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Thermochimica Acta 272 (1996) 131–137

thermochimica
acta

Decomposition of vinylidene chloride copolymers in the presence of selected transition metal halides[1]

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Received 26 September 1994; accepted 14 November 1994

Abstract

Because of their high barrier to the transport of oxygen and flavor and aroma molecules, vinylidene chloride polymers occupy a position of prominence in the polymer plastics packaging industry. However, at processing temperatures these polymers tend to undergo degradative dehydrochlorination. The dehydrochlorination reaction is a typical chain process which is initiated at a defect site (allylic dichloromethylene unit), present in the polymer as a consequence of random dehydrohalogenation during polymerization, drying, etc. This initial dehydrohalogenation is thought to be catalyzed by metal ions formed by interaction of the polymer with equipment walls or present by other means. To test this, a series of blends of metal halides (5 wt%) with a vinylidene chloride/methyl acrylate (5 mol%) copolymer has been examined by thermogravimetry in nitrogen. All the polymer/metal halide blends were more prone to degradation than the untreated polymer. The effectiveness of the metal halide in promoting the degradative dehydrochlorination correlates well with the Lewis acidity/Pearson hardness of the metal ion.

Keywords: Vinylidene chloride copolymers; Transition metal halides

1. Introduction

Vinylidene chloride copolymers, particularly copolymers with alkyl acrylates, find widespread and significant application in the barrier plastics packaging area. These materials display a high barrier to the transport of oxygen and other small molecules, as well as flavor and aroma constituents [1,3]. However, when subjected to the temperatures necessary for processing, these polymers undergo degradative dehydrochlorination [1].

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[1] Presented at the 23rd North American Thermal Analysis Society Conference, Toronto, Ont., Canada, 25–28 September, 1994.

SSDI 0040-6031 (95) 02604-5

This thermally induced dehydrochlorination is greatly facilitated by the presence of allylic dichloromethylene defect sites within the polymer [4,5]. Initial unsaturation may be introduced into the polymer in a variety of ways. Interaction of the polymer with Lewis acids, metal cations in particular, has long been recognized as being sufficient to induce initial dehydrochlorination and, as a consequence, to promote the degradation of the polymer [1,6]. Such catalysis is of particular concern during the processing of these polymers. Hydrogen chloride evolved during the degradation can interact with the walls of the process equipment to form metal chlorides which may then facilitate the degradation by introducing new defect sites (unsaturation, allylic dichloromethylene units) from which the degradation reaction may propagate. To better characterize the effectiveness of metal cations in facilitating the thermal dehydrochlorination of vinylidene chloride polymers, a series of blends of metal halides (5 wt%) with a standard vinylidene chloride/methyl acrylate copolymer (5 mol%) has been examined by thermogravimetry.

2. Experimental

2.1. Materials

The vinylidene chloride/methyl acrylate copolymer was prepared by suspension polymerization and characterized as previously described [7]. The polymer was of uniform molecular weight distribution (size exclusion chromatography) with $M_n = 57\,000$, $M_w = 102\,000$ and $M_w/M_n = 1.79$. The unanealed polymer displayed melting behavior characteristic of vinylidene chloride copolymers with endotherms at 164.6° and 172.4°C. The melted/quench-cooled sample displayed a glass transition, T_g, at 5.9°C, a crystallization exotherm, T_c, at 68.4°C and a melting endotherm, T_m, at 172.4°C. Analysis by ^{13}C NMR spectroscopy confirmed the random distribution of the methyl acrylate in the polymer and established that it had been incorporated at the intended 5 mol% level [7,8].

The metal halides were commercial materials from the Aldrich Chemical Company and were used as received.

