Effect of Formulation Variables on Coating Properties and Performance in the Deep Draw Process

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This study demonstrated correspondences between certain coating properties and observed failure modes in the deep draw process. Mode I failure, coating delamination at the cup edge, correlated with residual compressive stresses in the drawn coating. Neither crosslinker concentration nor prepolymer molecular weight in the ranges studied significantly affected residual stresses. However, residual stresses were strongly affected by the amount of wax in the coating formulation to the extent that coatings with less than 1.5% wax exhibited mode I failure, whereas coatings with 1.5% or more did not fail. Some of the coatings that exhibited mode I failure also exhibited mode II failure. Loss of adhesion on the cup wall, mode II failure, correlated with adhesive strength of the coating to the metal substrate, which in the present study was most strongly affected by crosslinker concentration. Coatings with 15 and 20% crosslinker exhibited extended areas of mode II failure, whereas coatings with 10% crosslinker showed no mode II failure. Increasing the molecular weight of the prepolymer improved adhesion somewhat, but not enough to affect the failure mode in the coatings tested, and wax had no measurable effect on the adhesion.

INTRODUCTION

The use of epoxy coatings on metal containers for protective and decorative purposes has been practiced for over 60 years. The coatings can be applied to the metal either before or after deformation depending on the forming method. Deep drawing and wall ironing are two modern can-making processes. The amount of metal deformation in the wall ironing process is considerable with substantial insult to the surface during forming. In this process the can body must be coated after fabrication. In deep drawing the coating is applied to the flat metal sheet before forming. The thin polymer coating must deform with the metal during the drawing procedure. This requires the coating to undergo extensive deformation without tearing, forming holes, or losing adhesion. During the process, the coated metal substrate is subjected to complex axial and shear stresses. The resulting strain distribution determines the stresses on the coating and the ensuing modes of coating failure.

Conventionally, the performance of candidate coatings is tested with a deep drawing apparatus that forms a cylindrical cup from a flat metal blank by means of a cylindrical punch and die set assembled in a power press.[1] The forming operation is intended to mimic the deformation that the coated metal would encounter during can manufacturing. After deep drawing, the coating is visually inspected for failure, and qualitative comparison is made with control materials that passed the forming operation without failure.

Various studies examined the relationship between chemical composition and specific properties that might affect coating performance, such as glass transition temperature (T_g), sub-T_g relaxations,[2-4] and flexibility.[5-7] It was recognized that adhesion is an important characteristic that affects coating response during processing.[8-10] Several methods have been proposed for measuring adhesion of the coatings to various substrates.[11-14] However, in these studies no correlations were attempted between adhesion and coating behavior in the deep draw process. The importance of residual compressive stresses was also recognized in the literature.[15,16] Other attempts have been made to correlate coating structure with practical aspects of coating performance such as abrasion resistance, surface lubricity, scratch resistance, and heat resistance.[17,18] However, empirical tests are relied upon to evaluate coating performance in the absence of a more fundamental approach.

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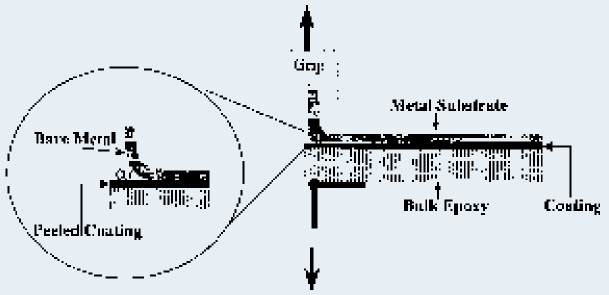

Figure 1—Schematic diagram of the modified peel experiment.

To design improved coatings that will undergo extensive deformation in the deep draw process without failure, it is useful to identify the modes of coating failure and, subsequently, to relate observed failure to key properties of the coating material. To understand the factors that control coating failure on the deep drawn cup, deformation of the uncoated metal substrate subjected to the deep draw process was characterized, and the deformation of the metal substrate was correlated with the failure modes of a thin epoxy-type polymer coating.[19] Subsequently, the effect of prepolymer molecular weight, crosslinker concentration, and amount of a wax on coating failure was studied, and the results were correlated with the adhesion of the coating to the substrate and residual stresses in the coating after the deep draw.

