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Thermal stability of vinylidene chloride/methyl acrylate copolymers in the presence of metal decanoates

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Abstract

The thermal degradation of a vinylidene chloride/methyl acrylate (5 mol%) copolymer in the presence of various metal decanoates (5 wt%) has been examined by thermogravimetry. The stability of the polymer is little affected by the presence of metal decanoates containing nonacidic cations. In contrast, the presence of metal decanoates containing acidic cations [iron(II), cobalt(II), copper(II) and, in particular, zinc] has a distinct and generally negative impact on the stability of the polymer. Copper (II) decanoate, containing a moderately acidic cation, displays the greatest potential for development as a stabilizer for vinylidene chloride copolymers. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Vinylidene chloride copolymers, particularly copolymers with alkyl acrylates, occupy a place of prominence in the barrier plastic packaging industry [1,2]. These materials exhibit extremely low permeability to small molecules, principally oxygen, and to flavor and aroma constituents of food items. Thus multilayer plastic packages in which a vinylidene chloride copolymer is present as the barrier layer permit long storage life with minimal spoilage or loss of flavor for a variety of food items [3]. The formulation of such packages is complicated by the propensity of these polymers to undergo thermal degradative dehydrochlorination in the vinylidene chloride sequences at process temperatures, 150–200°C [4]. Allylic dichloromethylene units introduced during polymerization or processing are principal labile structures responsible for the initiation of sequential loss of hydrogen chloride from the polymer mainchain [5–7]. Conversion of the allylic dichloromethylene groups to less reactive moieties might be expected to have a strongly stabilizing influence on the polymer. Indeed, the stability of these polymers is enhanced by the presence of certain metal formates, principally, copper(II) formate [8,9]. The nature of both the metal cation and the carboxylate anion are important for effective stabilization. The cation must be capable of sufficient interaction with bound chlorine to enhance the electrophilicity of allylic dichloromethylene units within the polymer but not so acidic as to strip chlorine from the polymer. The carboxylate anion must be sufficiently nucleophilic to displace metal-ion-activated chlorine. Formates are somewhat atypical in that they do not contain aliphatic functionality. It might be anticipated that metal carboxylates derived from long-chain fatty acids might display greater compatibility with the polymer and, therefore, more effective stabilization. Therefore, the stability of a series of blends of a standard vinylidene chloride/methyl acrylate (5 mol%) copolymer with divalent metal decanoates (5 wt%) has been examined by thermogravimetry.

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2. Experimental

2.1. Materials

The vinylidene chloride/methyl acrylate copolymer was prepared by suspension polymerization and characterized as previously described [10]. 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 unannealed polymer displayed melting behavior characteristic of vinylidene chloride copolymers [4] with endotherms at 164.6°C 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 [10,11] confirmed the random distribution of the methyl acrylate in the polymer and established that it had been incorporated at the intended 5 mol% level.

Decanoic acid was obtained from the Adrich Chemical Company. It was converted to metal salts by dissolving the appropriate amount of decanoic acid in toluene, adding a stoichiometric amount of metal carbonate, and stirring the mixture at solvent reflux with constant removal of water formed for 6–10 h. In a typical preparation 7.66 g (0.044 mol) of decanoic acid was dissolved in 250 ml of toluene and 5.38 g (0.024 mol) of copper(II) carbonate was added. The mixture was stirred at toluene reflux under a Dean–Stark trap for 8 h. The mixture was allowed to cool and the solvent was removed by rotary evaporation at slightly elevated temperature (40°C) and reduced pressure (15 torr). The sample was dried at 30°C and 20 torr for 4 h.

2.2. Vinylidene chloride copolymer/metal decanoate blends

In general the appropriate amount of metal decanoate was dissolved in methanol, 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) decanoate was dissolved in 50 ml of methanol 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) 0.50 h at room temperature. The solvent was removed by rotary evaporation at reduced pressure (approximately 20 torr). The residual polymer/decanoate blend was transferred to a Pyrex boat and dried at approximately 20 torr and 30°C for 16 h.

