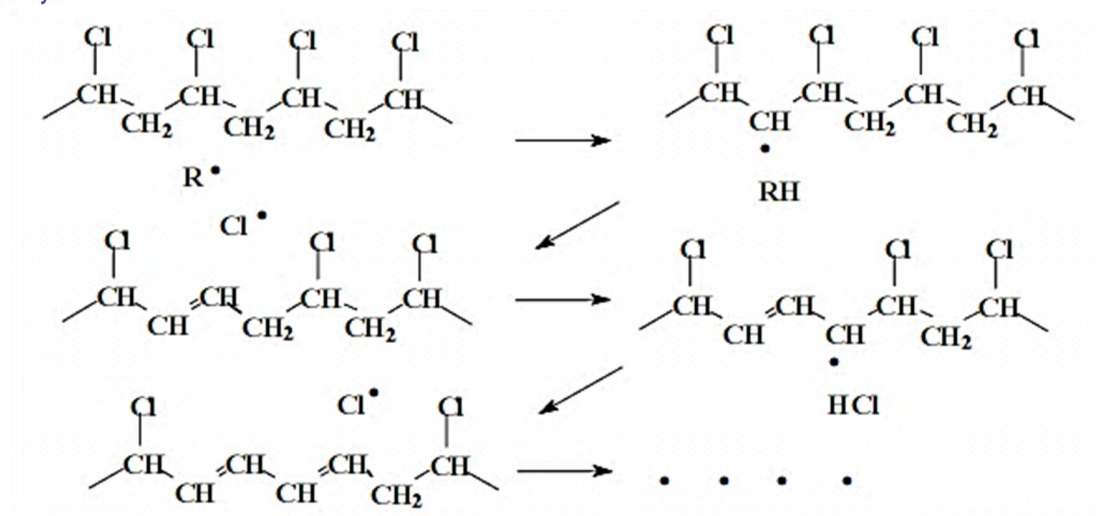
Figure 4: Dehydrochlorination through ionic mechanism

The major problem with this mechanism is that the chlorine atom is known to be so reactive as to be non-selective. Data on model compounds showed that the allylic hydrogen atom, $(>C=CH-CH_2-CCl<)$, has only slightly higher reactivity toward abstraction by a chlorine atom that is free to diffuse throughout the polymer matrix than does a hydrogen atom from a secondary carbon $(-CH_2-CCl<)$.

The above mechanism consequently generates primarily isolated double bonds and not the observed sequences of conjugated polyenes, owing to the much higher concentration of hydrogen on secondary carbon atoms. This radical mechanism also fails to explain the very important catalytic role of HCl. In addition, there are no reliable proofs that radicals are intermediates in PVC degradation in the absence of initiators and/or oxygen. [6]

The thermal degradation of unstabilized poly vinyl chloride (PVC) irradiated with γ-rays has been investigated by dynamic thermogravimetry in a nitrogen atmosphere. The overall effect of irradiation is to render PVC more susceptible to thermal degradation. The change in activation energy of degradation with dose showed a behavior parallel with the change of intrinsic viscosity with dose. The minimum and maximum Ea values were found to correspond with the minimum and maximum observed on [η] versus dose curves. This behavior indicates an inverse relationship between the rate of thermal degradation and molecular size. [10]

1.1.1.1. **Thermal Oxidative Degradation of PVC**

During processing, in addition to thermal dehydrochlorination, the polymer is exposed to thermo-oxidative degradation resulting from oxygen; in addition, mechanical stress may cause chain scission. The main feature in thermo-oxidative degradation is dehydrochlorination as in thermal degradation. The presence of oxygen causes the dehydrochlorination process to accelerate,

