Epoxidized linolenic acid salts as multifunctional additives for the thermal stability of plasticized PVC

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ABSTRACT: Calcium and zinc salts of epoxidized linolenic acid were synthesized and used as multifunctional additives, to minimize or prevent the reaction of epoxidized soybean oil (ESO) with liberated hydrochloric acid (HCl) during the thermal degradation of poly(vinyl chloride) (PVC) in particular. These metal epoxy salts were incorporated as thermal stabilizers for both diisodecyl phthalate and ESO–plasticized PVC blends that underwent thermal degradation studies at 170°C. The overall performance of these metal epoxy salts was examined by thermal gravimetric analysis and visual color retention of the PVC blends. The weight loss profiles of the metal salt stabilized PVC were comparable to those of blends containing metal stearates. There were, however, vast improvements in color retention of the plasticized PVC using these novel additives. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41736.

INTRODUCTION

Untreated poly(vinyl chloride) (PVC) is a hard, brittle solid, limiting its direct industrial application without the incorporation of various additives to improve its mechanical properties.[1] Chief among these additives is the use of a plasticizer which serves to increase the flexibility, workability, and distensibility of the polymer system. One class of plasticizers commonly used is phthalate esters made from long-chain branched alcohols. These include diisodecyl phthalate (DIDP) and bis(2-ethylhexyl) phthalate. It is the unique combination of the nonpolar and dipolar components of these plasticizers which results in their PVC compatibility. In essence, they behave as an internal lubricant that allows greater flexibility and mobility between polymer chains. However, phthalates are petroleum-based and, in addition, exhibit negative environmental and health effects. As a result, there has been a growing interest in developing alternative bio-based plasticizers for PVC as more sustainable options compared to the petroleum-derived phthalates.[2,3] One such bio-plasticizer is epoxidized soybean oil (ESO) (Figure 1). The soybean oil has a high content of nonconjugated double bonds that are easily epoxidized using standard and inexpensive reagents. Similar to the already mentioned phthalate plasticizers, ESO has been shown to be sufficiently compatible with PVC and an effective plasticizer, but only when used in combination with mixed metal soap as heat stabilizer to prevent acid-catalyzed oxirane ring opening.[4–6]

When choosing a plasticizer, there are several characteristics of the additive which must be taken into account in order to be considered for end-use applications. These include its solubility in the PVC, its UV-Vis absorption characteristics, and its tendency to undergo migration within the polymer matrix. Despite its environmental advantages over its phthalate counterparts, ESO's performance as a primary plasticizer suffers from the ease with which the strained oxirane rings react with the HCl generated during polymer degradation to produce the corresponding chlorohydrins.[2,7–9] These chlorohydrin derivatives have less compatibility with the polymer matrix. Hence, in the absence of metal soap stabilizers (Zn and Ca stearates), the effectiveness of ESO as a plasticizer is greatly diminished.[6]

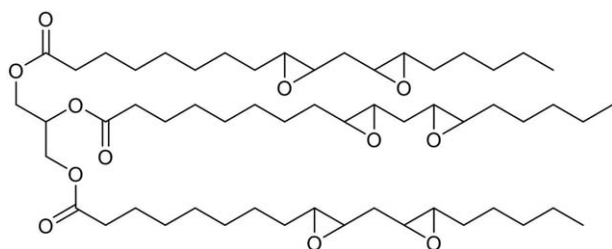Additional Supporting Information may be found in the online version of this article.

Figure 1. ESO—a bio-based PVC plasticizer.

Structurally, PVC is characterized by chlorine substituents located at alternating secondary carbons along the polymer chains [Figure 2(a)]. There are also allylic and tertiary chlorine sites [Figure 2(b,c)]. These latter sites, while few and far between, are considered "weak links" and a major source of the inherently low thermal stability of PVC at normal processing temperatures (170–200°C). At these temperatures, dehydrochlorination is readily initiated from these weak links.[10,11] In addition, the decomposition process can become catastrophic, since the HCl produced is a known catalyst for further dehydrochlorination processes (Figure 2d). Thus, autocatalysis can ensue accompanied by the formation of conjugated polyalkenes. The phenomenon is termed "chain unzipping." As a consequence of increased conjugation, the thermal degradation of PVC is normally accompanied by discoloration of the material which is undesirable for consumer and industrial applications.

A large number of additives designed for the thermal stabilization and color retention of PVC have been reported in the literature. The general approach has been to develop additives which can promote substitution reactions incorporating more stable substituents on the polymer backbone to retard or prevent elimination processes, and/or simply sequester the generated HCl via neutralization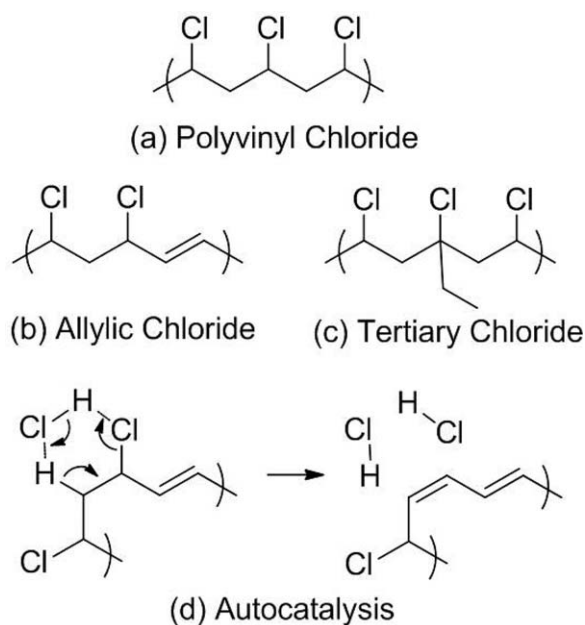 processes to promote long-term stability.[12–20] These additives include metal salts of fatty acids and molecules containing epoxide functionalities.[4–6,21,22] Traditional metal carboxylate additives, such as Ca and Zn stearates, have been synergistically used to slow the unzipping process. Metal stearate salts have been found to promote substitution at labile sites on the PVC backbone and to scavenge the thermally generated HCl via acid–base processes. Benanbiba and coauthor[2] found that epoxidized sunflower oil plasticizers exhibit a stabilization effect, citing the following two important stabilizing influences: (1) epoxides increase the induction time to rapid dehydrochlorination and (2) epoxides decrease the overall rate of dehydrochlorination after the induction time. Iida et al.[12,13] studied epoxidized polybutadiene as a thermal stabilizer alongside calcium and zinc stearate. Similarly, Odilora[23] showed that the time to reach one percent dehydrochlorination and the rate of dehydrochlorination at that time are both improved when metal carboxylates are used in addition to epoxidized oils. A study by Okieimen[15] examined the stabilizing effects of jatropha seed oil, khaya seed oil, and rubber seed oil along with metal soaps (Ba and Cd) of the epoxidized oils. These oils are comprised of mixtures of various fatty acids that include ∼5 wt % and ∼37 wt % linolenic acid for the jatropha seed oil and rubber seed oil, respectively. Worschech et al.[24] conducted a similar study, employing calcium and zinc salts of epoxidized metal glycerides. Overall, as the number of epoxy groups within the additive increase, the secondary stabilizing effects increase.