2.3. Thermal aging

To better assess the utility of the metal decanoates as potential stabilizers for vinylidene chloride copolymers, portions of the polymer samples containing the various metal decanoates were oven aged at 150°C for 0.25, 0.50, 1.0, 2.0, and 4.0 h prior to analysis by thermogravimetry.

2.4. Thermal degradation

The thermal degradation characteristics of the untreated polymer, the polymer containing various metal decanoates (5 wt%), and the polymer/decanoate blends oven-aged at 150°C for various lengths of time 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 20 mg, was contained in a platinum sample pan. The temperature was ramped at a rate of 5°C min^{-1} from 30°C to 350°C.

3. Results and discussion

To access the impact of typical metal carboxylates on the stability of vinylidene chloride copolymers, blends of a vinylidene chloride/methyl acrylate (5 mol%) copolymer with several metal decanoates (5 wt%) have been examined by thermogravimetry. As may be noted in Fig. 1, the thermal degradation of the polymer is influenced to varying degrees depending on the particular nature of the metal decanoate present. None of the blends displayed greater thermal stability than does the polymer alone. Table 1 contains the

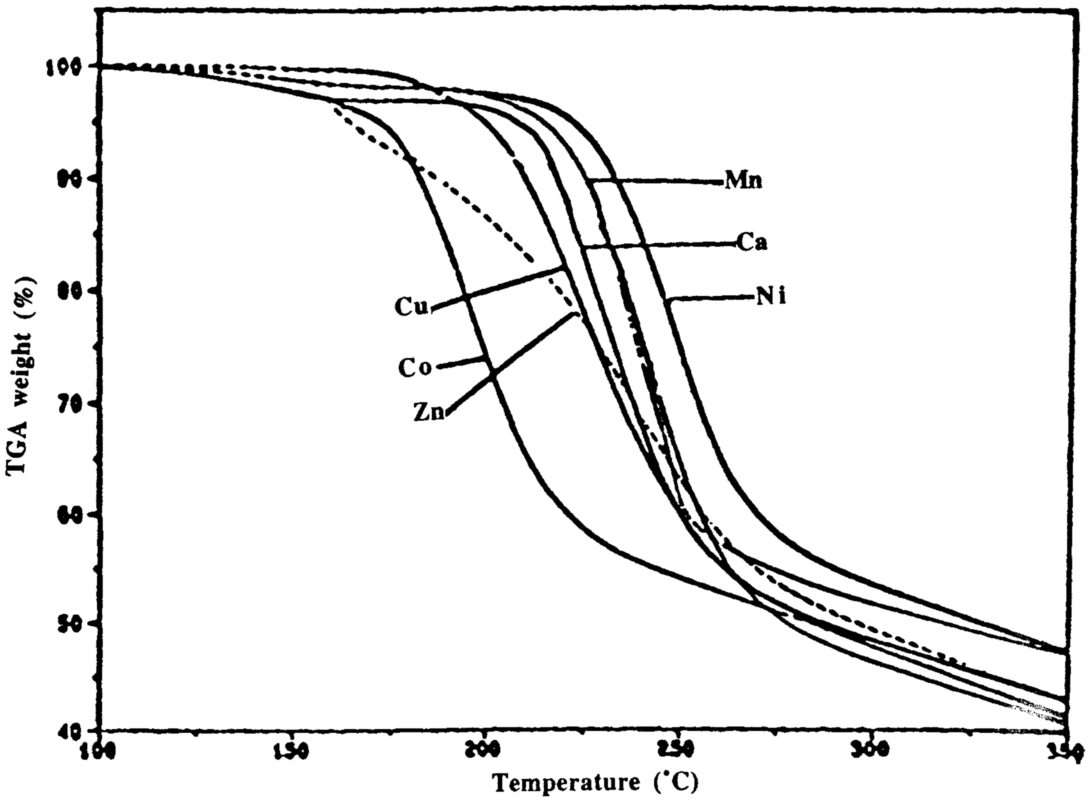

Fig. 1. Thermal degradation of a vinylidene chloride/methyl acrylate (5 mol%) copolymer in the presence of selected metal decanoates.