but the discoloration is not as severe as during thermal degradation. The polyene sequences are shorter as a result of the reaction between them and oxygen. The overall activation energy of dehydrochlorination is practically the same for thermal and thermo-oxidative processes. The initial dehydrochlorination proceeds by the same mechanism. The most significant damage during the commercial processing of PVC occurs as a result of mechano-chemical reactions in the presence of entrapped oxygen.
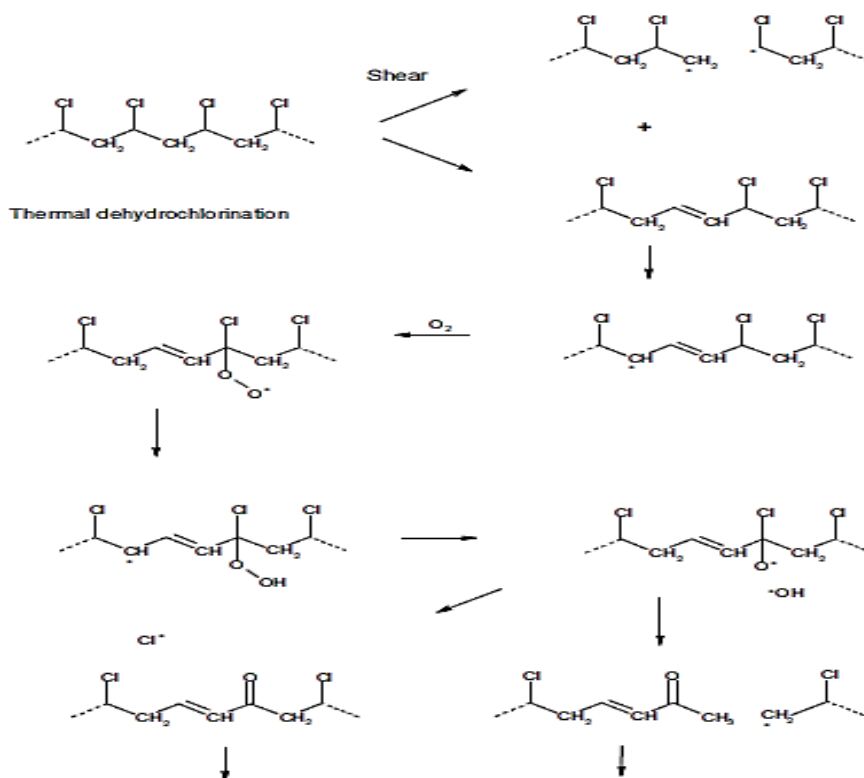
Figure 5: Thermal Oxidative Degradation of PVC

The shear forces cause chain scission, generating radicals. Thermally-initiated HCl loss is followed by radical oxidation of polyenes to form peroxy radicals and hydro peroxides. Hydro peroxides decompose to generate alkoxy and hydroxy radicals that accelerate the oxidation process and form ketones and acid chlorides. Keto-allylic chlorides initiate the thermal dehydrochlorination process.

1.1.2. Secondary Processes in PVC Degradation

In PVC degradation at low dehydrochlorination levels, polyene concentrations increase linearly and in parallel with HCl evolution. At higher dehydrochlorination levels, the increase in polyene concentration levels off. The plateau value is lower when degradation temperatures and oxygen pressures are higher. When the plateau is reached, dehydrochlorination level for all double bond sequences, show that no consecutive reactions to longer polyenes take place. In the absence of oxygen during the thermal degradation of solid samples, a measurable increase in molecular weight occurs and the molecular weight distribution becomes wider and shifts toward higher values. At some point during degradation, the melt viscosity increases considerably, as can be observed by increasing torque in a Bra bender Plastic order experiments. The cross linking process is catalyzed by HCl [34]. The most important cross linking reaction is the *Diels-Alder* condensation of *cisoid trans-trans* dienes with other polyenes.
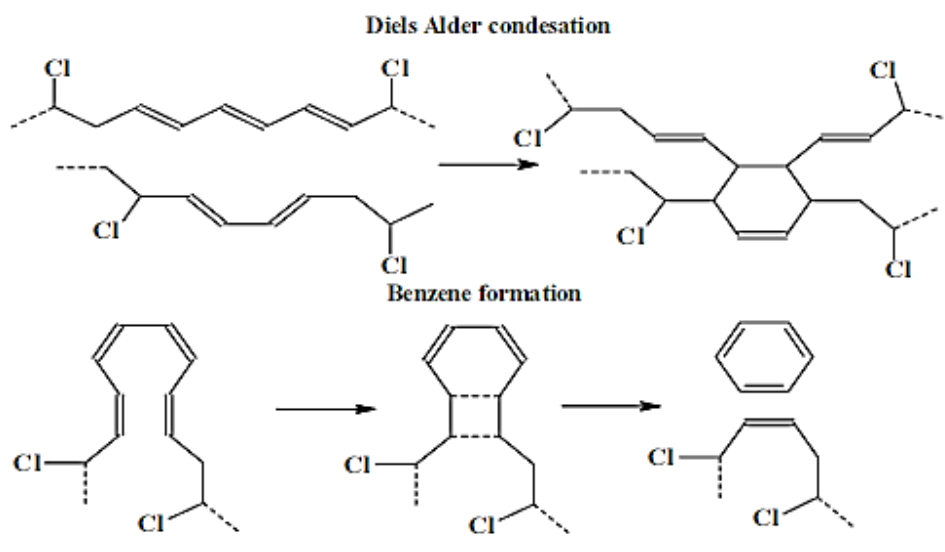
Figure 6: Secondary Processes in PVC Degradation