Herein, we present a new approach to PVC stabilization and introduce a multifunctional additive package—the Zn and Ca salts of epoxidized linolenic acid. The major advantages of this stabilizing system are the inclusion of both (1) epoxide functionalities to react with liberated HCl, thus protecting the epoxide groups of ESO, if present in the composition and (2) metal carboxylate functionalities to mimic the stabilizing behavior of zinc and calcium stearates. In this work, the novel zinc and calcium triepoxylinolenic acid salts (ZnEp and CaEp, respectively) were synthesized according to Figure 3 and subsequently used in thermal degradation studies of both DIDP- and ESO-plasticized PVC blends. Their ability to stabilize plasticized PVC was determined by means of thermogravimetric analysis (TGA) and the degree of visual discoloration of the bulk material. In addition, the HCl-promoted ring-opening reactions on model epoxides were also investigated.
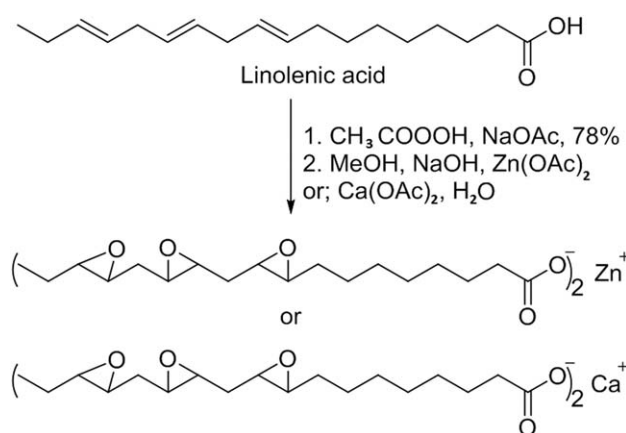

Figure 2. (a) Polyvinyl bhloride; (b) Allylic chloride; (c) Tertiary chloride; (d) Autocatalysis mechanism and chain unzipping.

Figure 3. Synthesis of Zn or Ca salt of 9,12,15-triepoxylinolenic acid.

MATERIALS AND METHODS

Materials

DIDP and zinc stearate ($ZnSt_2$, purum, 10–12% zinc metal basis) were obtained from Sigma-Aldrich. Calcium stearate ($CaSt_2$) was obtained from Alfa Aesar. The PVC powder (Oxy-Vinyls 240F suspension-grade homopolymer) was a product of Oxy Vinyls, LP and Plas-Chek 775 ESO was a product of Ferro Corporation. The properties of these grades of PVC and ESO have been reported elsewhere.[5] Helium and nitrogen were purchased from Airgas. All materials were >91% purity or ultra-high purity unless otherwise stated and used as received from the manufacturer.

Synthesis of 9,12,15-Triepoxylinolenic Acid

Neat linolenic acid (5.4 mL, 0.049 mol) added to reaction vessel and placed into an ice bath (0°C). Peracetic acid (18 mL, 0.069 mol) and sodium acetate (1.1 g, 0.069 mol) were then added to dropwise over 1 h, and the reaction was stirred for another 1 h at the same temperature. The organics were then extracted with diethylether (2 × 10 mL). The organic layer was washed with water (5 × 50 mL), dried over $MgSO_4$ and rotovapped under vacuum to give 4.6 g (yield 78%) of colorless semisolid product.

Synthesis of Zn or Ca Salt of 9,12,15-Triepoxylinolenic Acid (ZnEp or CaEp)

NaOH (0.5 g, 0.132 mol) in 15 mL water was added to a triepoxylinolenic acid (4.3 g, 0.0132 mol) dissolved in methanol (10 mL) at room temperature. The reaction was stirred for 15 min (homogeneous solution) after which $Zn(OAc)_2$ (1.2 g, 0.007 mol) (use $Ca(OAc)_2$ for the preparation of Ca salt) in 15 mL water was then added to the above homogeneous solution mixture. The appearance of a white precipitate was noted. The mixture was then cooled to 0°C. The solid was filtered and washed with water (3 × 20 mL), acetone (2 × 10 mL) and dried under vacuum to give 3.5 g (yield 76%) of Zn-triepoxylinoleniate (yield 51% Ca-triepoxylinoleniate) as a white solid. Elemental analysis for Zn—Calc. 9.13; found 9.33; Ca—calc. 5.80; found 6.17.

Blending of the PVC, Plasticizer, and Novel Additives

Dry-blended samples consisted of 3 g of PVC powder, 30 phr (0.9 g) plasticizer (DIDP or ESO), and 5 phr (0.15 g) additional additives ($ZnSt_2$ and/or $CaSt_2$ or novel additives ZnEp and/or CaEp). The PVC powder and one half of the plasticizer (0.45 g) were physically combined, heated to 95°C in an oil bath and thoroughly mixed by hand using a glass rod. In a separate vessel, the remaining plasticizer (0.45 g) and all other additives were combined and heated to 95°C. The two mixtures were then combined, heated to 95°C and thoroughly mixed in the same manner stated previously. This temperature is above the glass transition temperature of unplasticized PVC (83°C)[4] which facilitated the efficient absorption of the additive by the PVC. This two pot-blending technique of the plasticizer with the PVC afforded the complete uptake and uniform distribution of the additives. It should be noted that the ZnEp and CaEp additives are not readily soluble/compatible with the PVC and are therefore not incorporated into the PVC matrix without the plasticizers.

Thermal Analysis of PVC Blends

TGA was performed using a TA Instruments TGA Q50. Isothermal weight loss studies were conducted between 150°C and 180°C for up to 3h under a flow of nitrogen (100 mL/min). In all cases, approximately 20 mg of a dry blended sample was used in duplicate runs to confirm repeatability. Weight loss is reported with respect to only the PVC, excluding the additives. This is because the weight losses observed in the PVC blends are mainly attributed to dehydrochlorination of the PVC backbone (Supporting Information). This approach enables better determination of the overall effect of the additives on the plasticized PVC itself compared to untreated PVC.

