

Environmental Stability of Ethylene-Acrylic Acid Adhesive Copolymers Bonded to Metal Substrates

B. WARGOTZ, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974*

Synopsis

A study was conducted on the influence of high humidity and temperature on aluminum and copper sheet coated with ethylene-acrylic acid or ethylene-methacrylic acid copolymers. Infrared spectrometric and differential thermal analysis data indicate that a contributing cause to failure of the bond between the acrylic acid copolymers and copper is the solubilization of an underlying weak oxide layer under conditions of the test. No significant weakening of the bond of aluminum-adhesive copolymer was observed under high humidity. From oxygen uptake studies, thermogravimetric analysis in air, and infrared spectra of polymer bonded to metals, a general understanding of the thermal-oxidative stability of the ethylene-acrylic and ethylene-methacrylic copolymers has emerged. The acrylic acid copolymers are less stable in an oxidative environment than ethylene homopolymers and the ethylene-alkyl acrylate copolymers.

INTRODUCTION

Ethylene copolymers containing acrylic acid or methacrylic acid units as well as the partially neutralized form of these thermoplastic adhesive copolymers have been suggested for use in new communication cable designs.^{1,2} The use of these materials is of particular interest in metal-adhesive copolymer-polyethylene composites and in bimetallic laminates. Thermoplastic adhesive copolymers provide the contact adherence of a hot melt adhesive with the cohesive strength of a polymer.

The ethylene-acrylic acid (EAA) and ethylene-methacrylic acid (EMAA) copolymers are comparatively new materials. The mechanical properties and aging behavior of these materials are largely unknown.³⁻⁵ This paper presents information on the behavior of EAA and EMAA in contact with copper and aluminum under high humidity conditions; data on the thermal-oxidative stability of these copolymers alone and in contact with metal surfaces are also given.

EXPERIMENTAL

Laminates

Metal-polymer laminates were prepared by extrusion coating of polymer (0.001-0.002 in. thickness) on used as received copper (0.003 in. thick, full

TABLE I
Properties of Ethylene-Acrylic Acid and
Ethylene-Methacrylic Acid Copolymers

Sample	Melt index	Acid content, % by weight
EAA	5.0	7.5
EMAA	10.0	9.0

annealed Grade ETP) or aluminum (0.004–0.005 in., Grade 1145 or 1100). The melt index and acid content of the polymers prior to coating on the metal are shown in Table I.

Specimens 10 in. in length and 1 in. wide were exposed at 70°C and 95% RH. At various intervals up to 60 days, samples were removed and placed in a desiccator containing anhydrous MgSO₄. After one week of drying the specimens were examined by the following techniques.

Specular Reflectance Sampling. The device employed for obtaining the specular reflectance spectra of the polymer bonded to metal was a Wilks Scientific Corporation Model 22 specular reflectance attachment used with a Beckman IR-8 infrared spectrophotometer. The appropriate metal sheet was employed in the reference attachment.

Differential Thermal Analysis (DTA). The R. L. Stone Model KAW controlled atmosphere DTA unit was employed (helium atmosphere). The metal-polymer composite was examined. A Perkin-Elmer differential scanning calorimeter 1-A was used for more quantitative determination of the thermal properties of the polymer (nitrogen atmosphere).

Copolymers

EAA and EMAA of similar acid content (Table I) were purified by dissolving into reagent grade toluene under a nitrogen atmosphere. The polymers were precipitated with methanol and dried under vacuum.

Oxygen Uptake Studies. The unstabilized polymer was compression-molded at 120°C and 40,000 psi to films 0.010 in. thick. Samples approximately 0.1 g in weight were exposed at 60, 80, 100, 120, and 140°C in an oxygen-uptake apparatus.⁶

Thermogravimetric Analysis. The unstabilized EAA and EMAA samples (Table I) were heated in air from 25 to 500°C at a heating rate of 2°C/min in the programmed study and under isothermal conditions in air at 260, 310, 365, and 395°C. An apparatus described earlier was employed in this study.⁶

RESULTS AND DISCUSSION

Humidity Effects

Figure 1 shows the infrared absorption spectra of EAA and EMAA in the 900–2000 cm⁻¹ region. Both resins exhibit un-ionized acid carbonyl

