Wrinkling of Epoxy Powder Coatings

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ABSTRACT: Differential scanning calorimetry (DSC) and mechanical profilometry were used to study wrinkle formation in curing epoxy powder coatings. Powder coating formulations were studied that contained solid epoxy resins, methylene disalicylic acid (MDSA) crosslinker, and an amine-blocked Lewis acid catalyst. Both the crosslinker (MDSA) and the amine-blocked catalyst are required for wrinkle formation. Evaporation of the blocking amine from the free surface of the coating generated a depthwise gradient in the extent of polymerization and crosslinking, and hence in the degree of solidification, as evidenced by the formation of a mechanical skin prior to wrinkling. It is hypothesized that compressive elastic stress develops in the still swellable skin when unreacted low-molecular-weight material from beneath diffuses up into the monomer- or oligomer-depleted crosslinking skin and swells it. This compressive stress, if above a critical value, buckles the skin to produce wrinkles. Experimentally observed compositional requirements for wrinkle formation were consistent with the proposed mechanism. The size of the wrinkles can be controlled by varying formulation parameters such as the amount of catalyst or crosslinker. Increasing the amount of catalyst decreased both the wavelength and the amplitude of the wrinkle pattern. Increasing the amount of crosslinker initially increased the amplitude of the wrinkles; after reaching a maximum level, the wrinkle amplitude decreased. DSC was a useful tool to understand the critical reactions responsible for wrinkling in this system. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 116–129, 2005

Key words: crosslinking; blocked catalyst; wrinkling; gloss; differential scanning calorimetry (DSC)

INTRODUCTION

Powder coatings with wrinkled appearance that are low in gloss have found widespread use in the office furniture and laboratory equipment markets. Epoxy resin-based powder coatings that produce wrinkle finishes were discovered and patented by the Polymer Corp. in the early 1980s.[1] While wrinkling in epoxy and other chemistry-based powder coating systems has been known for over 20 years, a basic understanding of how the surface structure forms has been lacking.

Since wrinkle coatings were first introduced, many researchers have proposed different explanations for why wrinkles form in certain curing powder coatings. Lee et al.[2] found that wrinkles in epoxy- and urethane-based powder coatings appeared only after the coating had crosslinked enough to gel; wrinkles continued to develop after gelation. Huang et al.[3] observed fine wrinkling at late stages of curing in polyester resin-based powder coatings. Wrinkling, they thought, was due to local variations in shrinkage stress caused by lateral variations in the extent of reaction, which perhaps arises from compositional heterogeneity of the original powder. Foster et al.[4] and Jacobs et al.[5] studied surface wrinkling in powder coatings based on the reaction of hydroxyl functional polyester resins with tetramethyoxymethyl glycoluril and various amine-blocked sulfonic acids catalysts. They observed that wrinkled coatings resulted only when the acidity of the systems was high; they believed the crosslinking reactions are mostly inhibited at low values of acidity. They thought that wrinkles form somehow by build-up of stresses during network formation; they thought that all internal stresses balance except at the surface, and the effect of unbalanced stress at the surface would be manifested as wrinkling of the surface. They recognized the development of tensile stress in curing coatings, but did not explain why and how such stresses would produce wrinkling. Wrinkle finishes can also arise in ultraviolet-cured powder coating systems as described by Luciani et al.[6] In their system, the extent of wrinkling depended strongly on the time allowed for melting and leveling of the coating and on the irradiation procedures.[7]

Many questions regarding formation and control of wrinkling in epoxy powder coatings remain unanswered. A clear understanding about what components play the most important role and what reactions are critical in the process of wrinkle formation is lacking. Further, knowledge about how and to what extent the size of the wrinkle patterns can be controlled by varying the compositional parameters is needed. Most importantly, what is required is a comprehensive un-
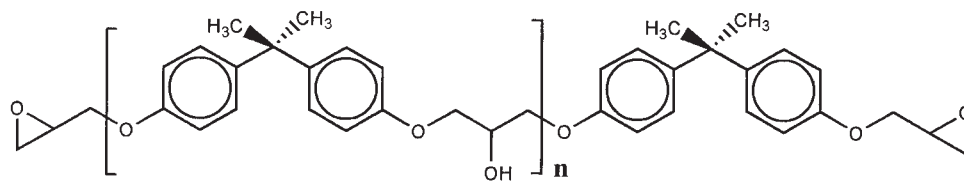
Figure 1 Structure of the bisphenol A diglycidyl ether resin.

derstanding of the physics of wrinkle formation in epoxy powder coatings.

In this paper answers to these questions are found by investigating the compositional requirements and critical reactions of wrinkle formation and deducing a conceptual mechanism that is consistent with the experimental observations. Both a crosslinker, methylene disalicylic acid (MDSA), and an amine-blocked Lewis acid catalyst are required for wrinkles to form. The effects of the reacting components and critical reactions on wrinkle size were evaluated by differential scanning calorimetry (DSC) and mechanical profilometry, and visual appearance was documented by optical photography. For a wrinkled surface to form, two reactions must take place: a Lewis acid-catalyzed self-cure of the epoxy resin and the reaction of the crosslinker, MDSA, with the epoxy resin. DSC was used to understand the relative importance of these two reactions in the wrinkling process. The patterns in the coating surface were characterized by mechanical profilometry, which yielded the surface roughness parameters, namely mean wrinkle wavelength and arithmetic and geometric average wrinkle amplitude.

The exotherms associated with the two main reactions were distinct so that DSC could be used to study the effects of catalyst and crosslinker loadings on the critical reactions of wrinkle formation.[11,12] The effects on wrinkle size of varying catalyst and crosslinker loadings were assessed. It was found that the higher the catalyst concentration, the lower both the wavelength and the amplitude of the wrinkles. Greater amounts of crosslinker made the wrinkle amplitude grow up to a maximum; beyond a critical amount, the amplitude decreased. Wrinkle wavelength appeared to be independent of crosslinker concentration.

Our earlier work,[10,13,14] leads to a conceptual model of the steps of wrinkle formation in the epoxy powder coating system. The first important step is the generation of a mechanical skin over a still-viscous underlayer. In the second step the skin absorbs unreacted material from below so that its stress-free state swells. In the third step swelling frustrated by the in-plain constraint of adhesion to the substrate generates compressive contribution to in-plane stress. After this reverses the tensile stress at first present in the skin it must grow compressive enough to buckle the skin and thereby produce wrinkles.[10,13,14] As demonstrated below, the observed compositional requirements for wrinkle formation in exper-

iments with epoxy powder coatings are consistent with the mechanism inherent by the model.

EXPERIMENTAL

Materials

The catalyst, a boron trichloride amine complex, was obtained from Huntsman (Salt Lake City, UT) under the trade name DY9577. It is a waxy solid with a melting point of about 28°C. For ease of handling, 10% by weight of catalyst was absorbed on barium sulfate (Polar Minerals, Mt. Vernon, IN) to prepare a catalyst master batch. GT-7013, a bisphenol A diglycidyl ether resin with an epoxy equivalent weight (EEW)[15] 650–725 was obtained from Huntsman (Salt Lake City, UT). GT-9496, another bisphenol-A diglycidyl ether resin with an EEW of 740–835 that contains 5 wt % of an acrylic flow control (ethylacrylate/2-ethylhexyl acrylate copolymer) was also used as received from Huntsman. The structure of a bisphenol A diglycidyl ether resin is shown in Figure 1. The crosslinker, MDSA, was synthesized as described in the U.S. patent[17] issued to Morton International. The MDSA obtained by this process is a mixture of dimer isomers as well as of trimers and higher oligomers that are produced by the sulfuric acid-catalyzed reaction of salicylic acid with formaldehyde.[17] Approximately 80% of the MDSA by weight was dimers and the remaining was trimers or higher oligomers. Some of the MDSA structures are shown in Figure 2.

