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The stability of vinylidene chloride copolymers in the presence of selected multifunctional amines

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Abstract

Vinylidene chloride copolymers, particularly acrylate copolymers, occupy a position of prominence in the barrier plastic packaging industry. They display excellent barrier to the transport of oxygen (to prevent spoilage of packaged food items) and flavor and aroma agents (to prevent 'scalping' during transport and storage). However, these polymers undergo thermally-induced degradative dehydrochlorination at process temperatures, 150–170°C. To scavenge evolved hydrogen chloride and thus prevent the formation of metal halides (Lewis acids) by interaction with the extruder walls, these materials are usually blended with a small amount of passive base prior to processing. To determine the suitability of selected commercially available multifunctional amines for this purpose, blends containing 1–10% of various amines with a standard vinylidene chloride/methyl acrylate (5 mol%) copolymer have been examined by thermogravimetry. In general, the amines studied are sufficiently basic so as to promote dehydrochlorination. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Vinylidene chloride polymers; Degradative dehydrochlorination; Lewis acid catalysis; Thermogravimetry

1. Introduction

Vinylidene chloride polymers have a variety of applications in the packaging industry. These polymers are used, often in connection with other structural polymers, as a barrier to prevent the entry of oxygen into food containers (to avoid food spoilage) and to limit the loss of flavor and aroma constituents (flavor scalping) during long periods of storage (warehouse, supermarket shelves, etc.).

Although these polymers display outstanding characteristics for use in food packaging, they suffer from sensitivity to thermal treatments during processing [1]. At their melt-temperature, these polymers

undergo thermally-induced dehydrochlorination. The loss of the first mole of hydrogen chloride generates a polymer main chain containing an allylic dichloromethylene unit. The carbon–chlorine bonds of this unit are quite susceptible to homolysis, much more so than the corresponding units in the initial polymer. As a consequence, the introduction of an initial double bond into the polymer main chain serves as the starting point for rapid sequential dehydrochlorination to generate polyene sequences. When sufficiently large, these polyene sequences absorb in the visible portion of the electromagnetic spectrum and impart a yellow coloration to the polymer. The loss of the initial mole of hydrogen chloride is strongly accelerated by the presence of Lewis acids. Since most process equipment is constructed of metal alloys, the potential for the generation of Lewis acids (metal halides) by interaction of evolved hydrogen chloride with the

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walls of this equipment is always present. To prevent Lewis acid formation and consequent acceleration of the degradation process, the stabilization package for these polymers usually contains a passive base to scavenge hydrogen chloride. The additive must be sufficiently basic so as to react with evolved hydrogen chloride but not so basic as to strip hydrogen chloride from the polymer. Several commercially available amines of varying base strength have been evaluated as potential stabilizing additives for vinylidene chloride copolymers.

2. Experimental

2.1. Materials

The vinylidene chloride/methyl acrylate (5 mol%) copolymer was synthesized and characterized as previously described [2]. The amines used were provided by the DuPont Company.

2.2. Sample preparation

Blends of various amines (1.0 and 5.0% by weight) were prepared by stirring the appropriate amount of polymer in a solution of the amine in hexane. The solvent was removed by rotary evaporation at reduced pressure and the blend was dried above room temperature at reduced pressure. As an example, 0.25 g of 2-methylpentamethylenediamine was dissolved in 200 ml of hexane in a round-bottomed flask. Polymer (24.75 g) was added and the mixture stirred for 15 min at 45°C. The solvent was removed by rotary evaporation at reduced pressure. The polymer/amine blend was transferred to a Pyrex boat and dried at 25 Torr and 50°C for 24 h.

2.3. Thermal degradation

2.3.1. General degradation procedure

The thermal degradation of a vinylidene chloride/methyl acrylate (5 mol%) copolymer blended with various amines was followed using a TA Instruments model 2950 TGA unit interfaced with a TA Instruments Thermal Analysis 2100 control unit. Blended samples (10–20 mg) were loaded onto a platinum sample pan. In a typical run, the TGA cell was swept

with nitrogen at 50 ml/min for 30 min prior to the beginning and during data collection. Weight loss was observed as either a function of temperature (dynamic experiment) or time (isothermal degradation). A 5°C/min ramp rate was used; isothermal decomposition was observed at 170°C using the isotherm feature (temperature controlled on oven thermocouple) of the Thermal Analyst 2100 software. Temperature control for isothermal runs was $\pm 0.02^\circ\text{C}$.

