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Thermal Stability of Poly (vinyl chloride) Formulations Containing Iron Additives as a Replacement for Antimony Oxide

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Abstract

Poly (vinyl chloride) [PVC] is a widely used commodity polymer with particular application for wire and cable coating, and for pipe and profile extrusion. For processing, PVC must be heavily plasticized. In addition, a number of other additives are usually introduced to promote thermal stability, to enhance processability and to inhibit flammability. Antimony oxide is often used in PVC formulations. However, the growing concern about the negative health and environmental impacts of antimony oxide has stimulated efforts to find suitable replacements. Iron compounds have been examined as suitable replacements for antimony oxide. PVC formulations containing 45 phr of Pevalen plasticizer, 50 phr of magnesium hydroxide and 2 or 10 phr of an iron additive were processed using a two-roll mill at 180°C. The thermal degradation and flammability of these materials have been evaluated utilizing thermogravimetry (TGA) and limiting oxygen index (LOI) measurements. All of the iron additives are effective in increasing LOI for combustion of the blends and in promoting char formation. The impact of the presence of all the iron additives is comparable and independent of the oxidation level of iron. Based on considerations of cost and availability, simple iron oxide may be the additive of choice.

Keywords: PVC additives; Antimony oxide replacements; Combustibility of formulated PVC; Impact of additives on the thermal stability of PVC;

Introduction

Poly(vinyl chloride) [PVC] is a large-scale commodity polymer produced around the world. It is the third largest volume commercial polymer. This is largely due to its superior mechanical and physical properties [1]. It is produced by radical polymerization techniques which leads to a relatively heterogeneous structure containing defect sites prone to initiation of thermal degradative dehydrochlorination [2]. This initial degradation occurs at relatively modest temperatures and hampers processing. In fact, the polymer was known as early as 1838 but it wasn't until the early

1930s when Semon discovered methods for plasticization that the polymer could be commercialized [3 - 5]. Today it is a large volume material of immense economic and societal importance. About half of the current production is used for pipe extrusion, 12% for vinyl siding, 4% for wire and cable coating, 6% for film and sheet and the remainder for smaller volume uses [6]. An important smaller use is in medical device applications [7]. It is valued for its toughness, strength, inertness and transparency.

For processing and subsequent use PVC must contain a number of additives. Among the most prominent of these are plasticizers.

Plasticizers are required in huge amounts for PVC formulation. Generally, esters, because of their ability to interact strongly with polar PVC, have been most commonly used as plasticizers. Among these, phthalate esters have been dominant [8]. Interaction with PVC occurs by both dipolar and π -type attractions. These materials have been effective, low-cost plasticizers for PVC. One phthalate ester, di-(2-ethylhexyl) phthalate (DEHP), has been predominant accounting for greater than 60% of usage. While phthalate esters are effective plasticizers, they tend to migrate from a polymeric matrix into which they have been incorporated. This creates two problems. The first is flammability and the other toxicity. Unformulated PVC is effectively nonflammable (LOI 49.8) [9]. In contrast, plasticized PVC is often quite flammable as a consequence of plasticizer volatilization. Further, migration of phthalate plasticizers from polymeric matrices has led to widespread distribution in the environment. As a consequence, human populations around the world have been exposed to these compounds, particularly DEHP [10 -12]. Human exposure to phthalates has been associated with a number of diseases. Because of this, there is growing resistance to the use of phthalates [13, 14]. An attractive approach to phthalate replacement is the development of effective plasticizers from nontoxic, renewable biosources. [15 - 17]. The flammability problem is often addressed by the incorporation of antimony oxide into the PVC matrix [18, 19]. In the presence of hydrogen chloride generated from the degrading polymer, the oxide is converted to the corresponding chloride or oxychlorides which are volatile and are effective in carrying chlorine to the gas phase where it scavenges combustion propagating radicals [20]. Although, antimony oxide is effective in this role, availability, cost and toxicity may limit its continued use. Because of concerns about exposure to toxic antimony oxide, particularly as the powder, replacements are being sought. Over the years other metal salts, principally tin, zinc, bismuth, molybdenum and some iron compounds have been considered without remarkable success [20 - 39]. The most successful have been two tin compounds, zinc hydroxystannate and zinc stannate [21, 22]. However, as yet no universal replacement for antimony oxide has been identified. Iron compounds are particularly attractive for a variety of reasons. They are readily available in a variety of forms, are inexpensive and nontoxic. Even if they were required at a much higher level than antimony oxide to be effective, they might still be preferred. Although, various iron compounds, principally iron (III) oxide, have been used as additives in PVC no systematic evaluation of iron additives has been carried out. In this case, the impact of the presence of four different iron additives at two different concentrations, on the thermal properties of PVC has been assessed using thermogravimetry and limiting oxygen index evaluation.

