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THERMAL DEGRADATION OF VINYLIDENE CHLORIDE/VINYL CHLORIDE COPOLYMERS IN THE PRESENCE OF N-SUBSTITUTED MALEIMIDES

Bob A. Howell[*] *and Jin Zhang*

Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI 48859-0001

As a consequence of their excellent barrier properties vinyl chloride/vinylidene chloride copolymers have long been prominent in the flexible packaging market. While these polymers possess a number of superior characteristics, they tend to undergo thermally-induced degradative dehydrochlorination at process temperatures. This degradation must be controlled to permit processing of the polymers. Three series of N-substituted maleimides (N-alkyl-, N-aralkyl, and N-aryl) have been synthesized, characterized spectroscopically, and evaluated as potential stabilizers for a standard vinyl chloride/vinylidene chloride (85 mass%) copolymer. As surface blends with the polymer, these compounds are ineffective as stabilizers. However, significant stabilization may be achieved by pretreatment of the polymer with N-substituted maleimides. The most effective stabilization of the polymer is afforded by N-aralkyl- or N-arylmaleimides, most notably, N-benzylmaleimide and N-*p*-methoxyphenylmaleimide.

Keywords: *N-substituted maleimides, stabilization, thermal processing, thermogravimetry, vinyl barrier polymers*

Introduction

Vinyl chloride/vinylidene chloride (VC/VDC) copolymers containing a predominance of vinylidene chloride (85–90%) have long been important barrier polymers widely used in the plastics packaging industry. These materials display excellent barrier to the ingress of oxygen and other small molecules (to prevent food spoilage) and to the loss of food flavor and aroma constituents (to prevent flavor scalping on the supermarket shelf) [1]. While these polymers have many outstanding characteristics which have made them commercial successes, they tend to undergo thermally-induced degradative dehydrohalogenation at process temperatures [2]. The dehydrochlorination occurs at moderate temperatures (120–200°C) and is a typical chain process involving initiation, propagation and termination phases. Defect structures, namely internal unsaturation (allylic dichloromethylene groups), serve as initiation sites for the degradation. These may be introduced during polymerization or during subsequent isolation and drying procedures. If uncontrolled, sequential dehydrohalogenation can lead to the formation of conjugated polyene sequences along the polymer mainchain. If sufficiently large, these polyenes absorb in the visible portion of the electromagnetic spectrum and give rise to discoloration of the polymer. For many applications color formation in the polymer is undesirable and must be controlled through the use of additives which interrupt propagation of the degradative dehydrohalogenation reaction or remove conjugated polyenes [3, 4]. Additives capable of interacting with the polymer to remove diene structures should enhance the stability of the polymer. The impact of the presence N-substituted (N-alkyl, N-aralkyl, N-aryl) maleimides on the stability of a typical vinylidene chloride/vinyl chloride (15 mass%) copolymer has been examined.

Experimental

Methods and instrumentation

Additives and polymers were characterized by spectroscopic, thermal, and chromatographic methods. Infrared spectra (IR) were obtained using solid solutions (1%) in anhydrous potassium bromide (as pellets), dilute solutions (5–10%) in carbon tetrachloride or thin films between sodium chloride discs and a model 1600 Perkin-Elmer FTIR instrument. Absorption intensities were classified as weak (*w*), medium (*m*), strong (*s*), very strong (*vs*), relative to the most intense spectral band. Thermal degradation characteristics were obtained by using a TA Instruments Inc. model 2950 TGA unit interfaced with the TA Instruments Thermal Analyst 2100 control unit. The TGA cell was swept with nitrogen at 50 ml min^{-1} during degradation runs. The temperature was ramped at a rate of 2–10°C min^{-1} or for isothermal kinetic runs held at a specified temperature.

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[*] Author for correspondence: bob.a.howell@cmich.edu

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Springer, Dordrecht, The Netherlands

Additives

Aromatic maleimides were synthesized in two steps from maleic anhydride. In the first step a solution of maleic anhydride in anhydrous methanol maintained at 0°C was treated with an aromatic amine to generate the corresponding N-arylmaleamic acid. N-arylmaleimides were prepared by dehydration of the corresponding N-arylmaleamic acid in the presence of acetic anhydride/sodium acetate. Aliphatic maleimides were synthesized in one step from maleic acid by treatment with the appropriate aliphatic amine in the presence of phosphoric acid.

