

Thermal degradation of vinylidene chloride/methyl acrylate copolymers in the presence of radical scavengers¹

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Abstract

Vinylidene chloride copolymers have a number of superior properties, most notably, a high barrier to the transport of oxygen and other small molecules. As a consequence, these materials have assumed a position of prominence in the packaging industry. At processing temperatures these copolymers tend to undergo degradative dehydrochlorination. It has previously been established that the dehydrochlorination reaction is a typical chain process with distinct initiation, propagation and termination phases. The chain-carrying species is a tight carbon–chlorine radical pair. To evaluate the impact of simple radical scavengers on the dehydrochlorination reaction, degradation of several surface blends of potential scavengers with a methyl acrylate (5 mol.%) / vinylidene copolymer has been examined by thermogravimetry. Of the several compounds evaluated including triphenylmethane, 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO), *N*-chlorosuccinimide, 9,10-dihydroanthracene, *N,N*-diethylhydroxylamine, and *N*-bromosuccinimide, none displayed a significant stabilizing influence with respect to degradative dehydrochlorination.

INTRODUCTION

Because of the prominence of vinylidene chloride copolymers in the barrier plastics packaging industry [1,2], interest in the degradation and stabilization of these materials remains high [3]. When subjected to thermal stress, these polymers undergo degradative dehydrochlorination [4]. This thermal dehydrochlorination is a typical radical chain process with distinct initiation, propagation and termination phases [5,6]. Initiation of degradation is promoted by the presence of any of a variety of agents capable of introducing random double bonds into the polymer backbone [4]. Unsaturation

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ration in these polymers appears to be a principal defect structure (allylic dichloromethylene units) responsible for degradation. The chain-carrying species for the propagation reaction is a tight radical pair (chlorine atom–allylic carbon radical) [7]. The presence of an agent capable of efficiently intercepting the components of this radical pair should have a strong stabilizing influence during processing of the polymer. To evaluate the impact of simple radical scavengers on the dehydrochlorination reaction, the degradation of several surface blends of potential scavengers with a vinylidene chloride/methyl acrylate (5 mol.%) copolymer has been examined by thermogravimetry.

EXPERIMENTAL

Materials

Monomers and reagents

Distilled vinylidene chloride and hydroxymethylcellulose (Methocel K4M cellulose ether) were obtained from the Dow Chemical Company. The methyl acrylate (MA) used was commercial material from Hoechst Celanese and contained 200 ppm MEHQ (monomethyl ether of hydroquinone) as stabilizer. Azobisisobutyronitrile (AIBN; VAZO 64) was obtained from the DuPont Chemical Company. Potential radical scavengers *N*-bromosuccinimide (NBS), *N*-chlorosuccinimide (NCS), *N,N*-diethylhydroxylamine (DEHA), 9,10-dihydroanthracene (DHA), 2,2,6,6-tetramethyl-1-piperidinyl-oxy free radical (TEMPO), and triphenylmethane (TPM) were obtained from Aldrich Chemical Company. Common solvents were obtained from Fisher Scientific Company.

Polymerization

Suspension polymerization was carried out to high conversion in a glass-lined reactor at 65°C. The aqueous phase contained 0.2 wt.% hydroxymethylcellulose as suspending agent. The initiator (AIBN; 0.5 wt.%, 0.3 mol.%) was dissolved in the monomer phase. A phase ratio of 1.5:1 (water mass to monomer mass) was maintained. The polymer generated was washed repeatedly with deionized water to remove residual monomer and suspending agent, collected by filtration at reduced pressure, and dried in an oven at 50°C.

Polymer characterization

Size-exclusion chromatography

Molecular weights were determined by size-exclusion chromatography relative to narrow molecular-weight polystyrene standards (Polymer Laboratories, Inc.) using solutions in tetrahydrofuran (THF) and a Waters

Associates modular chromatographic system which included a model M-6000 pump and a model 410 differential refractive index detector. Two 5 μm mixed-bed columns from Polymer Laboratories, Inc., (No. 5M-M-35-59, 60) were used in series. The polymer was of uniform molecular-weight distribution with $M_n = 57\,000$, $M_w = 102\,000$ and $M_w/M_n = 1.79$.

