

IMPACT OF INITIATOR CHARACTERISTICS ON THE THERMAL STABILITY OF VINYLIDENE CHLORIDE COPOLYMERS

B. A. Howell^{1,2*}, M. J. Johnson^{1,2}, D. E. Player², L. J. Hahnfeld^{1,2}, S. M. Kling² and M. L. Mounts²

¹Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI 48859-0001, USA

²Barrier Resins Research, Dow Chemical Company, Midland, MI 48667, USA

Two standard vinylidene chloride copolymers, the first containing approximately 9 mass% methyl acrylate and the second containing vinyl chloride at a nominal 15 mass% were prepared by radical suspension techniques using a series of peroxide and azo initiators (all of approximately the same half-life temperature for decomposition).

The nature of the initiator could impact the stability of the resulting polymer in two ways. Instability could be introduced either via end-group effects or by attack of residual initiator fragments on the finished polymer during isolation and residual monomer stripping. In this case, the relative thermal stability of the resins produced was assessed by exposing samples to heat and shear in an air environment in a two-roll mill (Brabender Prep-Mill). The rate and extent of degradation was most readily apparent from color development during this treatment. The more thermally stable polymers were produced using initiator radicals that did not attack the polymer during isolation/stripping processes.

Keywords: defect structures, polymer thermal stability as a function of chain-end structure, processing damage, radical reactivity

Introduction

Vinylidene chloride copolymers are specialty commercial materials important to the barrier plastic packaging industry [1]. The most prominent are copolymers of alkyl acrylates (4–10 mol%) and vinyl chloride (5–15 mol%) [2]. These polymers are produced by conventional chain growth polymerization. Suspension techniques are most commonly employed for the production of extrusion grade resins. Both because of the relative stability of the propagating radical and the steric demands of the halogen substituents on the monomer, polymerization occurs exclusively in a head-to-tail fashion to generate a very regular polymer free of defects except for a low level of unsaturation introduced as a consequence of the polymerization environment [3, 4]. Because of the uniformity of the vinylidene chloride sequences in these polymers they exhibit a high degree of crystallinity. This regular structure may also account for small free volume even in the amorphous regions of the polymer. As a consequence, mass transport in these materials is slow [5]. This makes them almost ideally suited for barrier plastic packaging applications. They may be used both in flexible packaging (wraps for meats, cheeses, etc.) and as components in rigid containers (pudding packs, bottles, jars, etc.).

While the vinylidene chloride sequences impart good barrier characteristics they, at the same time, ac-

count for a relatively low thermal stability of the polymers. This means that processing must be done at relatively low temperatures (150–170°C) and in the presence of lubricants and stabilizing additives. The main degradation reaction is a thermally-induced radical chain dehydrohalogenation. Degradation is initiated at allylic dichloromethylene units present in the polymer mainchain as a consequence of double bond formation (probably from chemically-induced dehydrohalogenation during polymerization or thermally-induced dehydrochlorination during monomer stripping and drying of the raw resin) during production. Initiation of degradation is followed by rapid propagation of the dehydrohalogenation reaction such that polyene sequences of sufficient size to absorb in the visible are formed [2, 3]. This thermal dehydrochlorination is a typical radical chain process with distinct initiation, propagation and termination (Fig. 1).

Thermal homolysis of an allylic carbon–chlorine bond generates a tight carbon chlorine radical pair. The chlorine atom most generally abstracts an adjacent hydrogen atom to extend the unsaturation by one unit, to regenerate an allylic dichloromethylene group, and to propagate the dehydrochlorination reaction. This is illustrated in Scheme 1.

