

Review

Thermal stabilizers for poly(vinyl chloride): A review

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Poly(vinyl chloride) (PVC) is one of the most important commercial plastic materials, but it is thermally unstable at processing temperature. Processing of PVC at elevated temperatures requires the use of thermal stabilizers. Widely used thermal stabilizers for PVC incorporate toxic heavy metal and organotin compounds that have been severely criticized based on environmental concern. In order to address this issue, several organic and inorganic compounds that are compatible with the polymer had been investigated. When introduced at relatively low amount, they function as excellent thermal stabilizers for PVC. The compounds function as primary and secondary stabilizers and also as co-stabilizers. These classes of chemical compounds would lead to ideal PVC thermal stabilizers that could be termed "green thermal stabilizers".

Key words: Poly(vinyl chloride), organic stabilizers, inorganic stabilizer, stabilization, thermal stabilizers.

INTRODUCTION

Poly(vinyl chloride), PVC, is a common commodity plastic, and its production is the third largest, after polyethylene and polypropylene (Yoshioka et al., 2008). It is cost-effective, highly versatile and is used in many construction applications as water, sewage and drainage pipes, and a variety of extruded profiles (Van Es et al., 2008). Thousands of rigid, semi-flexible and flexible (plasticized) materials and products based on PVC are widely used in practically all spheres of the world economy and will remain so for a very long time. From volume estimates, the world production of PVC grew from a few hundred million pounds to about 44 billion pounds in 2000 (Skip, 2006) as new uses and markets were developed. However, it is known that PVC degrades at elevated temperatures, giving off hydrochloric acid (HCl) that in turn accelerates the degradation process. Depending on the number of conjugated double bonds formed, it becomes yellow, orange, red, brown and finally black (Sabaa and Mohamed, 2007). The splitting-off of HCl from the polymer backbone affects the physical, chemical and the mechanical properties of the polymer. Until the discovery of thermal stabilizers, PVC was not an industrially very useful polymer, as it could not be

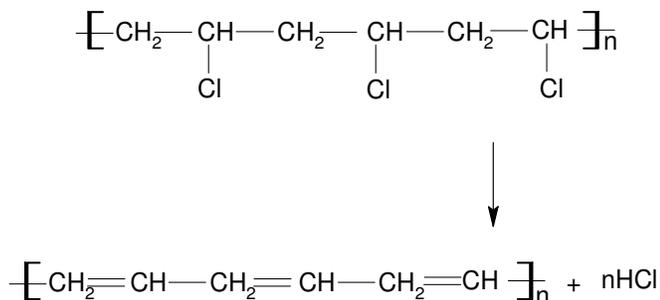
processed to useful articles without degradation at elevated temperatures. Quantum improvements in extrusion and injection moulding machinery and extrusion die design, together with significant improvements in stabilizers and lubricant technology have all contributed to increased tonnage production and usage of PVC. The aim of this review is to carry out the literature survey of organic and inorganic compounds that have been proved scientifically to act as PVC thermal stabilizers.

THERMAL DEGRADATION OF PVC

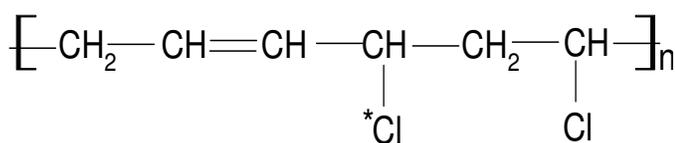
Thermal degradation is a process whereby the action of heat or elevated temperature on a material, product or assembly causes a loss of physical, mechanical or electrical properties (ASTM E 176). Thermal degradation of PVC (Scheme 1) occurs by an autocatalytic dehydrochlorination reaction (zipper elimination) with the subsequent formation of conjugated double bonds (Simon, 1990, 1992; Bacaloglu and Fisch, 1994; McNeill et al., 1995).

After the loss of the first HCl molecule, the subsequent unsaturated structure formed in a PVC chain is an allylic chlorine structure. However, this allylic chlorine (Scheme 2) stimulates the next loss of an HCl molecule and the repeated process leads to the chain or zip

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Scheme 1. Thermal degradation of PVC.



