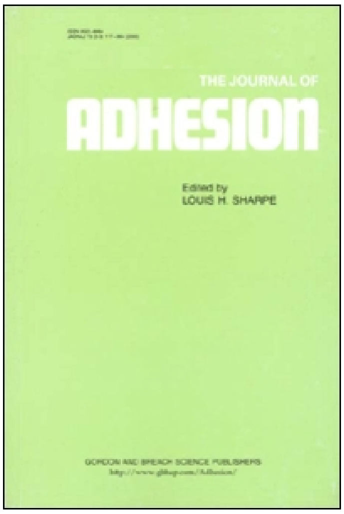

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Wang, P. C. , Moleski, J. J. and Baker, S. E.(1995) 'Influence of Paint Baking Exposure on the Lap-Shear Properties of a Polymer-Cored Laminated Steel', The Journal of Adhesion, 50: 4, 233 — 247
To link to this Article: DOI: 10.1080/00218469508014555
URL: http://dx.doi.org/10.1080/00218469508014555

J. Adhesion, 1995, Vol. 50, pp. 233–247
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Influence of Paint Baking Exposure on the Lap-Shear Properties of a Polymer-Cored Laminated Steel

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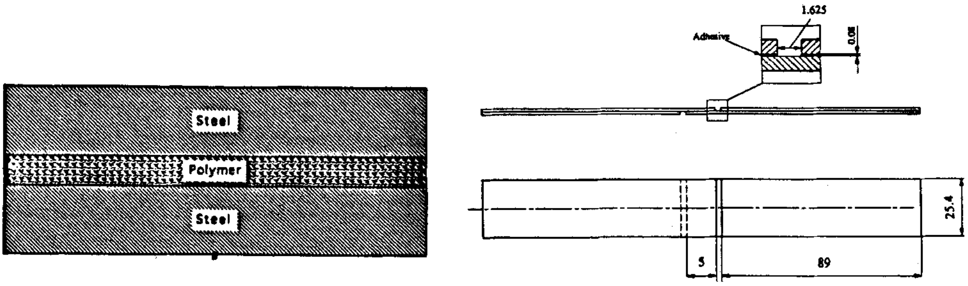
(Received August 5, 1994; in final form February 14, 1995)

Effect of thermal aging on the lap-shear properties of an acrylic-cored laminated steel was investigated by shear testing of specimens following exposure in air to the paint bake temperature of 180°C. The laminated steel consists of two thin steel layers bonded to a polymer core. It was found that thermal aging caused an increase in shear modulus and a decrease in ductility. Shear strength initially decreased, but then increased with aging time. Fractographic, thermal gravimetric, and differential scanning calorimetric analyses indicated that the decrease in shear strength and ductility is likely caused by void formation resulting from evaporation of the volatiles in the acrylic. These voids increased the local stresses. The subsequent increase in shear strength is attributed to the increase in adhesive cross-linking from thermal curing which hardens the adhesive. The increase in shear modulus with increase in aging time is ascribed primarily to thermal curing.

KEY WORDS: Acrylic-cored laminated steel; paint baking exposure; lap-shear properties; vehicle structural-borne noise; sound damping; volatile evaporation; thermal curing; automotive application.

INTRODUCTION

Polymer-cored laminated sheet steels are becoming increasingly popular for automotive application due to their combination of high strength-to-weight ratios[1–3] and good vibration-damping properties.[4–6] They have been used for the oil-pan, rocker cover, wheelhouse inners and dash lower to reduce vehicle structure-borne noise and engine noise.[7] They are also being considered for future applications where the fatigue properties are critical. Despite these advantages, there is an increasing concern about the deterioration of steel-to-polymer lap-shear strength that would jeopardize the long-term integrity of laminated steels. One of the major requirements of the laminated steel is the ability to withstand temperatures encountered during the paint bake cycle. Constant lap-shear strength between the steel and polymer (see Fig. 1(a)) throughout the automotive assembly process is considered to be a necessary condition for translation of constituent properties into both sound damping[8] and fatigue properties.[9] In order to utilize the full potential of laminated steels, a fundamental understanding of polymer-steel lap-shear properties is required.



(b)

FIGURE 1 (a) Polymer-cored laminated steel, and (b) shear test specimen (Dimensions in millimeters).

While there have been some studies[5, 6, 10] concerning the lap-shear strength of laminated steels, very little information is available concerning factors that influence the lap-shear properties of laminated steels after a paint bake cycle (Electrophoretic Priming Operation (ELPO) baking oven). In this paper, results from lap-shear property measurements of a polymer-cored laminated steel aged for varying times at 180 °C (ELPO oven) are presented, and factors contributing to their property degradation are identified.