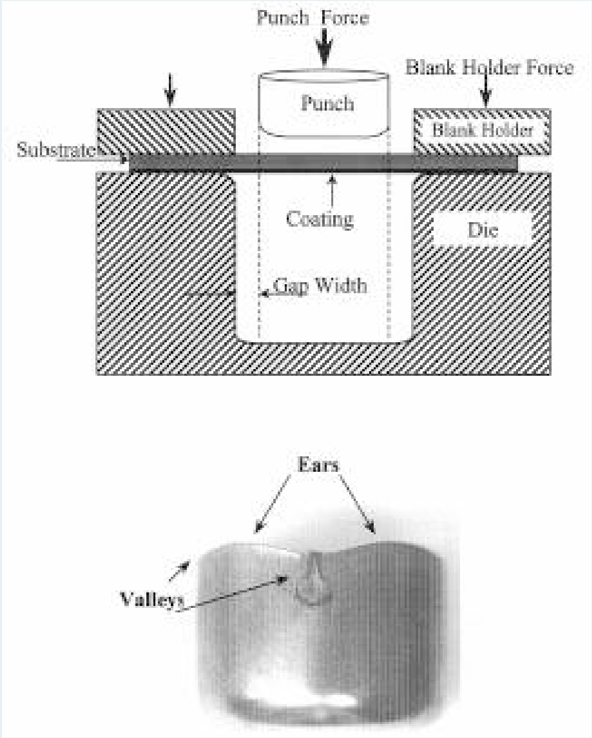

Figure 2—Schematic diagram of the deep drawing process and photograph of the deep drawn cup.

MATERIALS AND METHODS

Materials

Epoxy coatings used in this study were supplied by ICI Paints (Cleveland, OH). The metal substrate was 0.2 mm thick tin-free steel. Crosslinker concentration, prepolymer molecular weight, and a low molecular weight polyethylene wax were varied in the coating formulations used in this study. The compositions of the epoxy coatings are given in *Tables* 1-3.

Methods

The metal substrate was cleaned with methyl ethyl ketone before coating application. The epoxy coating was cast on the metal with a #20 coating bar for the high molecular weight prepolymer epoxies and with a #14 coating bar for the low molecular weight prepolymer epoxies. The dry film thickness in all cases was ~ 6 µm. The coated metal sheets were baked in a forced air oven at 210°C for 10 min. The epoxy-coated metal blanks were deep drawn in the Erichsen cupping machine and the coating failure modes were identified.

The Altec mobility/lubricity tester model 9505A was employed to measure a dimensionless friction force. The friction test was performed by dragging a 250 g weight with a 25 cm^2 contact area along the surface of the coated metal at a rate of 40 cm/min for a distance of about 40 cm. The dragging force was monitored digitally and averaged over 600 points.

A modified peel test was developed to measure adhesion between the coating and metal before deep drawing. A rectangular mold fabricated from a silicon mold resin (GE Co.) was filled with a room temperature curing epoxy. The epoxy was allowed to cure for zero, one, two, or three minutes before a strip of coated metal 1 cm × 6 cm × 0.02 cm was suspended in the mold. Precuring was intended to reduce diffusion of the epoxy into the coating. The epoxy with the embedded metal strip was removed from the mold after the epoxy had cured for a total of five minutes. A notch was introduced at the metal-coating interface with a fresh razor blade. The specimen was further cured for one hour at 40°C. A hinge was glued to the bulk epoxy and the specimen was loaded in the Instron at a rate of 2.0 mm/min. The modified peel experiment used to measure adhesion of the coating to the undeformed metal blank is shown in *Figure* 1. Changes in the peel angle were monitored during the experiment with a video system. With a precuring time of three minutes, the bulk epoxy did not adhere to the coating. Precuring times of zero, one, and two minutes produced specimens that failed at the metal-coating interface. The peel strength was not affected by the precuring time within experimental error ± 15%. It was concluded that diffusion of the epoxy was not a significant factor, and therefore, precuring of the bulk epoxy was not used to prepare subsequent specimens.

Fracture surfaces from the peel experiment were coated with 50Å of gold for scanning electron microscope (SEM) observation in a JEOL JXA instrument. Fracture surfaces for X-ray dispersive analysis (EDAX) were coated with 20Å of carbon.