Differential scanning calorimetry (DSC)

Analysis by DSC was accomplished using a Du Pont Instruments, Inc., 9900 thermal analyzer coupled to a model 912 DSC unit equipped with a liquid nitrogen cooling accessory (LNCA). The cell was calibrated using an indium sample ($T_m(\text{onset}) = 156.63^\circ\text{C}$, $\Delta H_f = 28.42 \text{ J g}^{-1}$). DSC plots (heat flow versus temperature) were generated using a model 7440 Hewlett-Packard plotter supplied by Du Pont Instruments. In general, 8–12 mg samples and closed aluminum sample pans were used. The cell was subject to a constant nitrogen purge. After equilibration at -40°C , the temperature was ramped to 200°C at $10^\circ\text{C min}^{-1}$. To observe a sharp glass transition temperature, samples were held at 185°C for 75 s and quenched in liquid nitrogen prior to analysis. The unannealed polymer displayed melting behavior characteristic of vinylidene chloride copolymers [4] 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 . By making reference to a calibration plot of melting point versus composition for vinylidene chloride/methyl acrylate copolymers for which the MA content had been determined rigorously by ^{13}C NMR spectroscopy, it could be established that the polymer contained methyl acrylate at the intended 5 mol.% level.

Nuclear magnetic resonance spectroscopy (NMR)

NMR spectra were recorded using solutions in $\text{THF-}d_8$ and a Nicolet NT-300 spectrometer. Carbon spectra were observed at 75.5 MHz with a pulse width of 18 μs (90°), a pulse delay of 10 s, an acquisition time of 0.41 s, gated decoupling without nuclear Overhauser effect, a sweep width of 20 kHz, and an acquisition size of 16K. The ^{13}C NMR analysis [8] confirmed the random distribution of the methyl acrylate in the polymer and established that it had been incorporated at approximately the distribution in the initial monomer mixture.

Vinylidene chloride copolymer / stabilizer blends

In general, the appropriate amount of stabilizer was dissolved in methanol or methylene chloride, 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 at reduced pressure. In a typical example, 5.00 g of TEMPO was dissolved in 200 ml of

methylene chloride in a round-bottomed flask. Polymer (45.00 g) was added and the resulting mixture was stirred for 0.25 h at 40°C. The solvent was removed by rotary evaporation at reduced pressure and 40°C. The residual polymer/stabilizer blend was transferred to a Pyrex boat and dried at approximately 20 Torr and 40°C for 16 h.

Thermal Degradation

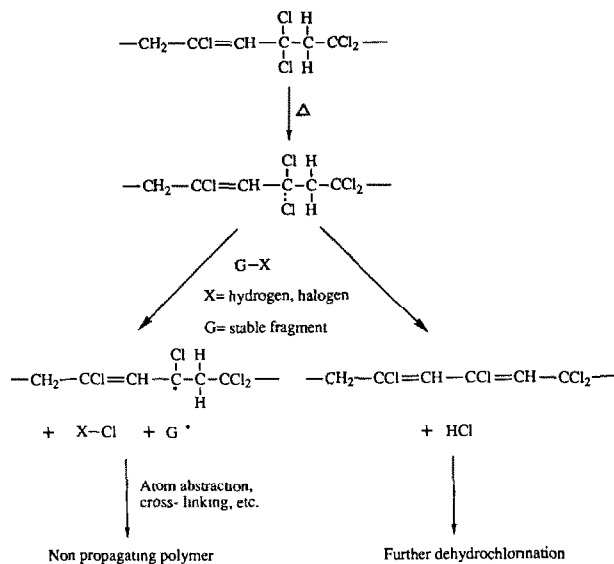
The thermal degradation characteristics of both untreated polymer and samples containing 1–10 parts per hundred (pph) of an appropriate radical scavenger were examined by thermogravimetry using either a TA Instruments 2100 thermal analyzer coupled with a 2950 TGA unit or a Du Pont 9900 thermal analysis system coupled to a 951 TGA unit. In a typical run the temperature was ramped at a rate of 5°C min⁻¹ from 30 to 350°C. The TGA cell was swept with nitrogen at 40 ml min⁻¹ during degradation runs and the sample, approximately 20 mg, was contained in a platinum sample pan. Decay plots, weight loss versus time (or temperature), were generated by feeding the analyzer output (TA Instruments or Du Pont software was used for all data manipulation) to a model 7440 Hewlett-Packard plotter.

