



Synergistic effect of co-stabilizers on the thermal stability of polyvinyl chloride

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Abstract

In this research work synergistic effect between layered double hydroxide (LDH) and epoxidised sunflower oil (ESO) on the thermal stabilization of poly-vinyl chloride has been investigated. Synthesis of zinc glutarate and epoxidation reaction on sunflower oil was carried out in the laboratory. The Ca/Zn based soap compounds were used for the primary stabilizer for PVC. Synergistic effect of LDH with Ca/Zn stabilizer on the thermal stabilization of PVC with and without ESO was studied. Thermal stability of PVC was determined by Congo red test as a stability time (ts) while discoloration of the PVC sheets were examined using static oven test. Likewise thermal degradation of PVC was evaluated by Thermogravimetric analyzer (TGA) in terms of onset temperature from TGA curves. The results shows the enhancement in the thermal stabilization of PVC in presence of LDH and ESO. However, stabilizing effect of LDH with ESO on the thermal stability of PVC was more pronounced due to the mechanism of synergism by scavenging liberated HCl which obstructs the further degradation of PVC.

Keywords: Dehydrochlorination, Thermal stabilization, Stabilizers, Synergists, Congo red.

Introduction

Poly-vinyl chloride (PVC) is one of the most versatile commodity thermoplastic polymer useful in variety of applicative fields such as wire and cable industry, automobile, rigid pipe, flexible sheets and window profiles etc. Despite the fact that, thermal instability of PVC is a major drawback during its processing which is due to the degradation of polymer and its deteriorating effect on the end use properties¹. Thermal degradation of PVC is a result of a “zipper dehydrochlorination” reaction (evolution of HCl) that involves the generation of polyene sequences of double bonds which causes the change in color of the PVC from white to yellow to brown and finally to black^{2,3}. The problem of thermal instability of PVC can be solved by using thermal/heat stabilizers. Stabilizers are used in PVC to stop the thermal degradation either reacting with labile chlorine atoms of PVC as a primary stabilizers or with autocatalytic HCl which is liberated by PVC as a secondary stabilizers⁴.

More often thermal stabilizers of heavy metal based lead, tin and cadmium compounds are considered as suitable solution for the degradation problem of the PVC. However the environmental concerns prevent the use of these heavy metal based compound as PVC heat stabilizers. Attempts are being carried out towards environmentally friendly and economical substitutes for these heavy metal based stabilizers. Many researchers reported the non-toxic Ca/Zn based mixed metal soap stabilizers as an alternative for heavy metal based compounds^{1,5,6}. Generally mixed compounds of calcium and zinc stearate have been widely used to prevent

dehydrochlorination reaction in the course of PVC processing. These stabilizers exhibit a worthy effect on the thermal stability of PVC.

More often metal soap stabilizer prolongs the long-term heat stability of PVC but causes subsequent discoloration to the polymer by zinc burning. This impaired thermal stabilization effects of mixed metal soaps is frequently prevented by the use of synergists^{7,8}. Therefore success of these mixed metal soap is undoubtedly ascribed to the additives of some synergists or secondary stabilizers. A range of organic compounds such as β -diketones, polyols, epoxidized oils as well as zeolites and LDH as hydrotalcites have been used as a synergists along with metal soaps to prevent the thermal degradation of PVC^{9,11}. Layered double hydroxides (LDHs) are layered inorganic material having an intrinsic hydrogen chloride (HCl) absorption capacity and thus can improve the thermal stability of PVC resin. Due to the non-toxic nature of LDH, it is now used as synergists with other thermal stabilizers for stabilization of PVC.

This study aimed to investigate synergistic effect between LDH and epoxidized sunflower oil in the enhancement of stabilizing efficiency of ca-stearate/zn-glutarate based stabilizer on the degradation of PVC.