Scheme 2. (*) Allylic chlorine atom.

dehydrochlorination. The process starts at the glass transition temperature (70 °C) by elimination of HCl, which is the main volatile product up to about 330 °C (Klaric et al., 1996). However, traces of benzene have been reported at temperatures as low as 150 to 160 °C (Levchik and Weil, 2005) and at 200 to 360 °C, about 15% of the polyene is converted to benzene (Grimes et al., 2007). The formation of benzene in this temperature range results from an intra-molecular process involving cyclization of polyene segments (Starnes, 2002). The primary process of thermal degradation includes three main steps viz: (1) initiation of dehydrochlorination (2) elimination of HCl and simultaneous formation of conjugated double bond and (3) termination of dehydrochlorination. The evolution of HCl takes place by elimination from the polymer backbone and discolouration is due to the formation of conjugated polyene sequences of 5 to 25 double bonds (Hjertberg et al., 1988; Minsker et al., 1989; Ivan et al., 1990). There is no consensus among researchers on the cause of thermal instability of PVC as many factors had been attributed to it. The leading candidates have been structural defects containing allylic or tertiary chlorine (Ivan et al., 1990), ketoallylic chlorine atoms – $\text{CO}(\text{CH}=\text{CH})_n\text{CHCl}$ - ($n \geq 1$) resulting from incidental air oxidation (Minsker, 1994), GTTG (G = gauche, T = trans) isotactic triads because of their favourable conformation (Martinez et al., 1993), terminal end groups such as double bonds ($-\text{CH}=\text{CH}_2\text{CCl}=\text{CH}_2$) (Hjertberg and Sorvik, 1983), peroxide residues (Nagy et al., 1980), head-to-head structures, β -chloroallyl groups ($-\text{CH}_2\text{CH}=\text{CHCHCl}$ -

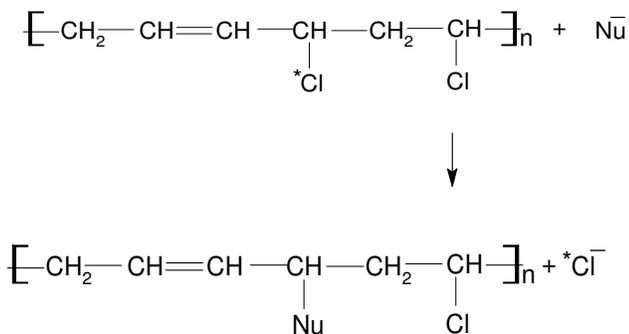
(Minsker and Zaikov, 2001) while adventitious α,β -unsaturated ketone segments have been suggested to function as true catalysts for the thermal dehydrochlorination of ordinary monomer units (Lukas and Pradova, 1986). Albeit, a universal consensus still remains to be reached, most researchers in this field now consider internal allylic and tertiary chlorine segments to be of prime importance (Starnes, 2002). However, sometimes it is believed that the lack of consensus is deliberate, though, it is not clear why that is so (Minsker and Zaikov, 2001). The mechanism of degradation of PVC is still as controversial as the cause; many mechanisms had been proposed. In spite of the disagreement in literature on the exact mechanism, it seems generally accepted that the thermal degradation of PVC proceeds with evolution of HCl via a chain mechanism called “zipper elimination” or unzipping” (Levchik and Weil, 2005). Many different kinds of mechanism have been proposed. These include unimolecular/concerted (Amer and Shapiro, 1980; Fisch and Bacaloglu, 1999), ionic (Starnes and Edelson, 1979; Starnes, 2002), free radical (Winkler, 1959; Stromberg et al., 1959), one-step unzipping (Meier and Kip, 1992) and mixed ion-radical (polaron) (Tran, 1998). All these mechanisms are based on experimental evidence.