Epoxide Ring-Opening Studies

HCl (g) was bubbled (3 min) through o-dichlorobenzene (o-DCB, 35 mL) at room temperature. The amount of HCl complexed with the o-DCB was determined by weighing the reaction vessel before and after HCl addition. The epoxide (cyclohexene oxide, 1,2-epoxyhexane or ESO) in a 1:1 or 20:1 (epoxide/HCl) molar ratio dissolved in o-DCB (2 mL) was then added to the HCl solution. The reaction was stirred at room temperature, and an aliquot of the mixture was taken and analyzed for the epoxide conversion and corresponding product formation by ^{1}H-NMR spectroscopy.

UV-Visible Spectroscopy Study of PVC

UV-visible studies of PVC were performed using an Agilent Cary 100 UV-visible spectrophotometer and 10 mm path length Quartz cuvettes. Scans were recorded over a range of 200–800 nm. PVC samples (~50 mg) were first loaded into the TGA, and an accurate mass was recorded. The TGA was used to precisely heat the sample to 180°C for a specific time. The heated samples were immediately removed from the TGA upon completion of the run and quantitatively dissolved in THF to obtain equal PVC concentrations. UV-visible spectra were obtained in triplicate to ensure repeatability between samples.

Polymer Discoloration Analysis of PVC Blends

Photographs of the PVC blends were taken during post-thermal treatment. These photographs were used to qualitatively compare the discoloration of the PVC polymer.

RESULTS AND DISCUSSION

Susceptibility of ESO to Hydrogen Chloride

Epoxide functionalities are strained ring systems that are highly reactive with both electrophilic and nucleophilic reagents. It follows that a PVC plasticizer, such as ESO, would be highly susceptible to reaction the HCl liberated during the thermal decomposition of PVC (Figure 4). The products of such a reaction would severely reduce the effectiveness of the plasticizer. As a consequence, it was instructive to set up a model system in
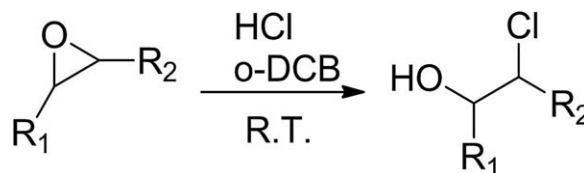
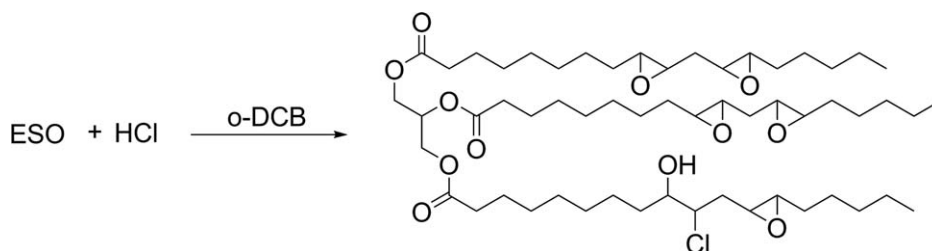**Figure 4.** Example epoxide ring-opening reaction.

Figure 5. Structure of chlorohydrin formed from the reaction of ESO with HCl.

order to investigate how rapidly and how completely ESO would scavenge HCl. ESO, dissolved in 1,2-dichlorobenzene, was reacted with dry HCl at room temperature to determine the reactivity of the epoxide groups. It should be emphasized that the ESO structure illustrated in Figure 5 is an idealized picture of the molecule. The fatty acid components of the glycerides could be saturated (containing no epoxy groups) or monounsaturated containing only one epoxide. The ^{1}H-NMR spectrum of the ESO used in this study is shown in Figure 6. The signals corresponding to the C-H protons bonded directly to the epoxide ring appear 2.70 and 2.89 ppm; these absorptions are labeled A. The absorptions at 2.12, 4.10 and 4.28, and 5.27 ppm are assigned to the hydrogens labeled B, C, and D. Based upon the relative peak integrations, each hydrogen accounts for 1.28 area units. As a consequence, it can be estimated that there are 4.5 epoxide groups per ESO molecule and not the idealize number of six.

At a molar ratio of 1:1 ESO/HCl, the epoxides completely reacted within a 5-min period at room temperature. This is clearly shown in Figure 7; the ^{1}H-NMR spectrum of the system after reaction shows the disappearance of the peaks at 2.70 ppm and 2.89 ppm (labeled A in Figure 6) and the appearance of peaks between 3.5 ppm and 4.0 ppm. These peaks are attributed to the ring-opened products and correspond to the protons adjacent to hydroxyl and chloride groups formed after HCl reacts with the oxirane rings. When a ratio of 20:1 ESO/HCl is

used, the ^{1}H-NMR spectrum of the reaction products shows a similar absorption pattern and the development of peaks between 3.5 ppm and 4.5 ppm are observed. It is concluded that even at this much reduced quantity of HCl, epoxy ring-opened products are formed. The ^{1}H-NMR spectrum of the reaction products is available in the supporting information, Figure S1. The experiments described previously provide strong evidence of the susceptibility of ESO to HCl and the need for an additive package, which preserves both the ESO structure and its function as an effective PVC plasticizer.

To demonstrate the effectiveness of the Zn and Ca salts of epoxidized linolenic acid, the results based upon the following experimental will be presented: (1) the thermal analyses of PVC and PVC plasticized with DIDP or ESO at 170°C and the accompanying visual appearance of the materials, (2) the corresponding activation energies for each of the aforementioned systems, and (3) the thermal analyses and visual appearances of the DIDP- and ESO-plasticized systems employing both the Zn and Ca salts of stearic acid and epoxidized linolinic acid.

TGA of Untreated PVC and PVC Plasticized with DIDP and ESO

Figure 8 shows the thermogravimetric profiles of untreated PVC and PVC plasticized with either DIDP or ESO at 170°C. The temperature of 170°C was chosen for these studies because it is well within the temperature range for typical industrial
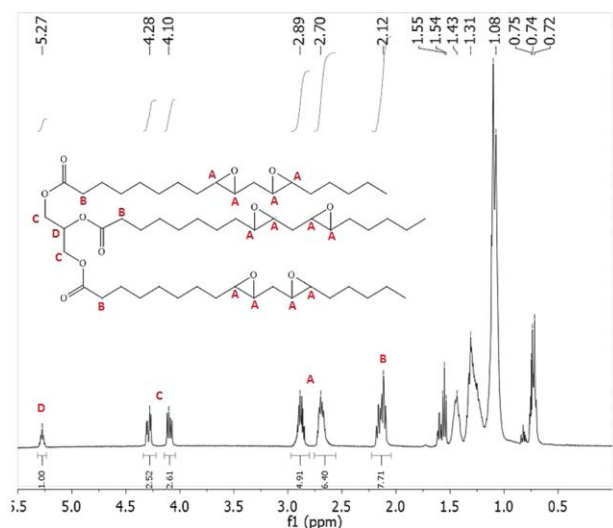