2.2. Vinylidene chloride copolymer/metal chloride blends

In general the appropriate amount of metal halide was dissolved in distilled water, polymer was added, the suspension was stirred, the solvent was removed by evaporation at reduced pressure and the blend was dried at slightly above room temperature and reduced pressure. In a typical example, 0.50 g of copper(II) chloride was dissolved in 250 ml of distilled water in a 500-ml, round-bottomed flask. Polymer, 9.50 g, was added and the resulting suspension was stirred (rotation of the flask on a rotary evaporator) 0.5 h at 40°C. The solvent was removed by rotary evaporation at reduced pressure (approximately 20 Torr) and elevated temperature (approximately 80°C, hot water bath). The residual polymer/metal chloride blend was transferred to a Pyrex boat and dried at approximately 20 Torr and 60°C for 48 h.

2.3. Thermogravimetry

The thermal degradation characteristics of the untreated polymer and the polymer/metal chloride blends were examined by thermogravimetry using a TA Instruments model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. Decay plots, weight loss versus temperature were generated by feeding the analyzer output (TA Instruments software was used for all data manipulation) to a model 7440 Hewlett-Packard plotter. The TGA cell was swept with nitrogen at 50 ml min^{-1} during degradation runs and the sample, approximately 30 mg, was contained in a platinum sample pan. The temperature was ramped at a rate of 5°C min^{-1} from 30° to 350°C.

3. Results and discussion

The degradative dehydrochlorination of vinylidene chloride copolymers is a typical radical chain process with distinct initiation, propagation and termination phases. A significant initiation site for the degradation reaction is an allylic dichloromethylene unit [5]. Interaction of the polymer with metal halides may strip hydrogen chloride from the polymer main chain and generate such units.

To access the effectiveness of metal chlorides in promoting the degradation of these materials, a series of blends of a vinylidene chloride/methyl acrylate (5 mol%) with metal halide (5 wt%) has been examined using thermogravimetric techniques. As can be seen from the data presented in Figs. 1–3, the promotion of the degradation of the polymer reflects the Lewis acidity of the metal halide [9].

Fig. 1 contains decay plots for blends of the copolymer with metal halides of low Lewis acidity. The degradation of these blends is only marginally more facile than that of the untreated polymer, particularly in the initiation region of the decay.

Metal halides of intermediate acidity (Fig. 2) have a definite detrimental impact on the stability of the polymer. Metal halides of greater acidity dramatically alter (Fig. 3) the degradation behavior of the polymer. Degradation begins at much lower temperature and is much more rapid in the presence of these metal halides.

As may be noted from Fig. 4, a reasonably good correlation of the onset temperature for the metal halide-promoted thermal degradation of the vinylidene chloride polymer with the Lewis acidity (taken as the Pearson hardness [9,10]) of the cation of the metal halide additive is apparent. This is certainly consistent with earlier observations for degradation of a vinylidene chloride polymer in the presence of formate salts [6].

The acidity of the metal halide reflects the ability of the cation to complex with the chlorine atoms of the polymer and to enhance the propensity of the atoms to be lost via thermal fragmentation. Complexation of the chlorine atoms by acidic cations (zinc, in particular) makes them a better leaving group.

Of particular interest might be the impact of the halides of iron(II), copper(II), cobalt(II), and zinc(II) since these are most likely to be present under process conditions for vinylidene chloride copolymers.

The degradation onset temperatures presented in Table 1 are fully supportive of the trends noted in Figs. 1–3. The onset temperatures for the degradation of blends contain-

