Chapter 2

Literature Review
2.1 Introduction

The field of polymer science is very much reliant on its diverse applications covering various areas of the developmental beneficiary sectors. Different types of polymers including thermoplastic as well as thermostetting one such as Polyethylene (PE), Polypropylene (PP), Styrene Butadiene Rubber (SBR), Teflon etc. are very much in demand in every aspect of usable life appliances. However the durability of the polymer always be kept in mind for its product use. This durability of polymer may suffer during the polymers ability to withstand under destructive external conditions such as elevated temperature, oxygen and shear deformation which may cause in the degradation of the polymer itself. The polymer degradation occurs according to the type, production conditions and application of the polymer end product. Among these polymers Polyvinyl Chloride (PVC) is considered to be the second largest commodity plastic after polyethylene with world production approximately over 18 million tonnes a year. It is used in different areas depending on its applicative field of the end product. Though PVC is very versatile polymer and has very vast applications in various field, the thermal degradation posed very serious problem to its processing at elevated temperature further this unwanted degradation of PVC affects the final properties of the end product. Therefore numerous attempts have been made in the understanding of thermal instability and the stabilization of the PVC degradation.

2.2 Thermal degradation of Poly(vinyl chloride) (PVC):

It is well known fact that PVC undergoes unwanted degradation during its processing at elevated temperature and also due to some other factors like UV and light radiations effects [1-7].
A simple process of PVC degradation is written as:

\[-(CH_2CHCl)- \rightarrow -(CH_2=CH_2)- + nHCl\]

Over the last fifty years, significant attempts have been made to understand the mechanism of this PVC degradation process, which critically affects the overall performance properties of the PVC polymer.

Loan and Winslow [8] reported that PVC degradation is the result of release of HCl and chain scissioning in the PVC molecule because of mechanical stress and the cross-linking of polymer. Hjerthberg, Minsker and Ivan et al. [9-11] reported that the prime reason for the PVC degradation is the evolution of HCl by elimination reaction from the PVC backbone and the formation of conjugated polyene sequences in the polymer. It has been also pointed out that PVC products with conjugated polyene sequences of more than 6 double bonds are generally colored [12-14]. Many research workers further reported that the polyene sequences are responsible for the discoloration of PVC polymer which may cause change in the physical and chemical properties of the final end product of PVC [15-17].

With this key concern, the concept of PVC degradation and its mechanism by stabilizer has been developed over the period following strict scientific lines as reflected in many more excellent scientific contributions [18-22].

Despite the considerable number of studies carried out by numerous researchers on the mechanism of PVC degradation, it is still not completely understood. Different views have been put forward by various researchers. Various degradation causes were proposed by number of researchers in PVC degradation step as primary and secondary degradation.
2.2.1 Primary degradation:

According to Benavides [23], evolution of HCl (dehydrochlorination) from PVC takes place as the primary degradation reaction which is independent of oxygen, followed by chain scissioning and cross-linking as secondary reactions which is very much depend on the processing temperature and availability of oxygen. The primary process of PVC thermal degradation basically includes three main steps viz:

(1) Initiation of dehydrochlorination (autocatalytic dehydrochlorination- zipper elimination)

(2) Elimination of HCl and simultaneous formation of conjugated double bond and

(3) Termination of dehydrochlorination.

It is to be expected that there are difficulties in making consensus among the researchers on the cause of thermal instability of PVC as many different factors had been attributed to it. It has been proposed that there are some possible defect structures present in PVC such as allylic chlorine, tertiary hydrogen and chlorine atom (structures given below), end groups such as double bonds, oxygen containing group, head-to-head structures [24-28] which are responsible and account for the low thermal stability of PVC as shown in following scheme 2.1.

![Allylic Chloride](image)

![Tertiary Chlorides](image)
Scheme 2.1 Dehydrochlorination of PVC by structural defects

The rate of dehydrochlorination during the degradation process is highly dependent on such structural anomalies of PVC such as the presence of allylic and tertiary chloride atoms. According to Fisch et al [29, 30] only cis-conjugated polyenes are reactive compared to its trans-conformation in the chain-propagation of the degradation process of PVC.