Figure 6. ^{1}H-NMR spectrum of ESO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
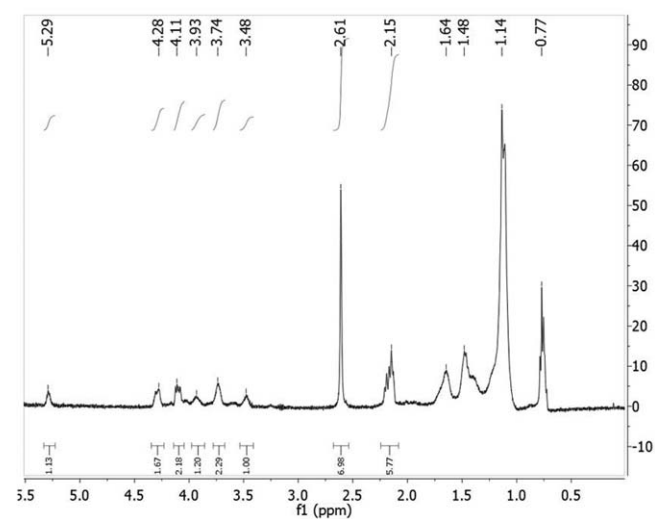

Figure 7. ^{1}H-NMR spectrum of the products from the reaction of ESO with HCl (1:1 molar ratio).
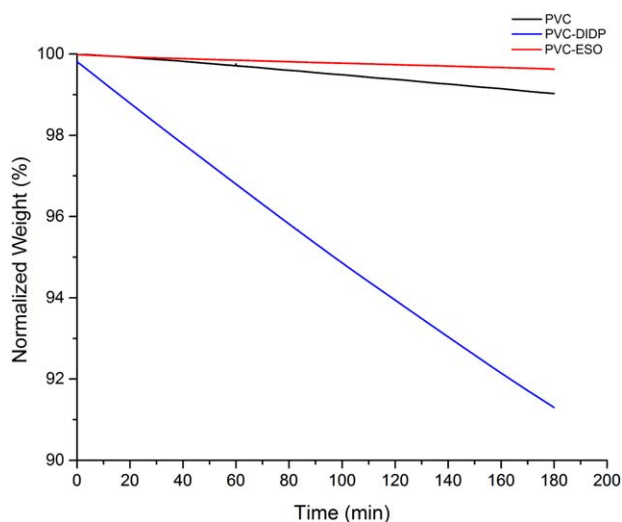
Figure 8. Weight loss at 170 °C over 2 h for PVC of PVC and plasticizer blends; weight normalized against the mass of PVC in each blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10. Color comparison of PVC and plasticizer blends after thermal treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

processing and it also affords adequate differentiation of performance between the different PVC blends. Untreated PVC, used as a base line for evaluating the plasticized blends, loses less than 1% of its starting weight over a period of 2 h. Since untreated PVC is too rigid and brittle for most applications, plasticizers such as DIDP and ESO are incorporated into the polymer matrix to increase flexibility and workability. From Figure 8, it is immediately obvious that DIDP-plasticized PVC loses significant weight during the 2-h period. To estimate how much of the weight loss is caused by volatilization/decomposition of DIDP, a TGA of neat DIDP was conducted at 170°C for a period of 2 h (Supporting Information, Figure S2). From these data, it was determined that the maximum loss of DIDP could only account for 0.027% of the overall weight loss of the DIDP-plasticized PVC. It was hypothesized, therefore, that this increased weight loss of PVC plus DIDP compared to untreated
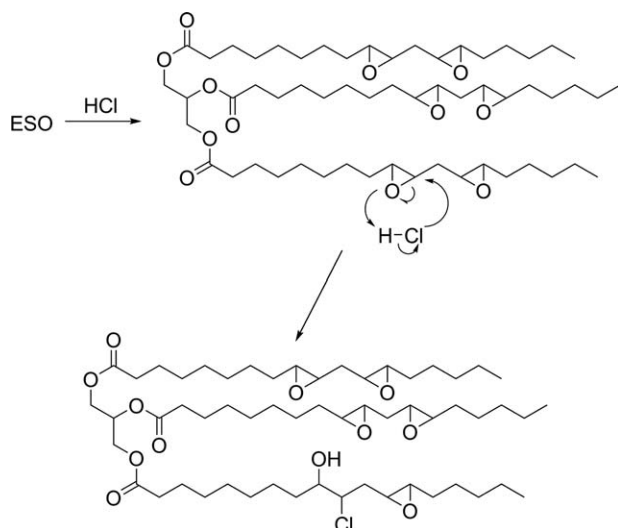
PVC was due to the increased flexibility of the polymer chains as a consequence of the plasticization of the polymer system. This flexibility allowed conformational changes in the polymer chains that would lower the activation energies for both the unimolecular and HCl-catalyzed elimination of HCl.

In contrast to DIDP, the ESO-plasticized PVC sample loses less weight after 2 h compared to untreated PVC; the ESO appears to exhibit a stabilization effect. This is attributed to the epoxide functionalities present in the structure. Based upon the previously discussed experiments, it is clear that the oxirane rings scavenge the thermally generated HCl at a rate substantially greater than the rate of HCl volatilization from the PVC sample (Figure 9). The point at which volatilization of HCl dominates over ring-opening reactions is not evident during the 2-h period. It is important to note that, in the absence of another heat stabilizer, the structure and plasticizer properties of ESO change as the HCl is scavenged leading to deleterious polymer-blend performance. Hence, maintaining the integrity of the ESO as a plasticizer is of primary importance.

In addition to the above quantitative thermal weight loss profiles, the visual appearance (change in color) of the bulk polymer provided a more complete picture of the degradation consequences. Figure 10 illustrates that DIDP-plasticized PVC displays poor color stability after 2 h. The discoloration is quite similar to that of untreated PVC. Indeed, the differences in the discoloration of untreated PVC and the plasticized PVC blends were minor. Nevertheless, of the three systems, it was clear that the ESO-plasticized PVC blend exhibits the least discoloration. Again, this is attributed to the scavenging of the thermally generated HCl by the epoxy functionalities. Figure 10 will provide a reference point for subsequent color retention observations of PVC systems containing a variety of stabilizing additives.