Preparation of coating powders

The ingredients—epoxy resins, MDSA, and catalyst master batch—were blended in given amounts depending on the experiment. A typical composition that produces a wrinkled coating is given in the last column of Table I. The blend was then extruded in a Buss-Ko-Kneader PLK 46 extruder (98 rpm, 82°C). The extrudate was ground and sieved. The fraction of particles smaller than 120 μm was used.

Preparation of coatings on panels

A Nordson (Westlake, OH) Versa Spray electrostatic spray cup gun set at 60 kV was used to spray the coating powders onto electrically grounded cold-rolled steel panels. The 7.6 × 12.7 × 0.082 cm panels
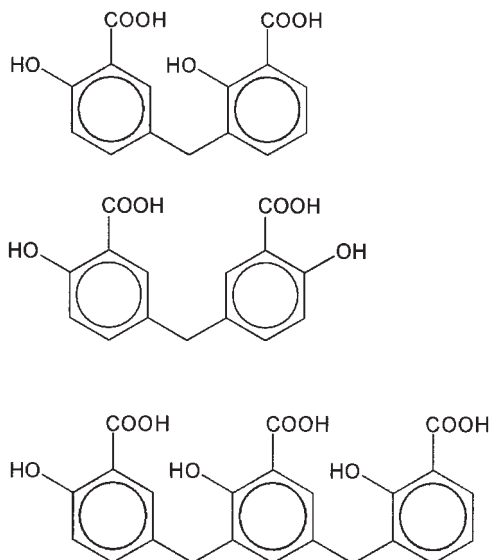
Figure 2 Structures of dimers and trimers of methylene disalicyclic acid (MDSA) synthesized by the reaction of salicylic acid with paraformaldehyde under acidic conditions.[17] All other possible isomers of these two structures are also present.

were obtained from Q-panel (Cleveland, OH). The coated panels were cured in a 190°C forced air convection oven (Blue M, Blue Island, IL) for 10 min. The cured coating thickness ranged from 75 to 110 μm.

Characterization methods

Thermograms of the samples were obtained with a TA Instruments 2920 DSC. DSC thermograms of polymers sometimes exhibit a strong hysteresis peak near the T_g that can make interpretation difficult.[11,18] To reduce this peak, the samples were exposed to the same thermal history by heating each past the T_g, at 20°C/min to 70°C, followed by cooling to room temperature. Data were then collected on the second scan to 300°C at a heating rate of 20°C/min.

The wrinkle wavelength and amplitude of the cured coatings were characterized with a stylus-based mechanical profilometer (Tencor P-10 surface profiler, KLA-Tencor, San Jose, CA). The wrinkle surface was scanned in straight lines—"1D"—with a carbide stylus having a 5-μm-radius hemispherical tip. A stylus contact force of 1 mg was used. The wrinkled surfaces were photographed with a digital camera (Nikon coolpix 990, 3.2 megapixel).

The gel time at a given temperature is defined as the time at that temperature required for a material to be transformed from a dry solid, through a liquid state, to a specified gel-like condition.[19] For the epoxy wrinkle formulations, gel time was measured at 190°C, which is the curing temperature for all samples. Gloss, a measure of surface reflectivity of the coating, was measured at 60 ° angle, as specified by ASTM D 523.

Standardization of mechanical profilometry techniques

Wrinkle coatings were characterized by calculating the average wrinkle wavelength and amplitude from the 1D mechanical profilometry scans. Several scans were taken at different regions on the surface of each coating sample. The average wavelength of a sample was obtained from the scans by counting the average number of peaks per unit length. The average amplitude was calculated in terms of arithmetic and geometric average roughness parameters, R_a and $R_{q'}$ which are defined as[20]

$$R_a = \frac{1}{L}\int_0^L |Y(X) - \bar{Y}| dX \approx \frac{1}{N}\sum_{i=1}^N |(Y_i - \bar{Y})| \qquad (1)$$

$$R_q = \left[\frac{1}{L}\int_0^L (Y(X) - \bar{Y})^2 dX\right]^{1/2} \approx \left[\frac{1}{N}\sum_{i=1}^N (Y_i - \bar{Y})^2\right]^{1/2} \qquad (2)$$

$$\bar{Y} = \frac{1}{L}\int_0^L Y(X) dX \approx \frac{1}{N}\sum_{i=1}^N Y_i. \qquad (3)$$

Here, $Y(X)$ is the coating height as a function of scan length X measured from an arbitrary baseline, L is the scan length, $\bar{Y}$ is the average coating height, and N is the number of data points in the scan length.

To evaluate the effects of scan length on roughness parameters, several scans of different lengths, all starting at the same point on the surface, were made. The scanning length was varied from 2 to 8 mm. As shown in Figure 3A, the roughness parameters calculated from different scan lengths showed only 0.2–0.3% standard deviation from the mean values. Based on this, it can be concluded that a 4- to 5-mm scan length is sufficient for wrinkled surfaces of powder coating.

To determine the number of scans i required to obtain a reliable value of mean roughness parameters, several scans of 5-mm length were made at different regions on the surface until a steady value was ob-

TABLE I
Composition of Coating Samples 1–3

Ingredients	Sample number		
	1	2	3
Epoxy resin GT 7013 (g)	850	850	850
Epoxy resin GT 9496 (g)	150	150	150
MDSA (g)	—	160	160
BCl$_3$:amine[a] (g)	9	—	9
Testing results			
60° Gloss	100+	86	4.1
Gel time (s)	300+	120	45
Appearance	Smooth	Smooth	Wrinkle

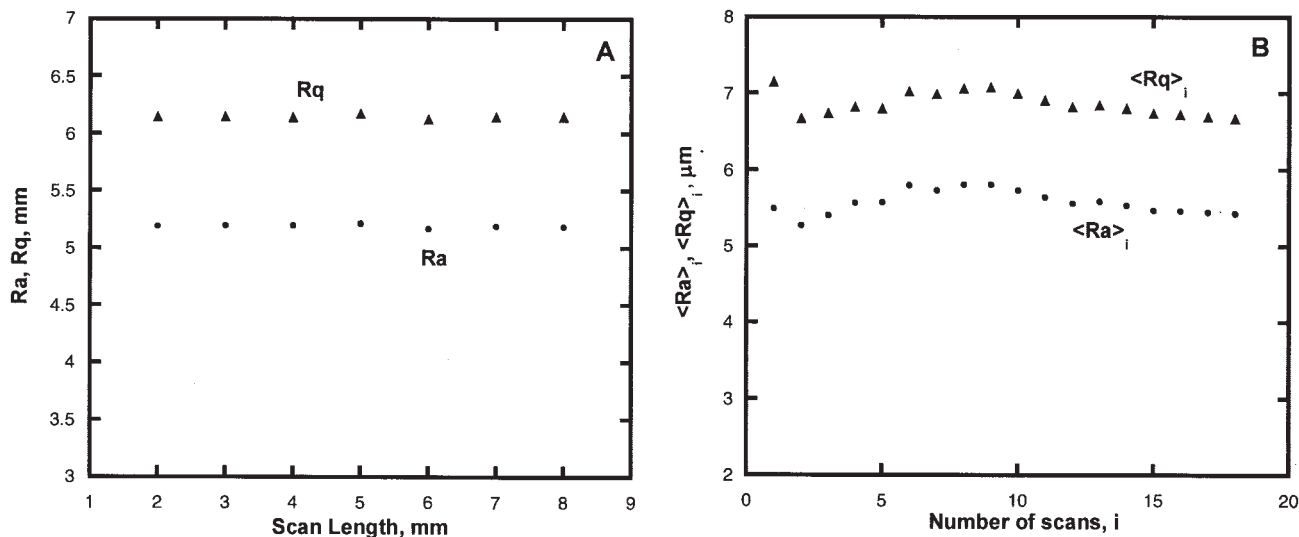[a] Weight listed is the amount of active catalyst present.

