

This article was downloaded by:

On: 22 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

Structure Mechanical Property Changes Occurring in Ethylene Acrylic Acid Copolymer Adhesive During Aging of Bimetallic Laminates

B. Wargotz^a

^a Bell Telephone Laboratories, Murray Hill, New Jersey

To cite this Article Wargotz, B.(1969) 'Structure Mechanical Property Changes Occurring in Ethylene Acrylic Acid Copolymer Adhesive During Aging of Bimetallic Laminates', *The Journal of Adhesion*, 1: 4, 282 – 289

To link to this Article: DOI: 10.1080/00218466908072190

URL: <http://dx.doi.org/10.1080/00218466908072190>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Note

Structure Mechanical Property Changes Occurring in Ethylene Acrylic Acid Copolymer Adhesive During Aging of Bimetallic Laminates

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

(Received May 23, 1969)

The increase in peel strength after thermal aging of aluminum and copper to tin-plated steel laminates was studied using adhesive samples recovered from copper to tin-plated steel laminates. Morphological changes of the ethylene acrylic acid copolymer adhesive were observed. Calorimetric and dynamic mechanical measurements on adhesive copolymers recovered from Cu-tin plated steel laminates suggest that the crystallinity of EAA increases due to thermal aging as well as oxidative processes. A higher degree of crystallinity and effective crosslink density are consistent with the higher elastic (E') modulus for aged specimens. Increase in crystallinity of an ethylene-acrylic acid copolymer resulted in a higher tensile strength, which appears related to the increase in peel strength of the laminate.

INTRODUCTION

Thermoplastic adhesive copolymers based upon an olefin and a carboxylic acid type monomer, such as the ethylene acrylic acid copolymers (EAA), are being employed in new packaging concepts and in communication cable designs. In one application, the ethylene acid copolymer adhesive is employed to laminate copper to tin-plated steel for use in a new broad-band coaxial cable [1]. Considerable development effort has been expended to understand the structural-mechanical property relationship [2, 3] and the environmental behavior of these adhesive copolymers in contact with metal surfaces [4].

Thermal aging of the adhesively bonded copper to tin-plated steel laminates has resulted in an initial drop [5] in peel strength followed by a small, gradual increase, Fig. 1. The initial reduction in peel strength was not observed with aluminum to tin-plated steel laminates, Fig. 2. The initial drop in peel strength was also observed after exposure of the copper to tin-plated steel laminate to humidity [1]. However, a more pronounced increase in peel strength was observed on further aging, with the maximum occurring in 40 days at 70°C/95% relative humidity [1]. It is believed [4] that the reduction in peel strength of the copper to tin-plated steel laminates observed initially in both environments is caused by formation of a weaker copper oxide layer than existed previously through oxygen diffusion into the joint. Assuming an environment resistant copper surface layer were present [6], one would not anticipate an initial drop in the humidity and thermal environments.

Property Changes Occurring in Ethylene Acrylic Acid Copolymer Adhesive

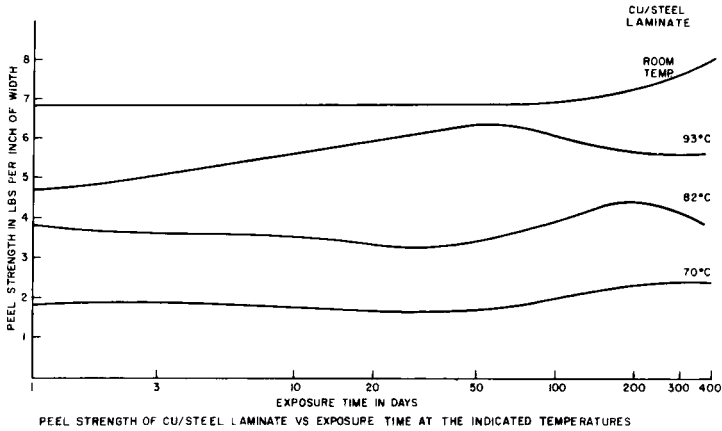


Figure 1. Peel Strength of Cu/Steel Laminate vs. Exposure Time at the Indicated Temperatures.