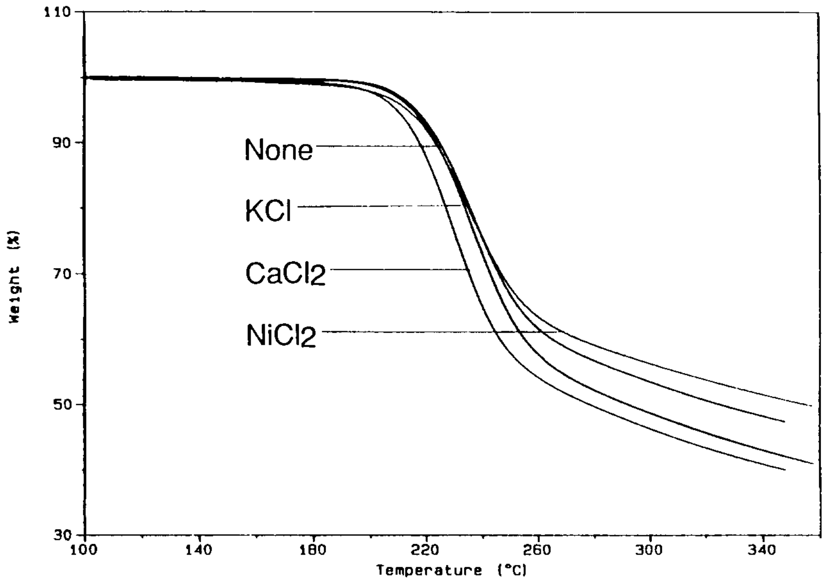

Fig. 1. Thermal degradation of blends of a vinylidene chloride/methyl acrylate copolymer (5 mol%) with metal halides (5 wt%) of low Lewis acidity.

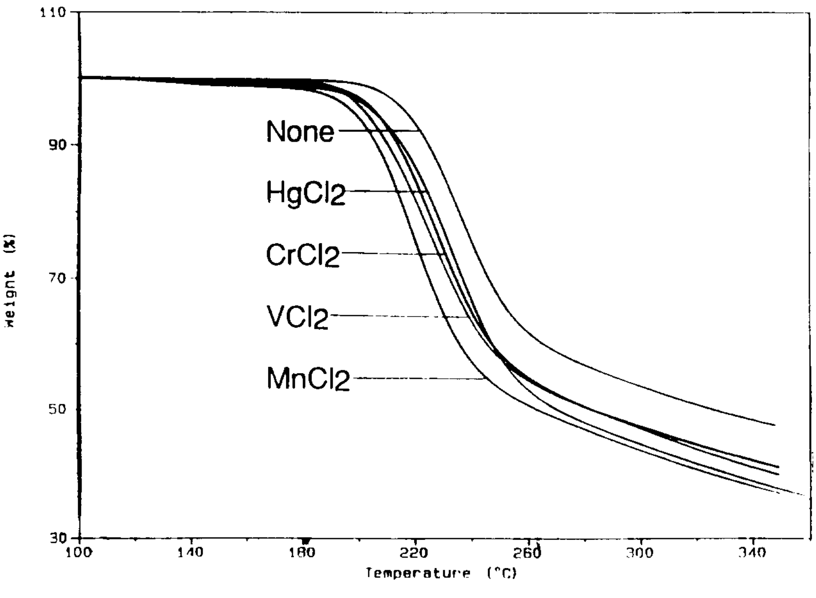

Fig. 2. Thermal degradation of blends of a vinylidene chloride/methyl acrylate copolymer(5 mol%) with metal halides (5 wt%) of moderate Lewis acidity.

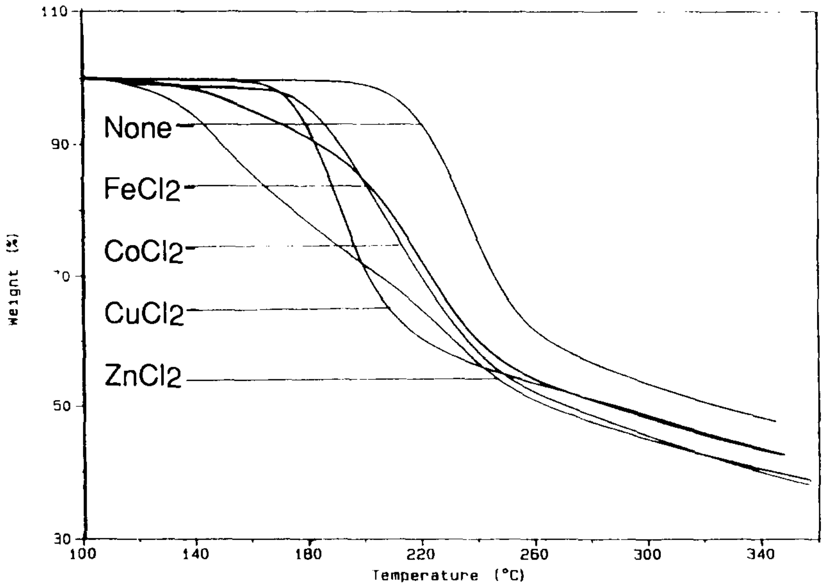

Fig. 3. Thermal degradation of blends of a vinylidene chloride/methyl acrylate copolymer (5 mol%) with metal halides (5 wt%) of high Lewis acidity