Benzene is formed in very small amounts even at temperatures as low as 160 to 170 °C by an intramolecular process. At higher temperatures, substituted benzenes and condensed aromatic hydrocarbons are formed by radical scission of *Diels-Alder* condensation products and radical cyclization of polyenes. In the presence of oxygen, the same reactions take place, but they are more complex because of the processes described earlier. Oxidative scission of the chain predominates and, in general, the molecular weight of the polymer decreases.

polymer and consists of dehydrochlorination, auto-oxidation, mechano-chemical chain scission, cross linking, and condensation reactions. This degradation must be controlled by the addition of stabilizers. The heat stabilizer must prevent the dehydrochlorination reaction that is the primary process in degradation. [6]

The polymer softens and melts eventually. The chains' kinetic energy exceeds intermolecular forces and the polymer becomes a highly viscous liquid mass but without any change in their chemical structure. [11]

1.1. Heat Stabilization of PVC

The degradation of PVC at elevated temperatures required in thermoplastic processing is an intrinsic characteristic of the

1.1.1. Alkyltin Stabilizers

The most commercially important Alkyltin derivatives are the mono and dimethyl, butyl and octyl

tin alkyl thioglycolates, mercapto-propionates and alkyl maleates. All these compounds react with HCl to form the corresponding tin chlorides.

However, their stabilization effect does not correlate with the amount of HCl reacted nor with the rate of this reaction. It has been es-tablished that in the stabilization of PVC with Alkyltin alkylthioglyco-lates, alkyl thioglycolates are re-leased by reaction with HCl. These Alkyltin compounds consequently function as secondary stabilizers, but this is not the main mechanism of their action.(Figure 7)
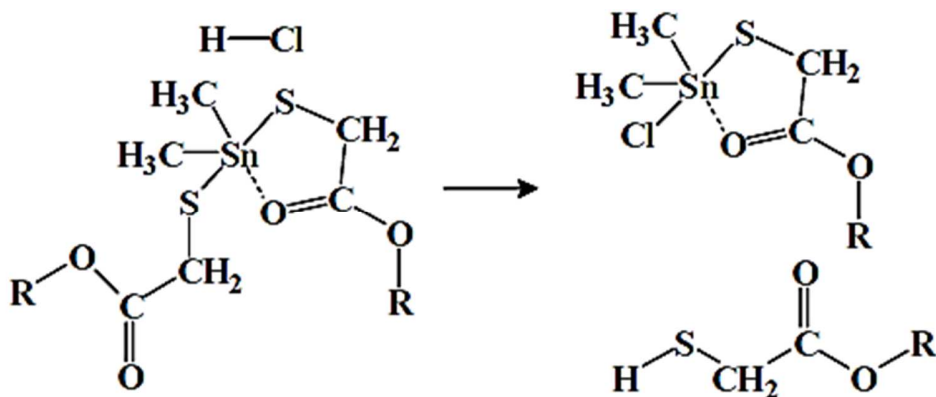