Determination of the Activation Energies for the Dehydrochlorination of Untreated and Plasticized PVC

Activation energies for the PVC degradation process were determined by TGA for PVC, PVC plus DIDP, and PVC plus ESO. In all cases, the PVC weight % was calculated with respect to the amount of PVC in the blend excluding the additives. Similar to DIDP, the weight of any ESO in the blend was assumed constant due to negligible weight losses (approximately 0.25%) of neat ESO at 180°C over a period of 2 h (Supporting Information, Figure S3). The Arrhenius equation was used to calculate the activation energy
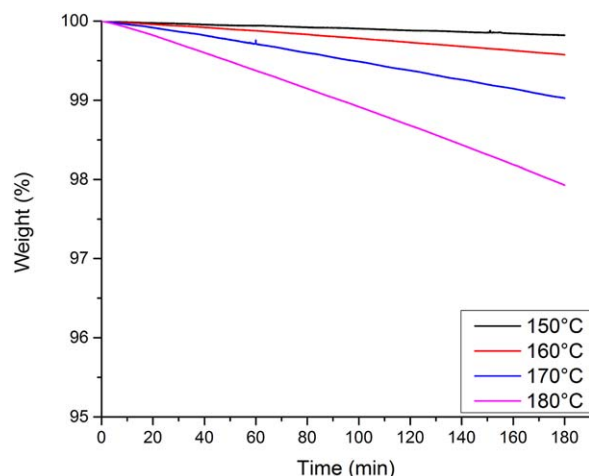

Figure 9. Scavenging of HCl by ESO.

Figure 11. Isothermal weight loss of untreated PVC over 2 h at 150°, 160°, 170°, and 180 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
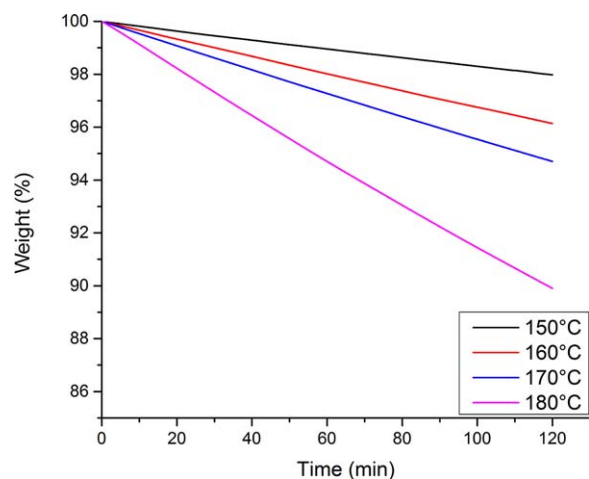

Figure 13. Isothermal weight loss of ESO-plasticized PVC over 2 h at 150°, 160°, 170°, and 180 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
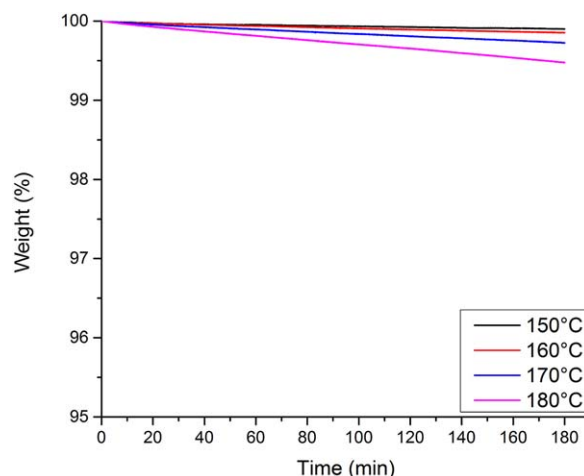
$$k = Ae^{-\frac{E_a}{RT}} \qquad (1)$$

where k is the rate of degradation at a particular temperature, A is the frequency factor, E_a is the activation energy for the degradation process, R is the gas constant, and T is the absolute temperature.

The isothermal weight loss data of untreated PVC, DIDP-plasticized PVC, and ESO-plasticized PVC at various temperatures are shown in Figures 11, 12, and 13, respectively. The weight loss during the first 30 min was used to determine the initial rate of degradation assuming first-order kinetics at each temperature. The Arrhenium plots for each of the samples are shown in Figure 14. The activation energy for the initial degradation for PVC is 106 ± 14 kJ mol^{-1} while that for PVC with 30 phr of ESO is 65 ± 7.8 kJ mol^{-1} and that for PVC with 30 phr of DIDP is 85 ± 3.5 kJ mol^{-1}.

Employing the ASTM E698[25] method for determining activation energies through the use of constant heating rate weight loss stud-

ies resulted in activation energies of untreated PVC and PVC with 30 phr ESO of 147 kJ mol^{-1} and 102 kJ mol^{-1}, respectively. In both ASTM method and the thermogravimetric weight loss method discussed previously, the activation energy for the untreated PVC was higher than that of the PVC with 30 phr ESO. However, the overall weight loss is less when PVC is mixed with 30 phr ESO than the weight loss of PVC alone. These observations suggest that when PVC is plasticized with ESO the release of HCl occurs more readily, but the ability of ESO to scavenge the HCl reduces the overall thermal weight loss. As indicated earlier, this is undesirable since the fundamental structure of the plasticizer is changed. Its hydrophilicity increases and its compatibility with the polymer matrix decreases. As a consequence, the ring-opened product has an increased tendency to migrate from the polymer matrix. In order to address these issues, it was conjectured that the new ZnEp and CaEp additive package could act as a
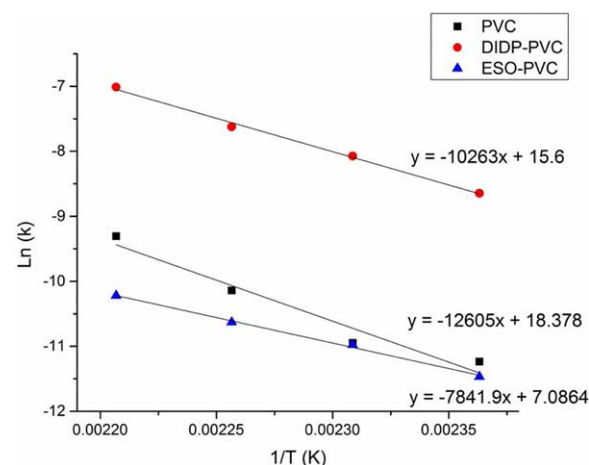