Assessment of stability of polymer/additive blends

The thermal degradation of blends of a standard vinylidene chloride/vinyl chloride (15 mass%) copolymer with various amounts of selected N-substituted maleimides was observed using a TA instruments model 2950 TGA unit interfaced with a TA Instruments Thermal Analyst 2100 control unit. Samples (6–15 mg) were loaded onto a platinum sample pan. In a typical run, the TGA cell was swept with nitrogen at 50 mL min^{-1} for 30 min prior to the beginning of and during data collection. Mass loss was plotted as either a function of temperature or time (isothermal degradation). A 5°C min^{-1} ramp rate was used; isothermal decomposition was observed at 180°C using the isotherm feature (temperature controlled on oven thermocouple) of the Thermal Analyst 2100 software. Temperature control for isothermal runs was ±0.1°C. Dynamic experiments were used to observe qualitative differences in initiation and propagation of degradative dehydrochlorination as a function of the amount of additive loaded. 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 a plot of $\ln[(w_\infty - w_o)/(w_\infty - w_t)]$ *vs.* time where w_∞ is the mass of the sample at infinite time (t_∞) taken as that mass that remains after 37.62% of the initial vinylidene chloride component mass (corresponds to the complete loss of one mole of hydrogen chloride per vinylidene chloride unit in the polymer) had been lost; w_o is the mass at time zero (t_0), i.e., the time at which the first data point was recorded and w_t is the mass at any time t, during the run.

Results and discussion

Vinylidene chloride/vinyl chloride (4–15 mass%) copolymers readily undergo thermally-induced degradative dehydrochlorination at process temperatures. This degradation process must be controlled to prevent the formation of polyene sequences which impart color to the polymer. Additives capable of preventing the formation of polyene sequences of extended length should be effective in preventing color development. One class of compounds which might be expected to display the necessary activity toward unsaturation in the polymer mainchain is the N-substituted maleimides. For examination as potential stabilizers for a typical vinylidene chloride/vinyl chloride (15 mass%) copolymer three series of N-substituted maleimides (N-alkyl-, N-aralkyl-, and N-aryl-) have been synthesized and used for both the preparation of polymer blends and polymer pretreatment. The stability of both simple surface blends of additive with the polymer and the polymer pretreated with additive was established using thermogravimetry [5]. No significant increase in stability was apparent from blending the additive with the polymer. In contrast, pretreatment of the polymer with additive markedly increased the stability of the polymer. The standard vinylidene chloride/vinyl chloride copolymer was treated with excess (two moles of maleimide per mole of vinylidene chloride units in the polymer) N-substituted maleimide in chlorobenzene at 130°C for two hours. The polymer was precipitated by pouring the chlorobenzene solution into an excess of methanol. The recovered polymer was dissolved in chlorobenzene and again precipitated in methanol. The dissolution/precipitation procedure was repeated at least twice. The polymer was collected by filtration at reduced pressure, dried at elevated temperature (60–80°C) and reduced pressure (20 torr) for 8 h, and examined by infrared spectroscopy and thermogravimetry. Infrared spectroscopy indicated that a portion of the maleimide had been bound to the polymer. The infrared spectrum of the copolymer after pretreatment with maleimide contains the characteristic maleimide band at 1708 cm^{-1}. Repeated dissolution/precipitation of the polymer does not remove this band from the spectrum.

Thermal curves for degradation of the polymer after pretreatment with the various N-substituted maleimides reflect the positive impact of this procedure. In these simple qualitative comparisons polymer pretreated with any maleimide displays greater stability than the untreated polymer. This is particularly true for the polymer pretreated with N-alkylmaleimides. Pretreatment with any of the N-alkylmaleimides leads to a higher temperature for the onset of degradation, i.e., the extrapolated temperature for the onset of degradation is higher for the polymer receiving treatment with any of the N-alkylmaleimides than for the untreated polymer. The temperature of maximum degradation rate is increased substantially by pretreatment with N-alkylmaleimide. The rate con-

Table 1 Rate constants for the thermal degradation of a vinylidene chloride/vinyl chloride (15 mass%) copolymer pretreated with a solution of N-alkylmaleimide (two moles per mole of vinylidene chloride units) in chlorobenzene at 130°C for 2 h

