ELSEVIER

Thermochimica Acta 357–358 (2000) 127–131

thermochimica acta

www.elsevier.com/locate/tca

The impact of high surface area magnesium hydroxide on the stability of vinylidene chloride copolymers

B.A. Howell*, F.M. Uhl, D. Townsend

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

Received 14 September 1998; accepted 10 January 1999

Abstract

Vinylidene chloride (VDC) copolymers display high barrier to the transport of oxygen, other small molecules, and flavor and aroma agents. For this reason they occupy a place of prominence in the plastic packaging industry. Unfortunately, these polymers undergo facile thermally-induced degradative dehydrochlorination at modest temperatures. To permit the processing of these materials at 150–170°C an effective stabilization package is required. One component of any stabilization system is a passive base to absorb evolved hydrogen chloride which can form accelerative Lewis acids by interaction with metallic surfaces of process equipment. The availability of a new high-surface area magnesium hydroxide offers potential for development as an effective additive for this purpose. Blends of this material and other commercially available magnesium hydroxides with a vinylidene chloride/methyl acrylate (5 mol%) copolymer have been examined by thermogravimetry to assess the utility of these materials as potential stabilizers for vinylidene chloride polymers.

Keywords: Vinylidene chloride copolymers; Degradative dehydrochlorination; Thermogravimetry

1. Introduction

Vinylidene chloride (VDC) polymers have a number of excellent characteristics which have placed them in a position of prominence in the plastic packaging industry [1]. The most notable of these is their high barrier to the transport of oxygen and other small molecules as well as to flavor and aroma constituents. This barrier to the transport of small molecules is reflective of the uniform microstructure of the polymers leading to highly crystalline materials and low free volume even in the amorphous regions.

Popular for many packaging applications are vinylidene chloride/methyl acrylate copolymers. These copolymers contain 5–15% methyl acrylate and as a consequence have melting temperatures low enough (150–170°C) that the materials can be melt processed. During processing degradative dehydrochlorination occurs in the vinylidene chloride sequences.

The loss of an initial mole of hydrogen chloride affords a polymer containing an allylic dichloromethylene unit. These units are more prone to thermally-induced carbon–chlorine bond homolysis than are those of the initial polymer. As a consequence, the dehydrochlorination event occurs successively along the polymer chain rapidly leading to polyene sequences long enough to absorb in the visible portion of the spectrum. This imparts an esthetically unpleasant coloration to the polymer. Further, the hydrogen chloride evolved may interact with the metallic walls of the process equipment to form Lewis acids, particularly iron chloride, which accelerate the dehy-

---

* Corresponding author. Tel.: +1-517-774-3582;
fax: +1-517-774-3883.
E-mail address: bob.a.howell@cmich.edu (B.A. Howell)

PII: S0040-6031(00)00380-4

drochlorination reaction. One way to control this unwanted catalysis of the degradation is to include a nonaggressive inorganic base in the stabilization package to scavenge hydrogen chloride as it is formed. The availability of a new high surface area magnesium hydroxide offers the potential for the development of a superior stabilizer for these polymers. The stability of blends of this new magnesium hydroxide as well as two established hydroxides (to act as controls) with a vinylidene chloride/methyl acrylate (5 mol%) copolymer [VDC/MA (5 mol%)] has been evaluated by thermogravimetry.

2. Experimental

2.1. Materials

2.1.1. Copolymers and reagents

The vinylidene chloride/methyl acrylate (5 mol%) copolymer was synthesized and characterized as previously described [2]. The magnesium hydroxides used in this study were obtained from the Dead Sea Periclase, LTD., Martin Marietta Magnesia Specialties, Inc., and the Dow Chemical Company.

2.1.2. Vinylidene chloride copolymer/magnesium hydroxide blends

In general, the appropriate amount of magnesium hydroxide was blended with the copolymer in a Waring blender for 5 min. Samples prepared contained 0.5, 1, 5, and 10 wt.% magnesium hydroxide. In a typical example, 2.0 g of magnesium hydroxide was blended with 18.0 g of VDC/MA (5 mol%) copolymer to give a 10 wt.% magnesium hydroxide blend.

2.2. Thermal degradation

2.2.1. General degradation process

The thermal degradation of blends of a vinylidene chloride/methyl acrylate copolymer (5 mol%) with various magnesium hydroxides was followed using a TA Instruments model 2950 TGA unit interfaced with a TA Instruments Thermal Analyst 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 of and during data collection. Weight loss was seen as either a function of temperature (temperature ramp 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 ±0.02°C.