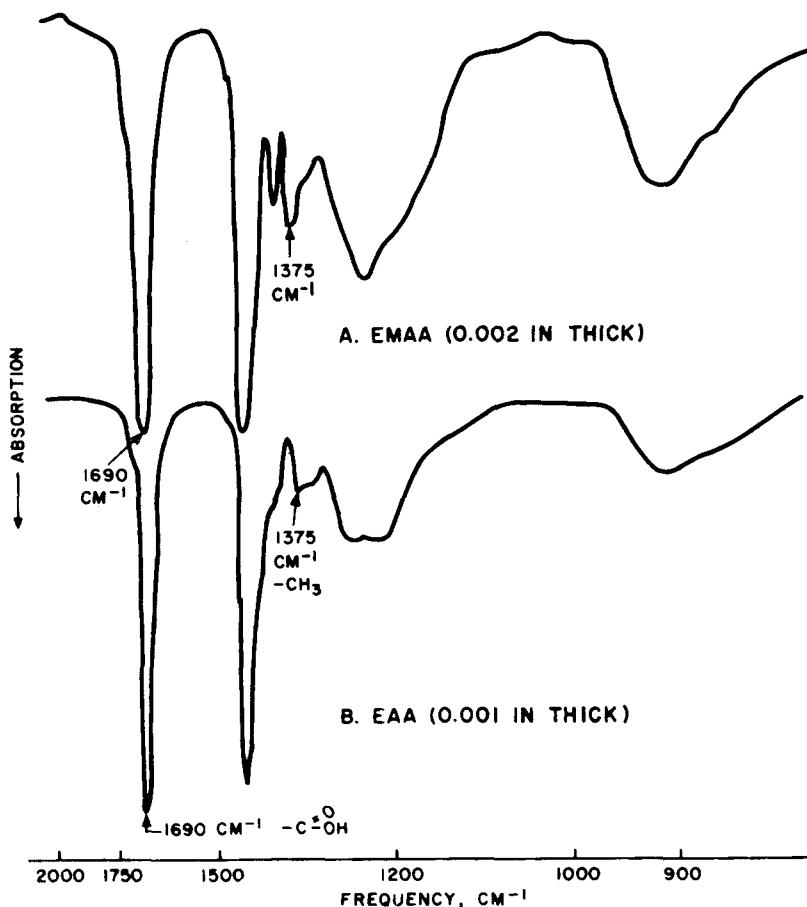


Fig. 1. Infrared spectra of EMAA and EAA.

absorption at approximately 1690 cm^{-1} . EAA and EMAA show slight differences in the region of the methyl group ($-\text{CH}_3$) absorption (1375 cm^{-1}). The increased intensity in this region for EMAA is probably due to the $-\text{CH}_3$ groups of the methacrylic acid and not to increased $-\text{CH}_3$ branching in the ethylene segments.

The specular reflectance spectra in the $1300\text{--}2000\text{ cm}^{-1}$ region of copper-EAA samples (copper reference) aged 5 days and 14 days are shown in Figures 2A and 2B. Of particular note is the development of an absorption band at 1600 cm^{-1} after only 5 days at 70°C and 95% RH. EMAA, when aged under the same conditions, also absorbs at 1600 cm^{-1} . As aging was continued, the intensity of this band increased with slight reduction of the acid carbonyl absorption. The differential transmission absorption spectrum (Fig. 2C) was obtained on EAA specimens aged 31 days and freed by chemically etching the copper in an ammonium persulfate solution. A control copper-EAA laminate treated in a similar manner gave

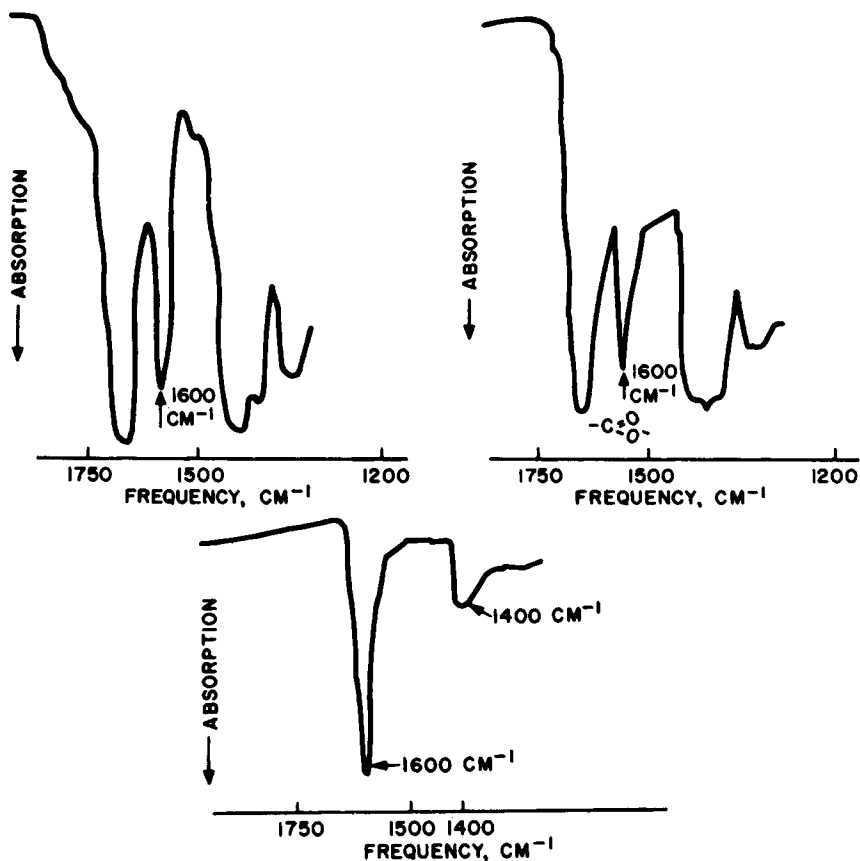


Fig. 2. Infrared spectra of aged EAA: (A) specular reflectance spectrum, Cu-EAA aged 5 days, 70°C/95% RH; (B) specular reflectance spectrum, Cu-EAA aged 14 days, 70°C/95% RH; (C) differential transmission spectrum, EAA aged 31 days, 70°C/95% RH.

EAA which was used as reference. Apparently, aging of copper-EAA and copper-EMAA at high humidity results in the formation of a copper salt of the acid function as indicated by carboxylate ion absorption⁷ at 1600 and 1400 cm^{-1} . The green-blue color observed is characteristic of the Cu^{+2} valence state. The green-blue color of the recovered film is not changed by prolonged immersion in distilled water; however, the color is lost when the film is exposed to cold, concentrated hydrochloric acid. The spectrum of film treated with the acid is identical to that of the control EAA and indicates no apparent decomposition.

The EAA-copper bond has deteriorated after only 5 days at high humidity since the EAA can be readily peeled from the copper surface by hand.* This is not true with control specimens.

* Frustrated multiple internal reflectance spectrum (KRS-5 crystal, -45°) sampling of the surfaces of the peeled, humidity-aged EAA showed the carboxylate ions to be concentrated at the copper-adhesive copolymer interphase.