Figure 7: Stabilization of PVC by alkyltin compounds

1.1.2. **Mixed Metal Stabilizers**

Metal carboxylates stabilize PVC by either mechanism, depending on the metal. Strongly basic carbox-ylates derived from metals such as K, Ca, or Ba, which have little or no Lew-is acidity are mostly HCl scavengers. Metals such as Zn and Cd, which are stronger Lewis acids and form covalent carboxylates, not only scavenge HCl, but also substitute carboxylates for the allylic chlorine atoms. It has been shown that when the concentration of the metal carboxylates is decreased, the ester group introduced into the back-bone by direct substitution can be elim-inated by reaction with HCl or by thermal degradation at higher tempera-tures (reversible blocking mechanism).
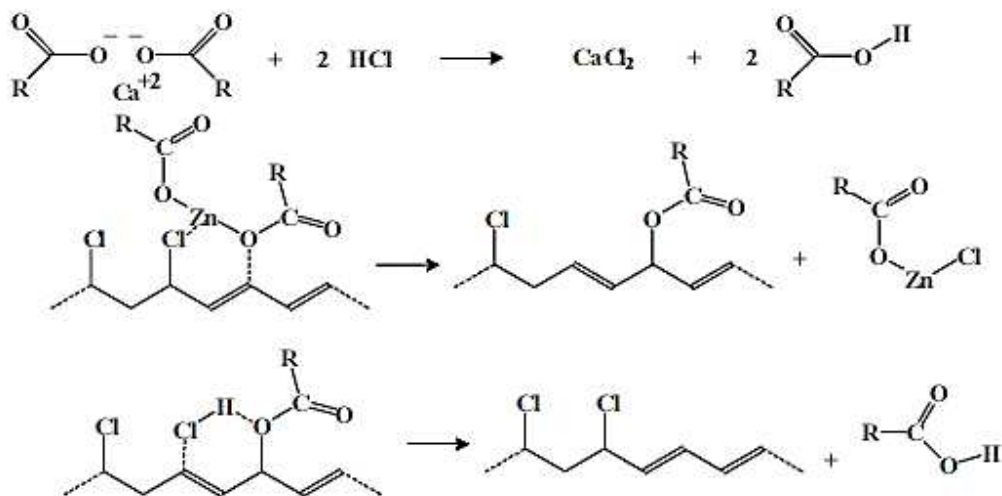
Figure 8: Stabilization of PVC by metal stearates

IR spectroscopy has shown that Zn carboxylates associate with PVC molecules at the surface of primary particles and are, consequently, very effective in the substitution of allylic chlorine. The synergism between Zn or Cd carboxylates and Ba or Ca carboxylates is attributed to fast exchange reactions between zinc or cadmium chlorides and barium or calcium carboxylates. These reactions regenerate the active zinc or cadmium carboxylates and also avoid the catalytic effect of zinc or cadmium chlorides in PVC degradation. However, it has been shown that the synergistic effect is increased by pre heating zinc and calcium stearate together. In this way, a complex zinc stearate is formed that is more active in allylic chlorine substitution.
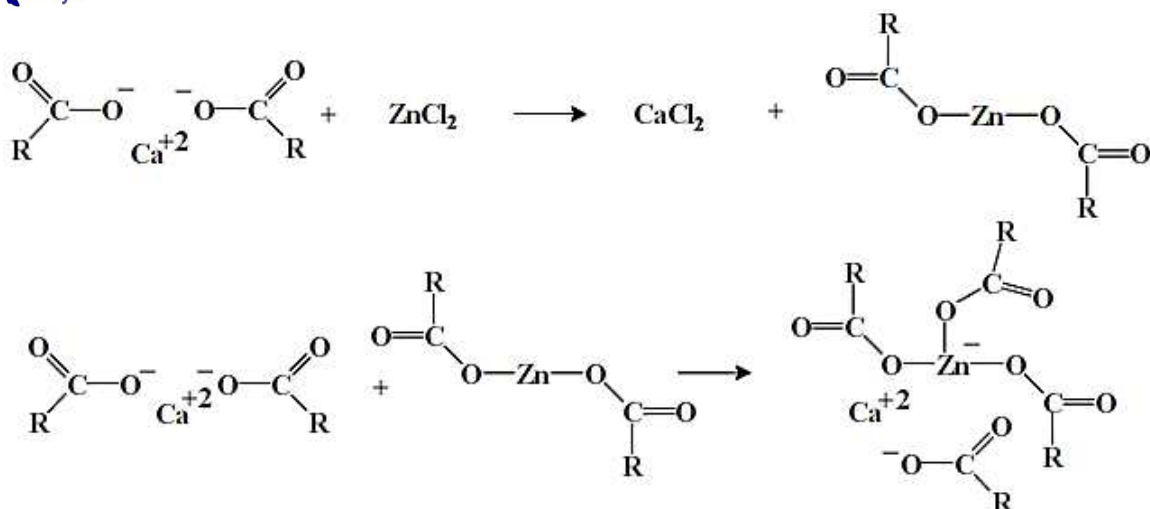
The damaging effect of Zn or Cd chlorides in PVC degradation can be considerably reduced by using co-stabilizers that form metal complexes with them. The most common co-stabilizers used with solid Cd and Zn carboxylates are polyols.