To measure residual stresses on the deep drawn coatings, the metal substrate was cleaned with methyl ethyl ketone and sprayed with Teflon® before epoxy coating application. The Teflon spray was used to assure polymer film detachment from the metal after the deep draw. The coating was applied to the metal as described previously.[19] The residual stresses in the coating after deep drawing were determined by punching a 2-mm diameter circular piece from a shallow valley region, 6-7 mm from the edge of the cup. The coating was peeled off the metal. The geometrical changes, after the circle was peeled from the substrate, were measured with an image analysis system.

For T_g measurements, the coatings were cast on tin foil. The tin foil was dissolved in mercury to obtain the free film. The T_g was determined by thermal analysis. A Perkin-Elmer Model 7 DSC with approximately 5 mg specimens was employed. The thermograms were obtained with a heating/cooling rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

The Deep Draw (Cupping) Process

The deep draw process for making cups uses a punch to force a flat circular blank of material into a cylindrical die as shown schematically in *Figure* 2. The blank is centered on the die, and a blank holder pressure is applied. The pressure is adjusted to prevent wrinkling but to allow the blank to slip easily into the die. To prevent ironing, the gap width between the die and punch should be larger than the blank thickness. The gap width used in the present study was about 20% greater than the thickness of the blank.

In the deep drawing of a cup, the metal is subjected to blank holder and punch forces. The metal at the center of the blank under the head of the punch wraps around the punch and experiences minimal stress. As the punch forces the blank into the die, the metal passes over the die curvature where it first bends and then straightens. Once it enters the cup wall, the metal experiences a tensile stress. Concurrently, metal in the outer portion of the blank is drawn inward toward the die. The outer circumference is forced to continuously decrease from that of the original blank to that of the finished cup. The constraint of the blank holder prevents wrinkling, instead the metal responds to the compressive stress in the circumferential direction with a continual increase in thickness as the blank moves inward.

The final product of the deep draw process is a cylindrical cup. The photograph in *Figure* 2 shows a deep drawn cup 22 mm in diameter, formed from a circular blank 44 mm in diameter. The top of the cup is undulating with ear and valley regions. The characteristic ears and valleys at the top of the cup and buckling of the metal in the valley regions result from instabilities raised during the cupping process.[19] The earing instability is well known from the literature. A general theory of earing was first proposed by Hill.[20] The origin of earing lies in the crystallographic unit cell of the metal blank and the planar anisotropy introduced by rolling. The body-centered cubic (bcc) metals used in most can-making processes can generate four, six, or sometimes eight ears.[21] The contributions of the crystallographic unit cell and the planar anisotropy to the final earing profile can be separated using analytical procedures.[22] The buckling instability is deeply related to earing. At the end of the deep draw the metal blank loses contact with the blank holder first in the valleys, while the ears and shallow valleys remain constrained. At this point, the unconstrained valleys are free to buckle. The buckle is forced into a waveform when it enters the gap. Buckling is an elastic instability that occurs when the valleys lose constraint before the ears.

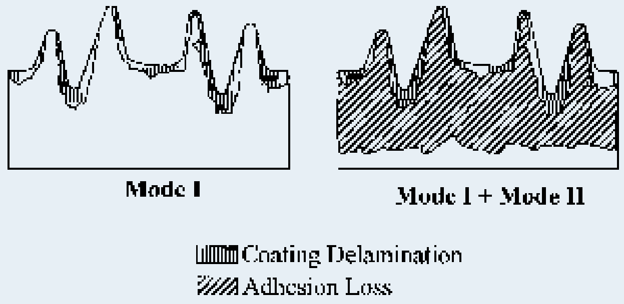

Figure 3—Coating failure modes.

As a consequence of the stresses imposed on the coating by the metal deformation, two types of coating failure are observed on the deep drawn cups (*Figure* 3). In mode I failure, the coating delaminates from the metal at the top of the cup. This failure mode dominates in the buckled valley region. Mode I debonding failure initiates during the buckling instability when the cup is drawn to about 90% of its final height. In mode II failure, the coating loses adhesion to the cup wall. Mode II failure is not as apparent as mode I. The coating remains in contact with the metal surface after forming, however, it can easily be peeled away from the cup wall. Mode II failure occurs at the end of the deep draw process when the cup loses all constraint of the blank holder. The type and degree of failure are expected to depend on the initial adhesive strength of the coating to the undeformed metal substrate.