Materials and methods

A suspension grade Polyvinyl Chloride (K-67, Reon) was supplied by Reliance Ind., India. Calcium stearate, DOP, processing aid (PA) and stearic acid were kindly provided by Aryavarat Chemicals, Jalgaon. Refined sunflower oil was

purchased from local commercial market. Layered double hydroxides (LDH) as Hydrotalcite was purchased from Sigma Aldrich. All other chemicals and solvents such as glutaric acid, zinc oxide, toluene, Amberlite IR 120 resin and hydrogen peroxide (30%) were of A.R. grade and used as received from s.d.fine chemicals, Mumbai.

Preparation of zinc glutarate: Zinc glutarate was synthesized in the laboratory from zinc oxide and glutaric acid as per the procedure given elsewhere⁸. Glutaric acid (0.10 mol) was dissolved in requisite amount of toluene in a 250 ml round bottom flask equipped with Dean- Stark trap and a reflux condenser. Then, zinc oxide (0.10 mol) was added into the glutaric acid in toluene. After the addition was completed, the slurried mixture was stirred vigorously at 50°C for 4 hours and cooled to room temperature. Then the reaction mixture was filtered off and washed with acetone several times. The zinc glutarate in powder form was obtained which was dried in a vacuum at 100°C for 24 hours.

Preparation of epoxidised sunflower oil (ESO): Epoxidation reaction of sunflower oil was carried out at 50°C by per-acetic acid which was prepared in-situ by reacting hydrogen peroxide (30% V/V) with excess glacial acetic acid in the presence of Amberlite IR 120 resin and level of epoxidation was determined by standard analytical method^{12,13}.

Preparation of PVC sheets: PVC formulations with varied stabilizer content were given in Table-1. Prior to processing, each formulations were dry blended using high speed domestic mixer for homogenized blend. Then homogenized dry blended formulations were compounded on Brabender Plastograph (Type W-50 EHT, GmbH, Germany) at 160°C for 5 mins. at 45 rpm mixing speed. The lump samples obtained from Plastograph were compressed in a compression molding press at 170 °C for 10 minute to obtain PVC sheet with 1mm thickness. The sheets were used for further analysis.

Table-1: PVC formulations with stabilizers contents.

Expt. No.	Compounds	Quantity (phr)
0.	PVC	100
1.	PVC+ Cast/Zn gl	100+ 1
2.	PVC+ Cast/Zn gl+ LDH	100+1+1
3.	PVC+ Cast/Zn gl+ LDH	100+1+2
4.	PVC+ Cast/Zn gl+ ESO	100+ 1+3
5.	PVC+ Cast/Zn gl+ LDH+ESO	100+1+1+3
6.	PVC+ Cast/Zn gl+ LDH+ESO	100+1+2+3

Each formulation contains fixed amount of plasticizer, lubricants and processing aid.

Characterization: Determination of thermal stability of PVC by Congo red test: Determination of static thermal stability of PVC was studied according to ISO 182-1 method¹⁴. In this process, a test tube containing PVC formulation was heated in an oil bath at 180°C ± 2°C temperature. Afterwards the emitted vapor are passed through a tube containing Congo red paper. HCl gas is liberated during the degradation of PVC which changes the color of Congo red paper to blue at specific time. This period indicates the thermal stability of PVC as stability time (ts).

Determination of thermal stability by static oven test: The compressed PVC sheets were cut into 1 cm x 1 cm strips and placed in a hot air oven at 180°C ± 2°C temperature. These PVC strips were then subjected to static thermal test for visual discoloration comparison. Strips were removed at 10 minute interval for initial 1 hour and 20 minute interval for 2 hour interval which were then subjected to visual examination as per ISO standard and interpreted using Ocskay et. al. method¹⁵.

Determination of thermal stability by thermogravimetric analysis (TGA): Thermo-gravimetric analysis was carried out to investigate the thermal degradation behavior of PVC sheets using thermo-gravimetric analyzer (TGA-Shimadzu, 50 HT Japan) within the range between room temperature to 600 °C with constant heating rate at 20 °C/min. The variation in onset temperature during the weight loss of PVC sheets was considered as a measure for improvement in the thermal stability of PVC.