EXPERIMENTAL PROCEDURE

Material

The material selected for this study is polymer-cored laminated steel manufactured by Pre Finish Metals Inc., Elk Grove Village, Illinois, USA. Polymer-cored laminated steel composite is composed of two 0.46 mm thick, low carbon, bare steel skins (SAE 1006) and 0.08 mm thick core adhesive. The core adhesive was manufactured by 3 M, St. Paul, MN. Tensile properties of polymer-cored laminated steel are listed in Table I.

Characterization of Polymer Core

Fourier transform infrared spectroscopy was used to identify the polymer core. The polymer core was dispersed in chloroform and centrifuged. A few drops of the clear chloroform solution were pipetted onto a 45°, 25 × 5 × 2 mm, KRS-5 prism and the

TABLE I

Tensile properties* of acrylic-cored laminated steel

0.2% Yield strength (MPa)	180
Tensile strength (MPa)	279
% Elongation (in 107 mm)	18.7

* Stroke rate = 0.1 mm/sec.

chloroform evaporated. The prism with the chloroform-soluble portion of the adhesive was mounted in a Spectra-Tech model 10–405 beam condenser, located in the sample compartment of a Nicolet model 5S × B spectrometer. Spectra of the polymer were obtained by co-adding 36 scans at 4 cm^{-1} resolution.

Specimen and Thermal Aging

Shear test specimens were machined in accordance with ASTM standard D 3165-91 (see Fig. 1(b)). Grooves were cut in opposite sides of the test specimens to give an overlap bond. The specimens were exposed in a high temperature chamber held at 180 ± 1°C and for 0.5, 5, 26, 34 or 50 hours, and then air cooled to room temperature. The lap-shear properties were measured at room temperature.

Shear Testing

Specimens were gripped in self-aligning hydraulic grips. A load-displacement curve was recorded as the sample was deformed at a stroke rate of 0.02 mm/second. The load divided by the bond area was taken to be the shear stress. The shear strain (γ) was calculated according to $\gamma = \delta/t_a$, where δ is the displacement and t_a is the adhesive core thickness (*i.e.*, 0.08 mm). The shear modulus was determined from the initial slope of the shear stress-strain curve. Duplicate tests were conducted to ensure the reproducibility of test results.

Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis on a DuPont 2100 analyzer was used to identify the temperature at which decomposition of the adhesive takes place. A 40 mg sample of unaged adhesive was placed in an aluminum pan and the temperature raised to 480°C at a rate of 10°C/minute.

Differential Scanning Calorimetry (DSC)

Extent of cure was determined using the 910 DSC unit of a DuPont 2100 Thermal Analyzer under a nitrogen environment. Adhesive specimens were taken from the unaged and aged laminated steels for investigation. Temperature scans were made from − 85 to 250°C at a heating rate of 10°C/minute.

Fractography

Post-failure fractographic analysis was performed with scanning electron microscopy (SEM). Following the shear testing, specimens were cut from the broken overlap sections. Before SEM examination, each specimen was sputter-coated with gold-palladium.

RESULTS

Characterization of Polymer Core

Figure 2 shows the infrared spectrum of the polymer core. The exact formulation of this polymer is proprietary to 3M, St. Paul, MN, USA but by comparing these spectra with reference spectra, the polymer is believed to be a solvent-based, one-part acrylic adhesive consisting of acetate, acrylate, and polystyrene. Toughened acrylics (*e.g.*, Loctite Steelbonder 340®) have been shown to have good bond strength and to cure quickly at room temperature.[11, 12]

Stress-Strain Curve

A typical lap-shear stress-strain of acrylic-cored laminated steel is plotted in Figure 3 (a). The curve shows a region of linear stress increase (from point 0 to A), followed by a region of non-linear stress increase to a maximum stress (point D) and a sharp decrease in stress after the maximum stress was reached. The change in slope at point *A* is believed due to the formation of microcracks and debonding between the adhesive and adherend and/or to microcracking within the adhesive itself. Details of the fractography are described later, and will not be elaborated here. Increase in stress caused the crack to propagate. The stress build-up occurred (point B) when the crack front appeared to have arrested and the sudden stress drop (point C) accompanied the detachment of a creased region of adhesive (see Fig. 3(b)). The next portion of the stress-strain curve (from point C to D) is due to cracks growing in the adhesive. The major loss of strength of the specimen occurs at *D*, when the specimen failed completely.

Effect of Thermal Aging

Shear tests were conducted at room temperature from specimens that had been aged at 180 ± 1°C for various aging times. These data are summarized in Figure 4; each datum

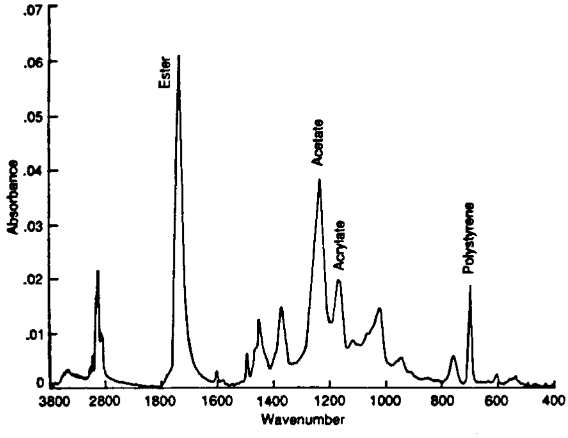


FIGURE 2 Fourier transform infrared spectrum of polymer core.