Figure 3 Standardization of mechanical profilometry for powder coatings: (A) Effect of scan length on roughness parameters; (B) Effect of number of scans on average roughness parameters.

tained. The mean roughness parameters were averages of i scans ($i = 1, 2, 3...$),

$$\langle R_a \rangle_i = \frac{1}{i} \sum_{j=1}^{i} R_{a_j} \qquad (4)$$

$$\langle R_q \rangle_i = \frac{1}{i} \sum_{j=1}^{i} R_{q_j}. \qquad (5)$$

The number i of scans finally selected was that beyond which adding one more scan did not change the mean value of the roughness parameters ($<R_a>_i$ and $<R_q>_i$) by more than 2% from its previous value. As shown in Figure 3B, at least 12 to 15 separate surface scans were needed before both roughness parameters satisfied this criterion.

RESULTS

Formulation requirements for wrinkling

To isolate the effects of the different reactions on wrinkling, three samples (1, 2, and 3) were prepared whose compositions, 60° gloss, and gel times are shown in Table I. Sample 1 contained only epoxy resins and catalyst, whereas Sample 2 contained only epoxy resins and crosslinker (MDSA). Sample 3 contained all three active components: resins, catalyst, and crosslinker. Profilometry traces of all the cured coating samples are shown in Figure 4. Samples 1 and 2 did not show any wrinkling; however, Sample 3 did. Samples 1 and 2 produced a smooth, glossy coating compared to the wrinkled, low-gloss coating produced by Sample 3. Thus, wrinkle formation appears to require the presence of all three components: epoxy resin, crosslinker, and the boron trichloride amine catalyst.

The DSC thermograms of Samples 1, 2, and 3 are shown in Figure 5. That of Sample 1 establishes that the catalyzed epoxy self-cure reaction has an exotherm at about 150°C. This reaction can be called the epoxy homopolymerization reaction. In Sample 2, the uncatalyzed addition reaction between MDSA and the epoxy groups peaks at about 220°C. This epoxy-MDSA crosslinking reaction can be called the epoxy heteropolymerization reaction. In the absence of catalyst, the epoxy homopolymerization peak at 150°C is absent. In Sample 3, two exothermic peaks are evident, one at 150°C and the other at 187°C. That at 150°C is due to epoxy homopolymerization, as in Sample 1. That at 187°C must be due to epoxy heteropolymerization, which appears at a lower temperature in the presence of catalyst. The decline in the peak temperature indicates that boron trichloride-amine acts as a catalyst for the epoxy heteropolymerization.

As displayed in Figure 1, the epoxy resin has two reactive functionalities, viz. epoxy and secondary hydroxyl. As shown in Figure 2, the crosslinker, MDSA, also has two reactive functionalities, phenolic hydroxyl and carboxylic. The epoxy functionality can react with other epoxy and secondary hydroxyl functionalities of epoxy resin molecules, as well as with phenolic hydroxyl and carboxylic functionalities of MDSA molecules. The secondary hydroxyl functionalities, apart from reacting with epoxy functionalities, can also react with carboxylic functionalities of MDSA molecules. The phenolic hydroxyl and carboxylic functionalities of MDSA can also react among themselves. The presence or absence of the Lewis acid catalyst can further influence the probability of occurrence of all of these possible reactions.

To understand which of these possible reactions can take place under what conditions, a study with model compounds was made. Phenol and salicylic acid were chosen as surrogates that contain the same functionalities as MDSA. Samples of various combinations of phe-
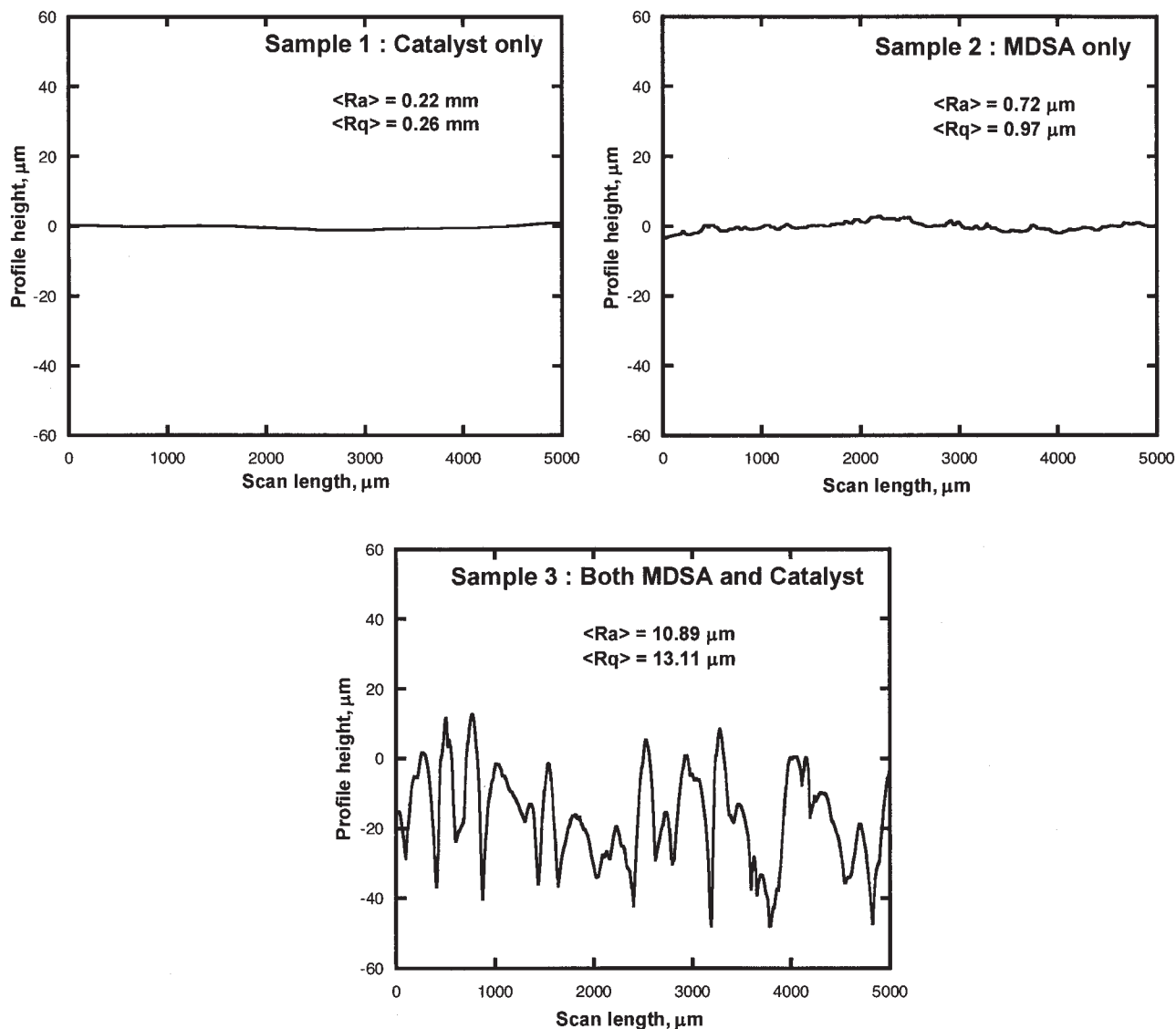
Figure 4   Mechanical profilometry traces of Sample 1 formulation with catalyst only, Sample 2 formulation with MDSA only, and Sample 3 formulation with both MDSA and catalyst.

nol or salicylic acid with epoxy resin (GT 7013) in the presence or absence of the amine-blocked boron trichloride catalyst were prepared to clarify the reactions that should be associated with the exotherms that appear in the DSC thermograms of epoxy wrinkle coating powders. The peaks observed when the samples were heated in the DSC to 300°C at 20°C/min are recorded in Table II. In separate DSC experiments on samples containing just MDSA (not shown in Table II), there was no reaction exotherm but a melting peak was evident near 240°C. These tests with model compounds conclusively established which reactions should be associated with which exotherms of DSC thermograms.

