

DEGRADATION OF VINYLIDENE CHLORIDE/METHYL ACRYLATE COPOLYMERS IN THE PRESENCE OF METAL FORMATES

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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. The dehydrochlorination reaction is a typical chain process with distinct initiation, propagation, and termination phases. It has been demonstrated that initiation of degradation is strongly facilitated by the presence of unsaturation along the backbone. Such unsaturation may be introduced via interaction of the polymer with a variety of agents which might commonly be encountered during polymerization or processing. The presence of an unsaturated unit within the polymer generates an allylic dichloromethylene which may function as a major defect (labile) site for the initiation of degradation. The conversion of these dichloromethylene units into non-reactive groups would interrupt propagation of the dehydrochlorination reaction and lead to the stabilization of the copolymer. Potential stabilization in the presence of metal formates has been examined using a vinylidene chloride/methyl acrylate (five mole percent) copolymer and thermogravimetric techniques. The effect of the metal formate on the stability of the polymer reflects the relative halogenophilicity of the metal cation present. Metal formates (sodium, calcium, nickel(II) and to a lesser extent lead(II), cadmium, manganese(II) and magnesium) may be expected to be ineffective as stabilizers for vinylidene chloride copolymers. At the other extreme, metal formates which contain cations sufficiently acidic to actively strip chlorine from the polymer backbone, e.g., zinc formate, will function to enhance the degradation process. An effective carboxylate stabilizer must contain a metal cation sufficiently acidic to interact with allylic chlorine and to facilitate its displacement by the carboxylate anion. Copper(II) formate may possess the balance of cation acidity and carboxylate activity to function as an effective stabilizer for vinylidene chloride copolymers.

Keywords: copolymers, dehydrohalogenation, halogenophilicity, Lewis acidity, kinetics, stabilization

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 can be promoted by the presence of any of a variety of agents capable of introducing random double bonds into the polymer backbone [4]. Unsaturation in these polymers appears to be a principal defect structure (allylic dichloromethylene units) responsible for degradation [7]. Effective removal of allylic dichloromethylene units might be expected to exert a strongly stabilizing influence on the polymer [8]. To evaluate the potential of metal formates for the stabilization of vinylidene chloride copolymers, the thermal degradation characteristics of several surface blends of metal formates (sodium, calcium, nickel(II), lead(II), cadmium, manganese(II), magnesium, copper(II) and zinc) with a vinylidene chloride/methyl acrylate (5 mol%) copolymer have been examined by thermogravimetry.

Experimental

Materials

The vinylidene chloride/methyl acrylate copolymer was prepared by suspension polymerization and characterized as previously described [9]. 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° 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 [9, 10] confirmed the random distribution of the methyl acrylate in the polymer and established that it had been incorporated at the intended five mole percent level.

Vinylidene chloride copolymer/formate blends

In general the appropriate amount of metal formate was dissolved in distilled water, 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) formate was dissolved in 250 ml of distilled water 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 40°C. The solvent was removed by rotary evaporation at reduced pressure (approximately 20 torr) and elevated temperature (approximately 80°C; hot water bath). The residual polymer/formate blend was transferred to a Pyrex boat and dried at approximately 20 torr and 60°C for 48 hr.

Thermal aging

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

Thermal degradation

The thermal degradation characteristics of the untreated polymer, the polymer containing various metal formates (5 wt%), and the polymer/formate 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 time (or 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 30 mg, was contained in a platinum sample pan. For dynamic runs, the temperature was ramped at a rate of 5 deg·min⁻¹ from 30° to 350°C. For isothermal runs, the temperature of the cell was rapidly brought to 180°C (with the TA Instruments high intensity cell about two minutes was required for temperature equilibration) and weight loss was monitored as a function of time for at least two half-lives. Under these conditions, the clean loss of mass corresponding to dehydrochlorination was observed in every case [7]. Temperature control was ± 0.02°C. Rate constants were determined from the slope of a plot of