PVC THERMAL STABILIZERS

The main classes of thermal stabilizers in current use are lead salts, metal soaps and organo-tin compounds. Some of these have disadvantages in terms of toxicity, environmental pollution and/or high cost (Lin et al., 2006). The metal soaps and organo-tin stabilizers are safer than lead salts, but their stabilization effects are usually lower than those of lead salts. In fact, calcium and zinc soaps of some seed oils had been investigated and proved to be save thermal stabilizers of PVC (Folarin, 2008). As a result of the worldwide increase in environmental awareness, attention is currently being focused on thermal stabilizers that are non-toxic and environmentally friendly (Bao et al., 2008). Thermal stabilizers of PVC possess one or more of the following features in addition to capacity for absorption and neutralization of HCl evolved by PVC during degradation:

1. An ability to replace or displace active, labile substituent groups, such as tertiary and allylic chlorine atoms;
2. A capacity to render pro-degradant substances e.g. heavy metal chlorides, inactive;
3. An ability to modify chain reactions, by interrupting conjugated polyene formation and inhibiting the elimination of HCl.

An ideal stabilizer should possess a number of desirable secondary attributes. Such stabilizers should be



Scheme 3. Mechanism of PVC thermal stabilizer by a primary stabilizer.

colourless, compatible and non-migrating. It should be relatively inexpensive, non-toxic, odourless and tasteless, and should not affect the polymer's physical and rheological characteristics.

CLASSIFICATION OF PVC STABILIZERS

As documented in the literature, PVC stabilizers could be classified based on mode of action into the following.

Primary stabilizers

These types of stabilizers function by reacting with allylic chlorine atoms, the intermediates in the zipper degradation chain, thereby preventing further dehydrochlorination (Scheme 3) (Fisch and Bacaloglu, 1999; Baltacioglu and Balkose, 1999; Okieimen and Sogbaike, 1995). This process should be faster than the chain propagation itself, requiring a very active nucleophile.

However, the reactivity of the nucleophile should not be so high as to react with the secondary chlorine of the PVC chain, a process that rapidly exhausts the stabilizer. To be effective, the stabilizer must be associated by complex formation with the polymer chlorine atoms, which means it should have a Lewis acid character (Fisch and Bacaloglu, 1999).

Secondary stabilizers

This type of stabilizers function by scavenging the HCl/Cl radical generated. HCl is a catalyst for the chain propagation reaction and the initiation step (Gonzalez-Ortiz et al., 2005). Scavenging cannot stop the degradation process completely since it is diffusion controlled. However, HCl scavenging considerably reduces the rate of degradation and avoids the very fast process that

eventually causes PVC blackening (Tamer et al., 2005).

Stabilization is complicated by the fact that primary stabilizers are strong Lewis acid, reacting with HCl that catalyzes the initiation and propagation of PVC degradation. To avoid this, secondary stabilizers should be present to react with HCl to protect the primary stabilizers.

ORGANIC THERMAL STABILIZERS

The high toxicity of majority of thermal stabilizers like lead salts, some metal carboxylates and some organo-tin compounds causes severe environmental problems. This has recently led to extensive search and use of compounds that are non-toxic, environmentally friendly and economical as PVC thermal stabilizers. Many organic compounds had been investigated and their stabilizing efficacy as PVC thermal stabilizers have been scientifically established.

In an attempt to find environmentally friendly thermal stabilizers, Sabaa et al. (1990) investigated *N*-substituted maleimides as thermal stabilizers for plasticized PVC at 180 °C in air by measuring the rate of dehydrochlorination and the extent of discoloration of the degraded polymer. The results revealed a higher stabilizing efficiency of the products investigated when compared with basic lead carbonate, dibutyl tin maleate and barium-cadmium stearate stabilizers, which are commonly used industrially. The induction period (T_s) was influenced by the nature and position of substituents in the aryl ring and the nature of the plasticizer used. Moreover, it was found that the stabilizers investigated, impart better colour stability to the degraded samples when compared with the stearate stabilizer. A synergistic effect was achieved when the compounds investigated were used as mixtures with the reference stabilizer in equimolar ratios. A radical mechanism was proposed which illustrated the stabilizing action of the products investigated.

Pielichowski and Hamerton (1998) reported on the secondary thermal stabilizing effect of 3-(2,4-dichlorophenylazo)-9-(2,3-epoxypropane) carbazole. Thermogravimetric analysis was used to evaluate the stabilizing effect of the compound. The report indicated its ability to hinder evolution of hydrogen chloride gas via an aromatic alkylation reaction.