Wrinkle size control

To discover how to control the size of the wrinkles, the concentrations of catalyst and the crosslinker were var-

ied. Using Sample 3[21] as the base case, two sets of samples were prepared. In one set the crosslinker concentration was kept constant and the catalyst concentration was varied; in the other set the catalyst concentration was kept constant and crosslinker concentration was varied.

Effect of catalyst loading

Five samples (A–E, compositions shown in Table III) were prepared to evaluate the effect of catalyst concentration on wrinkle size and appearance. These samples had the same amount of resin and crosslinker as the base case (Sample 3) but different amounts of catalyst. Photographs of the cured coating surfaces of four of five samples and typical mechanical profilometry scans of those surfaces are reported in Figures 6 and 7. Low catalyst loading leads to a coarser wrinkle;
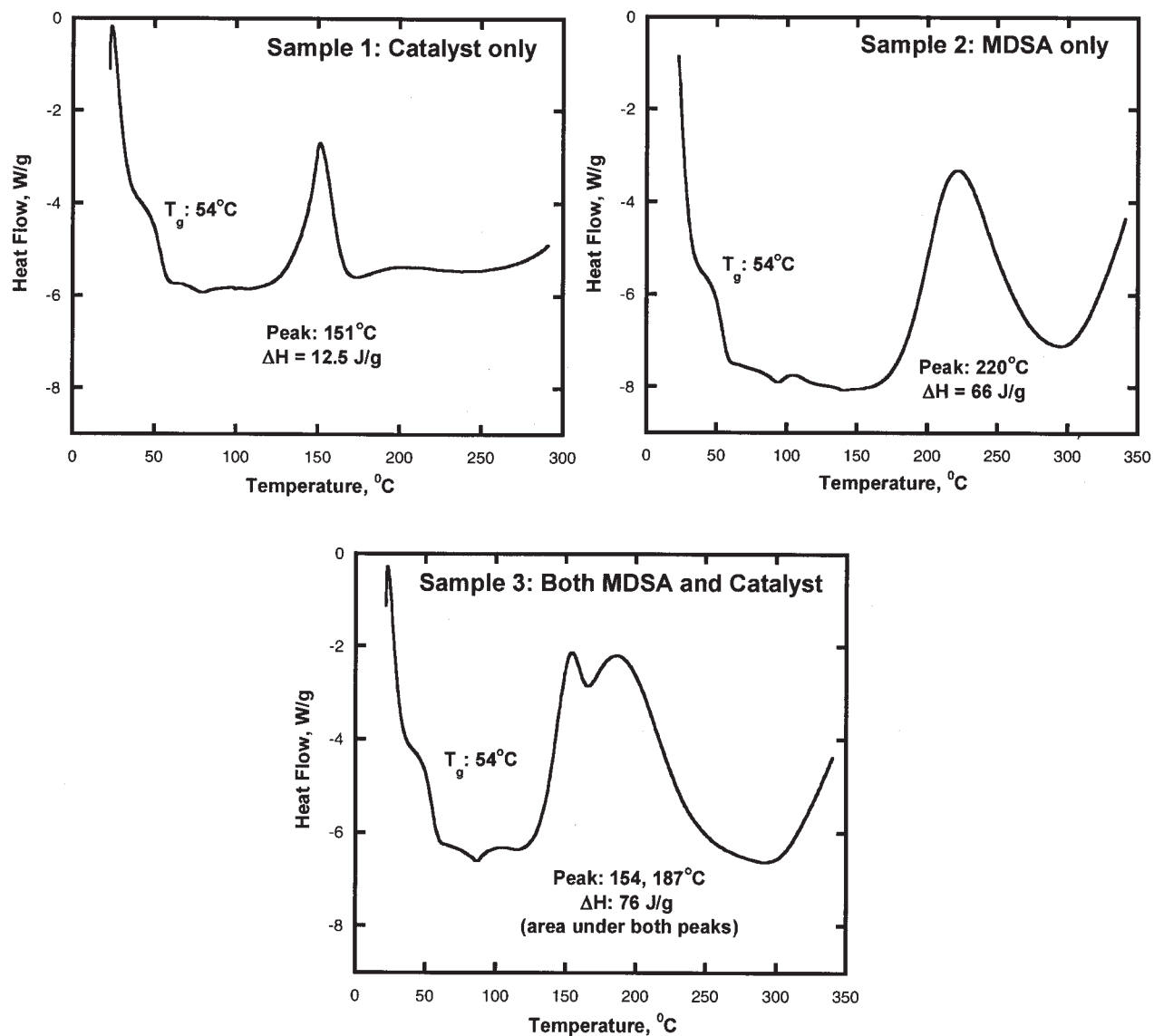
Figure 5 DSC exotherms of powders of Sample 1 formulation with catalyst only, Sample 2 formulation with MDSA only, and Sample 3 formulation with both MDSA and catalyst.
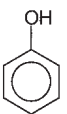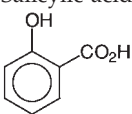
TABLE II
Model Compound Study

Phenol	Salicylic acid	Epoxy resin	BCl$_3$:amine	Exotherms in DSC (scan rate of 20°C/min, 25°C to 300°C)
		X		No exotherms
		X	X	153°C
X		X		No exotherms
X		X	X	150°C, 200°C
	X	X		203°C
	X	X	X	152°C, 185°C (excess salicylic acid)
				151°C, 189°C, 231°C (low amount of salicylic acid)

TABLE III
Composition of Samples A–E used in the Study[a]

Ingredients	Sample number				
	A	B	C	D	E
Epoxy resin GT 7013 (g)	850	850	850	850	850
Epoxy resin GT 9496 (g)	150	150	150	150	150
MDSA (g)	160	160	160	160	160
BCl_3:amine[a] (g)	5	9	12	18	24
Testing results					
60° Gloss	4.2	4.1	4.0	3.8	3.7
Gel time (s)	47	45	35	37	30
Appearance	Wrinkle	Wrinkle	Wrinkle	Fine wrinkle	Fine wrinkle

[a] Sample B has the same composition as Sample 3 in Table I.
[b] Weight listed is the amount of active catalyst present.

as it is raised, the patterns become progressively finer. As shown in Figure 8, both the wrinkle wavelength and the amplitude fell as the amount of catalyst increased. However, the wrinkle amplitude approached an asymptotic value in the samples that contained the highest amount of catalyst.