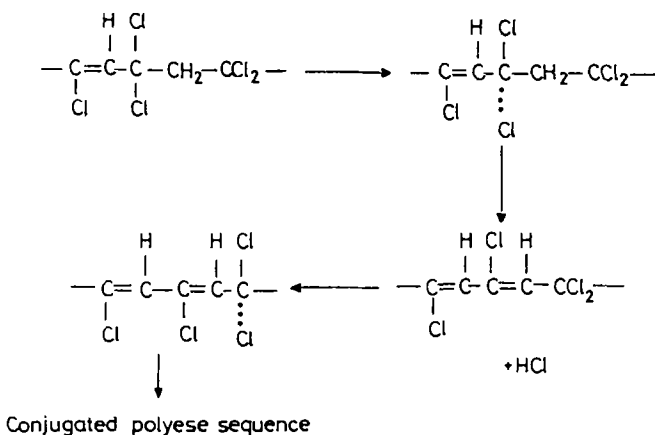
$$\ln \left[\frac{w_{\infty} - W_0}{w_{\infty} - W_t} \right] \text{ vs. time}$$

where w_{∞} is the weight of the sample at infinite time (t_{∞}) taken as that weight which would remain after 37.62% of the initial vinylidene chloride component

weight (corresponding to the complete loss of one mole of hydrogen chloride per vinylidene chloride unit in the copolymer) had been lost; w_0 is the weight at time zero (t_0), i.e., the time at which the first data point was recorded; and w_t is the weight at anytime, t , during the run. The initial portion of this plot was used to determine the rate constant for degradation initiation, k_i , and the later portion of the plot was used to obtain the constant, k_p , for the propagation segment of the reaction [9]. The values reported correspond to the linear, least-squares best fit of the data. In all cases, an excellent fit was observed.

Results and discussion

Because of their superior barrier to the transport of both small molecules, principally oxygen, and flavor and aroma constituents, vinylidene chloride copolymers occupy a place of prominence in the food packaging industry and as a consequence are commercially important materials [1-3]. At process temperatures these polymers tend to evolve hydrogen chloride with the consequent formation of double bonds along the polymer backbone. As shown below the introduction of this unsaturation generates an allylic dichloromethylene unit which is susceptible to thermally-induced loss of a chlorine atom which abstracts an adjacent hydrogen atom [7]. Propagation of the dehydrochlorination reaction in this way leads to the formation of a conjugated polyene sequence and resultant coloration of the polymer. For many applications



this color is objectionable and effective means to prevent its formation (and, subsequent, more extensive degradation) continue to be sought. Conversion of allylic dichloromethylene units to less reactive moieties would interrupt the propagation

sequence and enhance the thermal stability of the polymer. Removal of labile allylic chlorine in this way is analogous to the stabilization of poly(vinyl chloride) with lead, tin, or cadmium esters [8].

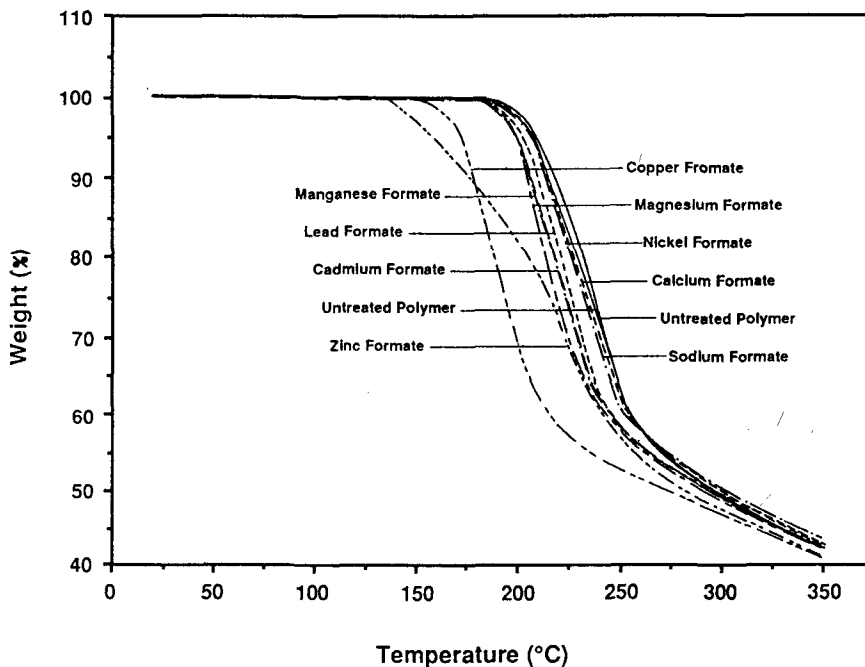


Fig. 1 Thermal degradation of a vinylidene chloride/methyl acrylate (5 mol%) copolymer in the presence of selected metal formates