1.1.3. Alkyl Phosphites Stabilizers

Dialkylphosphites have no effect on PVC degradation. Trialkyl phosphites scavenge HCl by an Arbuzov reaction and form dialkylphosphites. They react also with al-lylic chlorides, but this process plays a secondary role. When used alone, phosphites are secondary stabilizers, giving good long term stability but poor early color.

However, in the presence of zinc di (dialkylphosphites) formed from zinc salts and trialkylphosphites as stabilization proceeds, allylic substitution is considerably increased and becomes the dominant process in PVC stabilization. The early color is very considerably improved.
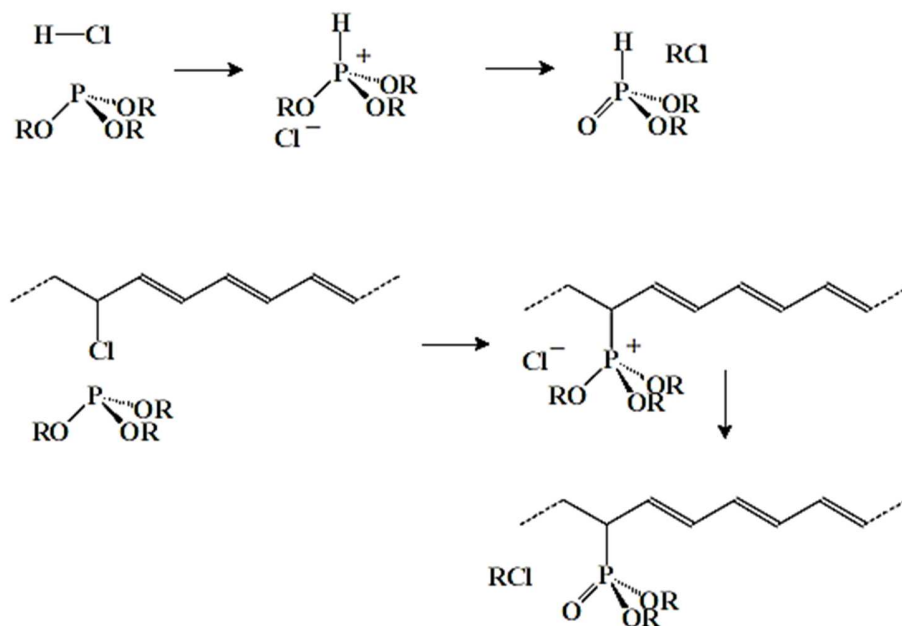
Figure 8: Stabilization of PVC alkyl phosphites

1.1.4. *β*-Diketones Stabilizers

β-Diketones and similar compounds with active methylenes react in the presence of Zn-carboxylates as catalysts with allylic chlorides generated by PVC degradation by a Ca-alkylation process. The stabilization effect increases with the CH acidity of these compounds.

1.1.5. Epoxidized Fatty Acid Esters Stabilizers

Epoxides are HCl scavengers and are also reported to be effective in allylic chlorine replacement in the catalytic presence of Zn and Cd salts. [6]
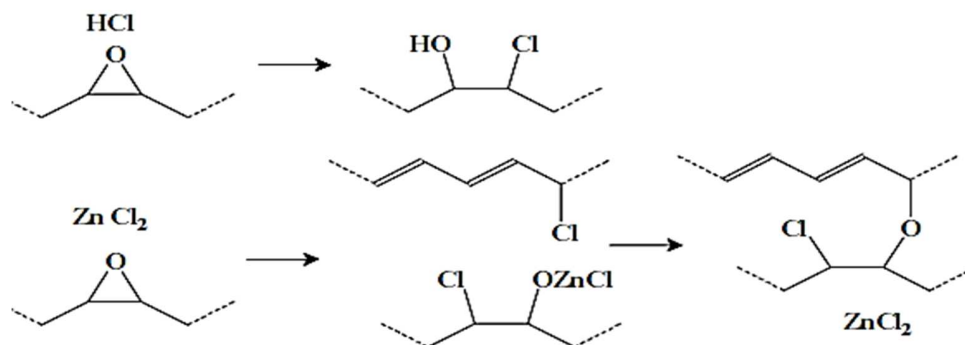