Oven aging

To assess the impact of prior interaction of the polymer with potential stabilizers, samples of each copolymer/stabilizer blend (1 pph) were held in an oven maintained at 65°C for 7 days prior to analysis by thermogravimetric methods.

RESULTS AND DISCUSSION

Vinylidene chloride copolymers are known to undergo thermal degradation via a tight radical pair. The propagation step for this reaction involves the decomposition of this radical pair to form a unit of unsaturation in the polymer backbone and to liberate hydrogen chloride. As depicted in Scheme 1, efficient interception of the radical pair by an external agent would shunt the dehydrohalogenation reaction and provide a means of stabilizing the polymer. A set of potential stabilizers of widely differing chain-transfer capability has been examined in this capacity. Polymer samples containing 1 pph of *N*-bromosuccinimide (NBS), *N*-chlorosuccinimide (NCS), *N,N*-diethylhydroxylamine (DEHA), 9,10-dihydroanthracene (DHA), 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) and triphenylmethane (TPM) were subjected to degradation using thermogravimetric techniques. As can be seen in Fig. 1, the presence of none of these agents has a significant impact on the stability of the polymer. In fact, the degradation behavior of all samples is quite similar. This is evident



Scheme 1. Thermal degradation of a poly(vinylidene chloride) segment in the presence and absence of an efficient radical stabilizer.

from both the slopes of the plots of weight loss versus temperature shown in Fig. 1 and the degradation onset temperatures presented in Table 1.

The behavior of the polymer in the presence of much higher loadings of these radical stabilizers is not unlike that observed for the samples containing 1 pph of the same material. As can be seen in Figs. 2 and 3, the

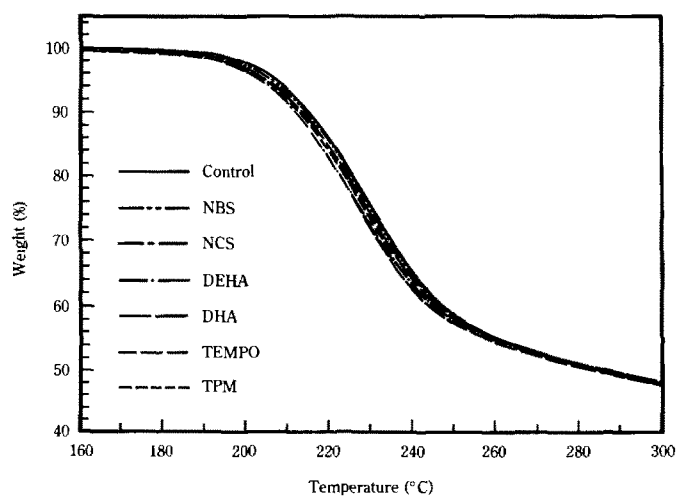


Fig. 1. Thermal degradation of a vinylidene chloride/methyl acrylate copolymer in the presence of 1 pph of selected radical stabilizers.

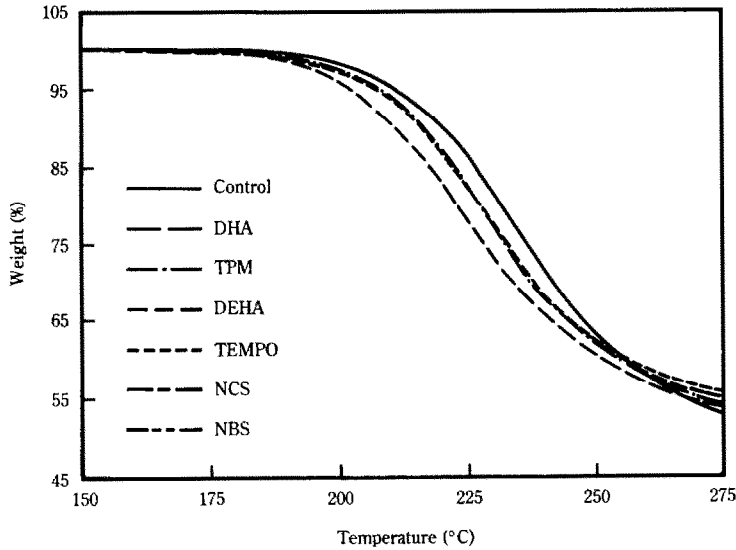


Fig. 2. Thermal degradation of a vinylidene chloride/methyl acrylate copolymer in the presence of 5 pph of selected radical stabilizers.

presence of 5 or 10 pph of the stabilizers has little impact on the degradation of the polymer. In no case is significant stabilization observed.