The DSC thermograms of the samples with different catalyst loading are shown in Figure 9. Raising the amount of catalyst lowered the peak tempera-

ture of the heteropolymerization reaction from 192 to 184°C. The peak temperature of the homopolymerization reaction fell marginally, from 156 to 152°C. The areas under the two peaks together remained about the same as the catalyst concentration was altered. However, the area under the homopolymerization peak grew and the area under the heteropolymerization peak shrunk with rising catalyst concentration.
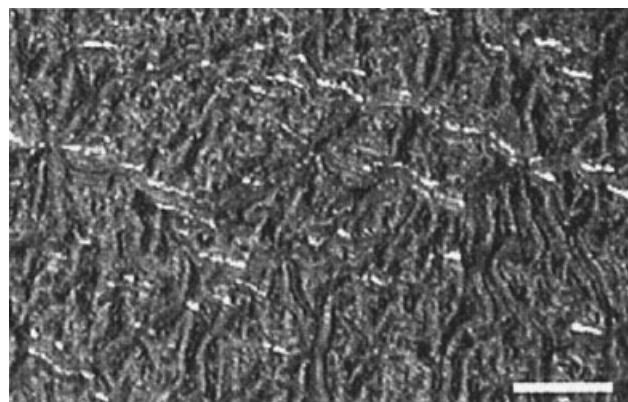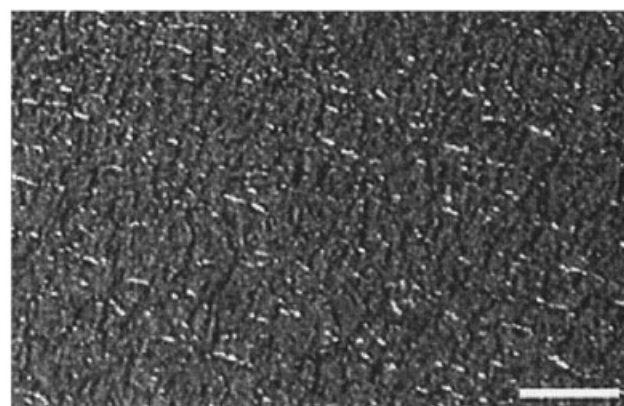

Sample A: 5 g Catalyst
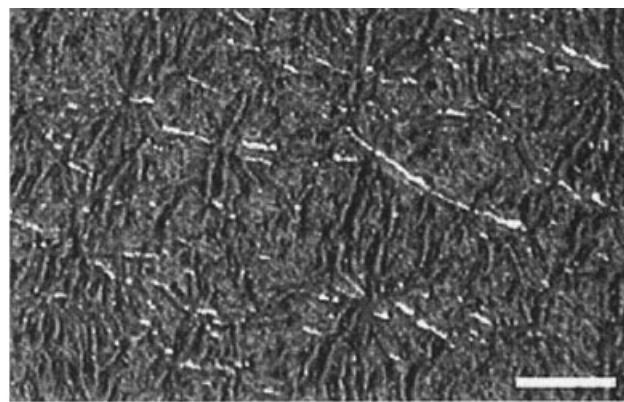
Sample B: 9 g Catalyst
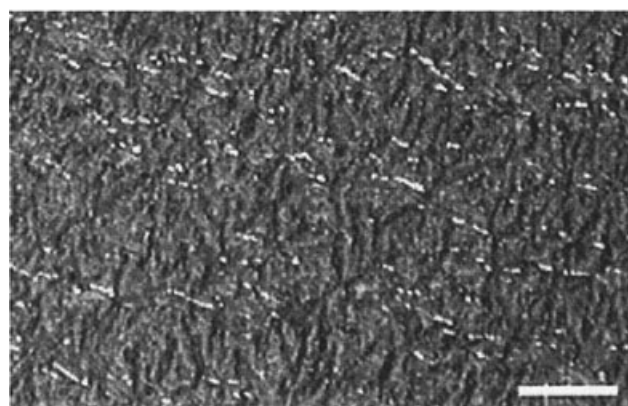
Sample C: 12 g Catalyst

Sample D: 18 g Catalyst

Figure 6 Optical photographs of coatings with different amounts of catalyst. The bar shown in each picture is 1 mm long.
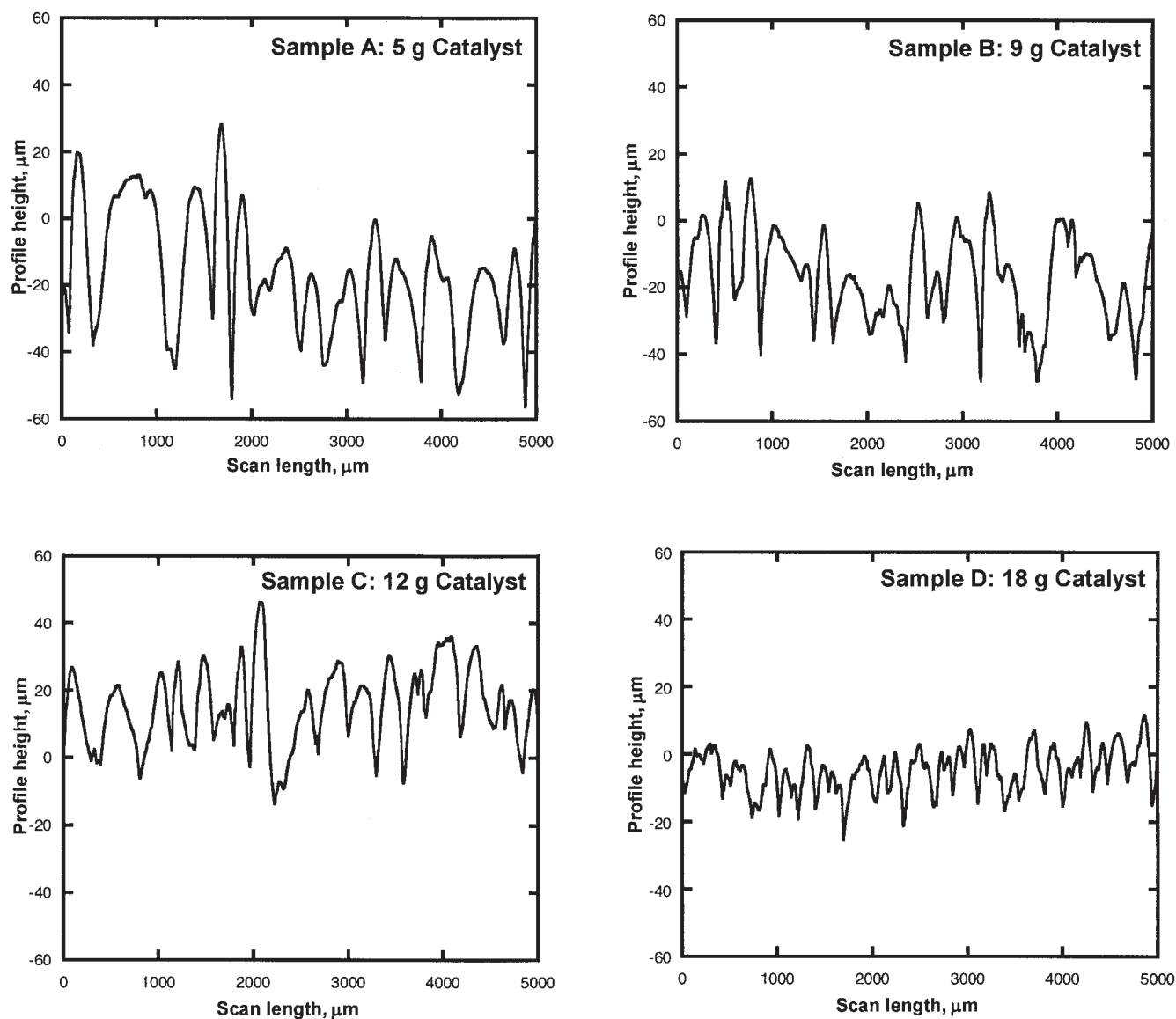
Figure 7   Mechanical profilometry traces for coatings with different catalyst loading. Traces whose wavelength and amplitude are close to the average value for that sample are shown here.