Figure 9: Stabilization of PVC by epoxidized fatty acid esters

A Review: Thermal Degradation and Stabilization of Poly (Vinyl Chloride)   744

1.1.6. Hydrotalcites Stabilizers

Hydrotalcites, a natural mineral, is the hydroxycarbonate of Mg and Al with the exact formula: Mg_6Al_2 (OH) $16CO_3$.$4H_2O$. It is constituted from infinite sheets of octahedral of Mg^{2+} six-fold coordinated to OH^-, sharing edges (brucite-like sheets), where Al^{3+} substitutes for some of the Mg^{2+} ions. A positive charge is generated in the hydroxyl sheet that is compensated for by CO_3^{2-} anions, which lie in the interlayer regions between two sheets. In the free space of this interlayer, there is water of crystallization, associated by hydrogen bonds with both OH^- and CO_3^{2-} anions. [12]

Hydrotalcites like clays with anions of weak acids react with strong acids such as HCl and exchange the anions with Cl^-. This reaction allows Hydrotalcites like clays to be used as HCl scavengers in PVC stabilization. [13-17]

1.1.7. Tin Stabilizers
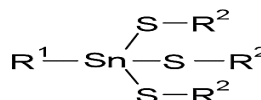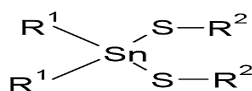
As early as 1936, Yngve recommended not only tetraalkyltin but also Alkyltin carboxylates as PVC stabilizers. In 1950, Firestone filed patent applications for organotinmercaptide-tides, which became extremely important in further developments in PVC technology. Organotin compounds with at least one tin-sulfur bond are generally called organotinmercaptide, sulfur-containing tin stabilizers, or thiotins. Organotin salts of carboxylic acids mainly maleic acid or half esters of maleic acid – are usually known as organotin carboxylates, and the corresponding stabilizers are sometimes called sulfur-free tin stabilizers. [20-22]

1.1.7.1. Organotinmercaptide and Organotin Sulfides

Sulfur-containing organotin compounds are among the most efficient and most widely used heat stabilizers. They can be described by the following structures;

Sn- R^1		**S**- R^2	
CH_3-/	Methyltin	-S-CH_2-CO-O-alkyl	thioglycolates (alkyl is mostly ethylhexyl or iso-octyl)
n-C_4H_9-	Butyltin	-S-CH_2-CH_2-CO-O-alkyl	mercaptopropionates
n-C_8H_{17}-	Octyltin	-S-CH_2-CH_2-O- CO alkyl	mercaptoethanol esters (so-called reverse esters)
		-S-alkyl	alkylmercaptides
		-S-	sulfides

Very efficient, solid stabilizers of a type not mentioned above are derived from ß-mercapto-Propionic acid
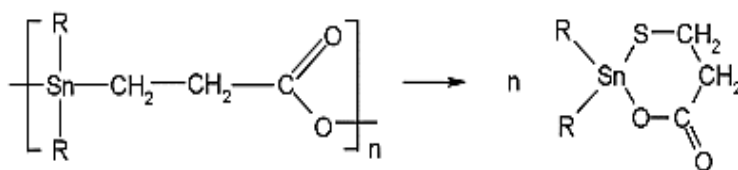
Organotinmercaptide are able to react with HCl, to annihilate initiating sites by substitution and also help impede auto-oxidation. The combination of these functions gives the organotinmercaptide exceptional thermo stabilizing properties not found in any other class of stabilizer

The organotin-sulfur stabilizers, especially as mixtures of mono- and dialkyl-tin i-octyl

Thioglycolates can be used in all PVC applications where high thermo stability is required. They can stabilize all homopolymers, emulsion, suspension, and bulk PVC (E-, S-, M- PVC), as well as copolymers of vinyl chloride, graft polymers, polyblends, and post chlorinated PVC (CPVC). [26-30]

1.1.7.2. Organotin Carboxylates

Only carboxylates with the following structures are of practical interest.
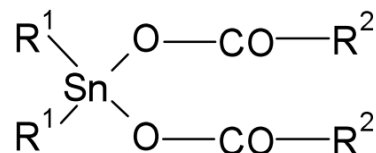
R^1 = Butyl or Octyl, R^2 = Alkyl or -CH=CH-CO-O-Alkyl

Organotin derivatives of maleic acid may have an additional stabilizer function, i.e., the Diels-Alder reaction. Their performance is good in all types of suspension, emulsion, and bulk PVC. Optimum results are obtained when they are combined with small amounts of phenolic antioxidants, particularly in plasticized PVC, impact-modified PVC, and PVC copolymers. Be-

cause stabilizers containing maleic acid occasionally lead to eye and mucous membrane irritations, there have been many attempts to replace them with other systems. For many years, organotin stabilizers free of maleic acid have been on the market. These consist of a combination of organotin carboxylates, e.g., laurates, and a small amount of an organotinmercaptide. Just as with sulfur free organotin stabilizers, when used in a suitable formulations, this combination gives rigid PVC high transparency and excellent weathering stability. [23-25]