Figure 12. Isothermal weight loss of DIDP-plasticized PVC over 2 h at 150°, 160°, 170°, and 180 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 14. Arrhenius activation energy plots for blends of PVC, PVC + DIDP, and PVC + DIDP. TGA weight loss data from 30 min of heat treatment was used for the rate determination in each case. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
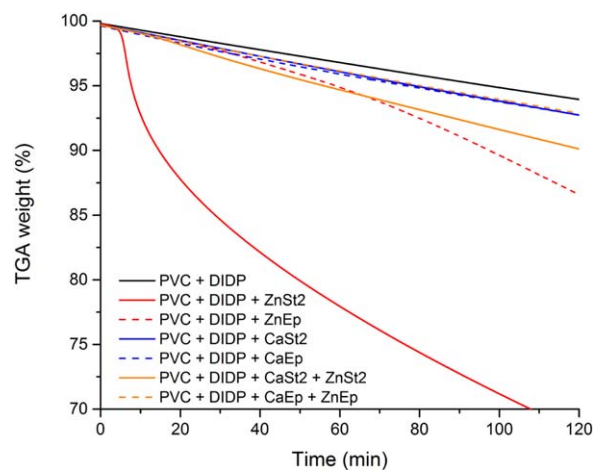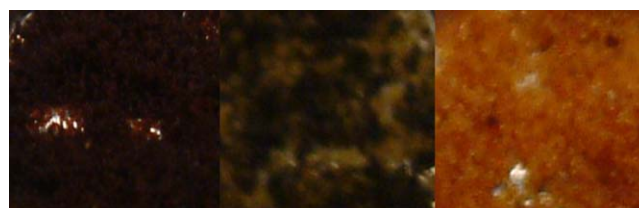
Figure 15. Weight loss of DIDP-plasticized PVC blends incorporating novel epoxide stabilizers during the heat treatment and degradation process at 170 °C; weight normalized against the mass of PVC in each blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 16. Color comparison of DIDP-plasticized PVC blends incorporating novel epoxide stabilizers after thermal treatment (2 h, 170 °C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

multifunctional additive by (1) promoting displacement reactions at labile chlorine sites (like the stearate additives) and (2) reacting with thermally generated HCl in a sacrificial capacity, thus protecting the plasticizer.

Effect of ZnEp and CaEp on DIDP-Plasticized PVC

Figure 15 summarizes the thermal behavior DIDP-plasticized PVC blends incorporating the ZnEp and CaEp as well as the standard Zn and Ca stearate (ZnSt and CaSt, respectively) additives. All blends containing ZnEp and CaEp exhibit similar or improved weight loss performance and color retention (Figure 16) compared to the blends containing the stearate stabilizers. It is interesting to note that DIDP-plasticized PVC blended with $ZnSt_2$ showed negligible weight loss during the first 10 min at 170°C. However, a catastrophic 30% weight loss occurred thereafter. This is attributed to the production of zinc chloride ($ZnCl_2$), a strong Lewis acid, formed from the zinc-promoted chloride substitution reaction of the stearate anion on the polymer backbone and/or from the reaction of the zinc stearate with the thermally generated HCl. The substitution process "stabilizes" the polymer toward further unzipping to form poly-conjugated structures and the acid–base reaction of stearate with HCl reduces the autocatalytic pathway for HCl loss. Nevertheless, both processes result in the formation of detrimental $ZnCl_2$. Further experiments probing the Lewis acid catalyzed degradation of the plasticized PVC with $ZnCl_2$ (added at the same molar quantity as the $ZnSt_2$ in other blends) showed a rapid weight loss of 51.5% (Supporting Information, Figure S4). Indeed, just in the time to heat the sample to 170°C an approximate 15% weight loss was observed. It is interesting to note that the weight loss profiles after approximately 10 min for DIDP-plasticized PVC with ZnSt and $ZnCl_2$ mirror one another, thus providing further evidence for the detrimental role of $ZnCl_2$. However, when $ZnSt_2$ was blended in combination with $CaSt_2$, the rate of weight loss was dramatically reduced, and color development was delayed by 90 min; no catastrophic weight loss was observed. The results support the following: (1)

the Lewis acidity of the zinc center in $ZnSt_2$ facilitates the initial stabilizing stearate substitution processes, (2) the zinc chloride formed as a consequence of these substitution processes then initiates the catastrophic weight loss, but (3) $CaSt_2$ present reacts with the $ZnCl_2$ to produce the desirable $ZnSt_2$ and innocuous $CaCl_2$ thus preventing the catastrophic weight loss.[12–20]

In contrast to the stearate additives discussed previously, the rate of PVC degradation is significantly reduced when ZnEp is substituted for $ZnSt_2$; a weight loss of less than 15% was observed over a period of 2 h at 170°C. Again the epoxy groups scavenge the free HCl inhibiting the formation of $ZnCl_2$, leading to the improved performance of the polymer. CaEp alone did not show any improvement when compared to $CaSt_2$ which lost 7.5% of its original mass, while the synergistic blend of both epoxide salts lost ~3% less weight compared to the analogous Zn and Can stearates, which had a 9.9% loss of weight.

The synergistic blend of ZnEp and CaEp additives was also the only DIDP-plasticized PVC to show reasonable color retention; all other blends changed from a white powder to a dark brown or black powder as shown in Figure 16. The mixture of $ZnSt_2$ and $CaSt_2$ afforded a heterogeneous mix of yellow and black powder while the ZnEp plus CaEp blend was a much lighter yellow-orange shade. This heterogeneous mixture is caused by inhomogeneity of the PVC blend with localized regions of Zn and Ca stearates. But despite this inconsistency in the PVC blend, the effectiveness of the Zn and Ca epoxide salts on the thermal stability of the DIDP–PVC system compared to the more traditional stearates are evident. (Additional images on the color retention of teach PVC blend can be found in the Supporting Information, Figures S5, S6, and S8)

Effect of ZnEp and CaEp on ESO-Plasticized PVC

The weight loss of ESO-plasticized PVC blends with stearate and epoxy salt additives is shown in Figure 17. It is immediately obvious that the overall weight loss of ESO-plasticized PVC is much less (less than 2% for all blends presented here) compared to DIDP-plasticized counterparts. However, there are some major differences in the general trends between the two plasticizers when metal stearates or metal epoxy salts are introduced. A drastic drop in weight is still seen for the ESO-plasticized PVC with $ZnSt_2$; however, it occurs much later—after approximately 2 h of thermal treatment. The sequestration of HCl via epoxy ring-opening mechanisms delays the onset of weight loss
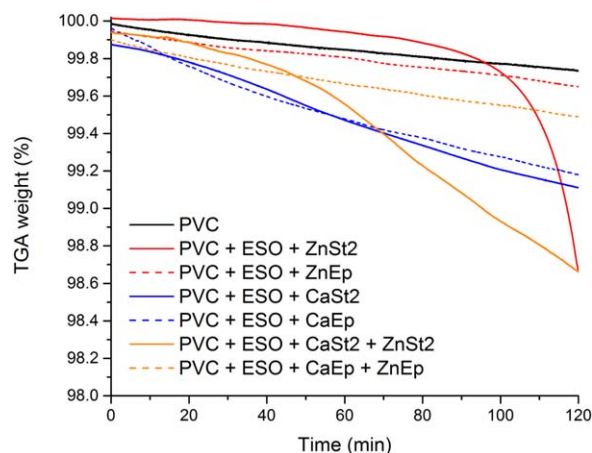
Figure 17. Weight loss of ESO-plasticized PVC blends incorporating novel epoxide stabilizers during the heat treatment and degradation process at 170 °C; weight normalized against the mass of PVC in each blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as seen in Figure 17. However, this drastic weight loss with $ZnSt_2$ is not observed in the ESO-plasticized PVC blend with ZnEp. This result supports the hypothesis that the multifunctional additive package presented here can protect ESO and its plasticization properties and thus prolong its effectiveness. It is conjectured that the ZnEp functions in a similar manner to the $ZnSt_2$ by replacing labile chlorines along the PVC backbone. This reactivity will potentially place the ZnEp in close proximity to the sources of HCL and thus scavenge the acid more efficiently to the ESO (thus protecting the plasticizer). It is very likely that both ESO and our ZnEp/CaEp additives are competitively reacting with released HCl. But this scenario would still