Effect of crosslinker loading

To investigate the effect crosslinker (MDSA) concentration on the wrinkle size and the reactions, six samples (F–K) were prepared. Their compositions are shown in Table IV. As before, the photographs and mechanical profilometry traces of four of the six cured coatings are shown in Figures 10 and 11. Figure 12 records plots of the wrinkle amplitude and wavelength as a function of MDSA concentration. Sample F, which had the least amount of MDSA, formed a coherent film but did not wrinkle appreciably. Samples G–K had a maximum in wrinkle amplitude at a critical MDSA concentration. The wrinkle wavelength, however, seemed not to depend on the concentration of MDSA.

The DSC thermograms versus MDSA concentration appear in Figure 13. The peak temperature of

the epoxy homopolymerization reaction was not affected by changes in MDSA concentration. The peak temperature of the catalyzed heteropolymerization reaction fell from 196 to 184°C as MDSA concentration was raised. A third exotherm at 235°C appeared only in samples that contained below 120 g of MDSA.

Wrinkle patterns also depend on factors other than formulation, including coating thickness, rate of heating, oven conditions, and substrate condition. The average values and the error bars of wrinkle wavelength and amplitude shown in Figures 8 and 12 are based on at least 12 scans on a single coating sample. The average values would be slightly different and error bars slightly wider, without any change in the trends or conclusions of the plots, if additional samples prepared separately
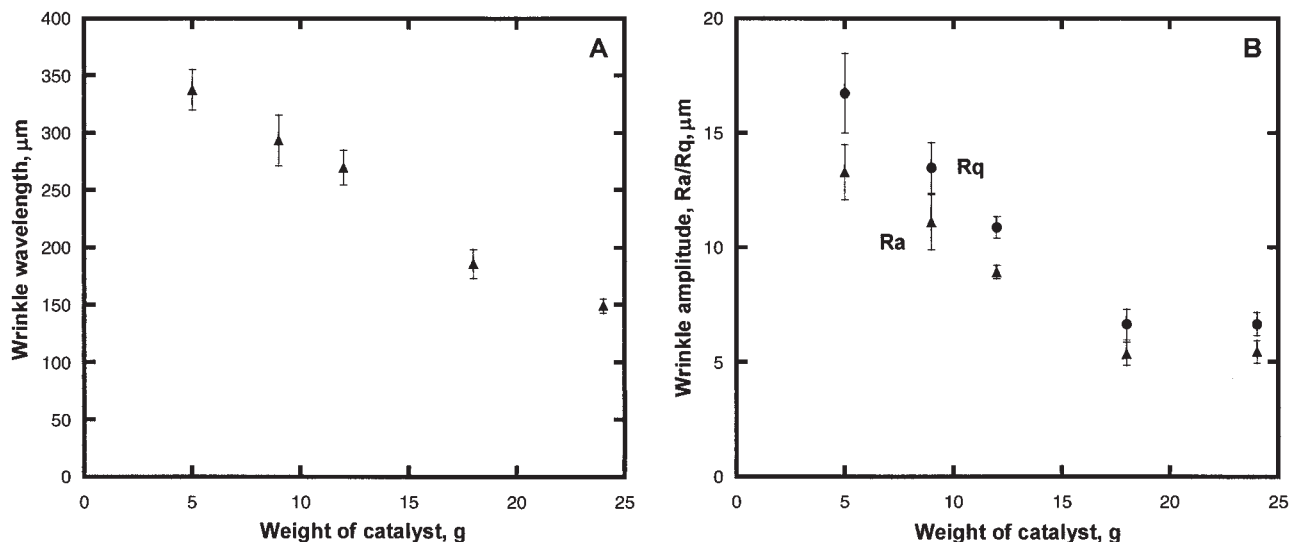
Figure 8 Variation of (A) wrinkle wavelength and (B) wrinkle amplitude with catalyst loading. The mean wavelength/amplitude and its standard deviation obtained from 12 different scans at different place of each sample are shown here.

from different batches of powders were also included.

DISCUSSION

Identifying the critical reactions from DSC results

Table II makes it clear that the epoxy homopolymerization requires a catalyst. The exothermic peak of this reaction system at 150°C in presence of catalyst may be due to epoxy–epoxy reaction or epoxy–secondary hydroxyl reaction. For simplicity, epoxy linear polymerization via activated chain end mechanism is referred to here as epoxy–epoxy reaction. Phenol reacts with epoxy resin only in the presence of catalyst and

Figure 9 DSC thermograms of powders with different amounts of catalyst (Samples A–D).

exhibits peaks at 150°C due to epoxy homopolymerization and 200°C due to epoxy–phenolic OH reaction. Salicylic acid reacts with epoxy resin in the absence of catalyst and displays a peak at 203°C due to epoxy–OH of salicylic acid reaction. Thus, the OH of salicylic acid is more reactive than that of phenol, which requires the catalyst to react with epoxy. Salicylic acid reacts with epoxy resin in the presence of catalyst and exhibits exotherms at 152°C due to epoxy homopolymerization and at 185°C due to epoxy–OH of salicylic acid reaction. The exotherm at 230°C in samples with low amounts of salicylic acid may be due to the reaction of the carboxylic acid functionalities of salicylic acid with the epoxy functionalities. It is expected that the reaction of the epoxy with the phenolic groups present on salicylic acid would be favored over the reaction of the carboxylic acid groups and the epoxy. However, when the system is starved of salicylic acid, the exotherms of the epoxy–phenol and epoxy–carboxylic acid reactions are both distinct. Because MDSA by itself displays no reaction exotherm, any reaction between phenolic hydroxyl and carboxylic groups of MDSA can be discounted.

From this study with model compounds it follows that the epoxy homopolymerization reaction, which appears only in the presence of catalyst and peaks at around 150°C, can be due to reaction both between epoxy and epoxy and between epoxy and secondary hydroxyl functionalities.[16] However, the reaction between epoxy and secondary hydroxyl functionalities is controversial. Whereas Tackie and Martin and others[22,23] claimed that the secondary hydroxyl functionalities on the epoxy chain are less reactive than the epoxy functionalities and do not react below 230 to 270°C, Li et al. and other authors[24–26] found hydroxyl functionality no less reactive than the epoxy function-
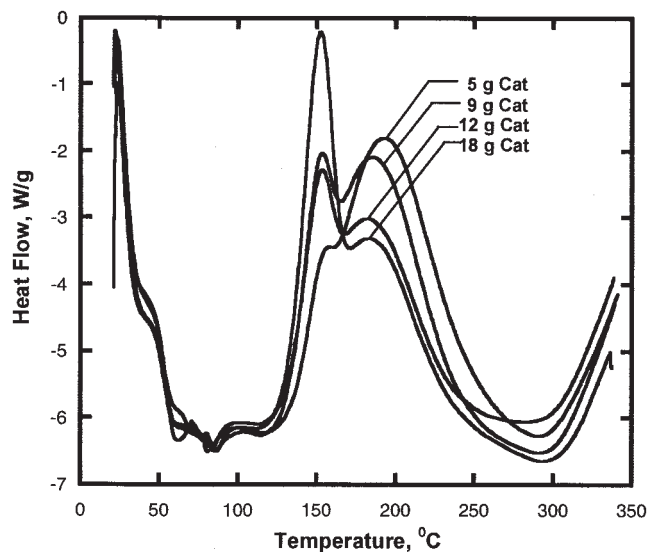
TABLE IV
Composition of Samples F–K used in the Study of Effect of Crosslinker Loading

Ingredients	Sample number					
	F	G	H	I	J	K
Epoxy resin GT 7013 (g)	850	850	850	850	850	850
Epoxy resin GT 9496 (g)	150	150	150	150	150	150
MDSA (g)	80	120	160	200	240	280
BCl$_3$:amine[a] (g)	10	10	10	10	10	10
Testing results						
60° Gloss	31	4.3	3.5	3.7	5.6	5.2
Gel time (s)	125	105	53	44	37	37
Appearance	Smooth	Fine Wrinkle	Wrinkle	Wrinkle	Wrinkle	Wrinkle

[a] Weight listed is the amount of active catalyst present.

ality and so did not neglect its participation in the homopolymerization reaction. If the participation of the secondary hydroxyl groups is negligible, the homopolymerization must result in essentially linear polymerization of the epoxy oligomers.