In the melt, PVC stabilized with Alkyltin maleates tends to stick to hot contact areas of the processing equipment. However, this problem can be prevented by suitable lubricants. Organotin carboxylates work especially well in the manufacture of rigid or plasticized PVC articles for outdoor use, as for example, transparent and translucent double-walled panels for greenhouses, siding, and window profiles , particularly when pigmented.[6]

1.1.7.3 Schiff bases

Vanillin–Schiff's bases (VSB) were examined as thermal stabilizers and co-stabilizers for rigid polyvinyl chloride (PVC) in air at 180^0C. Their high stabilizing efficiency were shown by their high thermal stability value (Ts), which is the time elapsed for the detection of HCl gas, if compared with dibasic lead carbonate and cadmium–zinc soap reference stabilizers used industrially, with better extent of discoloration. Blending these derivatives with reference stabilizers in different ratios greatly lengthens the thermal stability and the extent of discoloration of the PVC.

Condensation products of Vanillin with amines are very active biologically, besides having good complexation ability with metal ions. The Ni^{2+} and Co^{2+} complexes of VSB derivatives gave better thermal stability and less discoloration than the parent organic stabilizer. Also, blending these complexes with either of the used reference stabilizers in different ratios gave better thermal stability and lower extent of discoloration. Thermogravimetric analysis confirmed the improved stability of PVC in the presence of the VSB derivatives, compared to blank PVC, PVC stabilized with reference stabilizers and PVC stabilized with binary mixture of VSB derivatives with reference stabilizer.

The stabilizing efficiency of Vanillin–Schiff's base (VSB) derivatives is attributed to the replacement of the labile chlorine atoms on the PVC chains by a relatively more stable moiety of the organic stabilizer.[19]

Conclusion:

β-Diketones, Epoxidized Fatty Acid Esters, Alkyl Phosphites, Hydrotalcites, Tin Organotin Mercaptides, Organotin Sulfides and Organotin Carboxylates are mainly used as thermal stabilizers; these have adverse effect on environment. The Schiff bases used for thermal stabilization for PVC are comparatively better in this respect. The most recently studied inorganic compounds are layered double hydroxides (LHDs) and inorganic salts rare earth. The stabilizing effect of these compounds is attributed to their HCl scavenging ability, replacement of labile chlorine atoms and the electrostatic interaction between the chlorine atoms of the polymer chain and the positive layer of the hydrotalcite, thereby weakening the ability of the chlorine atoms to initiate dehydrochlorination. Synergism of stabilizer action between these classes of thermal stabilizers and Ca-Zn thermal stabilizers will eventually lead to evolution of ideal PVC thermal stabilizers.

Future plan

From the foregoing, future efforts would continue on the search for compatible, non-toxic and environmentally friendly organic and inorganic compounds that could function as PVC thermal stabilizers. In our own work we will focus on preparation of different PVC stabilizers and the effect of PH on their stabilizing effect.

References:

1. M. W. Allsopp, G. Vianello, "Poly (Vinyl Chloride)" in Ullmann's Encyclopedia of Industrial Chemistry, , Wiley-VCH, Weinheim. doi:10.1002/14356007.a21_717, **2012**

2. W. V. Titow. *PVC technology*. Springer. pp. 6–. ISBN 978-0-85334-249-6. Retrieved 6 October **2011. (31 December 1984)**

3. Chanda, Manas; Roy, Salil K *Plastics technology handbook*. CRC Press. pp. 1–6.ISBN 978-0-8493-7039-7. . **(2006).**

4. Galina Albertsson, Michel Galmohammadi and Arashk Mermapour**(1987)**

5. Burke, James; *Connections*, Little, Brown and Co., Boston, Fenichell, Stephen; *Plastic: The Making of a Synthetic Century*, HarperCollins, New York, **1996. 1978.**

6. Dr. R. Bacalogulu, Dr. M. H. Fisch, Polymer Additives, Crompton Corp.,

Tarrytown, NY, USA, Dipl. Chem. J. Kaufhold, Dipl. Chem. H. J. Sander*, Polymer Additives, Witco Vinyl Additives GmbH, Lampertheim, Germany**1988**