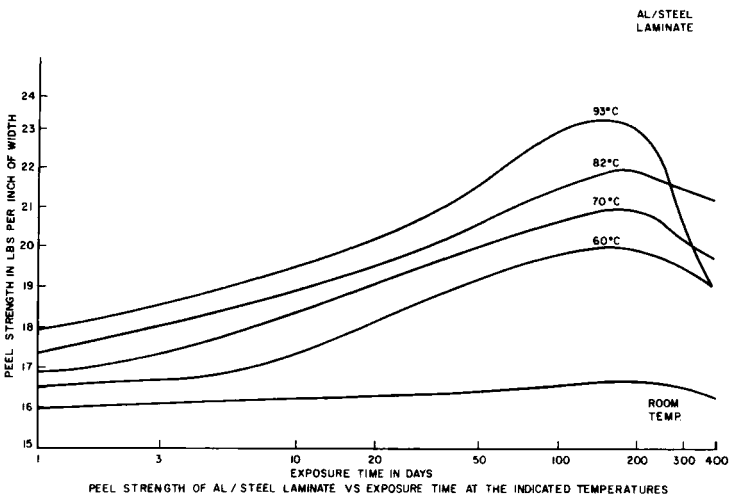


Figure 2. Peel Strength of Al/Steel Laminate vs. Exposure Time at the Indicated Temperatures.

Reduction in the peel strength of aluminum-aluminum bonded with EAA adhesive on conditioning of the specimens* prior to testing (88°C/1 hour) has been observed [7]. However, no correlation between increased crystallinity and a reduction in bond strength for EAA extrusion coated upon aluminum or copper and exposed to a temperature/humidity environment has been found [4]. It has also

* As these joints were compression molded, the influence of stress relief as a factor in joint strength reduction of the EAA was not discussed.

been observed that the bond strength of EAA on aluminum wire as a function of exposure to oxygen changes in a manner similar to that shown in Fig. 2 [8]. The rise in strength was associated with a toughening of the adhesive followed by cross-linking degradation [8].

It is of interest to explain the thermal behavior of these adhesive copolymers. This paper presents calorimetric and dynamic mechanical data on adhesive copolymer film recovered from aged copper to tin-plated steel laminates. Because of the harsh treatment (reacting aluminum with a base) required and possible adverse secondary effects (formation of metal salt) upon the adhesive, no attempt was made to recover the adhesive from aluminum to tin-plated steel laminates. The results obtained on the recovered adhesive from copper are assumed to be applicable to aluminum. The influence of the adhesive on the peel strength behavior of the copper-tin plated steel laminate during thermal aging is discussed.

EXPERIMENTAL

Laminates:

A copper or aluminum sheet containing a 0.002-inch-thick extrusion coated adhesive copolymer [4] (Dow Chemical PZ 4333.9, 8% acrylic acid content, 5 melt index EAA) is laminated to tin-plated steel employing two heated rollers. The temperature and speed of lamination are controlled so as to assure an exit temperature of the laminate of 185-195°C. Laminates are prepared from 0.003-inch-thick copper bonded to 0.01-inch-thick tin-plated steel with the 0.002-inch adhesive copolymer.

These laminates were then exposed in a forced air oven at 60, 70, 82, and 93°C for up to 400 days. Samples were removed at intervals, allowed to cool to room temperature, and 180° peel (copper or aluminum from tin-plated steel) tested on a Tinius Olsen test machine (Figures 1 and 2). Crosshead speed was 10"/minute. Tests were run on triplicate specimens. Comparable laminate specimens were removed from the various temperatures and times but not tested, being used instead in recovering the adhesive.

Recovery of the adhesive copolymer film from the copper-tin plated steel laminate was effected by amalgamation of the tin to yield copper coated with adhesive. The adhesive copolymer was freed by chemically etching the copper in an ammonium persulfate solution. The film was then rinsed in distilled water and dried for a few hours under vacuum at 50°C to remove absorbed water.

Calorimetry:

The melting point (T_m) and heat of fusion (ΔH_f) of the adhesive copolymer samples were determined on a Du Pont 900 Thermal Analyzer equipped with a differential scanning calorimeter (DSC) cell. Samples were punched from the center of the recovered films, placed in an aluminum pan and the DSC trace recorded from 23°C, heating at a rate of 10°C/minute in a nitrogen atmosphere. The melting point (T_m) was considered to be the point of maximum deviation from the base line.

Mechanical Testing:

The dynamic Young's moduli of the polymers were measured on a Vibron Dynamic Viscoelastometer [9] at a frequency of 110 cps and from -140°C to +80°C by J. H. Daane.