Results and discussion

Thermal Stability of PVC by Congo red test: Rate of dehydrochlorination of PVC was studied by Congo red test as stability time (ts). The data obtained as stability time from the Congo red test are collected in table 2 and also represented by graphical chart in Figure-1. The results show that use of synergist LDH with Ca-stearate/Zn-glutarate stabilizer system increases the stability time (ts) substantially. The lower stability time of Ca-gl/Zn-st stabilized PVC (expt. no. 1), could be explained on the basis that autocatalytic action of HCl and ZnCl₂ might be responsible for the increase in the rate of dehydrochlorination of PVC during degradation process.

The data show that addition of LDH (1 and 2 phr) in Ca/Zn stabilized PVC increases the stability time (ts) at around 24 mins and 32 mins (expt. no. 2 and 3) compared to only Ca/Zn stabilized PVC of 7 min. The thermal stability was supplementary improved in presence of epoxidised sunflower oil (ESO), which prevents the further dehydrochlorination reaction from PVC and stability time was increased at around 52 mins. This enhancement of the stability was due to the absorbance of HCl by LDH and subsequently the reaction of epoxy ring presented in ESO with liberated HCl produces the chlorohydrins which suppose to prevent the autocatalytic activity of HCl released during the degradation of PVC¹⁶. Also

the epoxy ring of ESO react with allylic chlorine groups present in PVC results in the esterification and etherification reactions which may prevents the further dehydrochlorination rate that was observed when Ca-stearate/Zn-glutarate and LDH stabilizer system is used in combination with ESO.

Table-2: Stability time (ts) of PVC formulations.

Expt. No.	Stability time in mins. (ts)
0.	3
1.	7
2.	24
3.	32
4.	11
5.	37
6.	52

Thermal stability by static oven test: Thermal static test gives the results of discoloration behavior in terms of blackening time of the PVC sheets during the degradation when thermally investigated in hot oven test. The results are illustrated graphically in Figures-2. Discoloration of the sheets was examined visually as described by the method of Ocskay et al. using Synmero scale¹⁵. This method indicated that there is a close connection exist between discoloration and the formation of hydrochloric acid in the metal soap stabilized PVC. Higher degree of discoloration with respect to blackening time show low thermal stability of PVC. It is observed that the blackening time of Ca-st/Zn-gl stabilized PVC was very early during the test at about 40 min. showing its high degree of discoloration having value between 6 and 8 as indicated in Figure-2.

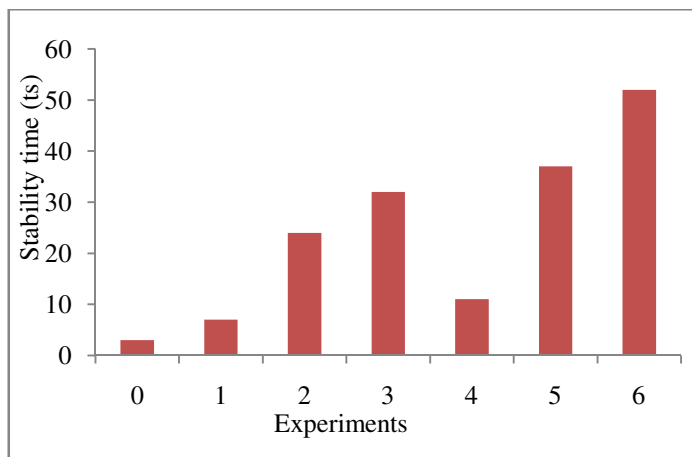


Figure-1: Stability time (ts) of PVC with LDH and ESO.

However, addition of LDH in Ca-st/Zn-gl stabilized PVC as synergist increased the blacking time which was goes upto 50 and 60 mins for 1 and 2 phr loading at low degree of discoloration respectively. Moreover LDH in combination with ESO in Ca.st/Zn.gl stabilized PVC (expt. no. 5 and 6) imparts better thermal stability resulting in low degree of discoloration as reflected in blackening time more than 80 mins. as shown in Figure-2. The effect show that ESO may work better synergistically with LDH to enhance thermal stability of PVC. This results were complimentary to the data of Congo res test. The HCl scavenging ability of LDH through ion exchange mechanism as well as reaction of epoxy ring with HCl and active site of the PVC prevents the further autocatalytic dehydrochlorination. It has been suggested that the presence of epoxy ring in ESO is act as excellent hydrochloric acid (HCl) scavenger and also able to substitute allylic chlorines that results in inhibiting the formation of long polyene, and hence imparting less degree of discoloration to the PVC sheets¹⁶. This results in the extension of blackening time imparts better long term thermal stability to the PVC. The overall reaction mechanism of synergists LDH with ESO on the degradation of PVC is suggested in Scheme-1.