To determine the impact of prior heat treatment on the interaction of the potential stabilizer with the polymer, samples containing the additives

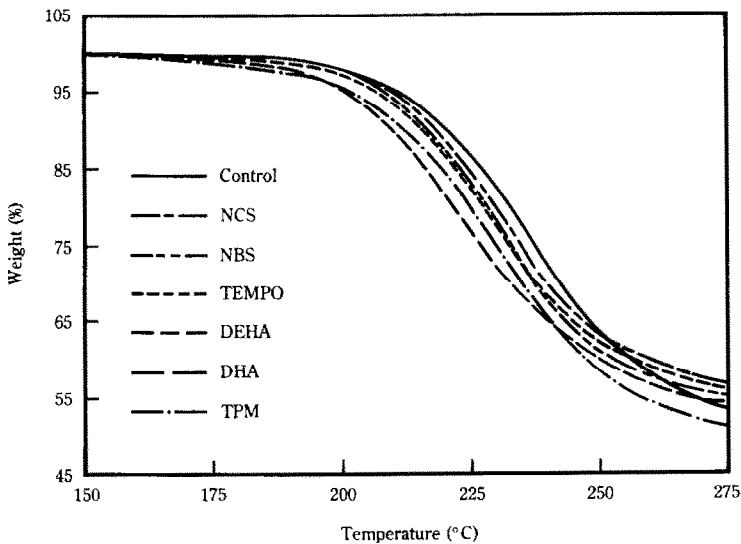


Fig. 3. Thermal degradation of a vinylidene chloride/methyl acrylate copolymer in the presence of 10 pph of selected radical stabilizers.

TABLE 1

Temperatures corresponding to 3% weight loss for the thermal degradation of a vinylidene chloride copolymer containing 1 pph of selected stabilizers

System	Temperature (°C)
Polymer	200.9
Polymer/NBS	199.6
Polymer/NCS	198.6
Polymer/DEHA	197.7
Polymer/DHA	197.2
Polymer/TEMPO	198.4
Polymer/TPM	198.8

were held in an oven at 65°C for 7 days. Analysis of these samples suggested that there was little difference in degradation characteristics before or after aging at 65°C. A comparison of the degradation behavior of aged and unaged polymer containing 1 pph DHA is presented in Fig. 4. Similar results were obtained for samples containing the other additives listed.

CONCLUSIONS

None of the potential radical stabilizers examined had any significant impact on the degradation characteristics of the vinylidene chloride polymer. This is consistent with the earlier observation that the propagating

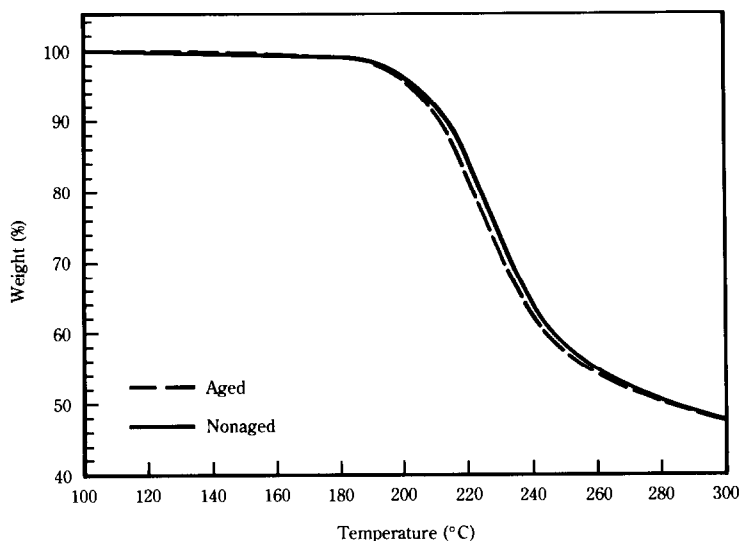


Fig. 4. Thermal degradation of a vinylidene chloride copolymer containing 1 pph DHA before and after oven aging at 65°C.

radical pair for the degradative dehydrochlorination reaction does not dissociate appreciably [7]. Consequently, the chlorine atom formed in the decomposition is never sufficiently free to interact with an added stabilizer.

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