To explore the potential offered by this approach, the degradation of several blends of metal formates with a vinylidene chloride/methyl acrylate (five mole percent) copolymer has been examined by thermogravimetry. The loading of formate was five percent based on the total mass of the blend in each case. In initial qualitative comparisons, all the polymer/formate blends were somewhat more prone to degradation than was the untreated polymer. This is illustrated in Fig. 1. The stability of the copolymer treated with sodium, calcium or nickel(II) formate is comparable to that of the untreated polymer. The presence of other metal formates, lead(II), cadmium, manganese(II) and magnesium formate, brings about a modest but noticeable destabilization of the polymer. Copper(II) formate and more specifically zinc formate have an even larger effect on the stability of the polymer. In fact, the presence of zinc formate has a strongly negative impact on the stability of the polymer.

Table 1 Rate constants for the thermal degradation of a vinylidene chloride/methyl acrylate (five mole percent) copolymer in the presence of metal formates at 180°C

| Metal formate | $k_i \times 10^4 (\text{sec}^{-1})^a$ | $k_p \times 10^4 (\text{sec}^{-1})^a$ |
|-----------------------|---------------------------------------|---------------------------------------|
| None | 0.36±0.05 | 1.35±0.11 |
| Sodium formate | 0.45±0.02 | 1.29±0.21 |
| Calcium formate | 0.28±0.01 | 1.26±0.18 |
| Nickel(II) formate | 0.37±0.01 | 1.22±0.14 |
| Lead(II) formate | 0.29±0.04 | 1.74±0.04 |
| Cadmium formate | 0.71±0.02 | 3.90±0.27 |
| Manganese(II) formate | 0.67±0.05 | 3.04±0.34 |
| Magnesium formate | 0.37±0.00 | 3.83±0.45 |
| Copper(II) formate | 0.39±0.03 | 20.00±0.01 |
| Zinc formate | 4.77 ^b | 166 ^b |

^a Averages of at least two determinations

^b Values by extrapolation from degradation at lower temperatures; $E_{ai} = 26.4$ kcal/mole and $E_{ap} = 39.5$ kcal/mole

Rate constants for the thermal degradation at 180°C of the polymer containing five weight percent of selected metal formates are presented in Table 1. In general, the impact of the metal formate on the stability of the polymer reflects the relative halogenophilicity of the metal cation present. Formate salts containing cations with little affinity for halogen (sodium, calcium, nickel(II)) have a very small impact on the thermal degradation of the polymer. As can be seen from the data presented in Table 1, neither the initiation rate constant, k_i , nor the propagation rate constant, k_p , for the degradation reaction is significantly influenced by the presence of these metal formates. As indicated by the increase in the magnitude of the propagation rate constant, the presence of formates containing metal cations capable of passive acceptance of chloride [lead(II), cadmium, manganese(II), magnesium] leads to a modest increase in the rate of degradation. Copper(II) is somewhat more effective in complexing chloride ion while, as has been previously noted [11], zinc ion actively strips chlorine from the polymer backbone and its presence brings about a dramatic increase in the rate of degradation for the polymer. The relative halogenophilicities of the metal cations as reflected by the onset temperature for degradation are shown in Table 2. To better assess the utility of these metal formates as potential stabilizers for vinylidene chloride copolymers, the polymer samples containing the various metal formates were oven aged at 150°C for 0.25, 0.50, 1.0, 2.0 and 4.0 hours prior to analysis by TG. At this temperature, the formate ion should be more effective in removing allylic chlorine than it is at room temperature. Based on the results of these studies the metal formates examined may be grouped into three categories: those that es-