Specular reflectance sampling of the aluminum-EAA or aluminum-EMAA laminates after aging up to 60 days at 70°C and 95% RH revealed no significant changes in the spectra of these composites. In addition, the EAA and EMAA coatings were not readily peeled from the aluminum surface after aging.

DTA data were obtained to determine if the loss of strength of the copper-EAA bond was due to the chemical interaction of EAA with copper, a morphological transformation in the bulk or at the metal-adhesive copolymer interphase (boundary layer),⁸ or a combination of these.

The general shape of the endotherm was found to be similar for EAA on aluminum or copper. Figure 3 shows a typical DTA curve. The progressive growth of the doublet observed in the melting endotherm as a function of aging (Fig. 4) occurred irrespective of the metal substrate employed.

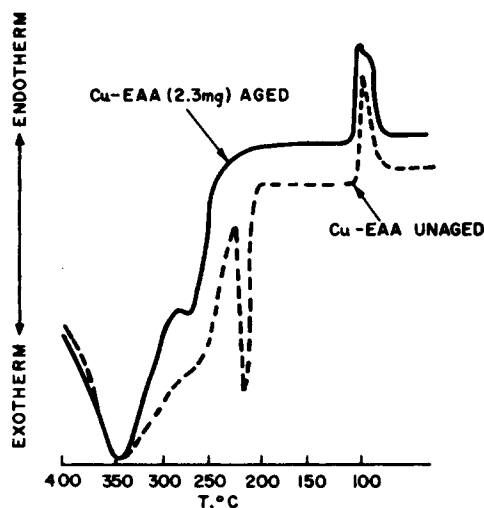


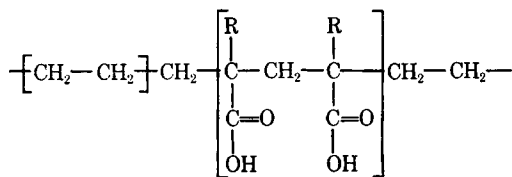
Fig. 3. Differential thermal analysis of aged Cu-EAA (14 days).

Figure 5 shows the differential scanning calorimeter (DSC) traces obtained with copper-EAA control. The sample was melted (Fig. 5A), crystallized (Fig. 5B), and conditioned at 87°C for 2 hr. Conditioning resulted in a doublet in the DSC trace (Fig. 5C). When the sample was remelted, the original trace (Fig. 5C) was obtained.

Figure 6 shows the same sequence for humidity aged copper-EAA. In the initial melting, the polymer exhibits a doublet as in Figure 3. Crystallizing and remelting of the sample gives melting endotherms similar to that of the original material shown in Figure 5A.

Heats of fusion (ΔH_f) for control and humidity-aged EAA of 14 and 17.6 cal/g, respectively, were obtained from DSC traces.

If adjacent units of the acrylic or methacrylic acid occur in an ethylene copolymer they could be represented as glutaric acid units (I):



Substituted
glutaric acid

R = H if EAA

R = CH₃ if EMAA

I

It has been demonstrated from dissociation constants in water⁹ of alkyl dicarboxylates that the order of stability of complexes with a number of bivalent transition metal ions is Zn < Cu > Ni > Co > Fe > Mn. Glutaric

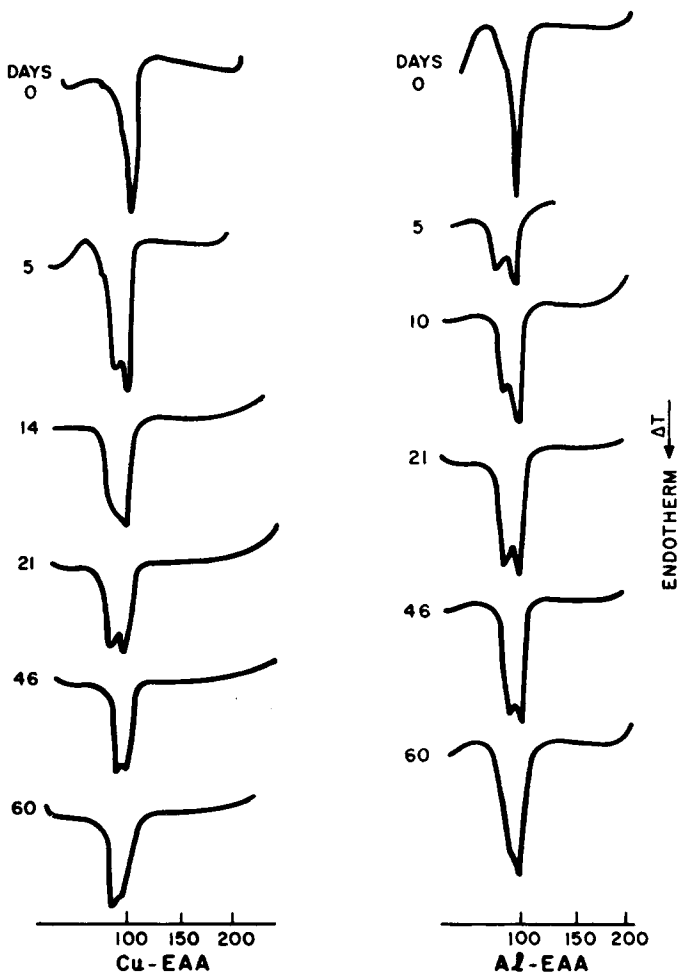


Fig. 4. Partial differential polymer analysis of metal-polymer aged 70°C/95% RH.

acid and, to a greater extent, substituted alkyl glutaric acids, as illustrated above, form exceptionally stable complexes with copper.