Table 1—Effect of Crosslinker on Coating Properties

Coating Designation	M_w of Prepolymer	Crosslinker (wt%)	Wax	Failure in Deep Draw (n=6)	T_g (°C)	Peel Force (N/m)	Recovery Strain	
							L_{II} (%)	L_I (%)
A/10	22 000	10	None	Mode 1	89	1070 ± 125	–2.6 ± 0.5	1.1 ± 0.6
A/15	22 000	15	None	Mode I + Mode II	91	650 ± 81	–2.1 ± 0.5	1.2 ± 0.5
A/20	22 000	20	None	Mode I + Mode II	96	600 ± 80	–2.7 ± 0.6	1.5 ± 0.3

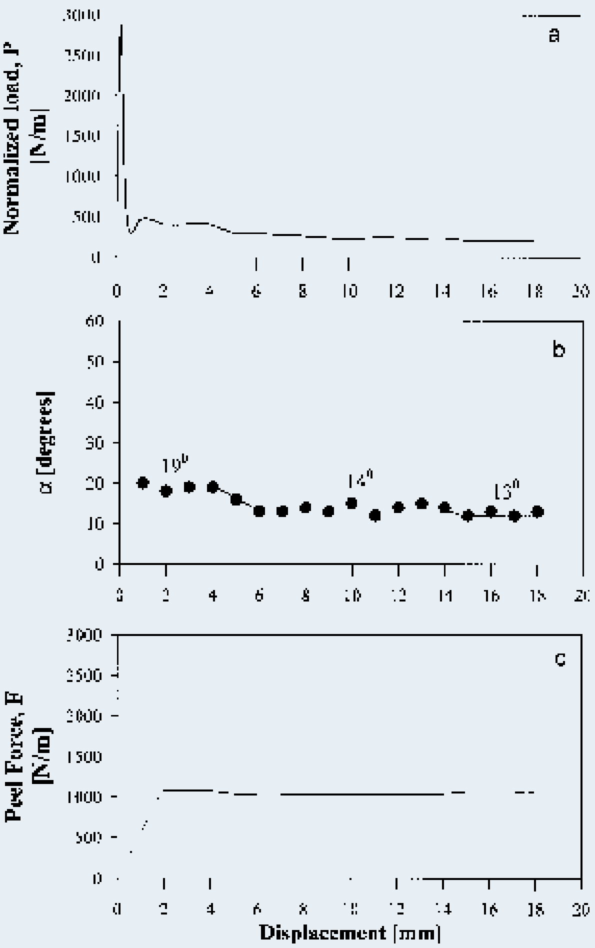

Figure 4—Results of a representative peel test: (a) normalized load vs displacement; (b) peel angle vs displacement; (c) peel force vs displacement after correction for changes in the peel angle.

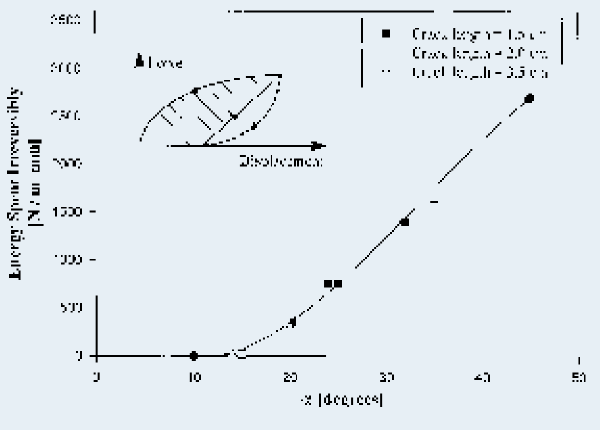

Figure 5—Calibration curve for irreversible deformation of the metal arm during the modified peel experiment.

Adhesion Measurements

In the modified peel experiment, the peel crack followed the coating-metal interface and the peel force represented the adhesive strength. A typical normalized load-displacement curve for the A/10 coating is shown in *Figure* 4a. The normalized load P was calculated as L/W, where L is the load and W is the width of the specimen. After an initial overshoot, the load gradually leveled off. The peel angle continuously decreased during the experiment (*Figure* 4b).