Table 2 Onset temperatures for the thermal degradation of a vinylidene chloride/methyl acrylate (five mole percent) copolymer in the presence of metal cations

| Metal cation ^a | Degradation onset $^{\circ}\text{C}^{\text{b}}$ | Temperature of maximum degradation $^{\circ}\text{C}^{\text{c}}$ |
|---------------------------|---|--|
| Ca^{2+} | 172.5 | 232.9 |
| Ni^{2+} | 171.6 | 231.6 |
| Na^{+} | 170.0 | 232.2 |
| Mg^{2+} | 165.6 | 210.2 |
| Mn^{2+} | 164.9 | 219.6 |
| Pb^{2+} | 162.6 | 224.0 |
| Cd^{2+} | 159.9 | 219.6 |
| Cu^{2+} | 141.3 | 188.4 |
| Zn^{2+} | 126.2 | 224.5 |

^aPresent as the formate salt at a level of 5% by weight

^bTaken as the change in slope for the derivative plot of weight loss vs. temperature

^cTaken as the maximum of the derivative plot of weight loss vs. temperature

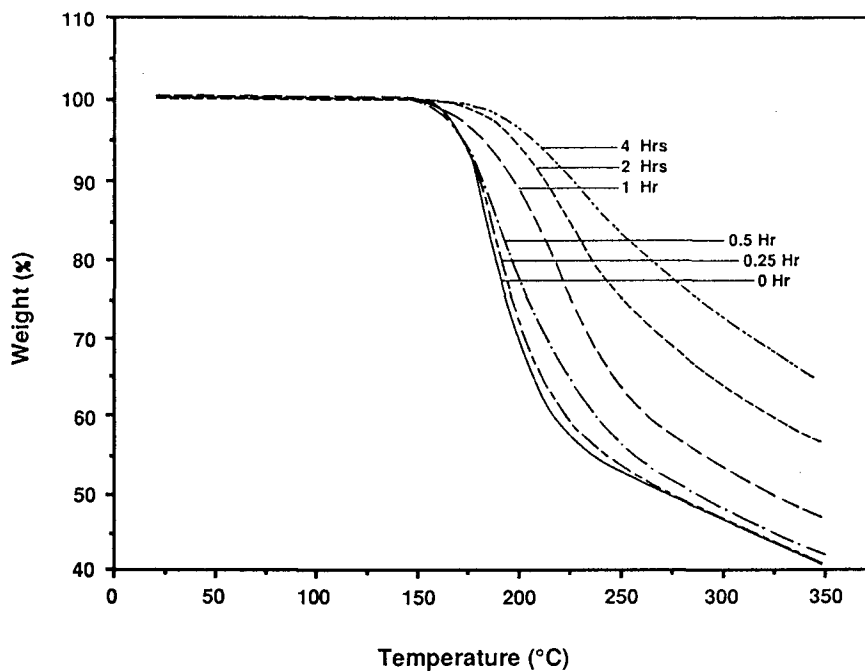


Fig. 2 Thermal degradation of a vinylidene chloride/methyl acrylate (5 mol%) copolymer aged at 150°C in the presence of five weight percent copper(II) formate for 0.25, 0.50, 1.0, 2.0 and 4.0 hours

sentially have no effect on the rate of degradation of the polymer (sodium, calcium and nickel(II) formate); those that modestly enhance the rate of initiation of degradation but modestly decrease the propagation rate for degradation (manganese(II), lead(II), cadmium, and magnesium formate); and those that markedly decrease both the initiation rate and more particularly the propagation rate for the degradation, i.e., which have a stabilizing influence on the polymer (copper(II) formate).