RESULTS AND DISCUSSION

Oxide Layer:

It is recognized that changes in the surface metal oxide (aluminum to tin-plated steel) can occur during aging and influence peel strength [4]. However, it has been observed that copper substrates prepared with oxidized and cleaned surfaces and bonded with EAA showed no differences in peel strength at low humidity [7]. It is assumed that under the conditions of the present study the initial drop in adhesion observed was from an oxide layer that degraded on thermal aging.

Differential Scanning Calorimetry (DSC):

The crystallinity of EAA reflected in the heat of fusion increases with time and temperature of aging (Table 1). In addition, the 25°C/400-day and 70°C/49-day recovered samples were completely soluble in trichlorobenzene at 110°C, while the 82°C/200-day and 82°C/400-day specimens appeared to be partially insoluble.

The DSC traces of EAA recovered from the copper-tin plated steel laminate after exposure to a thermal environment are shown in Fig. 3. These curves are similar to those obtained with samples exposed to a humid-temperature (70°C) environment in contact with copper [4]. The peak values of the melting endotherms are reported in Table 1 as T_m . The lower melting endotherms shown in Fig. 3 may be due to premelting of impure crystals of the EAA [10]. The development of the higher melting endotherms at 102°C and 105°C in the case of specimens aged at higher temperatures may be due to thickening of polyethylene lamellae [11].

Dynamic Mechanical Testing:

Otocka [2] and MacKnight [3] have employed dynamic mechanical measurements to characterize the ethylene acid copolymers. They have proposed that the acid copolymers consist of a crystalline ethylene segment phase and an amorphous phase consisting of ethylene and acid groups. These acid groups would form hydrogen bonds and, in effect, "cross-link" the polymer. On thermal aging, thickening of the polyethylene lamellae and/or more cross-linking can occur. Dynamic mechanical measurements may be useful to study the effect of aging. The loss modulus, E'' , and storage moduli, E' , of polyethylene and of EAA with 8 and 15 weight percent acrylic acid contents are shown [2] in Fig. 4. The loss modulus maxima occur at -21°C for polyethylene and 13 and 24°C respectively for the two EAA. These maxima are associated with the motion of ethylene branches present in the amorphous phase [3]. It is suggested [2] that the temperature corresponding to the transition peak is displaced by the presence of acid dimer cross-links which restrict

Table 1. Differential Scanning Calorimetry of Recovered Bimetallic Laminate Adhesive

Exposure Temperature—°C/Time—days	T_m °C	ΔH_f —cal./gm.
25°C/400	102	10
70°C/49	101	10.7
82°C/200	100	14
82°C/400	100.5	12

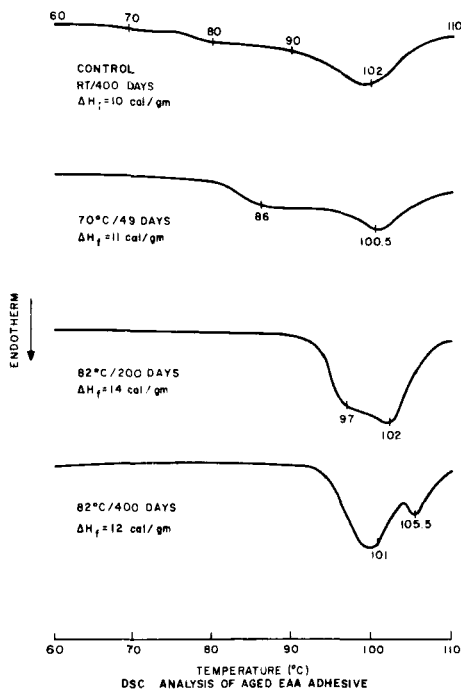


Figure 3. DSC Analysis of Aged EAA Adhesive.

this motion. This is shown in Fig. 4 for the polymer used in this study.

Comparison may be made of the traces in Fig. 4 of the loss (E'') and storage (E') moduli with those in Fig. 5 for the recovered EAA after aging at room temperature and 82°C for 200 days. In Fig. 5, the storage modulus, E' , values for the 82°C aged EAA are lower, below 0°C, and higher, above 0°C, than the room temperature aged sample. This behavior is the same as that exhibited in Fig. 4 as the acid content of EAA decreases. The implication is that in these regions the aged (82°C) EAA is behaving like an EAA of higher crystallinity. The higher crystallinity is confirmed from the heat of fusion data in Table 1, which increased during aging.