Mohamed et al. (2000) investigated the ability of barbituric acid (BA) and thiobarbituric acid (TBA) as PVC thermal stabilizers. The efficiency of these compounds as thermal stabilizers was evaluated by measuring the length of the induction period (T_s), during which no detectable amount of hydrogen chloride gas could be observed. The rate of dehydrochlorination, as measured by continuous potentiometric titration and the extent of discoloration of the degraded polymer were also used to measure the efficiency of BA and TBA. The evaluation procedure involved comparison of stabilizing efficiencies

of dibasic lead carbonate (DBLC), dibasic lead stearate (DBLS), barium-cadmium-zinc stearate (Ba-Cd-Zn stearate), n-octyl tin mercaptide (n-OTM) and dibutyl tin maleate (DBTM). With the exception of (DBTM), which showed a comparable stabilizing efficiency with BA and TBA, the organic stabilizers investigated exhibited a greater efficiency than those of all other reference stabilizers and they impart better colour stability to the degraded samples. The stabilizing efficiency was attributed to the replacement of the labile chlorine atoms on the PVC chains by a relatively more stable moiety of the stabilizers. A radical mechanism was also suggested for the stabilizing effect of the stabilizers.

In their efforts to find more environmentally friendly PVC thermal stabilizers, Mohamed et al. (2001) carried out studies on the ability of crotonal thiobarbituric acid (CTBA) and cinnamal thiobarbituric acid (CiTBA) in air at 180°C in order to prevent the degradation of PVC. The efficiency of these compounds as thermal stabilizers was equally evaluated by measuring the induction period (T_s), during which no detectable amount of hydrogen chloride gas could be observed, and also from the rate of dehydrochlorination as measured by continuous potentiometric titration and the extent of discolouration of the degraded polymer. The result revealed the higher stabilizing efficiency of the investigated compounds when compared with the industrially employed thermal stabilizers such as dibasic lead carbonate (DBLC), dibasic lead stearate (DBLS), barium-cadmium-zinc stearate (Ba-Cd-Zn stearate), n-octyl tin mercaptide (n-OTM) and dibutyl tin maleate (DBTM). The effect of blending CiTBA with either of the reference stabilizers on the stabilizing efficiency of the thermally degraded rigid PVC was also investigated. The results revealed that mixing of the stabilizers improved the T_s values, the rate of dehydrochlorination and the extent of discolouration. This improvement attained its maximum when both the investigated and the reference stabilizers were taken in equivalent weight ratios.

The effects of organic thermal stabilizers (EDTA; 1, 2-propane diol; benzoic acid and phenol) on the kinetics of degradation and stabilization of rigid poly(vinyl chloride) under nitrogen in the temperature range 160 to 190°C were studied (Taghizadeh and Fakhimi, 2005). The rate of dehydrochlorination at 1% degradation (R_{DH}) and the time required for dehydrochlorination to attain 1% conversion (t_{DH}) were used to assess the effect of the additives on the thermal susceptibility of PVC. The activation energies of the PVC degradation in the presence of the organic stabilizers and also in the absence of stabilizer calculated from the kinetics parameters EDTA (28), 1, 2-propane diol (27.5), benzoic acid (26.8), phenol (26) and PVC alone (24.5) kcalmol⁻¹, revealed the stabilizing effect of the organic compounds. The ability of some saturated polyesters to influence thermal and mechanical behaviour of flexible poly(vinyl chloride) was investigated (Tawfik et al., 2006). In the

study, poly(hexamethylene adipate), poly(ethylene adipate), poly(hexamethylene terephthalate) and poly(ethylene terephthalate) were prepared and the effect of blending these polyesters (5 and 10%) with poly(vinyl chloride) in the melt was investigated. The efficiency of the stabilizers was evaluated by studying weight loss after 50 min at 180°C, colour changes of the blend before and after aging for one week at 90°C, the variation in glass transition temperature and the initial decomposition temperature. The results gave proof of stabilizing role played by the polyesters investigated against the thermal degradation of PVC. The best results were obtained when PVC was mixed with aliphatic polyesters rather than with aromatic polyesters. The stabilizing effect of the polyesters on PVC was attributed to the interaction of the local dipoles between chlorines of PVC and the ester carbonyl groups in the polyesters which may delay the detachment of the labile chlorine atoms.