result in reduced degradation of the ESO and an extension of its beneficial properties.

In contrast with the DIDP-PVC, the ZnEp showed the best performance of all the blends, even including the synergistic blends of both metal salts (ZnEp and CaEp). This is likely due to the negative effect attributed solely to the CaEp. The Ca additives performed as good as the synergistic Zn/Ca blend in the DIDP-PVC blends while performing the poorest in the above ESO-PVC blends. This was not an expected result. The Ca ions of the additives form a benign calcium chloride product upon reaction with the liberated HCl. The $CaCl_2$ molecule should not affect the thermal decomposition of the PVC and thus have a similar effect on both the DIDP and ESO blends. A similar observation is seen by Karmalm et al.[21] during the thermal decomposition studies of PVC with ESO as a primary plasticizer.

The discoloration of the ESO-plasticized PVC blends with the novel epoxide stabilizers after thermal treatment is shown in Figure 18. The ESO-plasticized blend with no additive closely resembles that of PVC, as does the blend with $CaSt_2$. When $ZnSt_2$ and a combination of the stearates ($ZnSt_2 + CaSt_2$) are used, excellent color stability was observed. However, the weight loss after 2 h when employing $ZnSt_2$ is a critical limiting factor compared to the multifunctional ZnEp. The epoxide salts also exhibited similar trends in PVC color retention. Overall, the ZnEp showed the greatest color retention, while the combinations of the two epoxide salts yielded a red tint on the polymer.

Epoxide Ring-Opening Studies

At this juncture, it is clear that epoxide containing additives, such as ZnEp and CaEp, have beneficial effects with respect to weight loss and color retention for both DIDP- and ESO-plasticized PVC. From a structural point of view, both ZnEp and CaEp have internal epoxide functionalities. In an effort to develop a more
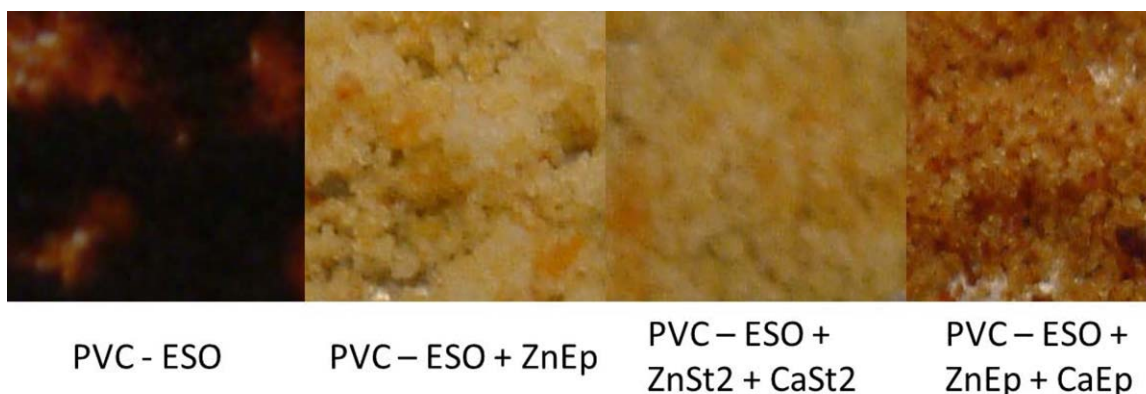

Figure 18. Color comparison of ESO-plasticized PVC blends incorporating novel epoxide stabilizers after thermal treatment (2 h, 170 °C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
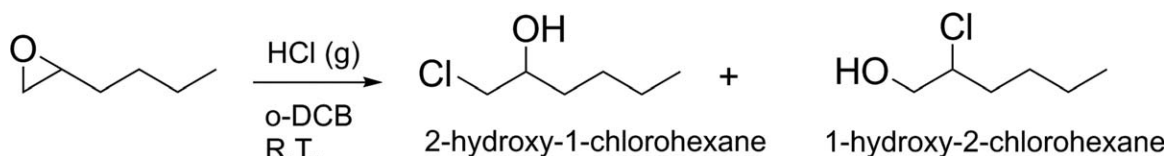

Figure 19. Epoxide ring-opening reaction of 1,2-epoxyhexane with dry HCl (g).
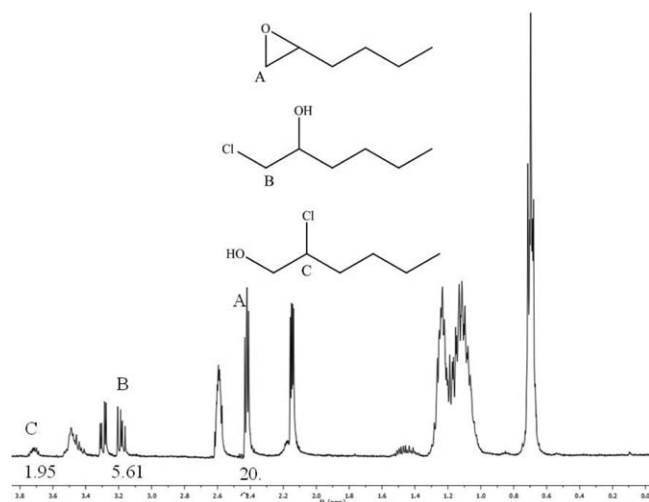
Figure 20. ^{1}H-NMR of the reaction of EH with HCl (1:1), room temperature, 90 min.