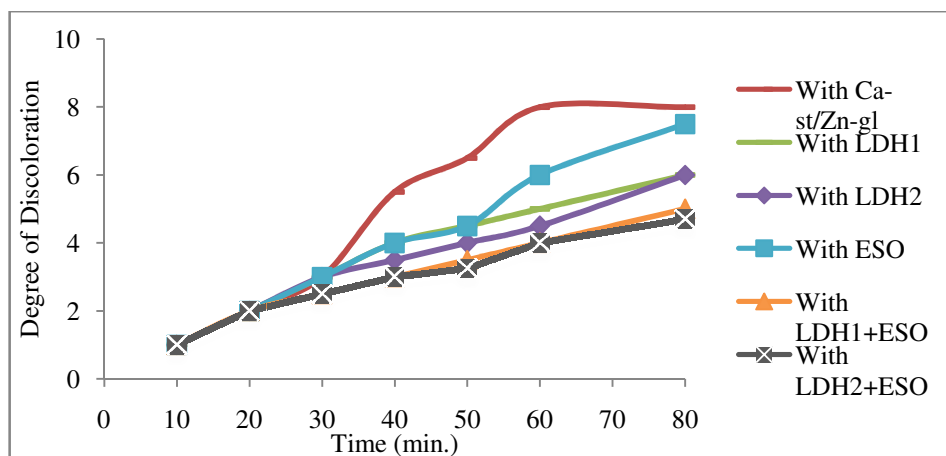
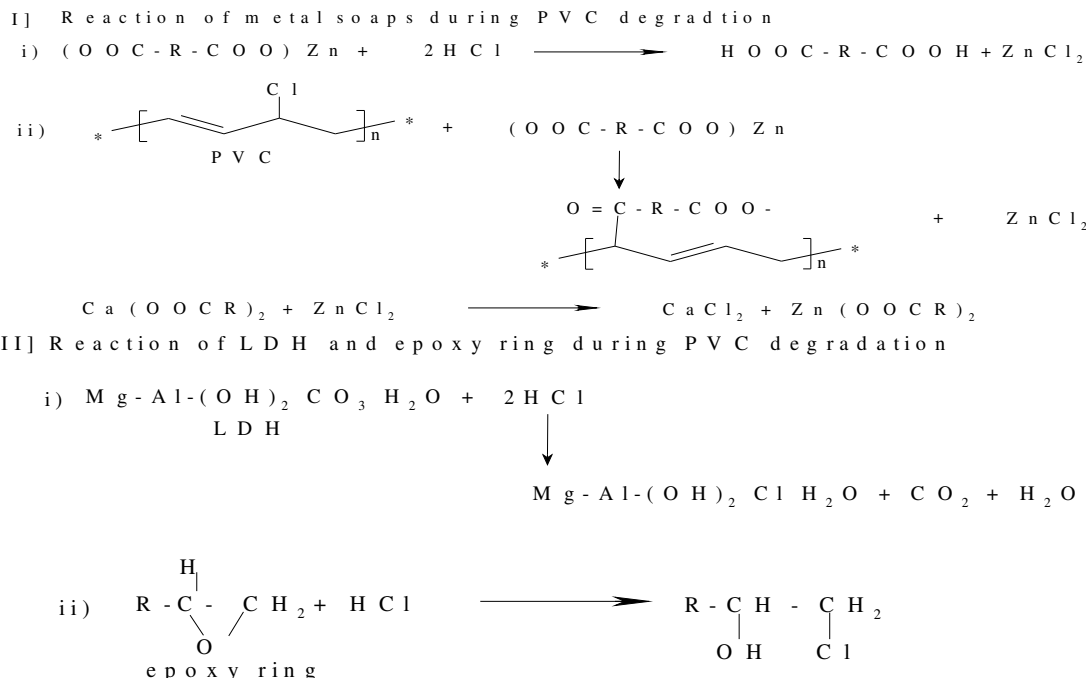


Figure-2: Discoloration of PVC sheets containing LDH and ESO.