In a study that examined the possibility of using organic thiols as PVC heat stabilizers, Starnes et al. (2006), synthesized and tested several organic thiols that contain one or more carboxylate ester groups that were highly compatible with the polymer. When introduced into PVC at high loading levels (30 to 35 parts by weight), the ester thiols were extremely effective as heat stabilizers and also useful as primary plasticizers. At a low loading level (3 parts by weight) they were still excellent heat stabilizers for both plasticized and rigid PVC. High potency was equally reported in the absence of any co-stabilizers that incorporate heavy metals. The stabilizing efficiency was attributed partly to the replacement of the labile chlorine atoms on the PVC chains by the ester thiol group and the addition of this group to the alkene double bonds. A free radical/an ion-pair mechanism involving HCl catalysis was proposed for the stabilization.

The long-term heat stabilization efficiency of (natural) polyol additives in heavy metal- and zinc-free poly(vinyl chloride) (PVC) was investigated (Steenwijk et al. 2006). The results showed that polyols, such as sorbitol and xylitol, markedly reduced the dehydrochlorination rate and improved Congo red values. Extraction experiments on unprocessed and ground-processed PVC-sorbitol mixtures after thermal degradation at 200°C revealed that in the ground-processed PVC-sorbitol system especially, sorbitol was partly converted into its mono- and di-anhydro-derivatives that is 1,4-sorbitan and isosorbide, respectively. Apparently, the HCl released during thermal degradation acts as the catalyst. Under these conditions, similar intramolecular cyclodehydration reactions also occurred with the natural polyols, erythritol and xylitol. Careful scrutiny of the measured dehydrochlorination rates and the Congo red values for ground-processed heavy metal- and zinc-free PVC-polyol mixtures showed that in particular polyols containing primary hydroxyl groups exert long-term heat stabilization and that they act as efficient HCl scavengers.

The potential of Eugenol (4-allyl-2-methoxy-phenol) as

PVC thermal stabilizer in air at 180°C was studied (Sabaa and Mohamed, 2007). This compound was reported to have higher stabilizing efficiency than common reference stabilizers, such as dibasic lead carbonate, calcium-zinc soap and octyl tin mercaptide. Blends of this compound with some reference stabilizers in different ratios were reported to exhibit synergism based on induction period, the rate of dehydrochlorination together with the longer extent of discoloration. The stabilizing efficiency was attributed partially to the stabilizer's ability to intervene in the radical chain degradation process of PVC and to the replacement of the labile chlorine atoms on PVC chains by a relatively more stable moiety of the organic stabilizer.

The effect of hydroxybenzylthioethers as novel organic thermal stabilizers for rigid PVC was investigated (Liu et al., 2007). The efficiency of these compounds as thermal stabilizers was evaluated by using Haake polydrive mixer and TGA. The stabilizing efficiency was compared with Ca-Zn soap and methyltin stabilizer. Hydroxybenzylthioethers exhibited greater efficiency than both of these stabilizers. This was attributed to the ability of these compounds to prevent the formation of polyene sequences. The hydroxybenzylthioethers stabilized PVC showed a slightly lower glass transition temperature (T_g) in comparison with the original PVC. Hydroxybenzylthioethers and epoxidized soybean oil (ESBO) exhibit synergistic effect on the stabilizing efficacy, when the mass ratios of ESBO to hydroxybenzylthioethers were less than 0.5. The stabilizing effect of hydroxybenzylthioethers was attributed to the replacement of labile chlorine atoms and addition to polyene sequences by thiols generated by thermolysis of hydroxybenzylthioethers.

The thermal degradation behaviour of poly(vinyl chloride) in the presence of poly(N-acryloylbenzhydrazide), PABH, was investigated (Mohamed and Al-mehbad, 2009). Continuous potentiometric determination of the hydrogen chloride gas evolved and the measurement of the extent of discoloration of the samples degraded were used to evaluate the efficacy of the compound. Poly(N-acryloylbenzhydrazide), PABH, proved to be a good thermal stabilizer for rigid PVC. Blending this polymeric additive with dibasic lead carbonate (DBLC), in different ratios was reported to have synergistic effects on both the thermal stability and the extent of discoloration of PVC. The efficiency of PABH was attributed to its ability to scavenge chlorine radicals resulting from the degradation of PVC and ability to block the odd electron sites created on PVC chains as a result of thermal degradation as it also scavenges the HCl released.