The assumption is made in the present study that water vapor and oxygen readily permeate the thin polymer coating and react with base copper or a copper oxide layer to solubilize it. The rate of oxidation of a cuprous

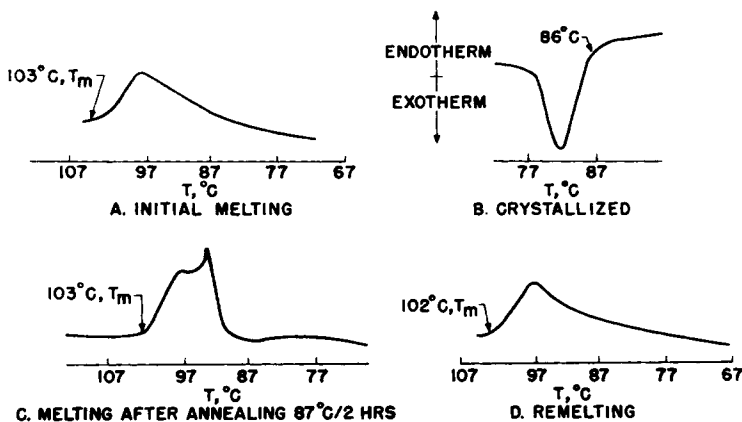


Fig. 5. Differential scanning calorimetric analysis of Cu-EAA (1.5 mg) control: (A) initial melting; (B) crystallized; (C) melting after annealing, 87°C/2 hr; (D) remelting. DSC-1 record; range 2 mcal/sec; scan rate 10°C/min; nitrogen; chart speed 1.0 in./min.

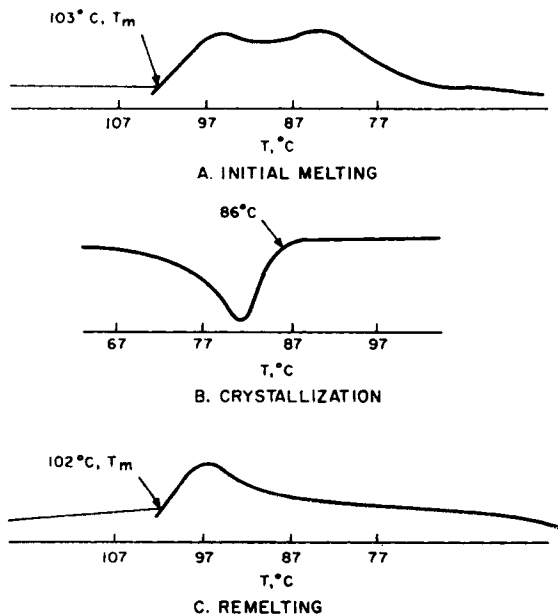
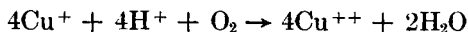


Fig. 6. Differential scanning calorimetric analysis of aged (31 days) Cu-EAA (1.63 mg). DSC-1 record; range 4 mcal/sec; scan rate 10°C/min (-10°C/min in crystallization); nitrogen; chart speed 4.0 in./min.

oxide or copper layer would be increased by the presence of hydrogen ions contributed by the carboxylic acid of the EAA ionized under humid conditions:



From infrared evidence, the acid functions of EAA or EMAA form an ionic complex with the cupric ion at the metal polymer interphase. A weak boundary layer also forms. With aluminum, under the conditions of testing, the oxide layer appears to be more stable than that on copper and does not react chemically with the EAA.

The DSC results indicate that an increase in the crystallinity of EAA and EMAA (as indicated from increased heat of fusion) can be anticipated on aging metal-adhesive copolymer composites or metal-adhesive copolymer-metal laminates. The doublet observed with DTA (Figs. 3 and 4) and with DSC traces (Fig. 6) for EAA appears to disappear as the metal-adhesive copolymer is aged (Fig. 4). Mandelkern¹⁰ and Bair¹¹ have observed the formation of a doublet in the DSC curves of conditioned single crystals of high-density polyethylene. Doublet formation is attributed to partial melting of crystals initially present, recrystallization of this material, and lastly complete melting of complex morphological structure formed. These structures are not present originally. In a similar manner one might interpret the doublet formation in the humidity aged EAA. However, the doublet shown in Figure 6A does not arise as in single crystals of high-density polyethylene during the DSC study but is originally present. The reduction in strength of the EAA-copper bond does not appear to be influenced by the increased crystallinity arising during the aging of EAA as evidenced by the retention in strength observed for aluminum-EAA bond with similar crystallinity changes (Fig. 4).

It is also possible that other mechanisms are affecting the copper-EAA bond and that the formation of a copper salt of the acrylic acid at the metal-adhesive copolymer interphase, occurs after failure of the bond.¹²

Thermal-Oxidative Behavior

In Figure 7, the amount of oxygen uptake increases with increasing acrylic acid content. Plotting t_{10} (time for 10 cm³ of oxygen to be absorbed by 1 g of polymer) versus the reciprocal of the absolute temperature is an arbitrary method to assess the ease of oxidation. The t_{10} values on low-density polyethylene, ethylene-ethyl acrylate copolymer (EEA), EAA (8% acrylic acid), and EMAA (9% methacrylic acid) are shown in Figure 8. It is apparent that the presence of the acid function in ethylene copolymers increases the susceptibility to oxidative attack.