Experimental

Materials

PVC (K70) was supplied by OxyChem, Avon Lake, Ohio. Iron

oxides were from LaXess; ferrocene from the Aldrich Chemical Company. Magnesium hydroxide was provided by Nuova Sima. Pevalen plasticizer was supplied by Perstorp.

Instrumentation and Techniques

Thermogravimetry was performed using a TA Instruments Q500 instrument. Typically, a heating rate of $10^{\circ}\text{C min}^{-1}$ was used. Samples (10-14 mg) were contained in a platinum pan. The sample compartment was purged with dry nitrogen at $60\text{ cm}^3\text{ min}^{-1}$ during analysis. Limiting oxygen index values were determined using a Fire Testing Technology, Ltd. (FTT) oxygen index unit and standard method, ASTM D2863-13.

Test Specimen

Formulation ingredients [resin, 45 phr Pevalen plasticizer (pentaerythritol tetravalerate), 50 phr magnesium hydroxide, and 2 or 10 phr of an iron additive] were dry blended and compounded on a two-roll mill at 453K. The material was compression molded at 453K into panels of 3.0 ± 0.2 mm nominal thickness. The panels were cut into specimen of width 10.5 ± 0.5 mm and length of 130 ± 2 mm for LOI testing.

Results and Discussion

Poly(vinyl chloride) [PVC] is an immensely important commercial polymer with applications across a range of areas essential to modern well-being. It is widely used for noncorrosive plumbing, for home siding, shingles and floor coverings, for wire and cable coating, for medical device fabrication and for a myriad of lesser uses. To permit processing and use, a number of polymer additives are required. One among these is often antimony oxide. Now that the toxicity and potential negative health effects of antimony oxide, particularly as a powder, are being recognized it has become increasingly important to find a replacement. Iron compounds are readily available, generally nontoxic and inexpensive. In this case, the impact of four different iron additives on the thermal stability of PVC has been assessed using thermogravimetry and limiting oxygen index. The additives used are identified in (Table 1). All samples

Sample	Additive	Level (phr)
PVC-0 ^a	Sb ₂ O ₃	10
PVC-1	FeOOH	2
PVC-2	Fe ₂ O ₃	2
PVC-3	Fe ₃ O ₄	2
PVC-4	Ferrocene	2
PVC-5	FeOOH	10
PVC-6	Fe ₂ O ₃	10
PVC-7	Fe ₃ O ₄	10
PVC-8	Ferrocene	10

a.The same formulation containing antimony oxide included for comparison

contain Pevalen plasticizer (45 phr) and magnesium hydroxide (50 phr). A commercial sample of PVC containing antimony oxide as additive is included for comparison.

The thermal degradation for PVC containing two parts of iron additive per hundred parts resin is illustrated in (Figure 1).

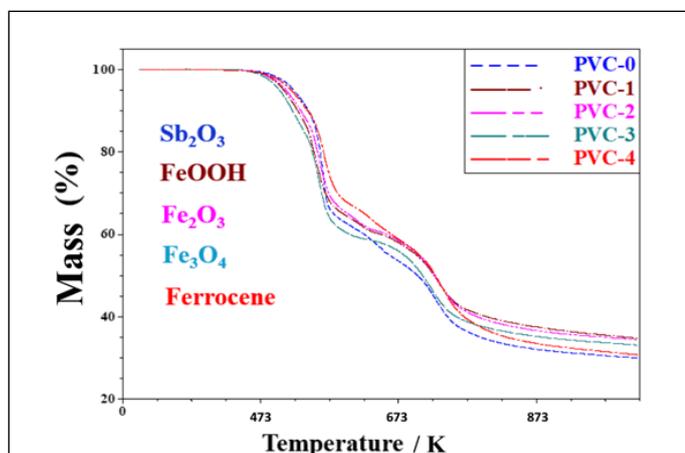


Figure 1: Thermal Stability of PVC Containing Iron Additives (2 phr)