The measured normalized peel load was corrected for plastic deformation in the metal arm. In order to measure the energy spent irreversibly in the peel experiment, a thin Teflon tape was placed between the bulk epoxy and metal to prevent adhesion. The crack length was fixed with a clip. The specimen was loaded to a certain crack opening angle α, then unloaded and loaded again to achieve the same force as on the first loading. The hysteresis area, insert in *Figure* 5, was taken as the energy spent irreversibly during loading to a crack opening α. As shown in *Figure* 5, this quantity depended on α but had no dependence on the crack length. Referring again to the example in *Figure* 4a, the area under the overshoot between 0 and 0.2 mm displacement was 287 N mm/m. For comparison, the initial peel angle α of 19° required an expenditure of 301 N mm/m in plastic deformation (*Figure* 5). The correlation demonstrated that the initial overshoot in the load-displacement curve was attributable to plastic deformation of the metal arm. Therefore, the initial overshoot was neglected in subsequent analysis of the adhesion strength. The normalized peel load P was corrected for the peel angle α to obtain the detachment force $F = P/\sin\alpha$. The quantity F was constant over the entire peel experiment (*Figure* 4c), and was taken as the adhesive strength of the coating to the metal.

Effect of Crosslinker Concentration and Prepolymer Molecular Weight

Three coating formulations that varied only in the crosslinker concentration were investigated (*Table* 1). All

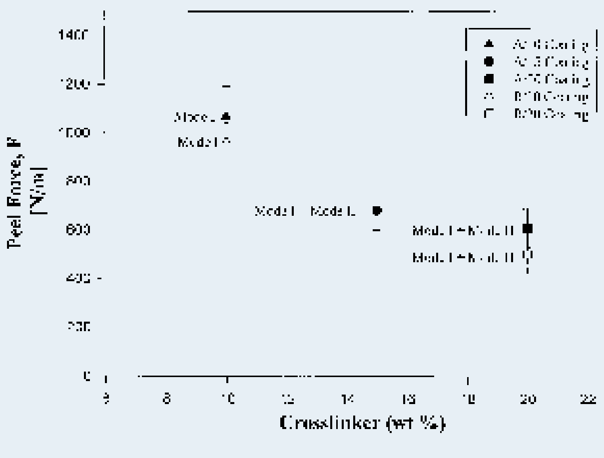

Figure 6—Effect of amount of crosslinker and prepolymer molecular weight on adhesion.

three coatings exhibited mode I failure, delamination at the top of the cup. The coatings with 15 and 20% crosslinker also exhibited extended areas of mode II failure, loss adhesion on the cup walls. However, the coating with 10% crosslinker showed no mode II failure. Adhesion measurements revealed that the coating with 10% crosslinker had significantly stronger adhesion to the metal than the coatings with 15 and 20% crosslinker, 1070 N mm/m compared to 650 and 600 N mm/m, respectively (*Figure* 6). Better adhesion of less-crosslinked epoxy coatings to metal substrates is usually attributed to better flowout and slower gelation time.[5,23]

The surface of the peeled metal was examined in the scanning electron microscope, and the features compared with those of the bare, uncoated metal. The uncoated metal was characterized by a striated surface texture that resulted from the rolling process (*Figure* 7a). The metal surface from which the A/20 coating had been peeled was indistinguishable from the uncoated metal surface (*Figure* 7b). The metal surface that had been coated with the A/15 coating showed areas of surface distortion (*Figure* 7c-d). The metal substrate was tin-free steel with a 1-2 µm thick layer of tin[18] followed by a monolayer of chromium oxide.[23] The damage probably occurred in the thin tin layer that covered the steel substrate. The metal with the A/10 coating exhibited similar surface damage and, in addition, small 2-4 µm flakes that had broken off the coating were adhered to the metal (*Figure* 7e-f).