2.2.2 Secondary degradation (thermo-oxidative degradation of PVC):

This secondary degradation of PVC occurs due to the presence of oxygen in addition to chain scissioning of PVC by mechanical stress which also results in dehydrochlorination. These results in the radical cyclization process of the polyenes formed in PVC which further generates low molecular weight compounds due to the decomposition of PVC. According to Starnes [31] this cause is less in the discoloration of PVC because of the less polyene sequences formation in the backbone of polymer. An increase in the amount of oxygen in the atmosphere, however, increases chain scission reaction at the cost of crosslinking of the PVC.

Due to the intrinsic scientific significance and technological applicability, the thermal degradation and stabilization of PVC has been the subjects of much interest. As is known that PVC is relatively thermally unstable and requires stabilization for processing, there are a large number of technical papers which propose the mechanisms of thermal decomposition of PVC including many reviews [32-35].
The main issue in the degradation of PVC is the type of mechanism by which the overall dehydrochlorination process due to the structural defects present in PVC takes place. Many researchers reported different mechanisms for the degradation of PVC. Fisch and other research workers have quoted that dehydrochlorination due to the autocatalytic action of evolved HCl initiated at the labile site in the polymer chains is the main cause for the degradation [36-39]. It is believed that after the loss of initial HCl from PVC, the subsequent unsaturated structure formed in a PVC backbone chain is an allylic chlorine structure. This allylic chlorine stimulates the next loss of HCl molecule and the process get repeated further which leads to the chain or zipper reaction of dehydrochlorination [40]. Further this leads to an extensive discoloration of the PVC polymer which may cause deterioration of its physical and mechanical properties [36-38].

Various schemes have been developed to understand the definite mechanism behind the degradation of PVC. The probable routes of the degradation mechanism of PVC are unimolecular/concerted, ionic and quasi ionic, free radical, mixed ion-radical (polaron) and other relevant mechanisms of degradation have been proposed for individual reaction steps based on different experimental evidences. According to Bacaloglu, Fish and other authors [41-44] unimolecular or six centered concerted mechanism is the most possible route for the dehydrochlorination process of PVC catalyzed by HCl (scheme 2.2)

**Scheme 2.2 Unimolecular mechanism of dehydrochlorination of PVC**
For some authors [45-46] the most probable mechanism for the growth of polyenes in PVC backbone by thermal dehydrochlorination reaction during the degradation is the ion-pair formation and quasi ionic environment by labile structural defects (scheme 2.3).

a)

\[
\begin{align*}
\text{HCl} & \quad \xrightarrow{\text{C-C}} \quad \text{HCl}^- \quad \xrightarrow{\text{C-C}} \quad \text{C} = \text{C} + \text{HCl} \\
\text{C-C} & \quad \xrightarrow{\text{C-C}} \quad \text{C} = \text{C} + \text{HCl}
\end{align*}
\]

b)

\[
\begin{align*}
\text{HCl} & \quad \xrightarrow{\text{C-C}} \quad \text{HCl}^- \quad \xrightarrow{\text{C-C}} \quad \text{C} = \text{C} + \text{HCl} \\
\text{C-C} & \quad \xrightarrow{\text{C-C}} \quad \text{C} = \text{C} + \text{HCl}
\end{align*}
\]

**Scheme 2.3** a) Ion-pair and b) Quasi-ionic mechanism of dehydrochlorination of PVC

Some workers have reported that the main support for an ionic process of PVC degradation arises from the observations that HCl catalyzes degradation and that the rate of dehydrochlorination in solution is influenced by the dielectric constant of the solvent [47-49]. Starnes [50] has suggested an ion-pair mechanism to account for experimentally demonstrated polyenyl cations in degraded PVC, with the positive charge located preferentially at the center of the polyene sequences as the chain length is increased.