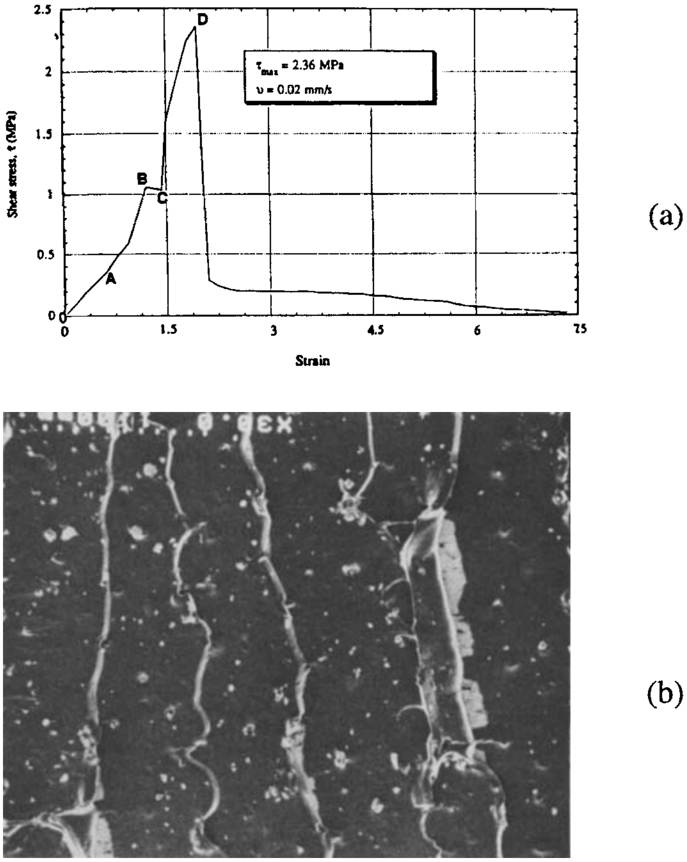


FIGURE 3 (a) Shear stress-strain curve for acrylic-cored laminated steel, and (b) scanning electron micrograph of fracture surface.

point in the figure represents an average value from at least three specimens. Lap-shear strength is defined as the maximum load divided by the overlap area. As shown in Figure 4(a), within the first 5 hours there was an initial decrease in shear strength followed by an increase. Figure 4(b) shows the shear strain (hereafter referred to as ductility) at the ultimate stress *versus* the aging time. It is shown that ductility initially decreased rapidly with a short induction period and then became relatively constant at aging time of 5 hours and longer. Figure 4(c) shows the shear modulus as a function of the aging time at 180 °C. It is observed that shear modulus increased with aging time and then became relatively constant at the aging time of 34 hours and longer.

Fractography

The effect of thermal aging on the fracture morphology was studied by observing the fracture surface with the scanning electron microscope after aging at 180 °C for various aging times. Figures 5 through 7 show the fracture surfaces of failed lap-shear