Ramp experiments were used to observe qualitative differences in initiation and propagation of degradative dehydrochlorination as a function of the amount of magnesium hydroxide 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 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 blend) had been lost; w_0 is the weight at time zero (t_0), i.e., the time at which the first point was recorded and w_t is the weight at any time, t, during the run.

2.3. Polymer degradation procedure

A series of temperature ramp experiments were done using the TGA instrument and samples of about 15 mg. Samples were weighted directly onto the sample pan after carefully taring 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 600°C. The effect of the presence of magnesium hydroxide on the blend loaded was displayed by plotting the decay curves as a composite.

Isothermal weight loss was 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 a period of 2 h. Initiation rate constants (k_i) were calculated by least squares analysis

Table 1
Surface areas of magnesium hydroxides blended with a VDC/MA (5 mol%) copolymer

Supplier	Designator	Surface area (m^2/g)
The Dead Sea Periclase, LTD.	MH-95-002	29
Martin Marietta Magnesia Specialties, Inc.	Magshield Type 5	12
Martin Marietta Magnesia Specialties, Inc.	Magshield Type M	15
The Dow Chemical Company	MHT 100	

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

Magnesium hydroxides from several sources were examined as potential stabilizers for VDC/MA copolymers. The magnesium hydroxides were of varying surface areas (Table 1).

Blends of the various magnesium hydroxides (0.5, 1.0, 5.0, 10% by weight) with a vinylidene chloride/methyl acrylate (5 mol%) copolymer were prepared and examined by thermogravimetry. Qualitatively, the impact of the presence of the magnesium hydroxides on the stability of the polymer may be seen from the plots displayed in Fig. 1. It is apparent from the collection of plots in Fig. 1 as well as from the corresponding plots for the blends of other compositions that (1) the impact of the presence of magnesium

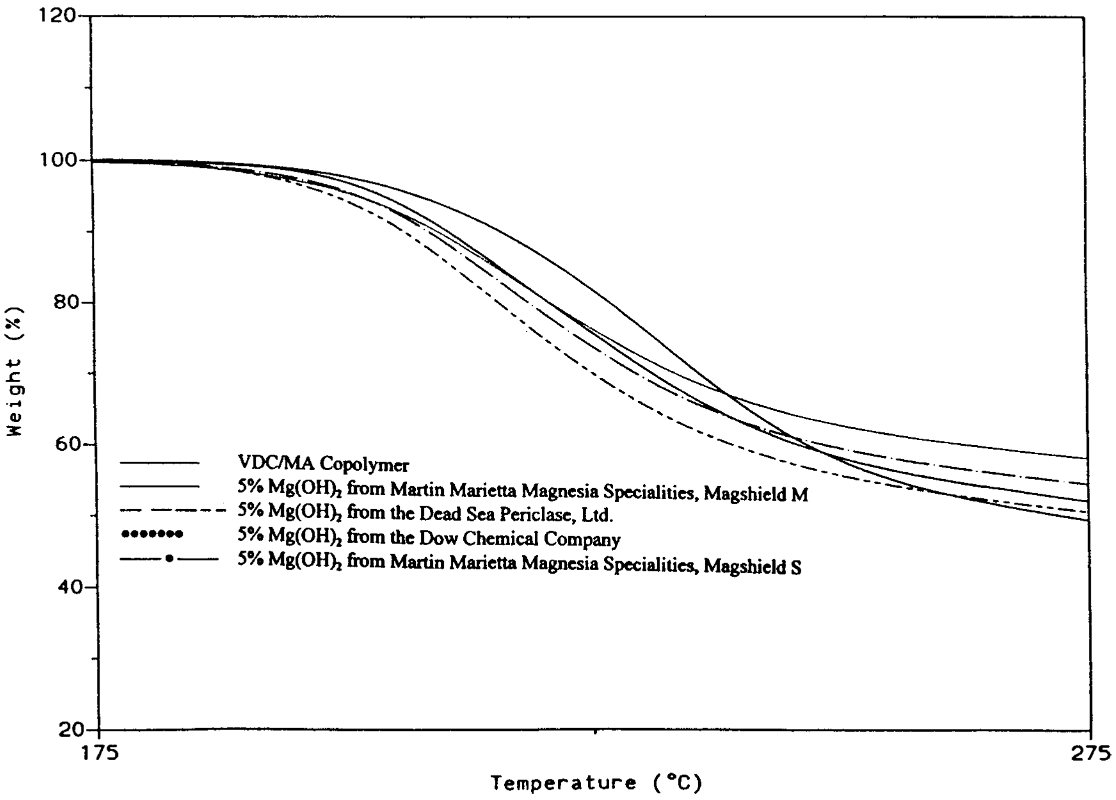

Fig. 1. Degradation of blends of various magnesium hydroxides (5 wt.%) with a vinylidene chloride/methyl acrylate (5 mol%) copolymer.