Table 3 Degradation temperatures for a methyl acrylate (five mole percent)/ vinylidene chloride copolymer oven-aged at 150°C in the presence of copper(II) formate (five weight percent)

| Aging time/h | Degradation onset/°C ^a | Degradation maximum/°C ^b |
|--------------|-----------------------------------|-------------------------------------|
| 0.00 | 140 | 188.4 |
| 0.25 | 145 | 190.6 |
| 0.50 | 165 | 192.5 |
| 1.00 | 185 | 222.0 |
| 2.00 | 195 | 225.3 |
| 4.00 | 205 | 227.6 |

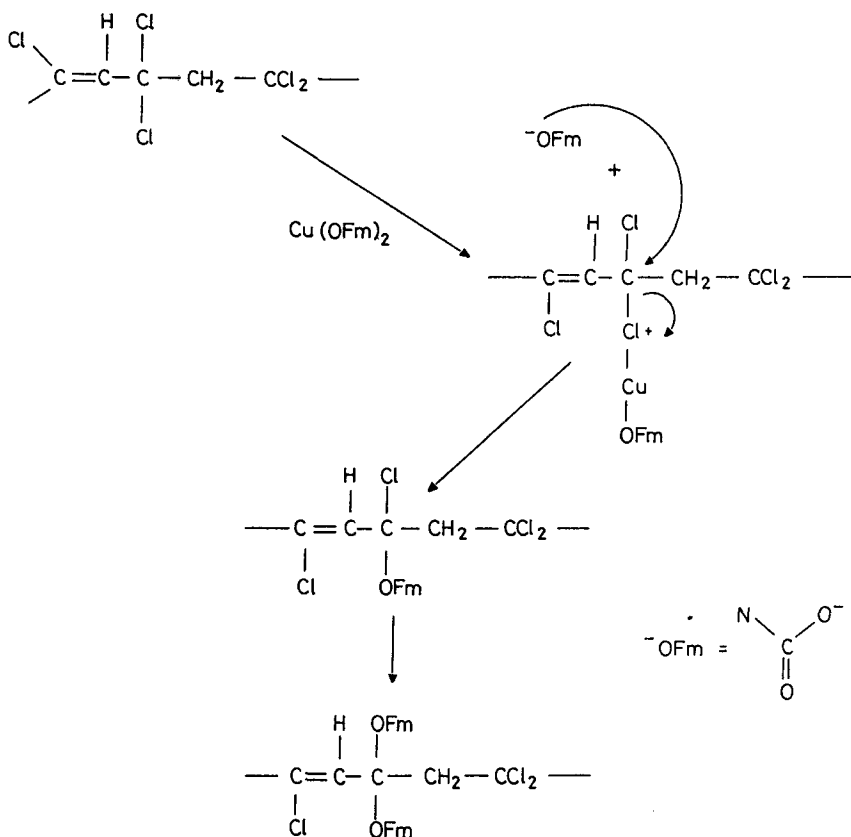
^aChange in slope of the derivate plot of weight loss vs. temperature

^bMaximum in the derivative plot of weight loss vs. temperature

As can be seen in Fig. 2, at a temperature (150°C) approximating process temperatures, copper(II) formate is effective in retarding the degradation reaction. The sample aged for two hours in the presence of copper(II) formate displayed considerably greater stability than did the unaged polymer containing copper(II) formate. Aging for longer times in the presence of copper(II) formate further enhanced the apparent stability for the polymer (Fig. 2). Although the polymer samples aged for times shorter than two hours in the presence of copper(II) formate are characterized by larger initiation rate constants and lower onset temperatures for degradation (Table 3) than those displayed by the unaged polymer containing copper(II) formate, the overall stability of these materials may be greater (lower rate of degradation propagation) than for the unaged polymer. Additionally, the polymer treated with zinc formate displays similar characteristics, i.e., with increased aging time at 150°C, the stability of the polymer does tend to increase. However, because of the high acidity of the zinc ion the effect is much less dramatic than that observed for copper(II) formate. The degradation of the polymer in the presence of manganese(II) and magnesium formate is also inhibited but to an even lesser extent. Of the formates examined, it is clear that only copper(II) formate may have the balance of cation acidity and anion reactivity required to function as an effective stabilizer for vinylidene chloride copolymers. Based upon the observations here, it would appear that the

cation must be capable of sufficient interaction with bound chlorine to enhance the electrophilicity of allylic dichloromethylene units within the polymer such that attack by formate acting as a nucleophile is effective, i.e., such that allylic chlorine atoms function as good leaving groups. If interaction of the metal cation with allylic chlorine atoms were not required, alkali and alkaline earth metal formates would be expected to function as good stabilizers in this system.