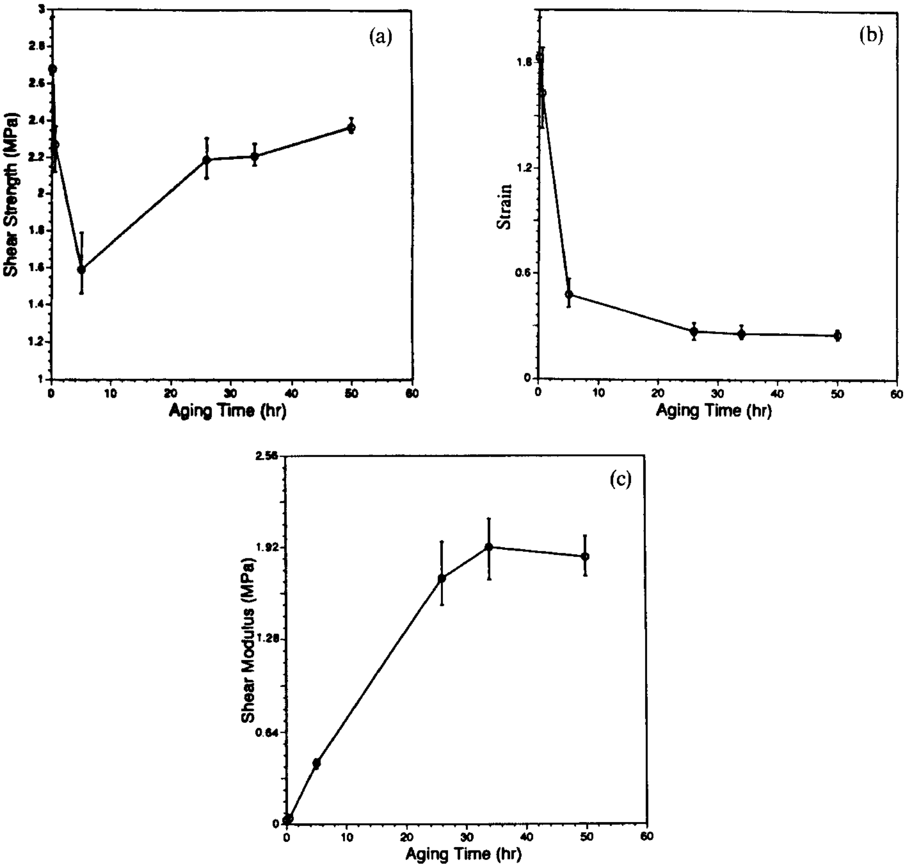


FIGURE 4 Lap-shear: (a) strength, (b) ductility, and (c) shear modulus *versus* aging time for acrylic-cored laminated steel.

specimens with different thermal exposures. Careful examinations of the unexposed (Fig. 5) and exposed (Figs. 6 and 7) fracture surfaces of the specimens revealed that the operative fracture mechanisms were dependent on thermal aging. As shown in Figure 5(a), the unexposed fracture appearance exhibited periodic marking that is preceded and followed by steps, which were relatively flat and almost featureless, in a direction perpendicular to that of the crack propagation. This topographical contrast suggests that two different fracture processes are involved. The periodic markings were generated when the crack appeared to have arrested, whereas the flat surfaces were formed by a fast-running crack. A higher magnification of a marking, indicated by an arrow in Figure 5(a), is shown in Figure 5(b). As shown, the plastic deformation occurs along the adhesive marking. In addition, lighter-appearing patches adjacent to the markings are also observed, as can be seen in Figure 5(b). This region was identified by X-ray micro-analysis in SEM to contain predominately iron. Figure 5(c) shows an iron X-ray dot map of the region in Figure 5(b). These results suggest that bonds between the acrylic core and adherend were stronger in those light-appearing areas than in the surrounding areas, which failed in the adhesive. Therefore, the failure occurring at acrylic-cored laminated steel is due to a mixed mode of cohesive (in the adhesive) and adhesive failures.

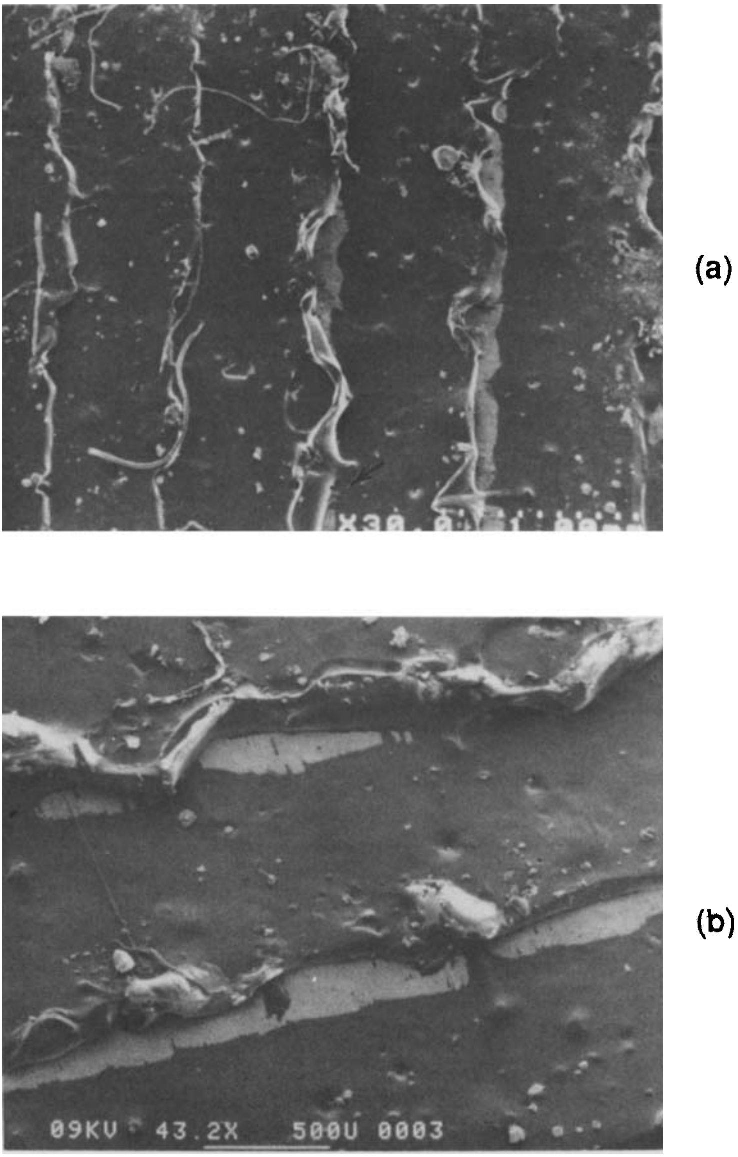


FIGURE 5 Scanning electron micrograph of fracture surfaces for: (a) bare laminated steel at ambient condition, (b) enlarged view of the region indicated by an arrow shown in (a), and (c) iron X-ray dot map (Light areas indicate the presence of iron).