Sabaa et al. (2009) examined Vanillin-Schiff's bases (VSB) as thermal stabilizers and co-stabilizers of rigid poly(vinyl chloride) (PVC) in air at 180°C. Their high stabilizing efficiency were shown by their high thermal stability value (T_s), which is the time elapsed for the

detection of HCl gas, when compared with dibasic lead carbonate and cadmium-zinc soap reference stabilizers used industrially, and with a better extent of discoloration. Blending these derivatives with reference stabilizers in different ratios greatly lengthened the thermal stability and the extent of discoloration of the PVC. 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 reference stabilizers used 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, when compared with the 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 was attributed to the replacement of the labile chlorine atoms on the PVC chains by a relatively more stable moiety of the organic stabilizer.

INORGANIC THERMAL STABILIZERS

Hydrotalcite stabilizers

Hydrotalcite (HT) is a double-layered inorganic complex. In its natural form, it is hydrated magnesium-aluminum hydroxycarbonate with a lamellar structure similar to that of brucite, with a general formula as $[Mg_{(1-x)}Al_x(OH)_2](CO_3)_{x/2} \cdot mH_2O$, where the stoichiometric coefficient (x) and the water content (m) can be varied over a wide range (Cavani et al., 1991). As Al^{3+} replaces some Mg^{2+} , an accumulative positive charge dominates.

This is balanced by OH^- anions that are situated throughout the structure (Yang et al., 2002).

This compound, also known as anion-exchanging clay and layered double hydroxide (LDH), has attracted a lot of attention in the search for efficient additives to enhance PVC thermal stability and to reduce the smoke emission during PVC flaming (Wang and Zhang, 2004; Zhang et al., 2006). HT is a non-toxic, environmentally friendly compound, which can be commercially produced by co-precipitation method (Bao et al., 2008). Kyowa chemical industries of Japan were the first to demonstrate 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 resin (Evans and Duan, 2006). HTs have been reported to have HCl absorption capacity and may be used as PVC thermal stabilizers (Liu et al., 2008). The role of the LDH in absorbing HCl was confirmed experimentally by Van der Ven et al. (2000) who measured the capacity of LDHs having the same M^{2+}/M^{3+} ratio and different counter-ions to react with HCl gas. They found a linear correlation between increasing HCl

capacity and thermal stability of the LDH in the order $SO_4^{2-} < Cl^- < OH^- < NO_3^- < CO_3^{2-} < C_{17}H_{35}COO^-$.

They suggested that the reaction between the LDHs and the HCl generally occurs in a two-step process: firstly, the interlayer anions react with the HCl gas, and secondly, the LDH layers themselves react with the HCl, leading to a complete destruction of the LDH structure and the formation of metal chlorides. Wang and Zhang (2004) investigated the effect of micro-sized hydrotalcite on PVC via melt blending. Congo red test and thermogravimetric analysis were used to evaluate thermal stability effect of the additive. The result indicated a significant positive improvement in the thermal stability of PVC. The stabilizing mechanism was attributed to the electrostatic interaction generated between the electron cloud of chlorine atoms in PVC chain and the positive layer charge of hydrotalcite, which resulted in a decrease in electron cloud density of chlorine atoms. This weakened the activity of the chlorine atoms and restricted the initiation of the dehydrochlorination. The additive was equally reported to exhibit flame retardant and smoke suppression effects.

Lin et al. (2005, 2006) studied the effect of varying the composition, structure and added amounts of LDH-hydrotalcite on the thermal stability of PVC. The investigation further confirmed the stabilizing effect of hydrotalcite on PVC. Thermal aging test was used to evaluate the effect of the additives. The results showed enhanced long-term stability and early colouring.

The effect of nano-sized hydrotalcite on the thermal stability of PVC was investigated by Liu et al. (2008) via solution intercalation process. The nanoscale exfoliated LDH particles were homogeneously dispersed in the polymer matrix. Thermal stabilizing effect of these particles based on increased dehydrochlorination time of samples containing the LDH particles was established. The results indicated increased stabilization with increased loading of LDH.