Figure 21. Epoxide ring-opening reaction of cyclohexene oxide with HCl.

fundamental understanding of the HCl scavenging efficiency of epoxides and potentially develop new and better additives, a series of simple experiments were conducted to determine the relative reactivities of two structurally different epoxides—a linear terminal epoxide (1,2-epoxyhexane, EH) and a cyclic epoxide (1,2-cyclohexene oxide, CHO). Individual and competitive reactions of each of these epoxides with dry HCl dissolved in 1,2-dichlorobenzene at room temperature were investigated. The reactions were analyzed by means of ^{1}H- and ^{13}C-NMR.

The epoxide ring-opening reaction of EH with dry HCl in *o*-dichlorobenzene (*o*-DCB), shown in Figure 19, resulted in two products. The major product is 2-hydroxy-1-chlorohexane and the minor product is 1-hydroxy-2-chlorohexane. From the ^{1}H-NMR spectrum, shown in Figure 20, the ratio of the major and minor products to the starting material can be easily determined by the unique signatures of various protons of each species. The peak areas of the protons used to determine yields of each product are labeled A (EH), B (major product), and C (minor product). The overall conversion of the EH was 52.2%
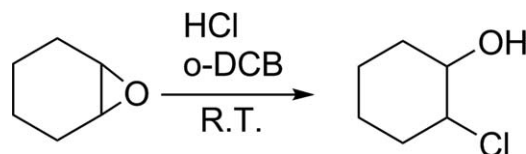
with yields of 35.9% and 16.3% of 1-hydroxy-2-chlorohexane and 2-hydroxy-1-chlorohexane, respectively, after 90 min at room temperature. (The ^{1}H- and ^{13}C-NMR spectra for EH is shown in the Supporting Information, Figures S9 and S10, respectively. The ^{13}C-NMR spectrum of the reaction products is shown in the Supporting Information, Figure S11)

The epoxide ring-opening reaction of the linear epoxide 1,2-epoxyhexane was compared with the cyclic epoxide cyclohexene oxide (CHO), shown in Figure 21. The reaction of CHO with HCl (molar ratio of 1:1 CHO/HCl) gave the product 2-chlorocyclohexanol. The molar ratio of CHO to 2-chlorocyclohexanol was determined by the ratio of the distinct peaks at 2.74 ppm (signal A) and 2.58 ppm (signal B) in the ^{1}H-NMR spectrum (Figure 22). From this spectrum, the conversion of CHO was calculated to be 45% after 90 min, comparable to the conversion of the linear epoxide (52% after 90 min). (The ^{1}H- and ^{13}C-NMR spectra of the CHO are shown in the Supporting Information, Figures S12 and S13, respectively. The ^{13}C-NMR spectrum of the reaction products is shown in the Supporting Information, Figure S14.)

In a competitive study performed with 0.5 equivalents each of EH and CHO and 1 equivalent of HCl, the CHO was consumed slightly faster than EH. After 90 min, 58.2% of the 1,2-epoxyhexane was converted to 2-hydroxy-1-chlorohexane and 1-hydroxy-2-chlorohexane while 78.4% of cyclohexene oxide was converted to 2-chlorohexanol. This supports our conclusion that epoxides, independent of structure and because of the associated ring strain, react with anhydrous HCl at rapid rates even at room temperature. (The ^{1}H-NMR spectrum of the reaction products in the competitive experiment is shown in the Supporting Information, Figure S15.)
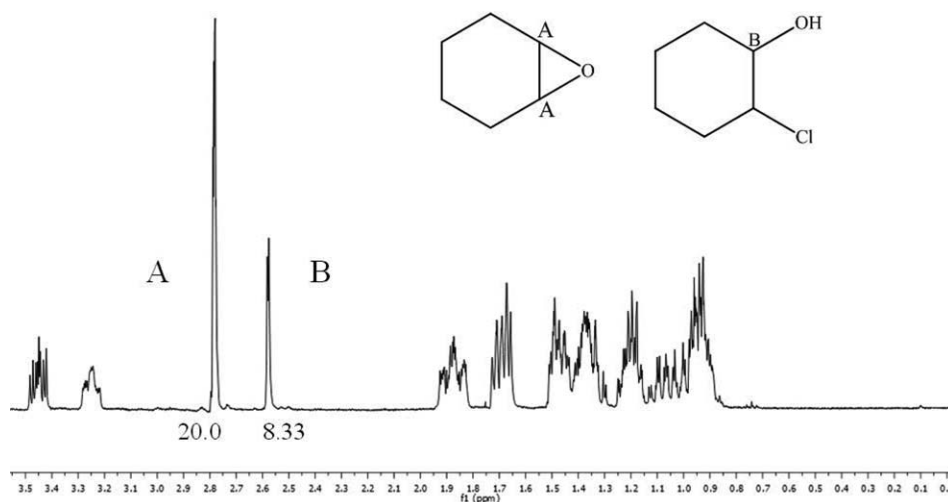

Figure 22. ^{1}H-NMR of the reaction of cyclohexene oxide with HCl (1:1), room temperature, 90 min.

CONCLUSIONS

Novel ZnEp and CaEp additives were created to have polyfunctional properties in the thermal stabilization of plasticized PVC. These properties include promoting (1) substitution reactions via the carboxylate nucleophile at "weak links" on the PVC backbone in order to retard degradation, (2) acid–base reactions between the basic carboxylate anion and the thermally generated HCl to decrease the autocatalytic pathways for dehydrochlorination, and (3) ring-opening reactions in order to preserve the plasticizing properties of ESO by competitively scavenging released HCl. Thermogravimetric analyses and visual color development for untreated PVC and PVC plasticized with DIDP or ESO are reported. Using these data as a base line ZnSt, CaSt, ZnEp, and CaEp additives were incorporated into DIDP- and ESO-plasticized PVC and comparatively evaluated with respect to rates of weight loss and accompanying visual color development. Compared to the stearate additives, ZnEp and CaEp showed superior weight loss performance and color stability in DIDP-plasticized blends. In ESO-plasticized PVC, these novel additives not only reduced the rate of weight loss of the PVC blend but, more importantly, dramatically decreased discoloration of the polymer.

AUTHOR CONTRIBUTION

F.S. Mohammed and C.L. Liotta drafted the manuscript. F.S. Mohammed oversaw the revision and editing process and contributed intellectually while analyzing and interpreting data. M. Conley, J. Switzer contributed equally in the blending of PVC additives and its thermal analysis. S. Saunders provided technical input and revised the manuscript, while R. Jha synthesized, purified, and characterized the epoxide salts used in this study. P. Pollet, B. Chaudhary, J. Cogen, C.L. Liotta, and C. Eckert are the principle investigators. They provided input regarding experimental design, scientific knowledge, and technical expertise, guiding the research as it progressed.

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