This reaction is well suited for study by thermogravimetry since the only process occurring at modest temperatures (120–200°C) is the loss of hydrogen chloride, i.e., no other volatile products are formed at

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

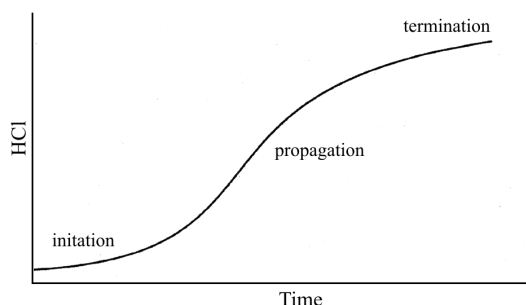
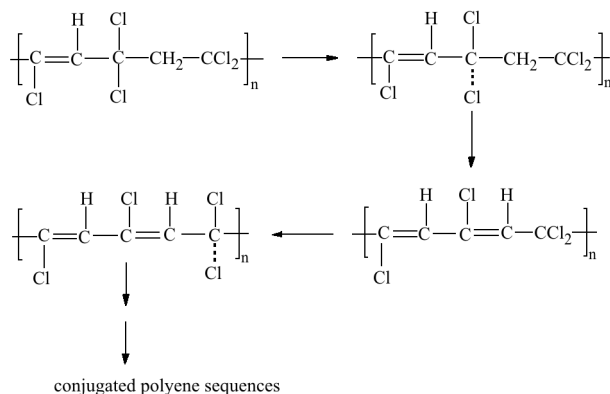


Fig. 1 Hydrogen chloride evolution for the thermal degradation of a typical vinylidene chloride polymer



Scheme 1 Mode of degradation of vinylidene chloride polymers

these temperatures [6, 7]. Therefore, the rate of change of sample mass accurately reflects the rate of degradation of a typical vinylidene chloride polymer as a function of temperature is shown in Fig. 2. As can be seen, degradation becomes prominent as the temperature approaches 200°C and occurs smoothly to reflect the loss of hydrogen chloride from each vinylidene chloride mer unit in the polymer. The curve for isothermal degradation of the same polymer at 180°C is displayed in Fig. 3. Both the initiation and propagation phases of the degradation are apparent in this plot. These regions are even more obvious in a plot of $\ln[(w_\infty - w_0)/(w_\infty - w_t)]$ vs. time where w_∞ is the mass of the sample at infinite time (w_t) taken as that mass which remains after 37.62% of the initial vinylidene chloride component mass (corresponding to the complete loss of one mole of hydrogen chloride per vinylidene chloride unit in the polymer) has been lost; w_0 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. This is illustrated in Fig. 4. Rate constants for both initiation (k_i) and propagation (k_p) may be obtained from the appropriate linear portions of this plot.

The degradation leads to color development even at very low levels of hydrogen chloride elimination (<1% of that available in the polymer). The level of unsaturation, i.e., potential sites for the initiation of degradation, is strongly influenced by the polymer-

ization environment. In addition, a number of other variables including the nature of the polymerization initiator [specifically the nature of the initiating radical, e.g., it has been suggested that polymer produced using a carbon radical as the initiating species exhibits greater thermal stability than does polymer generated from an alkoxy radical—presumably because of the presence of an alkoxy chain end (C–O bond) in the latter] and the level of residual polymerization aids may influence the stability of the polymer. To better define the influence of initiator choice on the

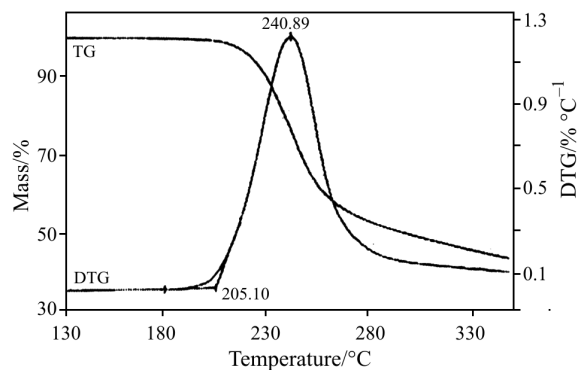


Fig. 2 TG/DTG curves for the degradation of a typical vinylidene chloride polymer