Scheme-1: Reaction mechanism of LDH and epoxy ring (oxirane) with HCl and PVC.

Thermal stability of PVC using thermogravimetric analysis (TGA): Thermal stability of PVC was studied by thermogravimetric analysis (TGA). The data obtained from TGA analysis are summarized in Table-3 while TGA thermogram of representative PVC samples are shown in figure 3. Increase in onset temperature (as $T_{\text{onset}}^{\circ\text{C}}$) during the degradation of PVC was considered as better thermal stability to PVC. It is reported that degradation of PVC occurs in two step^{3,17}. The first step occurs in between the temperature range of 200 °C- 350 °C which is mainly related to the dehydrochlorination i.e. loss of HCl from the polymer. Second step (up to 600 °C) involves the decomposition of polymer due to the more volatile compounds and pyrolysis of the PVC.

In TGA analysis onset temperature (T_{onset}) of primarily stabilized PVC (expt. No.1) was at 254 °C correspond to early degradation stride while addition of LDH in the stabilizer auxiliary increases the temperature around 256 °C as seen in Figure-3. Whereas the combination of LDH with ESO in primary stabilized PVC further enhanced the thermal stability by increasing onset temperature at around 260 °C as shown in Figure-3.

This increase in the onset temperature with better thermal stability of PVC can be attributed to the synergistic effect shown by LDH and ESO on thermal degradation of PVC. Both synergists involve in a better way to scavenge evolved HCl and hinder its autocatalytic action during the degradation reaction. Therefore it is concluded that the onset temperatures of the PVC stabilized with Ca/Zn stabilizer substantially increased with the addition of LDH and ESO as a synergist¹⁸.

Table-3: TGA data of PVC containing LDH with ESO.

Expt. No.	Onset temperature (°C)
1.	254
2.	255
3.	256
4.	255
5.	260

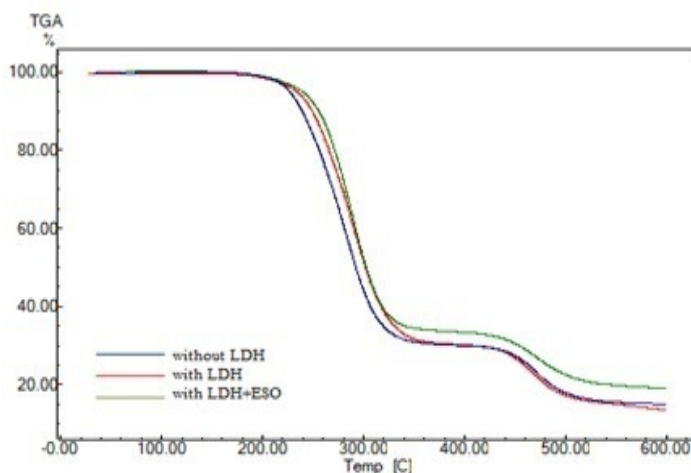


Figure-3: Thermograms of the primary stabilized PVC with LDH and ESO.

Conclusion

In this study synergistic effectiveness of LDH in combination of epoxidized sunflower oil (ESO) on the thermal stabilization of PVC were investigated. Thermal stability of PVC was studied in terms of dehydrochlorination rate, degree of discoloration by static oven and thermogravimetric analysis (TGA) as a criterion of onset temperature. The results suggest that combined use of LDH with ESO as a synergists enhanced the thermal stability of PVC by the effect of synergism which is attributed by scavenging of evolved HCl and reaction of epoxy group during the degradation of PVC. It is concluded that the use of synergists in Ca.st/Zn.gl stabilized PVC not only enhances the stabilizing efficiency of primary stabilizer but also improves the long term thermal stability by preventing the further degradation.

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