EAA can be described as a polyethylene backbone with pendant carboxylic acid groups. These acid groups are electron-withdrawing substituents which activate the hydrogens attached to the carbon atoms containing the carboxylic acid groups.¹³ By the sequence of reactions (1)-(5) these

hydrogens can be readily removed to give a free-radical species (1) which reacts with oxygen (2)

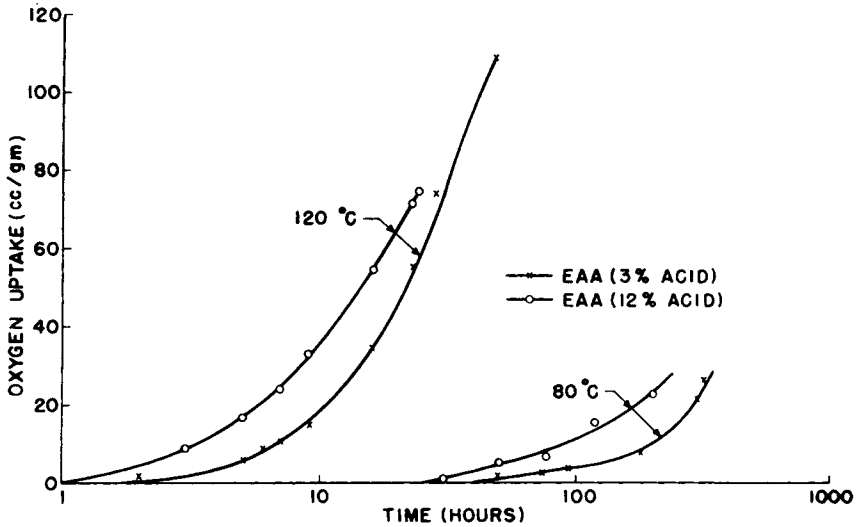
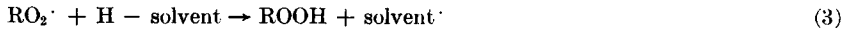


Fig. 7. Oxygen uptake of EAA as a function of acid content.

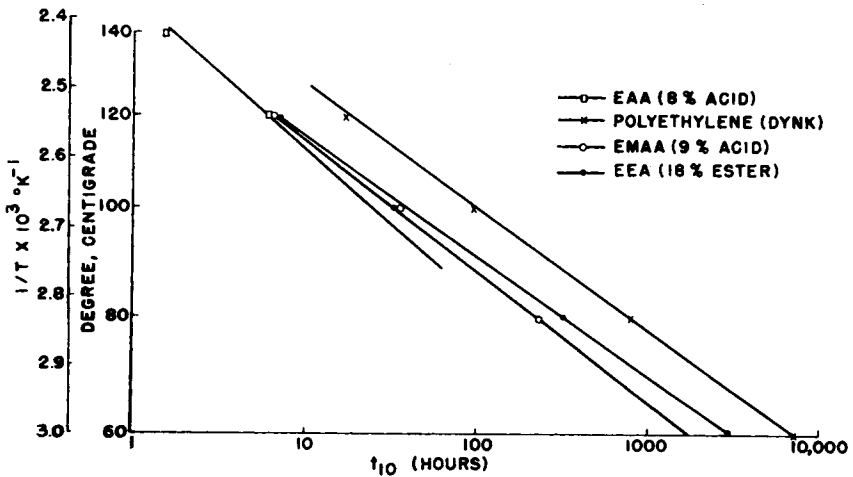


Fig. 8. Arrhenius plot. Induction period (t_{10}) of the thermal oxidation of polyethylene EAA, EMAA, and EEA as a function of the reciprocal of the absolute temperature.

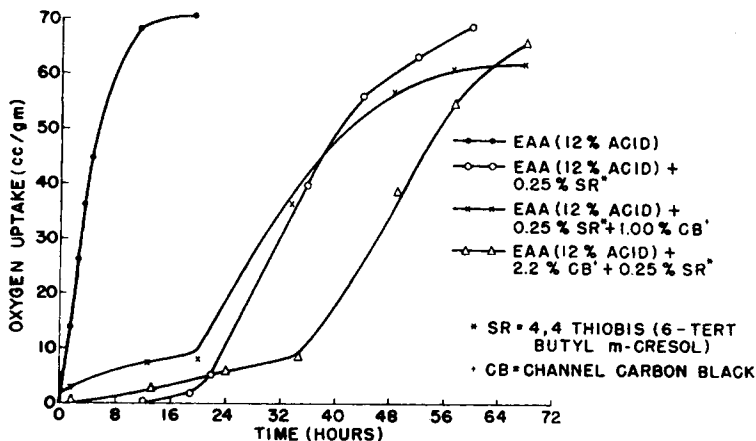


Fig. 9. Oxygen uptake of EAA (12% acid) containing antioxidant and channel carbon black at 140°C.

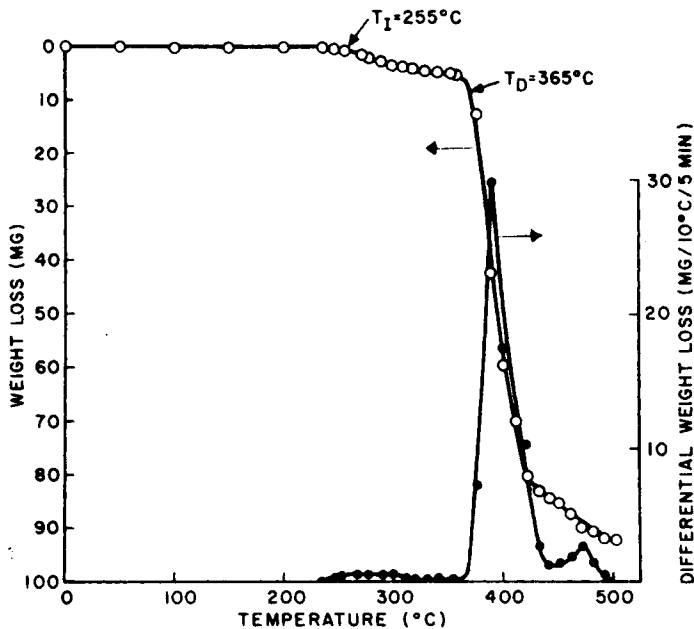


Fig. 10. Thermogram of the weight loss and differential weight loss as a function of temperature for EAA (8% acid).

