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Enhanced thermal stabilization and reduced color formation of plasticized Poly(vinyl chloride) using zinc and calcium salts of 11-maleimideoundecanoic acid

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ABSTRACT

Above certain temperatures, untreated PVC undergoes dehydrochlorination to produce conjugated polyenes in the polymer backbone. This is accompanied by formation of color in the polymer. In order to address both the thermally induced dehydrochlorination process and the accompanying color formation the dienophilic zinc and calcium salts of 11-maleimidoundecanoic acid (Zn11M and Ca11M, respectively) were synthesized and employed as stabilizing additives. The stabilizing effect of the Zn11M and Ca11M on PVC was studied at 170 °C in air. Evidence is presented which shows that this combination of salts performs a dual role of reducing both the rates of dehydrochlorination and formation of color in plasticized PVC.

1. Introduction

Polyvinyl chloride (PVC) is a thermally unstable polymer under certain conditions. At normal processing temperatures (170°–200 °C) PVC undergoes dehydrochlorination to produce unsaturation in the polymer backbone [1,2]. The HCl produced can further act as a catalyst for subsequent dehydrochlorination resulting in an autocatalytic increase in the formation of conjugated polyenes. This phenomenon is known as “chain unzipping.” These resulting polyenes can undergo a variety of intra- and intermolecular reactions leading to materials with poor physical and mechanical properties. In addition, conjugated polyene sequences of five or more double bonds result in the development of discoloration. Both the loss of mechanical properties and the discoloration pose limitations for industrial and consumer applications.

The structure of PVC is primarily characterized by alternating CH–Cl and CH$_2$ groups in a combination of isotactic, syndiotactic, and atactic regions of the polymer chain (Fig. 1a). In addition, there are also accompanying sites in which the chlorine atoms are located in allylic and/or tertiary positions (Fig. 1b and c). These are termed defect sites and are formed during the polymerization process. While these sites are relatively uncommon, the dehydrochlorination process from these positions requires lower activation energies compared to chlorines at the “normal” secondary carbons. As a consequence, it has been generally accepted that the thermal dehydrochlorination is initiated at these structural defect sites. Once HCl is generated it can act as a catalyst for subsequent dehydrochlorination processes. Fig. 1d illustrates the dehydrochlorination of an allylic chloride catalyzed by HCl generated from defect sites (autocatalysis). To develop a more robust PVC, both the thermal stability and the accompanying color formation must be addressed. In light of this, a wide variety of thermal stabilizers have been reported in literature [3–8]. Traditional metal carboxylate additives, such as Ca and Zn stearates, have been synergistically used to retard but not eliminate the unzipping process and are therefore limited by their inability to mitigate existing polyene concentrations.

If the extended conjugation of PVC during thermal degradation could be eliminated or effectively reduced, the associated embrittlement and discoloration could be controlled. A potential means of reducing conjugation is to employ an additive having an affinity

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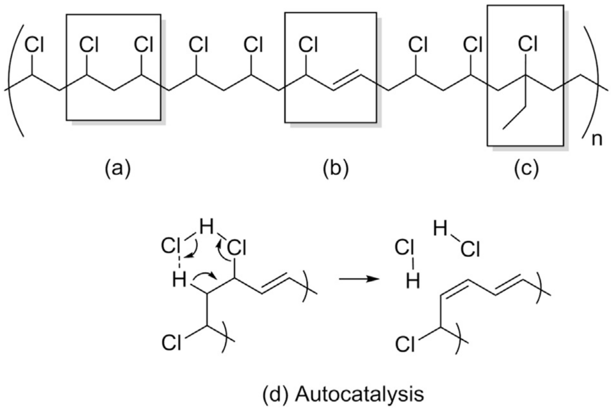

Fig. 1. (a) Polyvinyl chloride; (b) Allylic Chloride; (c) Tertiary chloride; (d) Autocatalysis and chain unzipping.

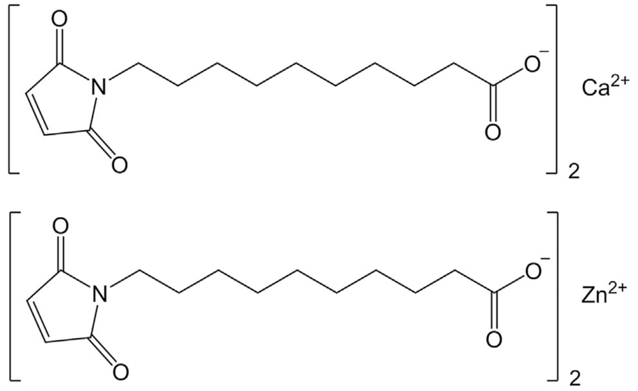

Fig. 3. Examples of the novel maleimide stabilizers: Zn11M and Ca11M.