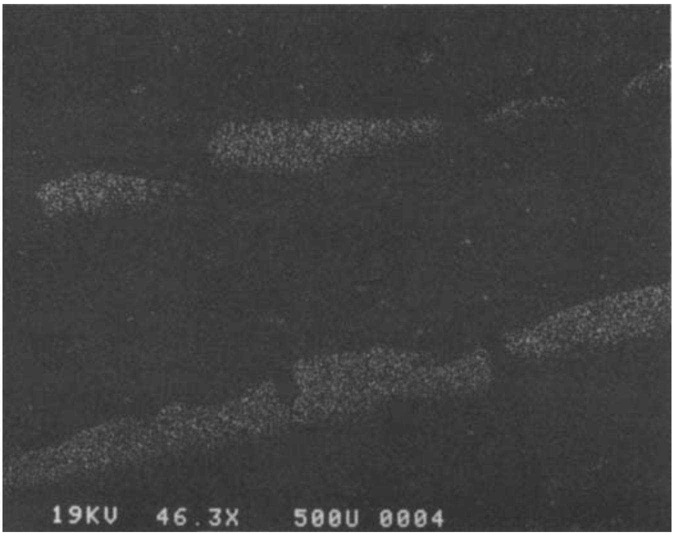


FIGURE 5 *(Continued).*

Figures 6(a) and 6(b) show the fracture surface for a specimen after aging at 180°C for 0.5 and 5 hours, respectively. It can be seen that the fracture surfaces are also characterized by the presence of markings, but slightly less pronounced. However, unlike in Figure 5, a large number of relatively uniformly distributed voids are observed throughout the fracture surfaces. These voids may result from the evolution of gases generated by evaporating the volatiles.[13] As much as 9.6% of the surface, shown in Figure 6(a), was actually covered with voids. The presence of these voids results in an increase in stress in the bulk adhesive and, thus, leads to lap-shear strength reduction. Comparing Figures 6(a) and 6(b), the increase in the number of voids with increasing time can be seen qualitatively.

Visual examinations of Figures 5 and 6 indicated that at longer aging times the voids became deeper and there were internal cracks between the voids. A fracture surface for specimen after 50 hours aging at 180 °C is shown in Figure 7(a). As shown, light-appearing patches are increased noticeably by extended aging time. X-ray microanalysis confirmed the existence of iron in these patches. Figure 7(b) shows the iron X-ray dot map for the region indicated by an arrow in Figure 7(a). A light area indicates the presence of iron. These results indicate a high shear strength at the interface between adhesive and adherend, suggesting that when a crack starts the fracture propagates, changes direction and enters the adhesive as well as the iron oxide. We assume that at a longer thermal aging, stronger bonds at the adhesive-iron interface region are created due to an increased degree of adhesive cross-linking. The higher shear strength observed after the 50 hours aging at 180°C will be discussed later.

Distribution of Voids

Measurements of the number and size of voids formed after exposure in air at 180°C for 0.5, 5 and 50 hours were made as a function of aging time. The observed area was