to give the peroxy radical ($RO_2\cdot$) followed by a combination of $RO_2\cdot$ with hydrogen (3) available, e.g., from trace solvent left from processing or oxidizing polymer, to give a hydroperoxide, $ROOH$. On slight heating, reactions (4) and (5) would occur to generate the polymer radical ($R\cdot$) which propagates by step (2). It has been demonstrated that the rate of autocatalysis in the presence of oxygen for polymers is related to the rate of

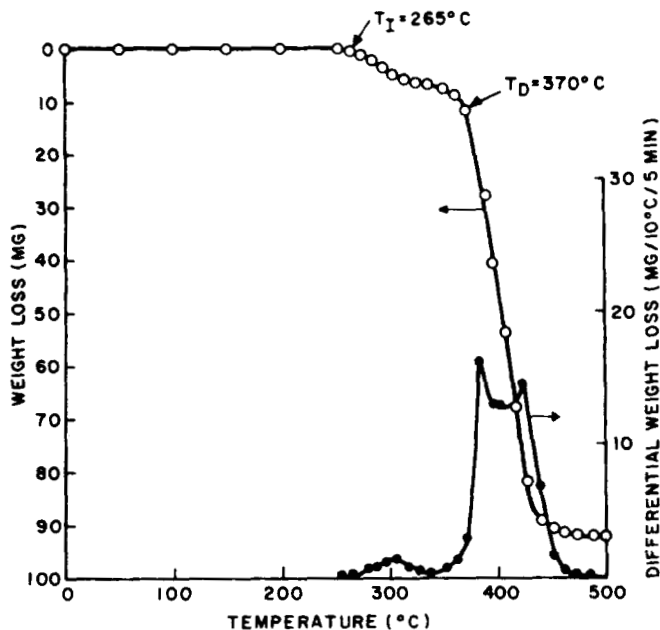


Fig. 11. Thermogram of the weight loss and differential weight loss as a function of temperature for EMAA (9% acid).

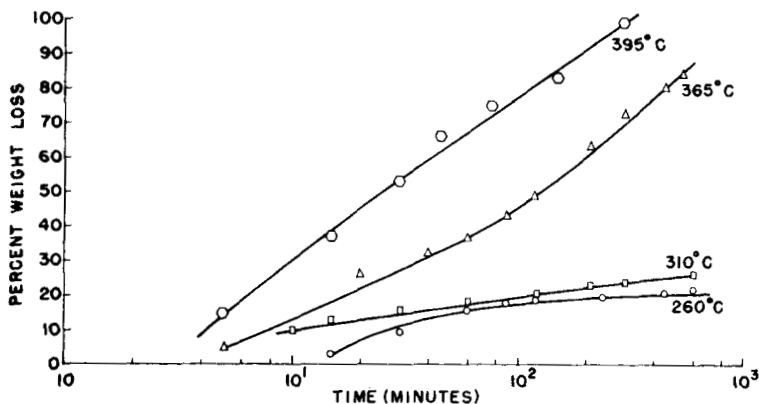


Fig. 12. Thermogram of per cent weight loss as a function of time of exposure under isothermal conditions for EAA (8% acid).

formation and homolytic decomposition of hydroperoxides. Hydroperoxides from the sequence of reactions depicted in eqs. (1) and (2) should be present in EAA to a greater concentration than present in ethylene homopolymer because more labile hydrogens are present.

The esters of these acids, EEA, are apparently more resistant to oxidation than EAA. This is apparent from the slope of the lines from Figure 8, where EEA with 18% acrylate is compared to EAA with 8% acrylic acid.

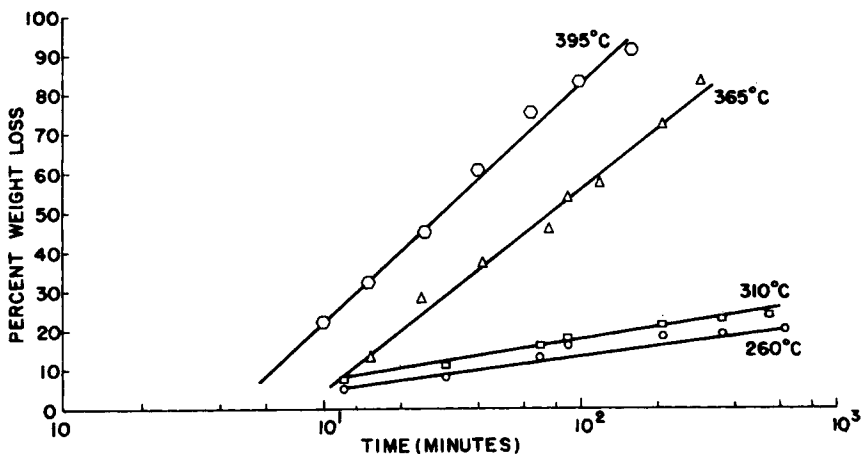


Fig. 13. Thermogram of per cent weight loss as a function of time of exposure under isothermal conditions for EMAA (9% acid).

It has been observed that over the temperature range of 60–140°C oxidation of EMAA (9% methacrylic) proceeds with a longer induction time than that of EAA (8% acrylic acid).¹⁴ This suggests that substitution of the labile hydrogens by $-\text{CH}_3$ groups is conducive to greater oxidation stability. The assumption is made that, in the synthesis of EAA and EMAA to equivalent acid content, the proportion of $-\text{CH}_3$ branching in the polyethylene portion of the ethylene copolymer is not altered.