Examination of the loss modulus, E'' , in Figure 5 reveals a lowering and a displacement to a higher value of the loss maxima of 82°C aged EAA. This is the same as that obtained with increasing acid content of EAA, Figure 4. The loss maxima in higher acid content EAA is believed to reflect the presence in the amorphous regions of higher T_g acrylic acid segments [3] and dimer crosslinks [2]. It has been demonstrated from infrared measurement [2, 3] that association of the carbonyl groups of EAA is complete at room temperature. Infrared spectra of the aged EAA indicates only minor changes in the regions of the carbonyl 1550-1750 cm^{-1} and the OH out of plane bending of the dimer at 940 cm^{-1} . No carboxylate ion absorption is observed at 1600 cm^{-1} which might have arisen were a metal salt of the copolymer formed in contact with copper [4].

The increased heat of fusion (crystallinity) accompanied by the increase in modulus would appear to be related to the increase in the peel strength of the

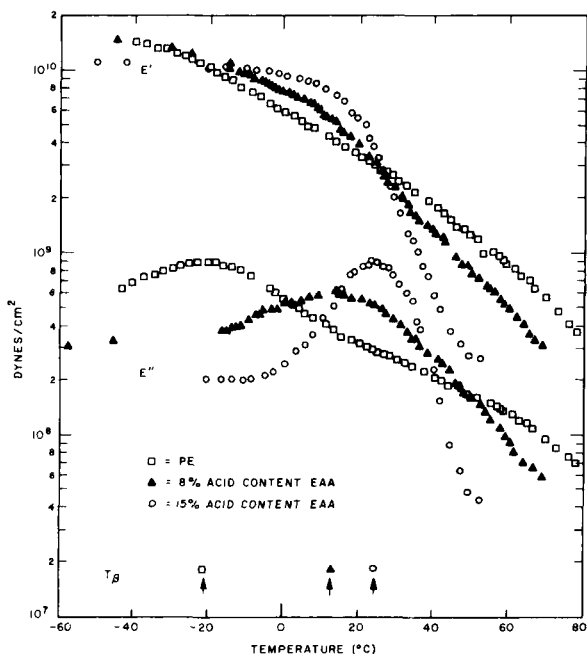


Figure 4. Dynamic Elastic (E') and Loss Moduli (E'') at 110 cps (from data of Otopcka and Kwei²).

copper to tin-plated steel laminate after aging. Since peel strength depends upon the modulus of the whole composite, the modulus increase in the adhesive would make a minor contribution, as shown in Figure 1. However, with increased modulus the tensile strength of the EAA will probably increase. This is indeed the case, as shown in Table 3. The higher tensile strength of the aged copolymer adhesive film appears related to the increased peel strength.

Cross-Linking:

There is evidence, based on the observed partial insolubility of aged EAA in hot trichlorobenzene, that the adhesive in copper-tin plated steel laminate is cross-linked during thermal aging. This cross-linking can arise from anhydride formation of acid functions or oxidative cross-linking of polyethylene segments. In both instances, the polymer would exhibit an increase in modulus during the early stages of cross-linking.

Results from differential scanning calorimetric analysis (Table 2) lend further support for the occurrence of partial cross-linking during aging. The T_m values on remelting the 82°C aged (partially insoluble) EAA is slightly lower than that of the 25°C (soluble) aged EAA and that of an EAA control film, which was not part of a laminate. In this remelting study all thermal history is removed, so all specimens are in the same state. Cross-linking would be expected to lower the T_m of EAA, which is observed.