Dynamic experiments were used to observe qualitative differences in the rates of initiation and propagation of polymer degradation as a function of the amount of amine present. Isothermal runs were used to obtain first-order rate constants for initiation and propagation of dehydrohalogenation. Rate constants were taken as the slopes of the appropriate linear portions of the plot of

$$\ln\left(\frac{(w_\infty - w_0)}{(w_\infty - w_t)}\right) \text{ versus time,}$$

where w_∞ is the weight of the sample at infinite time (t_∞) taken as that weight that remains after 37.62% of the initial vinylidene chloride component weight (corresponding to the complete loss of 1 mol of hydrogen chloride per vinylidene chloride unit in the polymer) has been lost; w_0 is the weight at time zero (t_0), that is, the time at which the first point was recorded and w_t is the weight at any time (t), during the run.

2.3.2. Polymer degradation procedure

A series of temperature ramp experiments were done using the TGA instrument and samples of about fifteen milligrams. Samples were weighted directly onto the sample pan after carefully tarring the platinum pan and the oven was closed by raising it around the pan. After 30 min of nitrogen purge (50 ml/min), weight loss was followed from ambient temperature to 450°C. The effect of the amine loaded was displayed by plotting the decay curves as a composite.

Isothermal weight loss as observed at 170°C by loading the sample (approximately 15 mg) and allowing the oven to equilibrate at 170°C (requiring about 3 min) and immediately beginning data collection. This method allowed data collection during the initial portion of the degradation process because the sample was brought to temperature in a few minutes. Data were collected over 2 h. Initiation rate constants

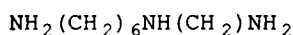
(k_i) were calculated by least squares analysis of the linear segment of the early portion (0–1400 s) of a $\ln((w_\infty - w_0)/(w_\infty - w_t))$ versus time plot with points plotted every 60 s. Propagation rate constants (k_p) were calculated in a similar manner from data acquired later (3000–6000 s) in the run (points were recorded every 60 s). Each run was carried-out in duplicate.

3. Results and discussion

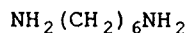
The impact of the presence of several amines of varied structure (see Fig. 1 below) on the stability of vinylidene chloride copolymers has been evaluated by thermogravimetry. Blends of amines (1.0, 5.0, 10 wt.%) with a vinylidene chloride/methyl acrylate (5 mol%) copolymer were prepared and subjected to thermogravimetric analysis (Fig. 1). In many cases, the effect of the presence of amine on the stability of copolymer was apparent from a color change (from white to yellow to tan to brown or black) which accompanied blend preparation. This is more prominently reflected in the plots collected in Fig. 2. As can

be seen, the presence of any amine has a detrimental impact on the stability of the polymer. This is most apparent in the region of the thermogram reflecting degradation initiation. This is consistent with earlier observations [3]. The effect is more prominent for blends containing more (5.0 and 10%) of the amine component.

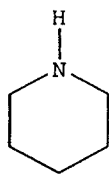
The extrapolated onset temperature for degradation (see Tables 1 and 2) is lower for all the blends than for the copolymer alone. Based on the degradation onset temperatures, the effectiveness of the amines in promoting degradative dehydrochlorination decreases in the order PDA>HMI>HMD>HMT>MPD. However, the differences among the degradation characteristics of the various blends are small. In fact, there is no structural basis for a strong difference in basicity for the amines. With one exception (a relatively non-hindered secondary amine) all are primary amines. The distinctions are somewhat blurred at higher amine loadings. For blends containing 10% of the amine component, the depression in degradation onset temperature is 10–20°C. The influence of the presence of the amines on the degradation of the polymer is



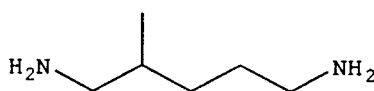
Bis(hexamethylene)triamine
(HMT)



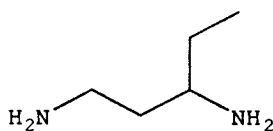
Hexamethylenediamine
(HMD)



Hexamethyleneimine
(HMI)



2-Methylpentamethylenediamine
(MPD)



1,3-Pentanediamine
(PDA)

Fig. 1. Amines used for the preparation of blends with a vinylidene chloride/methyl acrylate (5 mol%) copolymer.