The coating, which remained attached to the bulk epoxy after the peel experiment, was examined for adhered metal using EDAX. The EDAX spectrum of the metal substrate was characterized by a strong emission peak for tin at 3.6 keV and two iron peaks at 6.4 and 7.1 keV (*Figure* 8a). A weak peak at 5.4 keV in the enlarged spectrum revealed the presence of chromium (*Figure* 8b). The bulk epoxy showed a peakless signal that decayed toward the high eV region (*Figure* 8c). A weak chromium peak appeared in the spectrum of the epoxy that contained the peeled A/20 coating (*Figure* 8d). The chromium peak was stronger in the spectrum of the A/15 coating, and was strongest in the spectrum of the A/10 coating (*Figure* 8e-f). Furthermore, spectra of the peeled A/15 and A/10 coatings contained a pronounced tin peak. These spectra revealed a correlation between the strength of the coating-metal adhesion and the amount of metal from the steel substrate that adhered to the detached coating as it was peeled from the metal. The combined evidence from metal substrate (SEM) and detached coating (EDAX) analyses unambiguously

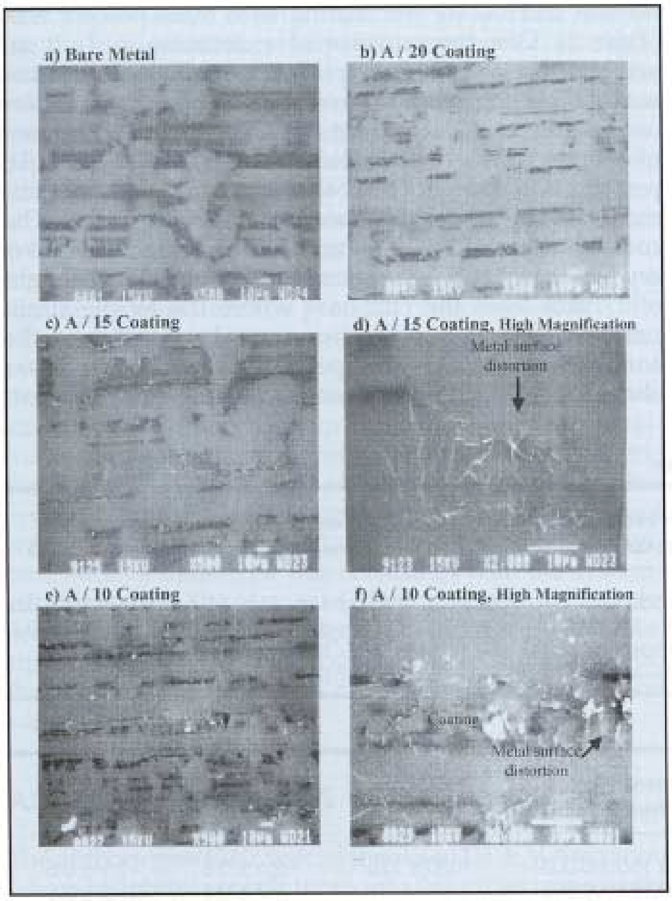

Figure 7—Scanning electron micrographs of the metal surface after the peel experiment: (a) unpeeled bare metal; (b) peeled from A/20 coating; (c) and (d) peeled from A/15 coating; (e) and (f) peeled from A/10 coating.