Oxygen uptake data of EAA (12% acid), with 4,4-thiobis(6-*tert*-butyl *m*-cresol) and in combination with channel carbon black are shown in Figure 9. Similar stabilizer systems but with lower antioxidant contents in polyethylene have been observed to give considerably longer induction time in oxygen uptake at 140°C.

Thermogravimetric data at 265–370°C (Fig. 10) for EAA show that there is a 5% weight loss prior to rapid degradation while EMAA exhibits a 10% weight loss in the same temperature range (Fig. 11). EAA and EMAA decompose in three stages during heating in air, as does polyethylene.¹⁵

From the differential curve (Fig. 11) for EMAA decomposition, it is evident that its maximum weight loss occurs in two stages at 385°C (15 mg/10°C/5 min) and 423°C (14 mg/10°C/5 min). For EAA, the maximum rate of weight loss (Fig. 10) occurs at 390°C (30 mg/10°C/5 min). The lower rate of weight loss for EMAA at the temperature of decomposition (T_D) indicates that after the initial volatilization, EMAA forms a more thermally stable residue. With EMAA and EAA, heating in air would be expected to result in the formation of an anhydride structure analogous to that arising during the thermal decomposition of poly(methacrylic acid).¹⁶ These anhydrides may form crosslinks between adjacent macromolecules and thereby increase the rigidity and thermal stability of the polymer. The above thermogravimetric data suggests that EMAA forms a more stable crosslinked structure.

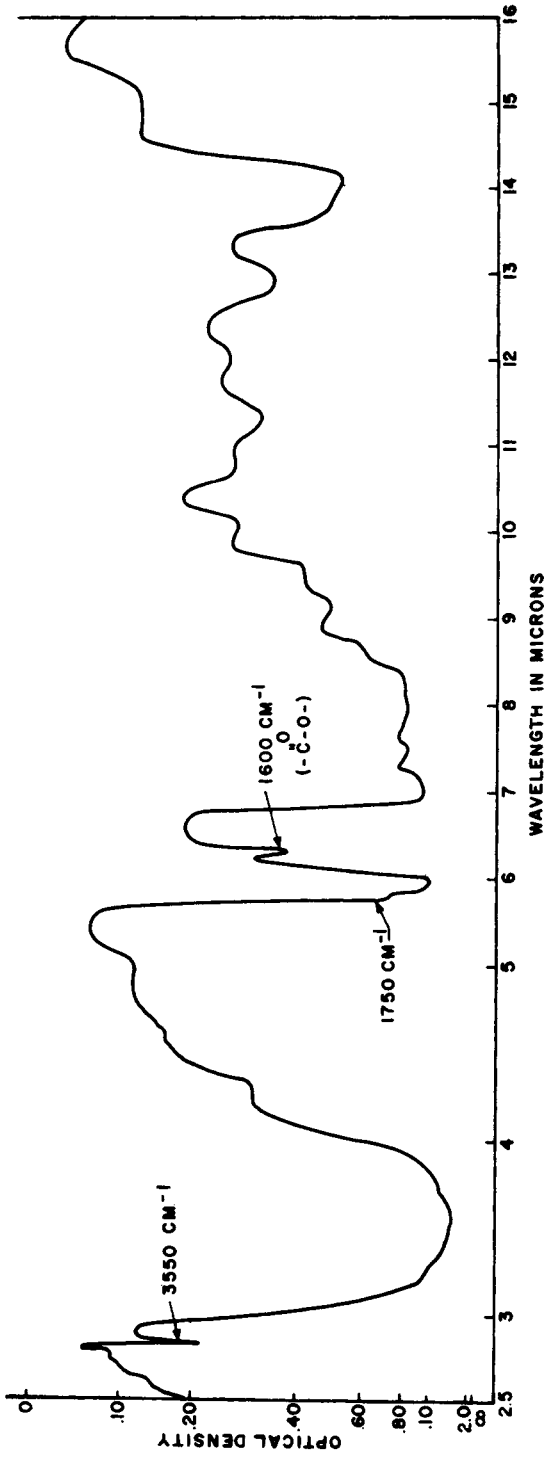


Fig. 14. Specular reflectance spectrum of EAA at 150°C after 1/2 hr contact with copper.