Table 1
Temperatures for the thermal degradation of a vinylidene chloride/methyl acrylate (5 mol%) copolymer in the presence of metal decanoates[a]

Metal decanoate	Degradation onset (°C)[a]	Temperature of maximum degradation (°C)[b]
None	209	240
Potassium	209	242
Calcium	208	223
Nickel (II)	215	248
Manganese(II)	215	236
Iron(II)	206	241
Copper(II)	190	223
Cobalt(II)	165	197
Zinc	149	248

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

[b] Maximum in the derivative plot of weight loss versus temperature.

degradation temperatures for the various blends. The presence of several metal decanoates [potassium, calcium, nickel(II), and manganese(II)] has very little impact on the degradation characteristics of the polymer. These salts contain relatively nonacidic cations. As has been previously observed the cation present must be sufficiently acidic to complex halogen but not so acidic as to strip halogen from the polymer mainchain [8,12]. Decanoate salts containing more acidic cations [iron(II), copper(II), cobalt(II), and zinc] have a much greater impact on the degradation of the polymer. In particular, the presence of zinc decanoate has a strongly negative effect on the stability of the polymer. This parallels the behavior of the polymer in the presence of metal formates [8]. The strongly acidic zinc cation promotes dehydrochlorination and thus the formation of allylic dichloromethylene groups which act as initiation sites for the thermal degradative dehydrochlorination. The other acidic cations, iron(II), copper(II), and cobalt(II), do this to a lesser extent.

Since copper(II) formate had displayed a stabilizing influence at higher temperature [8], the blend of the polymer with copper(II) decanoate was oven-aged at both 120°C and 150°C prior to analysis by thermogravimetry. The stabilizing influence of copper(II) decanoate increases with increasing pretreatment at 150°C.

4. Conclusions

The influence of various metal decanoates on the degradation characteristics of a vinylidene chloride/ methyl acrylate (5 mol%) copolymer has been examined by thermogravimetry. The stability of the polymer is little affected by the presence of metal decanoates containing nonacidic cations. Decanoate salts containing more acidic cations strongly influence the degradation of the polymer. The zinc salt, in particular, has a strongly deterimental effect on the stability of the polymer. Copper(II) decanoate, particulary at elevated temperatures, has the potential to function as an effective stabilizer for polymers of this kind.

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References

[1] G. Strandburg, P.T. DeLassus, B.A. Howell, in: W.J. Koros, (Ed.), Barrier Polymers and Structures, ch. 18, American Chemical Society, Symposium Series No. 423,Washington, DC, 1990.

[2] P.T. DeLassus, G. Strandburg, B.A. Howell, Tappi J. 71 (1988) 177.

[3] P.T. DeLassus, Barrier Polymers, Encyclopedia of Chemical Technology, vol. 3, 4th ed., Wiley, New York, 1992, pp. 931–962.

[4] R.A. Wessling, D.S. Gibbs, P.T. DeLassus, B.A. Howell, Vinylidene Chloride Polymers, Encyclopedia of Polymer Science and Engineering, vol. 17, 2nd ed., Wiley, New York, 1989, pp. 492–531.

[5] B.A. Howell, J. Polymn. Sci. Polym. Chem. Ed. 25 (1987) 1697.

[6] S. Gopalkrishnan, W.H. Starnes Jr., Polym. Prepr. 30(2) (1989) 201.

[7] P. Simon, Polym. Degr. Stab. 43 (1994) 125.

[8] B.A. Howell, C.V. Rajaram, J. Therm. Anal. 40 (1993) 575.

[9] B.A. Howell, B.S. Warner, C.V. Rajaram, S.I. Ahmed, Z. Ahmed, Polym. Adv. Tech. 5 (1994) 48.

[10] B.A. Howell, H. Liu, Thermochim. Acta 212 (1992) 1.

[11] B.A. Howell, P.B. Smith, J. Polym. Sci. Polym. Phys. Ed. 26 (1988) 1287.

[12] B.A. Howell, J.R. Keeley, Thermochim. Acta 272 (1996) 131.