The heteropolymerization reaction can be between epoxy–OH of MDSA and epoxy–COOH of MDSA.[16] In the present study, however, it was found that reaction between epoxy–COOH of MDSA takes place only when the system is starved of MDSA. Therefore, this reaction can be discounted in most of the cases of interest. In the absence of the catalyst, the heteropolymerization reaction peaks at around 220°C, whereas in the presence of the catalyst it peaks around 187°C. Hence, the catalyst not only is responsible for the homopolymerization reaction but also catalyzes the heteropolymerization reaction. These two reactions, which evidently predominate in the epoxy wrinkle formulation, are depicted in Figure 14. It is noteworthy that when the carboxylic acid groups of MDSA do not react considerably, only the trimers and higher oligomers of MDSA create crosslinks, whereas the dimers create linear polymers.
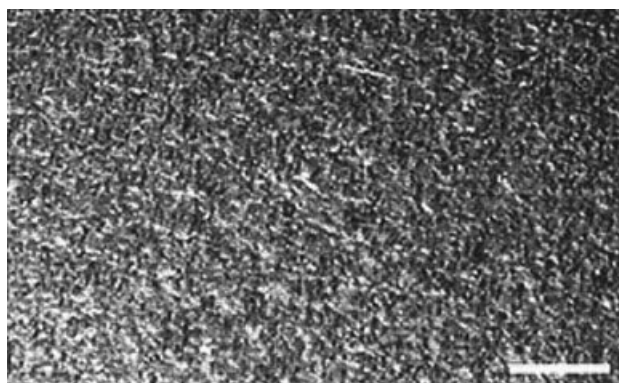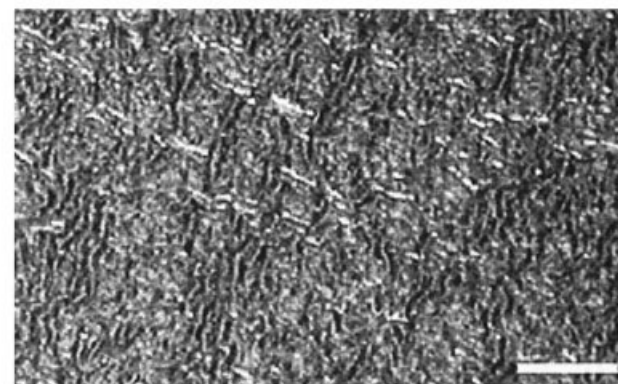

Sample F: 80 g MDSA
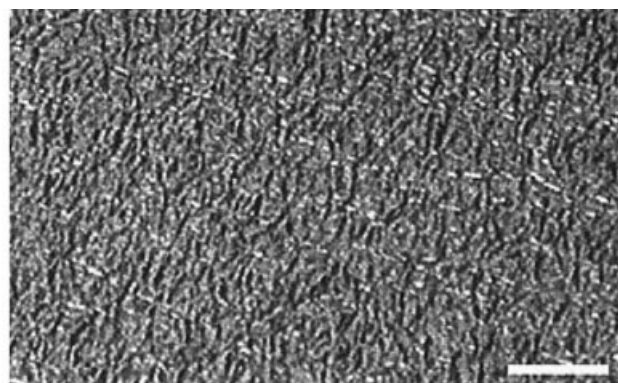
Sample G: 120 g MDSA
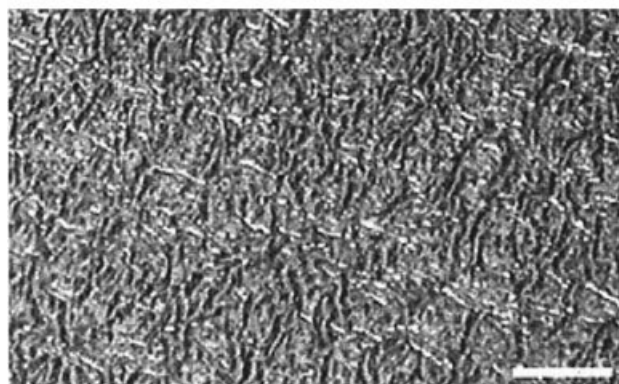
Sample I: 200 g MDSA

Sample K: 280 g MDSA

Figure 10 Optical photographs of coatings with different amounts of MDSA. The bar shown in each picture is 1 mm long.
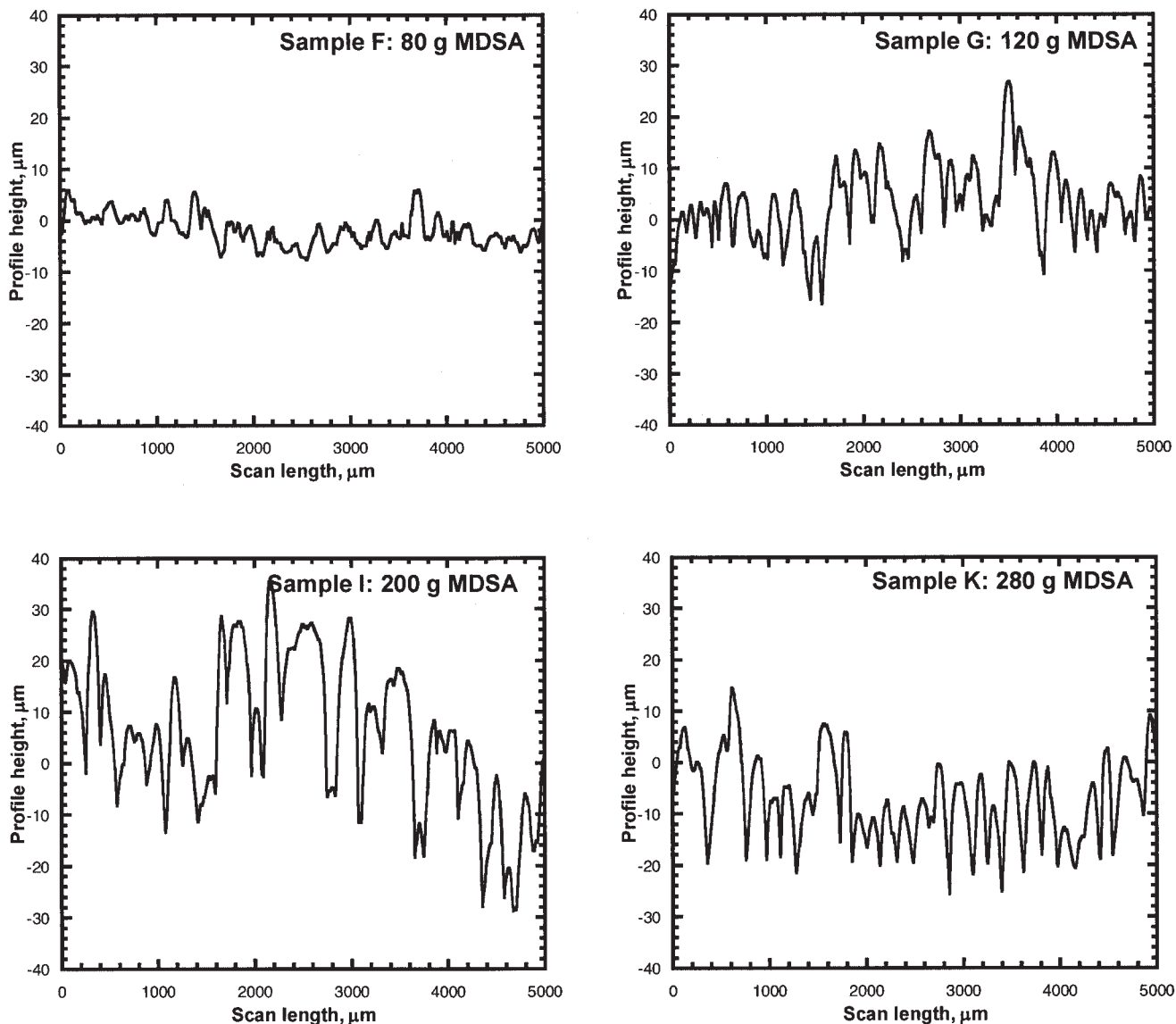
Figure 11 Mechanical profilometry traces of coatings with different crosslinker loading. Traces whose wavelength and amplitude are close to the average value of that sample are shown here.