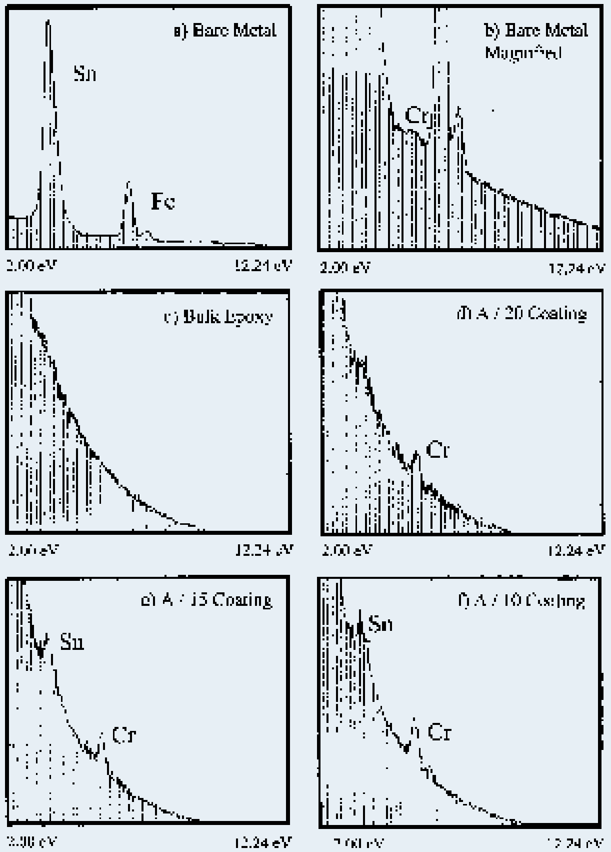

Figure 8—EDAX analysis of the epoxy surface after the peel experiment: (a) and (b) unpeeled bare metal; (c) unpeeled bulk epoxy; (d) peeled A/20 coating; (e) peeled A/15 coating; (f) peeled A/10 coating.

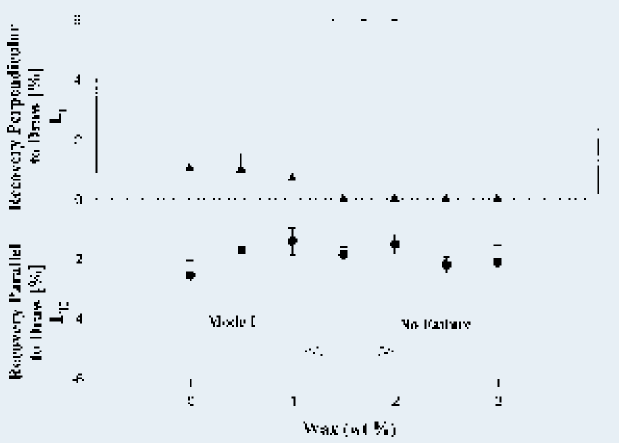

Figure 9—Effect of wax additive on recovery of the deep drawn coatings.

showed that the increase in adhesive strength that was achieved by decreasing the crosslinker content from 20 to 10% significantly increased the amount of damage during peeling. Moreover, the increase in adhesive strength that this represented was sufficient to prevent mode II failure during the deep draw process.

Increasing the prepolymer molecular weight from 12,000 to 22,000 did not affect coating failure in the deep draw. Coatings of both molecular weights with 10% crosslinker exhibited mode I failure, likewise coatings of both molecular weights with 20% crosslinker exhibited the combination of mode I and mode II failures (*Figure* 6). Although the increase in prepolymer molecular weight improved adhesion strength by about 20% (*Table* 2), apparently this was not enough to affect the failure.

Effect of Wax

Wax was added in varying amounts to the A/10 coating. Without the wax, this coating exhibited mode I but not mode II failure in the deep draw. Coatings with less than 1.5% wax also exhibited mode I failure. However, in four tests of the coating with 1.5% wax, only one exhibited mode I failure, the other three did not fail. Addition of more than 1.5% wax completely eliminated mode I failure.

Potentially, the wax can migrate to the coating surface and reduce friction between coating and die,[24] it can migrate to the coating-metal interface and affect adhesion, and it can act as a plasticizer to alter the bulk coating properties. All these possibilities were examined. The friction decreased sharply for all coatings with wax when compared to the coating without wax (*Table* 3). As little as 0.5% wax was sufficient to decrease the frictional force by a factor of 2; however, increasing the wax content further had very little effect on the frictional force. Although wax was shown to migrate to the surface, reduced friction between coating and die probably was not the major factor responsible for eliminating mode I failure. If it had been, 0.5% wax would have been sufficient for the purpose. Conversely, wax apparently did not migrate to the coating-metal interface because addition of up to three percent wax had no effect on the adhesion strength (*Table* 3).