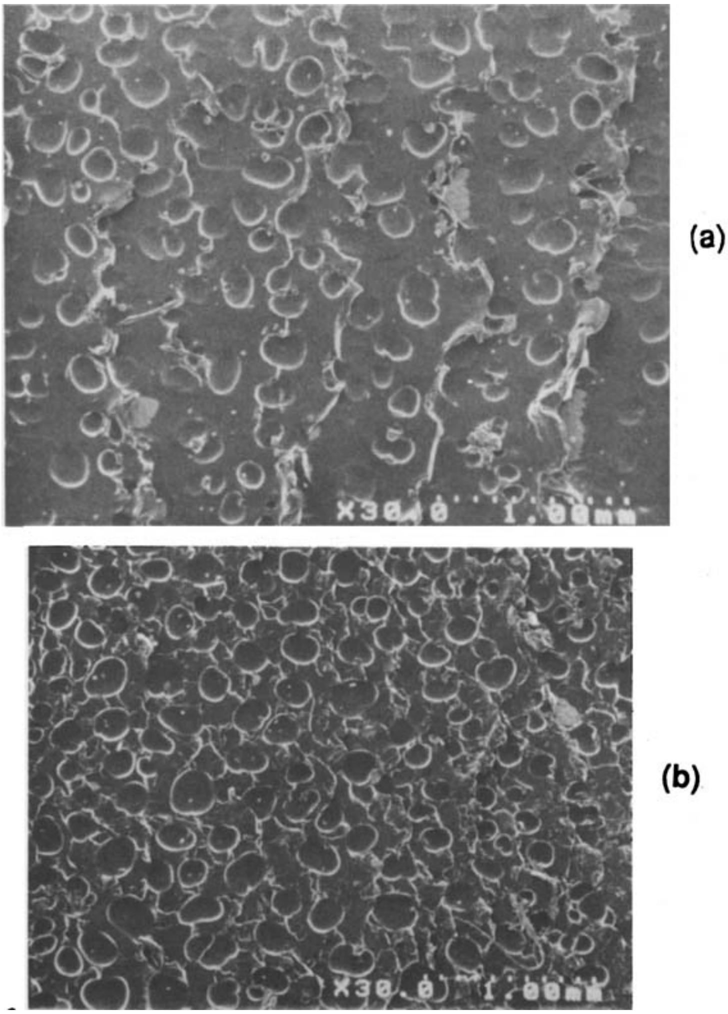


FIGURE 6 Scanning electron micrographs of the fracture surface for a laminated steel specimen after exposure to 180°C for: (a) 0.5 hour, and (b) 5 hours.

5 × 25 mm in size, to cover all of the voids on the fracture surface. Since for each aging time no significant change in fractography was found, only one fracture surface was analyzed. A summary of data is shown in Figures 8(a) and 8(b). As shown in Figure 8(a), within the first 5 hours there was an initial increase in number of voids/unit area followed by a slight decrease. Similar results were found for average void size shown in Figure 8(b), although the subsequent fall-off in the average void size was more pronounced. The key parameter for describing the voids is believed to be the area fraction of voids (A_V/A), where A_V is the total area of voids and A is the sampled area.

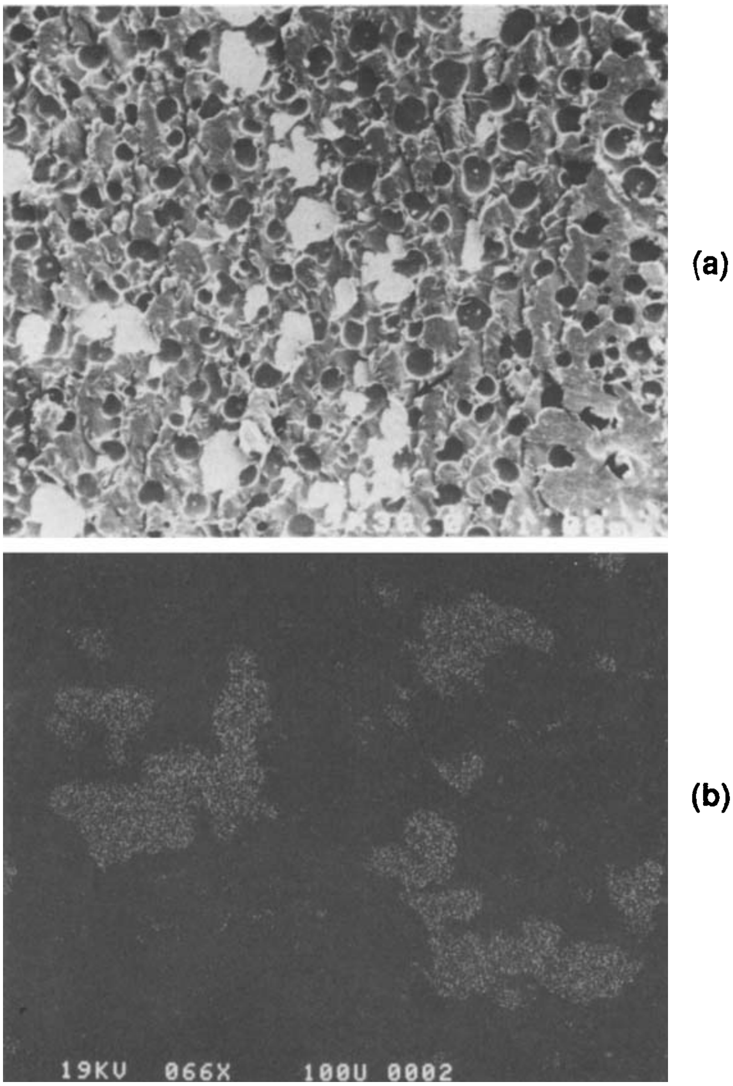


FIGURE 7 (a) Scanning electron micrographs of the fracture surface for a bare laminated steel specimen after exposure to 180°C for 50 hours, and (b) iron X-ray dot map of a region indicated by an arrow shown in (a). Light areas indicate the presence of iron.