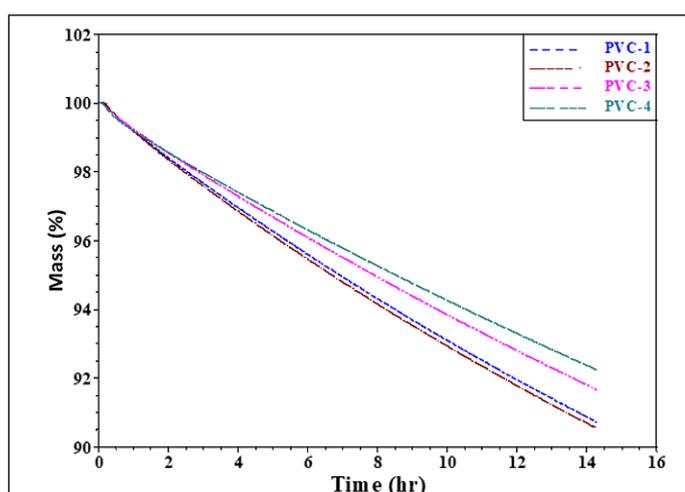


Figure 2: Plasticizer Volatility at 423K for PVC Formulations

As is readily apparent, the degradation profiles for all samples are quite similar and mimic that for the sample containing antimony oxide. For processing it is the initial dehydrohalogenation that is important. Extrapolated onset temperatures for degradation were obtained from the derivative plots of mass loss versus temperature and are listed in (Table 2).

At this temperature plasticizer volatility (Figure 2) is not great (less than 10% mass loss after 14 hours). Flammability of the PVC samples containing low concentrations of iron additives was determined by limiting oxygen index measurement. Results are presented in (Table 3). It is apparent that the volatility of the plasticizer (low) and the flammability of the PVC formulation

Table 2: Degradation Data for PVC Containing Iron Additives (2 phr)

Sample	Additive	Level (phr)	Degradation Onset Temperature/K ^b	Char Residue ^c (1023K)
PVC-0 ^a	Sb ₂ O ₃	10	545	30
PVC-1	FeOOH	2	531	35
PVC-2	Fe ₂ O ₃	2	538	34
PVC-3	Fe ₃ O ₄	2	533	33
PVC-4	Ferrocene	2	540	31

- Sample containing antimony oxide included for comparison.
- Extrapolated onset temperature from the derivative of the mass loss versus temperature plot.
- Percent of initial sample mass.

Table 3: Flammability of PVC Samples Containing Iron Additives (2phr)

Sample	Iron Additive	Level (phr)	Limiting Oxygen Index (LOI) ^a
PVC-0	Sb ₂ O ₃	10	39
PVC-1	FeOOH	2	33
PVC-2	Fe ₂ O ₃	2	33
PVC-3	Fe ₃ O ₄	2	34
PVC-4	Ferrocene	2	34

- Level of oxygen (%) in nitrogen required to support combustion

is largely unaffected by the iron additive present. The amount of stable residual char generated by complete degradation is somewhat greater in the presence of an iron additive than in the presence of antimony oxide. This is in accord with previous observations that the presence of iron additives may promote char formation [9,32,37,38]. This may reflect the promotion of cycloaddition reactions of unsaturated moieties generated by dehydrochlorination. The dehydrochlorination itself is not impacted by the presence of an iron additive (degradation onset is about the same for all samples). This is somewhat surprising since it is known that strongly acidic cations facilitate dehydrochlorination [40].

The stability of samples containing higher levels of the various iron additives was also investigated. The degradation of samples containing 10 phr of an iron additive is illustrated in Figure 3. The sample containing 10 phr of antimony oxide (PVC-0) additive is included for reference. The impact of the presence of the iron additives at higher loading is somewhat greater than for samples containing additive at 2 phr particularly on char formation. However, the impact on initial dehydrochlorination is small and comparable to that of antimony oxide. Complete degradation data for this set of samples are collected in (Table 4).