Plasticization of the coating by wax was indicated by the gradual decrease in T_g from 89°C for the coating with no wax to 79°C for the coating with three percent wax (*Table* 3). One consequence of a decrease in T_g is an acceleration of polymer relaxation processes that are responsible for relieving residual stresses.[25] To detect residual stresses in the deep drawn coating, the amount of coating recovery after deep draw was measured. To prevent adhesion of the coatings used in these experiments, the metal substrate was sprayed with Teflon. The coatings detached easily after deep draw and the recovery was measured. Measurements were made at a height of 17 mm from the cup base where the tensile strain parallel to the draw direction was about 30% and the compressive strain in the perpendicular direction was about –35%.[19] Residual stresses caused the detached coat-

Table 2—Effect of Prepolymer Molecular Weight on Coating Properties

Coating Designation	M_w of Prepolymer	Crosslinker (wt%)	Wax	Failure in Deep Draw (n=6)	T_g (°C)	Peel Force (N/m)	Recovery Strain L_{II} (%)	 L_I (%)
A/10	22 000	10	None	Mode I	89	1070 ± 125	–2.6 ± 0.5	1.1 ± 0.6
A/20	22 000	20	None	Mode I + Mode II	96	600 ± 80	–2.1 ± 0.5	1.5 ± 0.5
B/10	12 000	10	None	Mode I	89	900 ± 82	—	—
B/20	12 000	20	None	Mode I + Mode II	94	500 ± 80	—	—

Table 3—Effect of Wax on Coating Properties[a]

Coating Designation	Wax (wt%)	Failure in Deep Draw (n=4)	T_g (°C)	Dimensionless Friction Force	Peel Force (N/m)	Recovery Strain L_{II} (%)	 L_I (%)
A/10	None	Mode 1	89	0.165 ± 0.003	1070 ± 125	–2.6 ± 0.5	1.1 ± 0.6
A/10/0.5	0.5	Mode 1	—	0.087 ± 0.003	—	–1.7 ± 0.6	1.0 ± 0.5
A/10/1	1	Mode 1	—	0.086 ± 0.009	1065 ± 130	–1.4 ± 0.5	0.7 ± 0.2
A/10/1.5	1.5	None (n=3)/Mode 1 (n=1)	83	0.083 ± 0.008	—	–1.9 ± 0.3	0.0 ± 0.0
A/10/2	2	None	—	0.073 ± 0.010	—	–1.5 ± 0.3	0.0 ± 0.2
A/10/2.5	2.5	None	—	0.072 ± 0.003	—	–2.2 ± 0.3	0.0 ± 0.2
A/10/3	3	None	79	0.076 ± 0.008	1072 ± 123	–2.1 ± 0.6	0.0 ± 0.0

(a) Prepolymer M_w = 22 000, Crosslinker = 10 wt%.

ing to extend in the direction perpendicular to the draw direction and contract in the parallel direction (*Figure* 9). The amount of perpendicular recovery, and hence the magnitude of the residual compressive stresses, decreased as the amount of wax increased. Coatings with 1.5% wax or more did not exhibit any recovery in the perpendicular direction. This correlated with the amount of wax required to eliminate mode I failure. Residual compressive stresses in the coating were induced during the cupping process when the outer circumference of the coated metal was forced to decrease from that of the original blank to that of the finished cup. Unless the residual stresses were dissipated through relaxation processes, the resultant interfacial shear stress promoted adhesive failure and extension of the coating caused delamination from the metal.

SUMMARY

Correlations were found between certain formulation variables and coating performance in the deep draw process. In order to understand how certain variables affected failure, it was essential to have characterized the deformation of the metal substrate in the deep draw process, and to have established the failure modes of a thin epoxy coating on the metal substrate. Combined with a knowledge of certain coating properties, including the glass transition temperature, adhesion strength, and residual stresses, it was possible to understand the effect of formulation variables on coating failure. It was found that mode I failure, delamination at the cup edges, depended on residual compressive stresses in the drawn coating. In the present study, addition of a low molecular weight polyethylene wax was the formulation variable that affected the residual stresses. Crosslinker concentration and prepolymer molecular weight had no significant effect on this property. Mechanistically, the effect of wax was attributed to plasticization as indicated by a decrease in the glass transition temperature of the coating. In contrast, it was found that mode II failure, loss of adhesion on the cup wall, depended on metal-coating adhesion. In this study the formulation variable that most strongly affected adhesion was the crosslinker concentration. The effect was attributed to increased wetout and slower gelation with lower crosslinker concentration, a trend that was consistent with the systematic decrease in the glass transition temperature. Higher prepolymer molecular weight also increased the adhesion somewhat; the wax apparently did not migrate to the coating-metal interface because it had no effect on adhesion.

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