Table 2
Onset temperature and temperature of maximum degradation rate for vinylidene chloride/methyl acrylate copolymers blended with various magnesium hydroxides

Magnesium hydroxide (wt.%)	Extrapolated onset temperature for degradation (°C)	Temperature for maximum degradation rate (°C)
0%	190	232
Dead Sea		
0.5%	187	223
1%	185	219
5%	182	217
10%	181	217
Martin Marietta Magnesia Specialties		
Type S		
0.5	186	222
1	184	223
5	183	218
10	182	219
Type M		
0.5	187	224
1	186	223
5	185	220
10	182	218
The Dow Chemical Company		
0.5	187	224
1	185	220
5	180	219
10	179	219

Table 3
Rate constants for initiation and propagation of degradation for blends of a vinylidene chloride/methyl acrylate (5 mol.%) copolymer with high surface area magnesium hydroxides

% Magnesium hydroxide (wt.%)	$k_i \times 10^5$ (s^{-1})[a]	$k_p \times 10$ (s^{-1})[a]
0.0	2.73±0.09	4.37±0.02
The Dead Sea Periclase LTD.		
0.5	3.07±0.06	6.05±0.02
1	4.95±0.06	8.91±0.02
5	9.00±0.16	12.0±0.03
10	3.55±0.11	7.01±0.02
Martin Marietta Magnesia Specialties, Inc.		
Type S		
0.5	4.99±0.14	8.07±0.02
1	5.38±0.13	21.5±0.15
5	12.9±0.20	11.9±0.07
10	8.46±0.10	9.50±0.03
Type M		
0.5	3.85±0.11	6.82±0.02
1	4.68±0.08	7.73±0.01
5	5.14±0.10	8.61±0.02
10	8.45±0.14	11.0±0.03
The Dow Chemical Company		
0.5	2.49±0.03	3.68±0.04
1	2.62±0.04	3.8±0.01
5	5.70±0.03	4.76±0.02
10	4.51±0.03	4.23±0.01

[a] Averages of duplicate runs.

hydroxide on the degradation of the polymer is little effected by the surface area of the additive and (2) the presence of magnesium hydroxide enhances the onset of polymer degradation. These observations are reinforced by the data presented in Table 2. The extrapolated onset temperature for degradation is lower for the blends than for the polymer alone. The temperature at which the degradation rate is maximum is also lowered by the presence of magnesium hydroxide from any source. In this case, the impact is larger, 8–15°C.

Rate constants for decomposition of the blends at 170°C are collected in Table 3. Generally, the rate of initiation of degradative dehydrochlorination is enhanced by the presence of any magnesium hydroxide. This effect becomes more pronounced as the hydroxide loading is increased from 0.5 to 5%. The effect at higher loading (10%) is somewhat less clear and may reflect a limiting additive level. Propagation rate constants are generally parallel to those for initiation and reflect lower thermal stability for the blends than for the polymer itself.

4. Conclusions

As determined by thermogravimetry the presence of magnesium hydroxide has a small but negative impact on the stability of a vinylidene chloride/methyl acrylate copolymer. The main effect of the presence of hydroxide is an enhancement in the rate of initiation of degradative dehydrochlorination for the polymer. The surface area of the additive seems to have very little influence on the effectiveness of the additive.

Acknowledgements

The magnesium hydroxides used in this study were made available by Dead Sea Periclase, LTD., Martin Marietta Magnesia Specialties, Inc., and The Dow Chemical Company. Funding for the establishment of the Center for Applications in Polymer Science which permitted the purchase of the thermal analysis equipment used was from the Michigan Research Excellence Fund. All support is gratefully acknowledged.

References

[1] R.A. Wessling, D.S. Gibbs, P.T. DeLassus, B.A. Howell, Encyclopedia of Polymer Science and Engineering, 2nd Edition, Wiley, New York, 1989, pp. 492.

[2] B.A. Howell, B.S. Warner, C.V. Rajaram, S.I. Ahmed, Z. Ahmed, Polym. Adv. Technol. 5 (1994) 485.