The ability of nanoscaled hydrotalcite to inhibit thermal degradation of PVC was studied (Bao et al., 2008). The suspension polymerized PVC in the presence of the nano-sized particles showed that the majority of HT particles were dispersed in the PVC matrix in the nanoscale. The Congo red measurement and thermogravimetric analysis showed that the thermal stability time and the temperatures at 10% weight loss and at the maximum weight loss rate of PVC resins increased as the weight fraction of HT in the composite resins increased.

Gupta et al. (2008) synthesized nanosize Ca–Al LDHs and investigated their PVC thermal stabilizing efficacy. The thermal stabilizing efficiency of the LDHs was evaluated by volumetric measurement of the HCl evolved. Samples containing the LDHs were reported to have longer induction periods than PVC alone. The efficiency of these materials was attributed, predominantly,

to the adsorption capacity and the HCl scavenging by intercalated anions.

Zn–Al–LDHs synthesized via a clean-route procedure in combination with calcium stearate and β -diketone were investigated as thermal stabilizers of PVC (Tong et al., 2011). The LDHs were synthesized in three different Zn/Al ratios of 3:1, 2:1 and 1:1. The thermal ageing test of PVC in the presence of mixtures of the stabilizers was carried out using thermal ageing test box by observing the colour change. The authors reported that Zn–Al–LDHs significantly improved thermal stability of PVC due to the improved capacity to absorb HCl, ability to increase initial stability and ensure good-initial colouring due to the presence of the zinc element. The Zn–Al–LDHs were reported to bear synergistic effect with calcium stearate and β -diketone on the thermal stability of PVC. The mechanism of stabilization of the LDHs was attributed to their ability to react with labile chlorine atoms and prevent the growth of the polyene structure.

Organic modification of LDHs is often necessary to convert them into suitable precursors for synthesis of polymer nanocomposites. Being an anionic clay, the chemicals for modification of LDHs can be selected from a wide range of organic and inorganic materials, such as anionic surfactants, oxo- and polyoxometallates anions, organometallic complex anions, etc. The surfactants are normally selected according to their functionality and chain length (Costa et al., 2008).

Inorganic salts

Some inorganic salts had been reported to exhibit stabilizing effect on thermal degradation of poly(vinyl chloride). Most of these salts are alkaline-earth metals and rare earth metals salts. Liu et al. (2006) investigated the thermal stabilities of poly(vinyl chloride)/CaCO₃ composites with micro/nanosized CaCO₃ as fillers, prepared by solution blending method. The report showed that the addition of CaCO₃ fillers improved thermal stability of the polymer. It was also found that even with a smaller amount; the nanometer CaCO₃ filler provided better thermal stability than the micrometer fillers. The stabilizing efficacy of the CaCO₃ fillers was attributed to the adsorption of the HCl released. The superior effect of the nanosized CaCO₃ filler was associated with larger surface area of the nanoparticles.

Literature report about inorganic salt rare earth as PVC thermal stabilizer is scanty; however, it continues to attract more and more attention because it is non-toxic, environment-friendly, efficient and economical.

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) was investigated by Weiqing et al. (2009) using Congo red test method. Results showed that cerium carbonate could stabilize

PVC because cerium can coordinate with multi Cl atoms, which makes C-Cl bond in PVC stabilized.

FUTURE DIRECTIONS

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. At our own end, our research efforts would be on the preparation, characterization and evaluation of non-toxic, environmentally friendly metal carboxylates from fixed oils that can function as PVC thermal stabilizers.

CONCLUSIONS

In view of the global concern about the environmental implication of conventional PVC thermal stabilizers, this paper highlighted the use of organic and inorganic compounds as PVC thermal stabilizers. Various classes of organic compounds that had been investigated include acids, phenols, esters, amines, thiols, polyols and some heterocyclic compounds. Mechanisms of stabilization attributed to these stabilizers include replacement of labile chlorine atoms, scavenging chlorine radicals and HCl, addition across polyene sequences and aromatic alkylation. 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. These compounds have the potential of providing environmentally friendly thermal stabilizers for PVC. 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.

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