The probable mode of stabilization by copper(II) formate is depicted below.



If the cation is incapable of significant interaction with allylic halogen (sodium, calcium, nickel(II) and to a lesser extent lead(II), cadmium, manganese(II) and magnesium) no or little stabilization is observed. If, on the other hand, the cation is sufficiently acidic to remove allylic chlorine atoms without participation by the formate anion, rapid degradative dehydrochlorination is promoted. This would appear to be the case for zinc formate. It may well be that

degradative dehydrochlorination of vinylidene chloride copolymers in the presence of zinc ion is an ionic chain process [12].

Conclusions

In conclusion, metal formates (and other carboxylates) containing weakly coordinating cations may be expected to be ineffective as potential stabilizers for vinylidene chloride copolymers. At the other extreme, metal formates which contain cations sufficiently acidic to actively strip chlorine from the polymer backbone, e.g., zinc formate will function to facilitate the degradation process. An effective carboxylate stabilizer must contain a metal cation sufficiently acidic to interact with allylic chlorine and to facilitate its displacement by the carboxylate anion. The results of this study suggest that copper(II) formate may have the proper balance of cation acidity and carboxylate activity to function as an effective stabilizer for vinylidene chloride copolymers.

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Zusammenfassung — Vinylidenchloridkopolymere haben eine Anzahl hervorragender Eigenschaften, am auffallendsten ist der große Widerstand, der dem Transport von Sauerstoff und anderen kleinen Molekülen entgegengesetzt wird. Hieraus ergibt sich die Beliebtheit dieser Materialien in der Verpackungsindustrie. Bei den Fertigungstemperaturen neigen diese Kopolymere zu einer degradativen Dehydrochlorierung. Die Dehydrochlorierungsreaktion ist ein typischer Kettenprozeß mit ausgeprägten Phasen für Kettenstart, Kettenfortpflanzung und Kettenabbruch. Es wurde gezeigt, daß der Abbaubeginn durch die Gegenwart von Ungesättigtheiten entlang der Hauptkette stark erleichtert wird. Derartige Ungesättigtheiten können durch Wechselwirkung des Polymers mit einer Reihe von Stoffen eingebracht werden, die für gewöhnlich während der Polymerisation des Fertigungsprozesses anwesend sind. Die Existenz einer ungesättigten Einheit innerhalb des Polymers bildet ein Allyldichlormethylen, was als eine Hauptdefektstelle zum Abbaubeginn fungieren kann. Die Umwandlung dieser Dichlormethylen-Einheiten in nichtreaktive Gruppen unterbricht die Kettenfortpflanzung der Dehydrochlorierungsreaktion und führt zur Stabilisierung des Kopolymers. Mittels TG wurde eine potentielle Stabilisierung von Vinylidenchlorid/Methylmethacrylat (fünf Molprozent) Kopolymer in Gegenwart von Metallformiaten untersucht. Der Effekt der Metallformiate auf die Stabilität des Polymers widerspiegelt die relative Halogenophilie der anwesenden Metallkationen. Von Metallformiaten (Natrium, Calcium, Nickel(II) und in geringerem Maße Blei(II), Cadmium, Mangan(II) und Magnesium) kann man annehmen, daß sie als Stabilisatoren für Vinylidenkopolymere wirkungslos sind. Im anderen Grenzfall werden Metallformiate mit Kationen, die genügend sauer sind, um Chlor aktiv von der Polymerhauptkette zu entfernen, wie z.B. Zinkformiat, den Abbauprozeß begünstigen. Ein effektiver Carboxylatstabilisator muß ein Metallion enthalten, welches genügend sauer ist, um mit dem allylischen Chlor in Wechselwirkung zu treten und dessen Ersatz durch ein Carboxylatanion zu erleichtern. Kupfer(II)-formiat hält möglicherweise das Gleichgewicht zwischen Kationacidität und Carboxylataktivität, um als wirkungsvoller Stabilisator für Vinylidenchloridkopolymere zu fungieren.