The area fraction of voids and volume fraction of voids are identical for a random distribution of voids. Figure 8(c) shows the area fraction of voids observed as a function of aging time. The void fraction increases with aging time initially, then reaches a maximum and decreases. The maximum area fraction of voids observed was 14%.

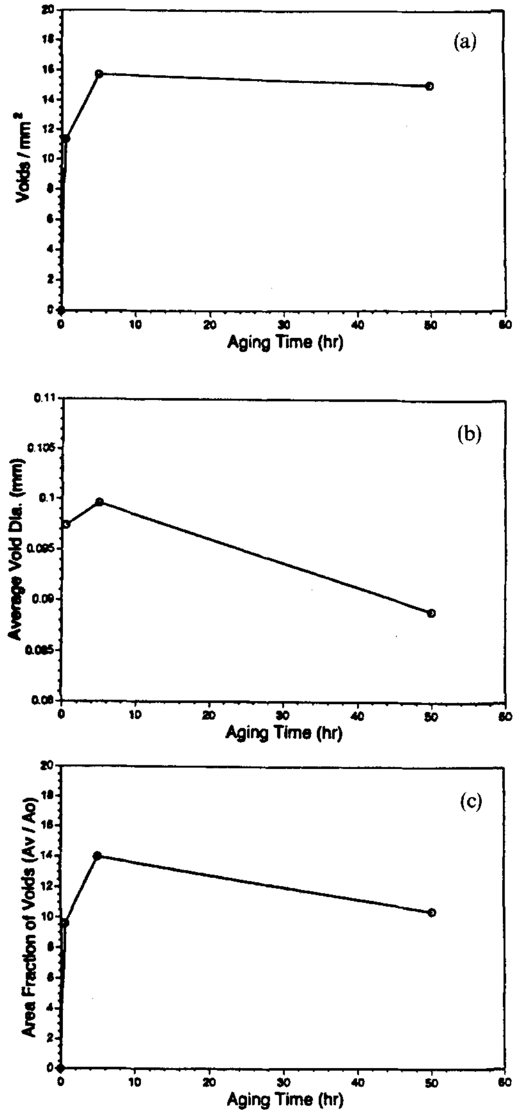


FIGURE 8 Void formation in acrylic adhesive: (a) void/unit area, (b) average void size, and (c) area fraction of voids (A_V/A) as a function of aging time.

DISCUSSION

The major purpose of this discussion is to provide an interpretation of the data presented above so that we can understand how thermal aging affects the lap-shear properties of the acrylic-cored laminated steel. Aside from the composition of the polymer core, two factors appear to control the lap-shear properties of acrylic-cored laminated steel: evaporation of volatiles and polymer curing. The relative importance of each factor on lap-shear properties will be discussed below.

Thermal gravimetric analyses (TGA) of acrylic adhesive in air and nitrogen are shown in Figure 9. At 180°C, weight losses in air and in nitrogen were identical at about 0.4%, which could be attributed to trapped volatiles and/or residues from incomplete adhesive reaction during the fabrication. Rapid decomposition occurs at about 250°C independent of atmosphere. Above 250°C, the rate of degradation in air was larger than in nitrogen, which is due to oxidation and pyrolysis. As shown in Figure 8(c), the acrylic adhesive had a maximum area fraction of voids, 14%, after aging at 180°C for 5 hours. The presence of these voids resulted in an increase in stress in the bulk adhesive; hence, the lap-shear strength is lowered. Simultaneously, the thermal exposure cures the acrylic adhesive, and tends to raise the lap-shear strength. Differential scanning calorimetry (DSC) measurements of unaged and aged acrylic adhesive are presented in Figure 10. As shown, aging increased the glass transition temperature (T_g), suggesting that thermal cross-linking developed. These two effects compete, with the volatile-induced voids predominating for short aging time. As the aging time increased, the acrylic adhesive cured further. Table II shows the glass transition temperature (T_g) as a function of aging time. As shown, T_g is approximately 25°C higher for a specimen with 50 hours exposure than for a specimen with 5 hours exposure, whereas area fraction of voids decreased slightly (see Fig. 8(c)). The subsequent increase in shear strength shown in Figure 4(a) suggests that the influence of thermal curing outweighs that of voids in acrylic-cored laminated steel with aging times longer than 5 hours. It is reasonable to conclude that the initial decrease and subsequent increase in shear strength with the aging time is the result of the competitive effects of local stress concentrations and adhesive cross-linking, with the first one predominating for short aging times and the second assuming greater importance as the aging time increases.