N-alkylmaleimide	$^{a}k_{i}\cdot 10^{4}/\mathrm{sec}^{-1}$	$^{a}k_{p}\cdot 10^{4}/\mathrm{sec}^{-1}$
None	2.59±0.02	3.85±0.02
N-propylmaleimide	1.27±0.10	2.24±0.20
N-butylmaleimide	1.11±0.02	1.69±0.10
N-isopropylmaleimide	1.07±0.01	1.94±0.01
N-*t*-butylmaleimide	0.76±0.09	2.37±0.07
N-octadecylmaleimide	0.67±0.10	2.52±0.00

[a] Average of at least two determinations

stants for both initiation and propagation of degradation of the polymer pretreated with N-alkylmaleimides are collected in Table 1. It is apparent that pretreatment with any of the N-alkylmaleimides enhances the thermal stability of the polymer. In particular, the rate of initiation of degradation is strongly diminished.

Considering all the data, pretreatment with N-butylmaleimide seems to afford the most effective stabilization of the copolymer.

N-aralkylmaleimides or N-arylmaleimides are even more effective in providing stabilization. Pretreatment of the polymer with any of these compounds leads to a material which displays an apparent stability greater than that of the untreated polymer (Tables 2 and 3). In particular, pretreatment with N-benzylmaleimide from among the N-aralkylmaleimides or N-*p*-methoxyphenylmaleimide from among the N-arylmaleimides has a strongly positive effect on the stability of the polymer. This is reflected in the rate constants for degradation at 180°C (Table 2). The initiation rate constants for the degradation of the polymer after treatment with N-benzylmaleimide and N-*p*-methoxyphenylmaleimide are $1.06\cdot 10^{-4}$ sec^{-1} and $2.01\cdot 10^{-4}$ sec^{-1}, respectively, compared to $2.59\cdot 10^{-4}$ sec^{-1} for the untreated polymer. The degradation onset temperature for the polymer pretreated with either N-benzyl- or N-*p*-methoxyphenylmaleimide (180°C) is fully 10°C higher than that for the untreated polymer (Table 3). All of these observations suggest that pretreat-

Table 2 Rate constants for the thermal degradation of a vinylidene chloride/vinyl chloride (15 mass%) copolymer pretreated with a solution of N-aryl- or N-aralkylmaleimide (two moles per mole of vinylidene chloride units) in chlorobenzene at 130°C for 2 h

N-aryl(aralkyl)maleimide	$^{a}k_{i}\cdot 10^{4}/\mathrm{sec}^{-1}$	$^{a}\mathrm{k}_{p}\cdot 10^{4}/\mathrm{sec}^{-1}$
None	2.59±0.02	3.85±0.02
N-phenylmaleimide	4.02±0.03	4.41±0.14
N-butylmaleimide	1.06±0.03	2.27±0.07
N-(2-phenylethyl)maleimide	2.59±0.16	4.41±0.18
N-*p*-methoxyphenylmaleimide	2.01±0.16	3.23±0.14
N-*p*-ethoxyphenylmaleimide	2.12±0.03	3.74±0.02

[a] average of at least two determinations

Table 3 Degradation temperature for a vinylidene chloride/vinyl chloride (15 mass%) copolymer pretreated with a solution of N-aryl- or N-aralkylmaleimide (two moles per mole of vinylidene chloride units) in chlorobenzene at 130°C for 2 h

N-aryl(aralkyl)maleimide	[a] Degradation onset temperature/°C	[b] Temperature of maximum degradation rate/°C
None	174	212
N-phenylmaleimide	175	221
N-butylmaleimide	178	212
N-(2-phenylethyl)maleimide	185	229
N-*p*-methoxyphenylmaleimide	185	221
N-*p*-ethoxyphenylmaleimide	176	213

[a] extrapolated onset temperature from the derivative plot of mass loss *vs*. temperature; [b] maximum in the derivative plot of mass loss *vs*. temperature

ment of this polymer with either of these maleimides affords significant stabilization. In fact, pretreatment with any of the N-aralkyl- or N-arylmaleimides, with the possible exception of N-phenylmaleimide, imparts stability to the polymer (smaller rate constant for the initiation of degradation; higher temperature for the onset of degradation).

Conclusions

The presence of N-substituted maleimides in blends with a standard vinylidene chloride/vinyl chloride (15 mass%) copolymer does not significantly impact the stability of the polymer. However, pretreatment of the polymer with selected N-substituted maleimides, particularly N-arylmaleimides, does impart significant stabilization for the polymer as indicated by significantly enhanced onset temperatures for degradation and decreased rates of degradation.

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