It is further stated that both the ionic and the unimolecular routes of dehydrochlorination process are highly allylic activated one. It is also evident that as the free radicals are created during PVC degradation, this might have been the probable mechanism for dehydrochlorination for the growth of polyene sequences [50-55]. As the attack of a chlorine radical on the PVC chain is supported by many of them, this mechanism is depicted in scheme 2.4.
Scheme 2.4 Free radical mechanism of dehydrochlorination of PVC

The chlorine radical abstracts a methylene hydrogen atom of PVC chain, forming HCl. The new macro-radical formed in PVC backbone will dissociate a chlorine radical adjacent to this radical and a new double bond is formed and the newly released chlorine radical will further attack the neighboring methylene group immediately. This cycle get repeated many times by evolving successive losses of HCl and yielding a polyene sequence in the polymer chain.

Another possible mechanism for dehydrochlorination of PVC is creation of Polaron (mixed ion-radical) which has been proposed by Tran and other research authors [56-60].

In Scheme 2.5 a mechanism, which involves an allylic cation radical, is shown. According to Tran et al. the ion-radical mechanism of thermal dehydrochlorination not only polarons can propagate dehydrochlorination, but also solitons and bi-polarons.

Scheme 2.5 Polaron mechanism of dehydrochlorination of PVC
2.3 PVC stabilization by thermal or heat stabilizers:

Many excellent reference texts cover the importance of PVC heat stabilizers including lubricants in literature. The main function of the stabilizer is to overcome thermal instability of PVC by preventing decomposition or degradation of it during processing and fabrication so that the finished product remains stable and suitable for the final applications [61-62].

For practical use PVC requires thermal and oxidative stabilization and there are number of technical publications available on the mechanism of stabilization of PVC. Degradation of PVC can be protected with a variety of stabilizer systems.

There are mainly two types of stabilizers namely primary and secondary depending on its function of PVC stabilization.

Primary stabilizers are chemicals which are capable of reacting with labile structures such as allylic and tertiary chlorides of PVC compound and absorb evolved HCl during the degradation process to inhibit the initiation of degradation.

According to Mesch [63] secondary stabilizers and/or co-stabilizers inhibit or reduce the degradation of PVC by accepting thermo-oxidative groups. The choice of stabilizer depends on the probable decomposition mechanisms involved. In some PVC stabilizers system primary and secondary stabilizers are generally used in combination to observe their synergistic effect on the stabilization of PVC.

The main classes of PVC thermal stabilizers in current use are lead salts, metal soaps and organotin based compounds including some organic compounds. Some of these heavy metals containing compounds have disadvantages in terms of their toxicity,
environmental pollution and/or high cost [64]. There are many literatures available on the thermal stabilization of PVC by heavy metal (lead, tin and cadmium) based stabilizers system along with some co-stabilizers. The metal soaps and some of organotin stabilizers are safer than lead salts, but their stabilization effects are usually lower than those of lead salts based stabilizers.

Keeping this view in mind, the present investigation has been made which is based on non-toxic and environmentally helpful PVC stabilizers system and majority of the literature given in this section is relevant to the mixed metal based (particularly Ca/Zn based) and other non-toxic stabilizers. Significant improvement is observed in the effectiveness of mixed metal based stabilizers in PVC degradation over the last fifty years. Still there has been continuous research going-on in the progress and new developments of synergistic PVC stabilizers system based on mixed metal and other non-toxic based compounds.

In the recent past some researchers reviewed the compatibility of PVC stabilizers containing heavy metals [65] and synergetic effects of mixed metal stabilizers on degradation of PVC [66]. Mixed metal stabilizers composition generally contains metal soaps of fatty acids or salts basically carboxylates. Strongly basic carboxylates of metals K, Ca or Ba that have weak or no Lewis acidity act as a HCl scavengers; however, carboxylates derived from metals Zn and Cd, which have stronger Lewis acidity, are able to scavenge HCl and also to react with allylic chlorine atoms in the degradation process of PVC [29]. This composition is used for the initial color and longer thermal stability of PVC which reacts with by Frye and Horst mechanism during the degradation of PVC.
Benavides et al. [67-69] have shown that a synergistic effect exists between Zn stearate (ZnSt$_2$) and Ca stearate (CaSt$_2$) because of the coordinative bonding between the ZnSt$_2$ and CaSt$_2$ molecules. Many researchers have worked on the synergism between Ca/Zn based stabilizers and reported many excellent observations.