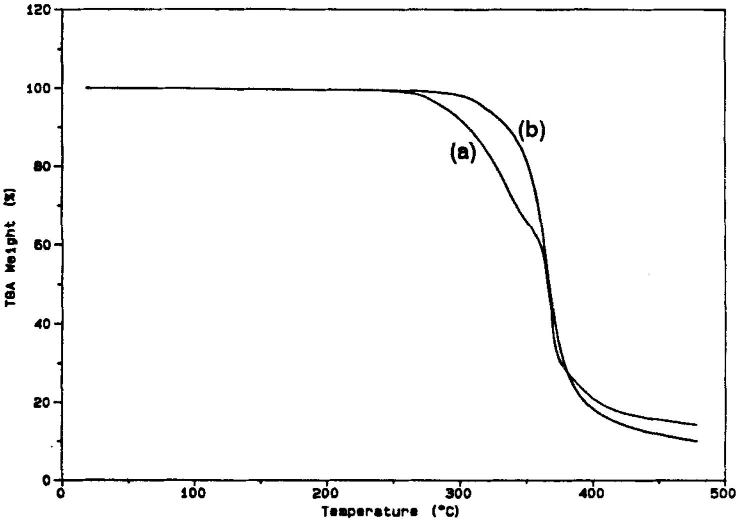


FIGURE 9 TGA thermograms of acrylic adhesive in: (a) air, and (b) nitrogen.

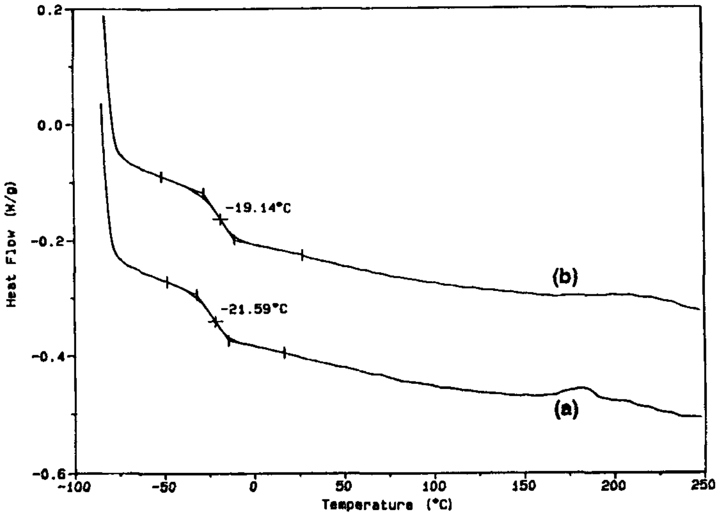


FIGURE 10 Differential scanning calorimetry thermograms (DSC) for acrylic adhesive: (a) unaged, and (b) aged at 180°C for 5 hours. Curve (b) was shifted along the Y axis for clarity.

TABLE II

Glass transition temperature of acrylic core as a function of aging time at 180°C

Aging Time hour	Glass transition temperature T_g(°C)
0.0	−21.59
5.0	−19.14
50.0	5.67

The decrease in ductility in the initial stages of exposure at 180°C can be attributed mostly to volatile-induced voids, as the area fraction of voids increases from 0 to 14% after 5 hours (Fig. 8(c)). There is also some contribution from acrylic adhesive embrittlement by thermal aging. We opened the DSC pan after the test and found that the samples were brown and brittle.

The observed increase in shear modulus with increasing aging time is consistent with previous observations. Dale *et al.* found a large increase in the storage modulus with an increasing amount of cross-linker.[14] Although there are volatile-induced voids in the adhesive, the effect of voids is nullified by the cross-linking that results from thermal aging.

The results found in this study are of particular importance due to the manufacturing process in which the laminated steel is applied. Laminated steel must be able to survive an electrocoat bath without fouling the paint or losing its material properties, and it must be capable of withstanding the baking temperature of the topcoat without deterioration. The temperature (180°C) and aging time (30 minutes) here are simulative of a baking environment (Electrophoretic Priming Operation) encountered by the laminated steel. It is evident from the results obtained in this study that the use of the acrylic-cored laminated steel under a thermal aging results in marked changes in the lap-shear properties of the material. The severity of these effects will depend on the temperatures and time involved. Therefore, it is recommended that the material properties of laminated steel used in vehicle structural design be adjusted to account for likely thermal effects.

CONCLUSIONS

1. Aging acrylic-cored laminated steel at 180°C (in Electrophoretic Priming Operation) caused an initial decrease in shear strength for times up to 5 hours. This was due to the void formation resulting from evaporation of the volatiles in the polymer, which increases the local stresses. Between 5 to 50 hours exposure in air at 180°C the shear strength increased. This increase in shear strength is attributed to the increase in adhesive cross-linking from thermal curing which hardens the adhesive.
2. Thermal aging at conditions experienced during paint bake cycle exposure of acrylic-cored laminated steel caused a decrease in ductility and an increase in shear modulus.
3. A mixed mode of cohesive and adhesive failure was observed in both ambient and thermal aging environments.
4. The properties of acrylic-cored laminated steel used in vehicle structural design should be adjusted to account for the paint baking degradation.

Acknowledgements

The authors are grateful to Dr. G. Banas and Prof. F. V. Lawrence, Jr. of University of Illinois at Urbana-Champaign for helpful discussions and technical assistance throughout this work.

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