toward conjugated polyenes which, when reacted, creates saturated carbon centers that effectively break up the conjugated network. A reactive dieneophile is such an additive which could initiate pericyclic processes to reduce the degree of conjugation and therefore the accompanying discoloration. These processes include the Diels–Alder reaction (Fig. 2a) and the ene reaction (Fig. 2b). Several reports have appeared in the literature in which maleic anhydride, chloromaleic anhydride, maleate esters, and maleimide derivatives have been employed for this purpose [9–14]. Al-Dossary et al. [15] reported the synthesis and use of N-(N'-arylamine)maleimide derivatives in which the aryl group contained highly electron withdrawing substituents which enhanced the acidity of the amino hydrogen. When incorporated into PVC with a variety of basic additives, the maleimide derivative was ionized and acted as both a nucleophilic species which performed substitution reactions of the PVC polymers and as a dienophile with the developing conjugated polyene. The authors state that the substitution of labile chlorines dominates in the early stages of PVC degradation leaving the maleimide portion of the additive to react in a Diels–Alder capacity at longer degradation times. Tran et al. [9]. reported the Diels–Alder reaction of maleic anhydrides with partially dehydrochlorinated PVC and beta-carotene using infrared spectroscopy, while Yi et al. [10]. have recently employed the zinc and calcium salts of maleic acid which they claim functioned as a dienophile in Diels–Alder reactions and as a nucleophile in substitution processes of labile chlorines. It should be emphasized that the reports sited above used either rigid PVC or base-treated PVC which produced a partially degraded polymer containing conjugated polyenes. None of the above studies employed plasticized PVC.

Herein is reported the effective use of a highly reactive dieneophile tethered to the Zn or Ca salt of a long chain carboxylic acid-11-maleimidoundecanoic acid (Fig. 3)- in reducing both the weight loss due to dehydrochlorination and the color production of PVC plasticized with either diisododecyl phthalate (DIDP) or epoxidized soy bean oil (ESO). Although the effects of plasticizers such as di(2-ethylhexyl) phthalate and epoxidized soy bean oil (ESO), and additives such as zinc and calcium stearate, on dehydrochlorination and thermal stability of PVC have been reported in the literature [11,12], the zinc and calcium salts of 11-maleimidoundecanoic acid have not previously been investigated as PVC stabilizers. To understand the behavior of Zn11M and Ca11M in relationship to the more conventional stabilizers the following will be presented: (1) the UV–Vis behavior of untreated PVC at 180 °C as a function of time, (2) a comparative visual and TGA analysis of DIDP plasticized PVC in the presence of a variety of stabilizing additives including Zn11M and Ca11M, (3) the UV–Vis behavior of DIDP plasticized PVC in the presence of stabilizing additives including Zn11M and Ca11 M at 180 °C as a function of time, and (4) a similar comparative visual and TGA analysis of ESO plasticized PVC containing these same stabilizer combinations.

2. Experimental section

2.1. Materials

Diisodecyl phthalate (DIDP), calcium acetate ($Ca(OAc)_2$), sodium acetate (NaOAc, anhydrous) and zinc stearate ($ZnSt_2$, purum,

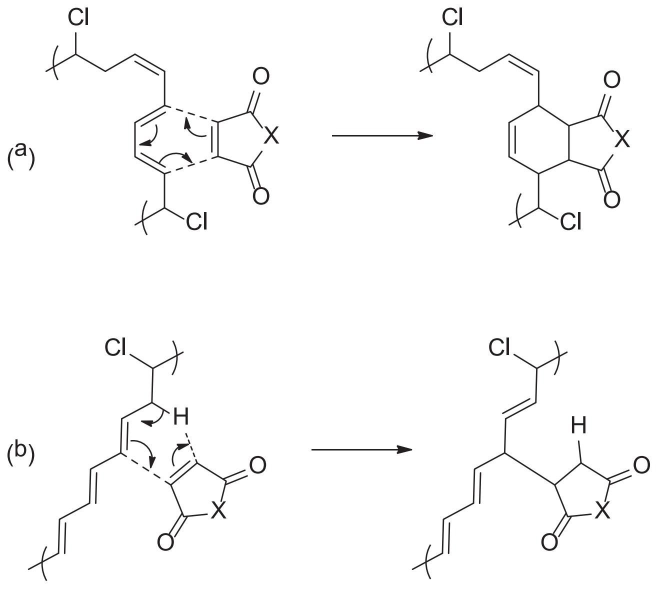

Fig. 2. Reaction of conjugated polyene with a dieneophile: (a) Diels–Alder reaction; (b) Ene reaction.

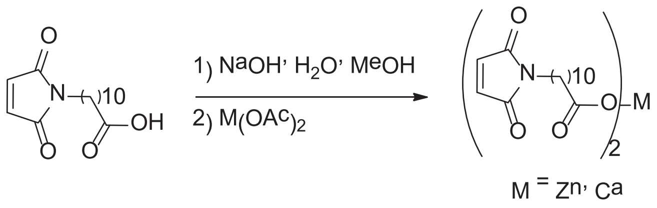

Fig. 4. Synthesis of Zn or Ca salt of 11-maliemido-undecanoic acid.