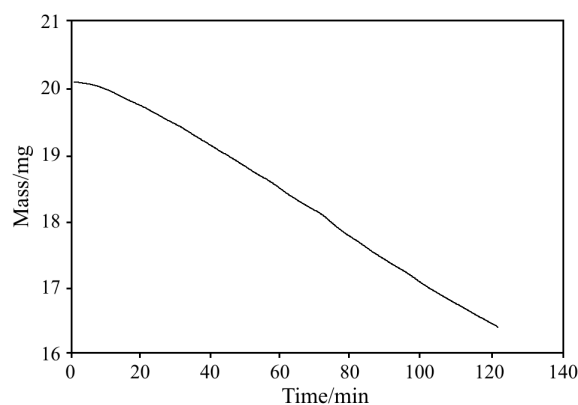


Fig. 3 Degradation of a typical vinylidene chloride polymer at 180°C

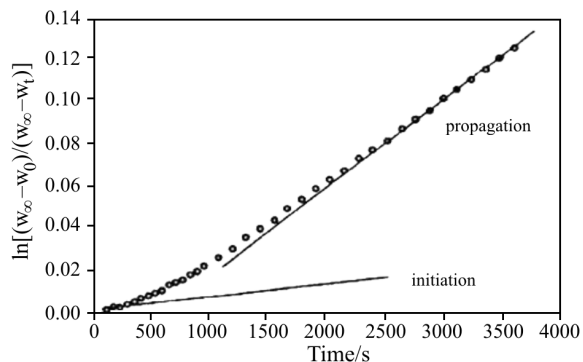


Fig. 4 Thermal degradation of a typical vinylidene chloride polymer at 180°C

stability of the finished polymer two sets of vinylidene chloride copolymers have been prepared using a series of initiators under virtually identical conditions and the stability of the resulting polymers when subjected to heat and shear in air evaluated by observing the rate of color formation.

Experimental

Polymers

Two standard vinylidene chloride polymers were prepared by radical suspension techniques using previously described methods [3]. The first was a vinylidene chloride/methyl acrylate (9 mass%) copolymer. Four initiators of similar decomposition temperatures were used: dilauroyl peroxide (LPO), 2,2'-azobis(2-methylbutronitrile) (AMBN), *t*-butyl peroctoate (TBPO) and *t*-amyl peroctoate (TAPO). The 10-h half-life temperature for the decomposition of these initiators is 61, 66, 72 and 73°C, respectively. The second was a vinylidene chloride/vinyl chloride (15 mass%) copolymer. Initiators used for the generation of this polymer were isopropyl peroxydicarbonate (IPP), 2,2'-azobis(2,4-dimethylpentanenitrile) (ADPN), and *t*-amyl peroxyvalate (TAPP). The 10-h half-life temperature for the decomposition of these initiators is 50, 52 and 55°C, respectively. Polymerization variables, other than the choice of initiator, were kept as nearly identical as possible. In all cases, the polymers produced had a mass average molecular mass of approximately 100000 with a polydispersity of about two.

Instrumentation/sample evaluation

A two-roll mill (Brabender Prep-Mill) was utilized for an evaluation of polymer thermal stability. The functional portion of the mill consists of two Duronickel rollers corotating at a speed differential of 1.3:1. The rollers may be operated at variable speed (0–30 rpm) and temperature (oil heated; up to 300°C). For this study a speed of 13 rpm and a temperature of 170°C were utilized.

Prior to exposure to heat and shear in the two-roll mill all samples were blended for two minutes with 1% epoxidized soybean oil, 0.9% ground high density polyethylene, 0.45% Allied 617A polyethylene wax and 0.18% Allied 629A polyethylene wax in a Prodex Herschel blender operating at 1800 rpm.