7. Dr. W. Lincoln Hawkins Polymer Degradation and Stabilization Polymers Properties and Applications 8, , pp 35-39, **1984**

8. Geddes, W. C., *Eur. Polym. J., 3 747.* Gupta, V. P. & St Piere, L. E., *J. Polym. Sci. Al, 8 37.* **(1967)** **(1970)**

9. Lieberman, A., Reuwer, J. F., Gollatz. K. A. & Nauman, C. D., *J.* Pofym. *Sci. Al,* 9 **(1971) 1823.**

10. Satilmiş Basan Olgun Güven Volume 11, Issue 1, , Pages 45–53,**1985**

11. J. Štěpek, H. Daoust Additives for Plastics Polymers 5, , pp 144-166, **1983**

12. Cavani F, Trifiro F, Vaccari A. Hydrotalcite-type anionic clays: preparation, properties and application. Catal Today;11(2):173e301, **1991**

13. van der Ven L, van Gemert MLM, Batenburg LF, Keern JJ, Gielgens LH,Koster TPM, et al. On the action of hydrotalcite-like clay materials as stabilizers in polyvinylchloride. Appl Clay Sci;17(1e2):25e34. **2000**

14. Lin YJ, Li DQ, Evens DG, Duan X. Modulating effect of MgeAleCO3 layered double hydroxides on the thermal stability of PVC resin. Polymer Degradradation Stability;88:286e93. **2005**

15. Lin YJ, Wang JR, Evens DG, Li DQ. Layered and intercalated hydrotalcite-like materials as thermal stabilizers in PVC resin. J Phys Chem Solids;67:998e1001. **2006**

16. Wang XD, Zhang Q. Effect of hydrotalcite on the thermal stability,mechanical properties, rheology and flame retardance of poly(vinyl chloride). Polym Int;53:698e707. **2004**

17. Zhang ZH, Zhu MF, Sun B, Zhang QH. The effect of hydrotalcite andzinc oxide on smoke suppression of commercial rigid PVC. J Macromol Sci A;43(11):**1807,2006**.

18. Mohamed N.A., Sabaa M.W., Khalil Kh.D., Yassin A.A., Organic thermal stabilizers for rigid poly(vinyl chloride) III. Contonal and cinnamal thiobarbituric acids, *Polym. Degrad. Stab.,* 72, 53-61 **(2001)**.

19. Magdy W. Sabaa *, Riham R. Mohamed, Emad H. Oraby European

Polymer Journal 45   3072–3080, **(2009)**

20. B. B. Troitskii,* L. S. Troitskaya, A. S. Yakhnov, M. A. Lopatinand M. A. Novikova Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod, Russia *(**Received 14 October 1996; accepted in final form 29 October 1996**)*

21. Emad Yousif, Nadia Salih, Jumat Salimon Received; accepted**24 May 2010**, **5 September 2010**

22. Yan-Jun Lin, Dian-Qing Li, David G. Evans, Xue Duan Received; received in revised form; accepted Polymer Degradation and Stability 88 286-293, **(2005)**

23. Radka Kalouskovaa,), Miroslava Novotnab, Zdenek Vymazal Received 4 February 2004; received in revised form **2 April 2004**; accepted **10 April 2004** Polymer Degradation and Stability 85 **(2004)** 903-909

24. Eromosele CO. Thermal stabilization of poly (vinylchloride) by Khaya senegalensis Oil and its Derivatives. Ph.D. Thesis, Chemistry **(1998)**

25. Klarić[1,*], U. Roje[1], M. Bravar Journal of Applied Polymer Science Volume 61, Issue 7, pages 1123– 1129, Department, University of Benin, Benin, City Nigeria. **15 August 1996**

26. D. Deur-Šiftar,   V. Mitrović, Issue 10, pp 573-575**(1972)**

27. C. Thaumaturgo, E. C. Monteiro, 49, Issue 1, pp 247-254, **1997**

28. Béla Ivan, Joseph P. Kennedy, Tibor Kelen, Ferenc Tüdős Polymer Bulletin, 6, Issue 3-4, pp 147-153, **December 1981**

29. B. Barić, T. Kovačić Journal of Thermal Analysis and Calorimetry 12- 54, Issue 3, pp 753-764, **1998**

30. M.   Beneš, N.   Milanov, G. Matuschek, A. Kettrup, V. Plaček,V. BalekJournal of Thermal Analysis and Calorimetry 11-78, Issue 2, pp 621-630, **2004**