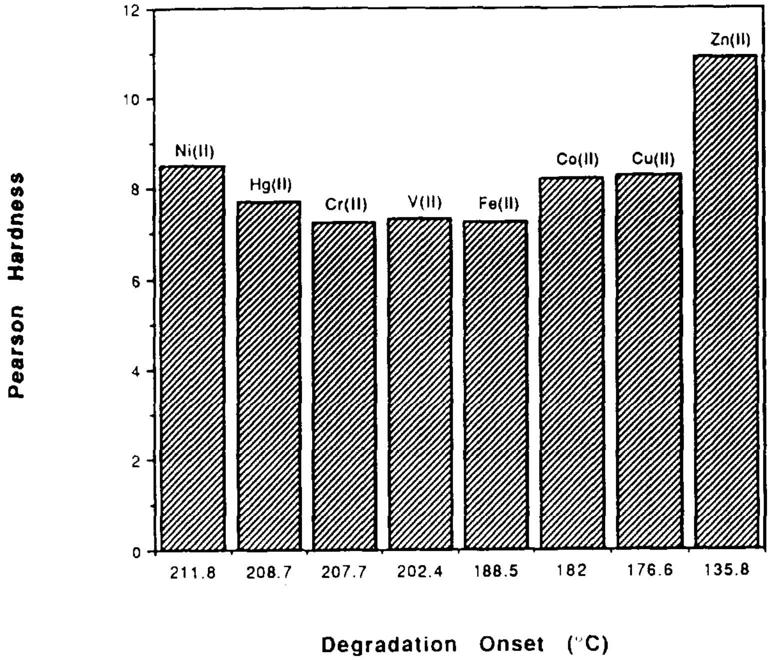

Fig. 4. Onset temperature for the metal halide promoted thermal degradation of a vinylidene chloride/methyl acrylate copolymer as a function of the Lewis acidity/Pearson hardness of the metal halide.

Table 1

Temperature of degradation for blends of a vinylidene chloride/methyl acrylate (5 mol%) copolymer with metal halides (5 wt%)

Metal halide	Degradation onset (°C)[a]	Temperature of maximum degradation (°C)[b]
None	218	236
KCl	214	231
$CaCl_2$	214	230
$NiCl_2$	212	230
$HgCl_2$	209	228
$CrCl_2$	208	227
VCl_2	202	225
$MnCl_2$	202	219
$FeCl_2$	189	221
$CoCl_2$	182	203
$CuCl_2$	177	191
$ZnCl_2$	136	145

[a] Extrapolated onset from the derivative plot of weight loss versus temperature.

[b] The maximum of the derivative plot of weight loss versus temperature.

ing halides of potassium, calcium and nickel(II) are quite similar and only marginally different from that of the untreated polymer, as seen in Fig. 1. The onset temperatures, as seen in Fig. 2, for the degradation of blends containing halides of mercury(II), chromium(II), vanadium(II) and manganese(II) are modestly lower than those for blends in Fig. 1. However, it is only the most acidic metal halides, those of iron(II), cobalt(II), copper(II) and zinc, which have a dramatic impact on the onset temperature for the degradation of the polymer.

4. Conclusions

The presence of metal halides can markedly accelerate the thermal degradation of vinylidene chloride copolymers. The effectiveness of metal halides in promoting the degradative dehydrohalogenation of these polymers is directly reflective of the Lewis acidity/Pearson hardness of the metal cation present.

Acknowledgements

The authors gratefully acknowledge funding from the Michigan Research Excellence Fund for the establishment of the Center for Applications in Polymer Science which permitted the purchase of the thermal analysis equipment required for this work.

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