Polymer (typically 200 g) was placed in the mill, the time to fusion noted, and samples removed at 3-min intervals for 0.5 h. All samples were pressed into square plaques and mounted, in order of removal from the mill, on white posterboard. The plaques were then evaluated for color, texture, gloss and clarity.

Results and discussion

While thermogravimetry represents the most ideal method for assessing thermal stability of vinylidene chloride copolymers other methods offer some advantage, particularly, with respect to the degradation to be expected under processing conditions where shear is a contributing factor.

The impact of the choice of polymerization initiator on the stability of two typical vinylidene chloride polymers, one a methyl acrylate copolymer and the other a vinyl chloride copolymer, has been examined by observing the progress of degradation for a polymer sample in air at 170°C under shear in a two-roll mill. The methyl acrylate copolymer was generated using four different initiators of similar decomposition temperature, dilauroyl peroxide (LPO), 2,2'-azobis(2-methylbutronitrile) (AMBN), *t*-butyl peroctoate (TBPO) and *t*-amyl peroctoate (TAPO). In terms of composition and molecular mass the polymer produced was essentially the same in each case. The stability of the polymer produced using the various initiators was assessed by noting the rate of color development for a fully fused sample in a two-roll mill. As a function of initiator used the polymer stability was LPO>TAPO>TBPO>>AMBN. This order was somewhat unexpected. The initiating radicals generated from LPO, TAPO and TBPO are all oxygen-centered radicals while that from AMBN is a carbon-centered radical. If the polymer stability reflected chain end structure, the polymer generated using AMBN should have displayed the greatest stability. It seems far more likely that the impact on stability arises as a consequence of damage to the polymer from radicals generated by the decomposition of residual initiator in the raw polymer during monomer stripping and drying. In fact, if a good radical scavenger was added to the resin after polymerization but prior to the finishing steps, the stability of the polymer was markedly improved. Similar observations were made for a vinylidene chloride/vinyl chloride copolymer produced using three different initiators, isopropyl peroxydicarbonate (IPP), 2,2'-azobis(2,4-dimethylpentanenitrile) (ADPN) and *t*-amyl peroxyvalate (TAPP). The polymer stability suggests an order of initiator suitability of IPP>TAPP>ADPN. This ordering is consistent with that observed for the vinylidene chloride/methyl acrylate copolymer and probably reflects the relative aggressiveness toward the polymer of radicals generated from residual initiator decomposition in post-polymerization operations.

Conclusions

As assessed by the degradation characteristics for the fused polymer under shear in air, the initiator utilized for polymerization clearly has an impact on the stability of vinylidene chloride copolymers. The effect probably arises as a consequence of residual initiator decomposition in the polymer during post-polymerization monomer stripping and drying.

Acknowledgements

A summer research internship (LJH) provided by the Dow Chemical Company is gratefully acknowledged.

References

- 1 P. T. DeLassus, W. E. Brown and B. A. Howell, *Encyclopedia of Packaging Technology*, 2nd Ed., John Wiley and Sons, Inc., New York, NY 1997, pp. 958–961.
- 2 R. A. Wessling, D. S. Gibbs, P. T. DeLassus, B. E. Obi and B. A. Howell, *KirkOthmer Encyclopedia of Chemical Technology*, Vol. 24, 2nd Ed., John Wiley and Sons, Inc., New York, NY 1997, pp. 883–923.
- 3 B. A. Howell, *J. Polym. Sci., Polym. Chem. Ed.*, 25 (1987) 1681.
- 4 B. A. Howell, *Thermochim. Acta*, 134 (1988) 207.
- 5 B. A. Howell, *J. Therm. Anal. Cal.*, 83 (2006) 53.
- 6 B. A. Howell and J. A. Ray, *J. Therm. Anal. Cal.*, 83 (2006) 63.
- 7 P. T. DeLassus, G. Strandburg and B. A. Howell, *Tappi J.*, 71 (1988) 177.

DOI: 10.1007/s10973-005-7486-x