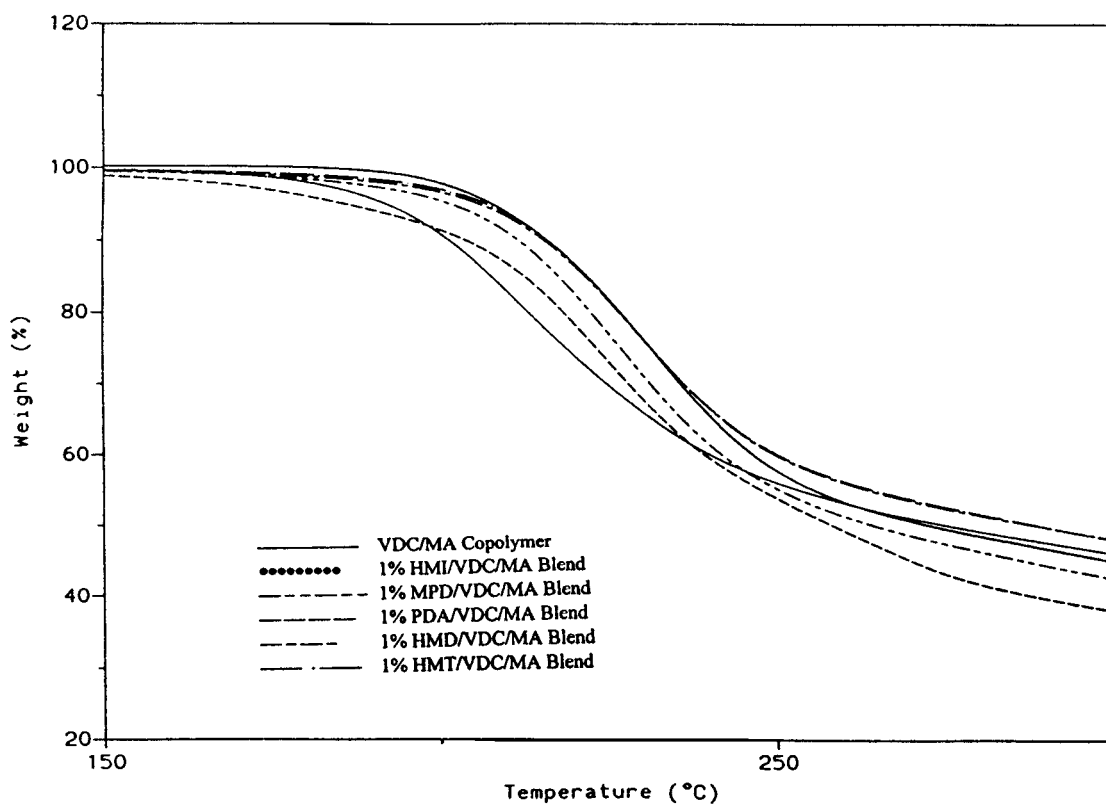


Fig. 2. Thermal degradation of blends of selected amines (1 wt.%) with a vinylidene chloride/methyl acrylate (5 mol%) copolymer.

Table 1

Degradation temperature for blends of selected amines (1 wt.%) with a vinylidene chloride/methyl acrylate (5 mol%) copolymer

Amine present	Wt.% of amine	Onset temperature of degradation (°C)	Temperature of maximum degradation rate (°C)
None	0	190	232
HMI	1	177	214
MPD	1	187	229
PDA	1	169	226
HMD	1	179	229
HMT	1	175	227

Table 2

Degradation temperatures for blends of selected amines (5 wt.%) with a vinylidene chloride/methyl acrylate (5 mol%) copolymer

Amine present	Wt.% of amine	Onset temperature of degradation (°C)	Temperature of maximum degradation rate (°C)
None	0	190	232
HMI	5	163	232
MPD	5	177	227
PDA	5	164	224
HMD	5	158	228
HMT	5	162	227

Table 3
Rate constants for the degradation of blends of selected amines with a vinylidene chloride/methyl acrylate (5 mol%) copolymer

Amine present	$k_i \times 10^5 \text{ (s}^{-1}\text{)}^a$	$k_p \times 10^5 \text{ (s}^{-1}\text{)}^a$
None	2.73±0.09	4.37±0.02
HMI	30.9±0.39	8.77±0.08
MPD	22.4±0.60	4.51±0.02
PDA	18.0±0.47	4.36±0.01
HMD	12.7±0.38	3.84±0.01
HMT	5.76±0.16	3.40±0.02

^a Averages of duplicate runs.

apparent from the rate constants presented in Table 3. As may be noted, the major impact is on the initiation rate constant, that is, the amines promote the initiation of degradation. Most probably the amines promote E2-type elimination of hydrogen chloride to introduce initial double bonds along the polymer main chain.

4. Conclusions

Blends of five commercially available amines with a vinylidene chloride/methyl acrylate (5 mol%) copolymer have been examined by thermogravimetry. In all cases, the presence of the amine had a detrimental

impact on the stability of the polymer. The amines are sufficiently basic so as to promote E2-type elimination to introduce double bonds and consequent allylic dichloromethylene units along the polymer main chain. These allylic units serve as initiation sites for sequential thermal degradative dehydrohalogenation.

Acknowledgements

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