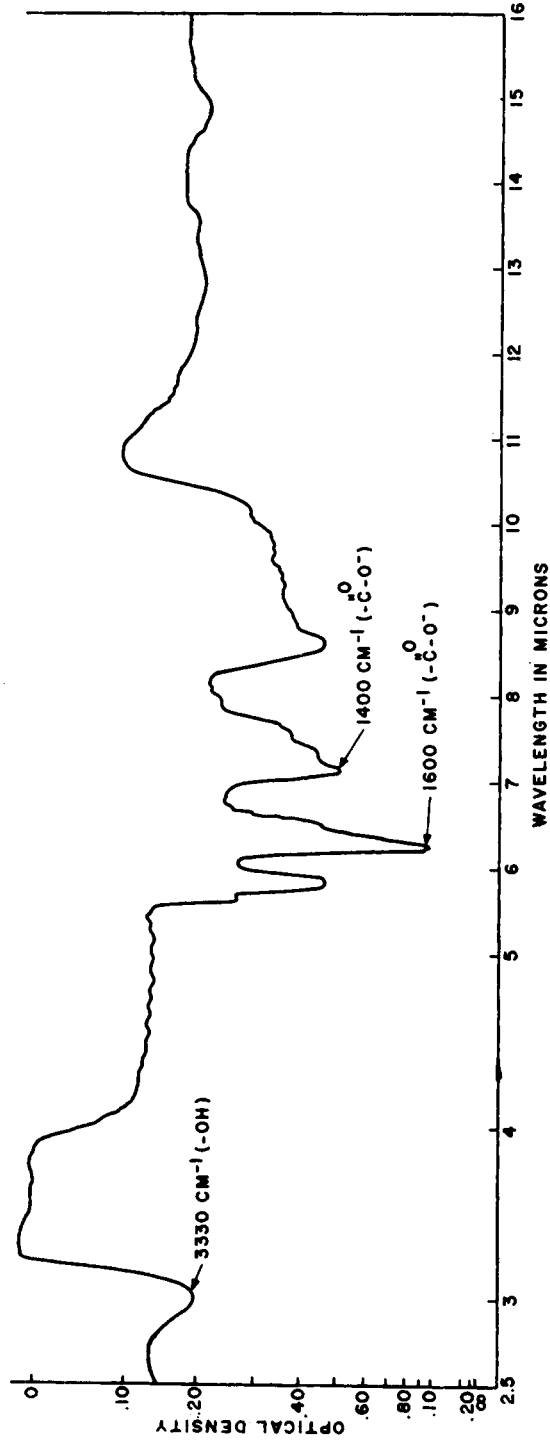


Fig. 15. Differential transmission spectrum of heat-aged EAA recovered from copper-EAA with control EAA as reference.

Thermograms of the behavior of EMAA and EAA under isothermal conditions were determined. The isothermal data were plotted on a semi-log scale in Figures 12 and 13. From the figures it appears that at temperatures above 310°C and short exposure time, volatiles would be produced sooner with EAA than with EMAA.

Figure 14 shows the specular reflectance spectrum of copper-EAA after $\frac{1}{2}$ hr of heating at 150°C in air. The spectrum at room temperature prior to heating has no bands observable at 1600, 1750, or 3550 cm^{-1} . The bands at 3550 and 1750 cm^{-1} in Figure 15 are detected at room temperature after heating to 120°C. After 2.5 hr at 150°C, the intensity at 150°C of the band at 1600 cm^{-1} increases but no significant change in the band at 3550 cm^{-1} occurs. When cooled to room temperature, the band at 1600 cm^{-1} is retained in the spectrum, while the bands at 3550 and 1750 cm^{-1} disappear. Further heating at 150°C of the sample in air for a total reaction time of 7.0 hr resulted in a broadening and increase in intensity of the band at 1600 cm^{-1} . The specular reflectance spectrum of copper-EMAA heated at 150°C in air showed similar behavior to that of the copper EAA system, except that the intensity of the 1600, 1750, and 3550 cm^{-1} bands in the spectrum of the aged samples was more marked. The transmission differential absorption spectrum of EAA recovered after 7 hr aging in air at 150°C as copper-EAA is shown in Figure 15. A similar spectrum is obtained when aged EMAA is compared to control samples. Absorption is observed at 3330 ($-\text{OH}$), 1600 (COO^-), and 1400 cm^{-1} (COO^-).

Specular reflectance spectra of tin-plated steel-EAA and aluminum-EAA obtained during heat aging at 150°C in air show the development of a band at 3550 cm^{-1} and a shoulder at 1750 cm^{-1} on the carboxyl band at 1700 cm^{-1} , but no band developed at 1600 cm^{-1} .

Recent work⁵ has suggested that the bands at 3550 and 1750 cm^{-1} observed during heating of EMAA, and in turn to be expected in EAA, are attributable to free hydroxyl stretching and monomeric carbonyl stretching vibration, respectively.

The author is indebted to W. L. Hawkins and L. H. Sharpe for comments and discussions concerning this work and to H. E. Bair for performing the DSC analysis.

References

1. G. E. Clock, G. A. Klumb and R. C. Mildner, paper presented at the 12th Annual Wire and Cable Symposium, Asbury Park, N. J., December 3, 1963.
2. General Cable Corporation, U.S. Pat. 3,233,036 (February 1, 1966).
3. E. I. Du Pont, Can. Pat. 655,298 (January 1, 1963); U.S. Pat. 3,264,272 (August 2, 1966).
4. R. W. Rees and D. J. Vaughn, papers presented to Division of Polymer Chemistry, 149th American Chemical Society Meeting, Detroit, April 1965; *Preprints*, **6**, No. 1, 287, 296 (1965).
5. W. J. MacKnight, L. W. McKenna, B. E. Read, and R. S. Stein, paper presented to Division of Polymer Chemistry, 154th American Chemical Society Meeting, Chicago, September 1967; *Preprints*, **8**, No. 2, 1130 (1967).
6. B. Wargotz, *Polym. Eng. Sci.*, **8** [1], 50 (1968).

7. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958, p. 174.
8. H. Schonhorn, *J. Polymer Sci. B*, **2**, 465 (1964).
9. R. H. Jones and D. I. Stock, *J. Chem. Soc.*, **1962**, 306.
10. L. Mandelkern and A. L. Allow, Jr., *J. Polymer Sci. B*, **4**, 447 (1966).
11. H. E. Bair, R. Salovey, and T. W. Huseby, *Polymer*, **8**, 9 (1967).
12. P. Walker, *J. Paint Technol. Eng.*, **37**, No. 491, 1561 (1965).
13. P. M. Norling, T. C. P. See, and A. V. Tobolsky, *Rubber Chem. Technol.*, **38**, 1202 (1965).
14. B. Wargotz and J. P. Creedon, Bell Telephone Laboratories, Incorporated, unpublished results.
15. S. Igarski and H. Kambe, *Bull. Chem. Soc. Japan*, **37**, 176 (1964).
16. D. H. Grant and N. Grassie, *Polymer*, **1**, 125 (1960).

Received November 30, 1967

Revised January 24, 1968