It has also been pointed out that the stabilization effects of synergistic metal soaps in case of Zn containing compounds is impaired by the excessive cool color producing metal chloride, that is, zinc blackening in PVC [70-73]. This creates labile chlorine and catalyzes the further propagation of PVC degradation by promoting sudden dehydrochlorination of PVC [38]. To avoid this abrupt blackening and masking the color of PVC, secondary or a co-stabilizer such as phosphates, β-diketones, polyols, amines, and epoxides have been used to protect the primary stabilizers [74-78]. It is also reported that the success of mixed metal based stabilizers is very much dependent upon the use of synergists. Folarin et al. reviewed in depth information on the use of non-toxic stabilizers, co-stabilizers and its synergism in PVC degradation [64].

Nowadays research has been focused on non-toxic compounds which may have positive effects on properties and should be in environmental friendly approach. Layered double hydroxides (LDH) or Hydrotalcite (HT) is one of the non-toxic, environmentally friendly anionic clay compound, which has attracted much attention in the recent time for the developments of efficient additives to enhance PVC thermal stability and to reduce the smoke emission during PVC flaming [80-86].

HTs have been reported to have HCl absorption capacity and may be used as PVC thermal stabilizers. Evans and Duan reported that Kyowa chemical industries of Japan were the first to reveal that adding Mg-Al LDHs to PVC in combination with
other additives such as zinc stearate and tin maleate lead to an enhancement in thermal stability of the PVC resin [86-87]. The role of the LDH in absorbing HCl was confirmed experimentally by Van der Ven et al. [80] who measured the capacity of LDHs having the same M\(^{2+}/M^{3+}\) ratio and different counter-ions to react with HCl gas.

Liu et al. investigated the effect of hydroxylbenzylthioethers as novel organic thermal stabilizers for rigid PVC [88]. The thermal stabilizing efficiency of these compounds as thermal stabilizers was evaluated by using Haake mixer and TGA comparatively with Ca-Zn soap and methylnit stabilizer. Hydroxylbenzylthioethers exhibited greater efficiency than both of the reference stabilizers. This was attributed to the ability of these compounds to prevent the formation of polyene sequences in PVC backbone during the degradation process.

Weiqing et al. [89] studied the thermal stability of poly(vinyl chloride) resin (PVC) upon doping cerium carbonate as well as compound binary-ingredient thermal stabilizer (that is, cerium carbonate and tribasic lead sulfate) using Congo red test method. In some literature suggestions have been also given for several alternatives, like binary blends containing poly(vinyl butyral), poly(acrylonitrile butadiene styrene), poly(methyl methacrylate butadiene styrene), poly(methyl methacrylate) [90-91], copolymers of poly(vinyl chloride-co-vinyl acetate) [92], or incorporation of nanoparticles such as layered silicates or calcium carbonate [93-95]. These have been studied especially to delay the dehydrochlorination process of PVC degradation for their different stabilizing modes.

It is said that there is no ultimate PVC formulation is available. A good PVC formulation in the form of stabilizer system has been continuously explored time to
time since its development. The details available on the degradation and stabilization of PVC through research findings continuously used for the meeting of constructive progress towards the development of appropriate PVC stabilizer system. As per the need of time and requirement, PVC stabilizer systems in the form of variety of formulations have been transforming for the implementation of proper application purpose. Therefore for the development of suitable stabilizer system for proper application a better understanding of formulation/ property relationship PVC and stabilizer need to be investigated.
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2. Literature Review


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