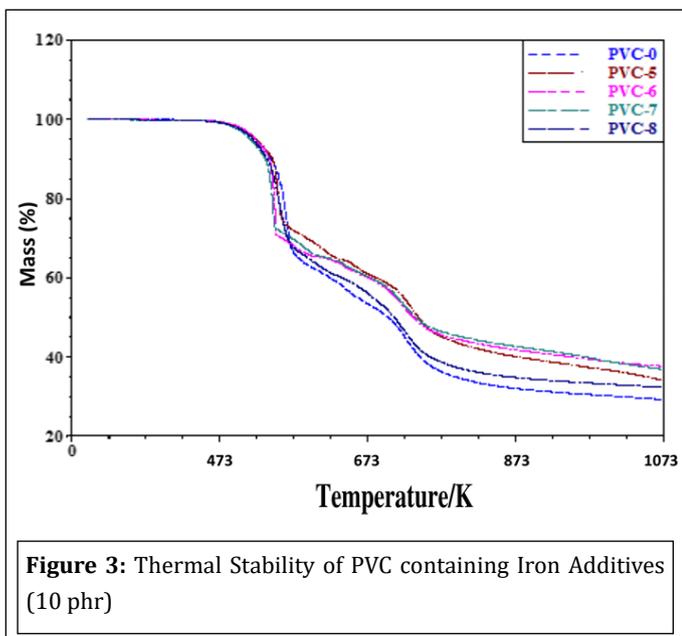


Figure 3: Thermal Stability of PVC containing Iron Additives (10 phr)

Table 4: Degradation Data for PVC Containing Iron Additives (10 phr)

Sample	Additive	Level (phr)	Degradation Onset Temperature/K ^a	Char Residue (1023K) ^b
PVC-0	Sb ₂ O ₃	10	545	30
PVC-5	FeOOH	10	542	36
PVC-6	Fe ₂ O ₃	10	542	38
PVC-7	Fe ₃ O ₄	10	536	38
PVC-8	Ferrocene	10	531	33

- a. Extrapolated onset temperature from the derivative plot of mass loss versus temperature.
- b. Percent of initial sample mass.

Table 5: Flammability of PVC Samples Containing Iron Additives (10 phr)

Sample	Additive	Limiting Oxygen Index (LOI) ^a
PVC-5	FeOOH	32
PVC-6	Fe ₂ O ₃	34
PVC-7	Fe ₃ O ₄	34
PVC-8	Ferrocene	34

a. Level of oxygen (%) in nitrogen required to sustain combustion.

The impact of the presence of iron additives at 10 phr is small and comparable to that for antimony oxide. While no extensive evaluation of the physical properties of the blends has been carried out, simple preliminary observations suggest that the presence of none of the additives has a negative impact on the properties of the polymer.

The flammability of the PVC samples containing the higher loading of the iron derivatives is illustrated in (Table 5).

The LOI values are lower for samples containing any of the iron additives than for that containing antimony oxide (Table 3, PVC-0) suggesting that the formation of iron chloride and its volatility are inferior to the same properties for antimony oxide. At equivalent loadings antimony oxide is superior to iron oxides for controlling the flammability of formulated PVC. However, because of the much lower cost, greater availability and lower toxicity of iron compounds they could be used to advantage at much higher levels. Two modes of action have been suggested for iron compounds in PVC. It has been widely observed that these compounds promote char formation [9,32,37,38]. Simple iron oxides may be converted to iron(III) chloride generated from the degrading polymer. Iron(III) is a strong Lewis acid which may promote cationic crosslinking and char formation. Iron chloride or oxychlorides may also be volatilized to the gas phase. In the gas phase iron species interrupt the combustion process [20]. It is likely that both phenomena are present for combustion of formulated PVC containing iron additives.

Conclusions

The thermal degradation of PVC containing four different iron additives at two different concentrations have been evaluated using thermogravimetry and limiting oxygen index determination. At the level incorporated, 2 and 10 phr, the iron compounds are not as effective as antimony oxide in increasing LOI, but does not need to be. Because of the much lower cost, greater availability, and much lower toxicity, iron additives may be used at higher levels of loading than can antimony oxide. The impact of the presence of additive seems to be largely independent of the oxidation level for iron. None of the iron additives promote degradative dehydrochlorination of PVC.

Author Contributions

Conceptualization was provided by B.A.H., F.J.B. and E.D.W.; project administration and manuscript preparation was provided by B.A.H.; experimental work and figure preparation was provided by Y.G.D.

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Conflicts of Interest

The authors declare no conflict of interest.

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