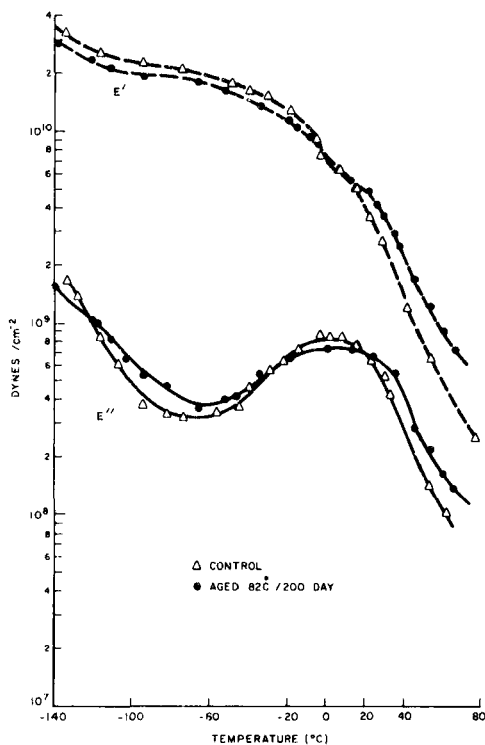


Figure 5. Dynamic Elastic (E') and Loss Moduli (E'') at 110 cps.

Table 2. Differential Scanning Calorimetric Analysis of Thermally Aged EAA

Sample	Melting T_m °C	Cooling T_c °C	Remelting T_m °C
22-25°C/400	103	93.5	104
82°C/200	102	91	102
82°C/400	102	90	101
Control 8% acrylic acid 5 melt index	103	94	104

Table 3. Tensile Properties of Thermally Aged EAA

Sample Temperature (°C)/Time (days)	Tensile Strength* (kg/cm ²)	Elongation (per cent)
22-25°C/400	138	360
82°C/200	157	290
82°C/400	153	240

* One-inch gauge length—crosshead speed 1 inch/minute.

It is believed that the cross-linking by anhydride formation does not contribute to the modulus increase in EAA during aging below 82°C. From other studies it has been observed that no volatiles were released by a high acid content EAA during thermal volatilization analysis [12] up to 135°C at a programmed heating rate.*

The increased crystallinity (heat of fusion) observed on aging (Table 1) may reflect thermal oxidative annealing. Chain scission reactions due to oxidation promote ordering processes. It has been demonstrated with polyethylene that oxidation-induced crystallization occurs at 100°C [13]. In the oxygen starved area of the glue line of the copper-tin plated steel laminate, chain scission would be accompanied by slight cross-linking. This could account for the partial insolubility of the aged EAA recovered from the copper-tin plated steel laminate. The loss in peel strength (Figs. 1 and 2) accompanied by a decrease in heat of fusion after 400 days' exposure at 82°C (Table 1) can be associated with extensive oxidative decomposition.

CONCLUSION

The observed increase in peel strength during thermal aging of the laminate of aluminum and copper to tin-plated steel is interpreted as arising from changes in the morphology of the EAA adhesive. An increase in peel strength similar in magnitude to that observed with aluminum would be expected with copper to tin-plated steel laminates if the copper oxide layer was resistant to the environment. Increased crystallinity (heat of fusion) from annealing as well as oxidative processes are reflected in higher modulus and loss maxima displacement observed with dynamic mechanical measurements. The cohesive strength of the copper to tin-plated steel laminate adhesive is also expected to increase and contribute to the increased peel strength.

BIBLIOGRAPHY

1. Nutt, W. G., Wargotz, B., and Biskeborn, M. C., *Bell Laboratories Record*, July 1969, p. 194.
2. Otocka, E. P., and Kwei, T. K., *Macromolecules*, 1, 244 (1968).
3. MacKnight, W. J., et al., *Poly. Eng. and Sci.*, 8, (4), 267 (1968).
4. Wargotz, B., *J. Appl. Poly. Sci.*, 8, 1873 (1968).
5. Schmieder, R. J., (unpublished results, Bell Telephone Laboratories).
6. Wargotz, B., *J. Appl. Poly. Sci.*, in press.
7. Smarook, W. H., and Bonotto, S., *Poly. Eng. Sci.*, 8 (1), 41 (1968).
8. Wargotz, B., (unpublished results, Bell Telephone Laboratories).
9. Matsuoka, S., *SPE Transactions Polymer Engineering and Science*, July, 1965.
10. Rees, R. W., and Vaughn, D. J., *Polymer Preprints*, 6, 287 (1965).
11. Bair, H. E., et al., *Polymer*, 8, 9 (1967).
12. McGaugh, M. C., and Kottle, S., *J. of Poly. Sci.*, 6, 1243 (1968).
13. Winslow, F. H., et al., paper presented at the Division of Polymer Chemistry ACS, April, 1963, p. 336.

* Pressure-temperature data are obtained in this technique. A rise in pressure at a particular temperature indicates release of a volatile (water to form anhydride) from the polymer under study.