Compositional requirements and mechanism of wrinkle formation

All samples that produced wrinkles formed a skin prior to wrinkling. The unblocking reaction of the Lewis acid amine complex occurs at a low temperature in the range of 85 to 90°C[22,27] and is reversible.[17] Evaporation of the amine from the surface of the coating[22] shifts the equilibrium there to create a higher effective catalyst concentration. Deeper beneath the surface, amine remains and keeps the effective catalyst concentration low. Consequently, the catalyst-dependent homopolymerization and heteropolymerization reactions are likely to take place preferentially at the surface. This results in a gradient in solidification with depth and causes a skin with modulus, able to support stress, to form.

Skinning appears to be a precursor to wrinkling. The presence of the skin can be demonstrated by

mechanically probing the coating surface.[10] A reasonable hypothesis of the cause of wrinkling is that once a skin of polymerized material is present, unreacted low-molecular-weight monomers and oligomers beneath it diffuse up into the monomer- or oligomer-depleted crosslinking material of the skin and tend to swell it; because the coating cannot swell laterally, compressive in-plane elastic stress develops in the skin even if it is at first in tension; and this compressive stress, once above a critical value, is relieved by out-of-plane deformation, i.e., buckling, into wrinkles that are solidified by subsequent reaction.

The experimentally observed compositional requirements for wrinkle formation are consistent with the hypothesis. In Sample 1, which had only catalyst, a skin presumably formed owing to evaporation of the blocking amine, with the skin resulting from homopo-
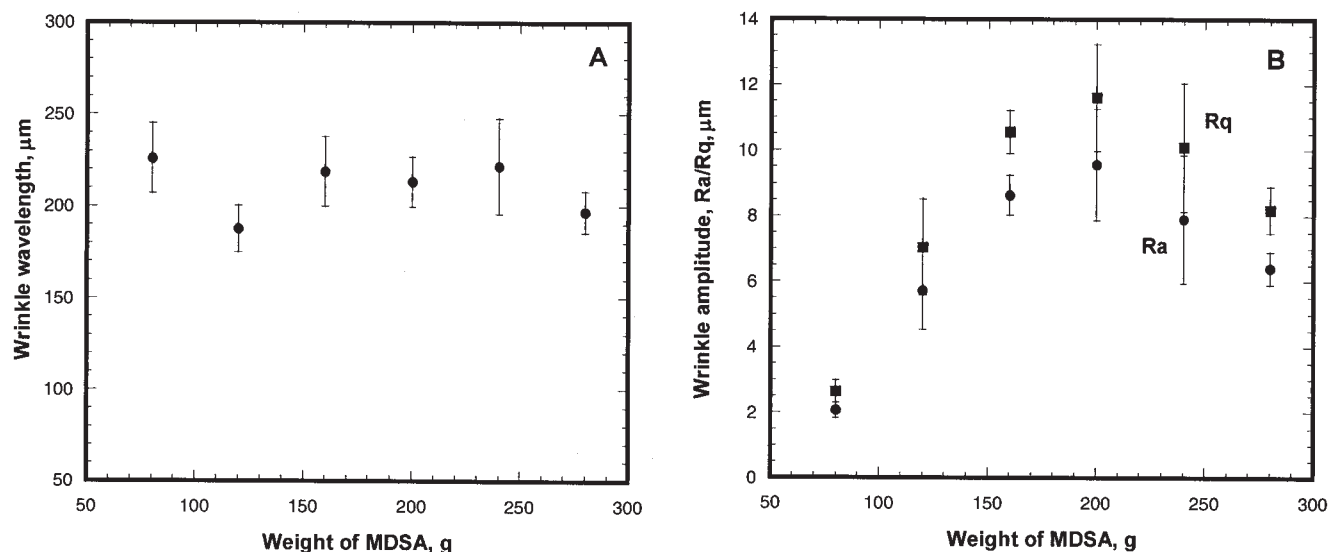
Figure 12 Variation of (A) wrinkle wavelength and (B) wrinkle amplitude with crosslinker loading. The mean wavelength/amplitude and its standard deviation obtained from 12 different scans at different place of each sample are shown here.

lymerization of the epoxy resin and therefore not being highly crosslinked. Such skin would presumably have neither the swellability nor the elastic modulus needed to develop enough compressive stress to buckle. In Sample 2, which had only crosslinker, a crosslinked coating with high modulus formed by the uncatalyzed heteropolymerization reaction, but in the absence of the volatile blocking amine, there could be no gradient in solidification, so that no skin formed and there was no possibility of wrinkling. In Sample 3, which had both the blocked catalyst and the crosslinker, evaporation of the blocking amine, led to a gradient in solidification by the combination of epoxy homopolyerization and catalyzed heteropolymer-

Figure 13 DSC thermograms of powders with different amounts of MDSA (Samples F–K).

ization. The resulting skin must have crosslinked enough to have the swellability and elastic modulus needed to develop sufficient compressive stress to buckle the skin into wrinkles that were locked in place as the polymerization proceeded to completion.

Thus, the observations are consistent with the postulates that generation of a depthwise gradient that leads to skinning, and that diffusion of unreacted material into the skin, are necessary for wrinkling. Plainly, the crosslinking reaction with the crosslinker MDSA must produce a skin of sufficient swellability and modulus, which tend to be contradictory properties, that it can develop high enough in-plane compressive stress to buckle into wrinkles. Nevertheless, formation of a wrinkle finish in epoxy powder coating systems is not limited to the reactions of MDSA with epoxy resins under the influence of amine-blocked Lewis acid catalysts. Wrinkle finishes also result from the reaction of homologues of MDSA, such as methylene bis(3-methylsalicylic acid), with solid epoxy resins in the presence of amine-blocked Lewis acid catalysts.[28] Various other amine-blocked Lewis acid catalysts can also be used to achieve a wrinkled coating. For example, boron trifluoride triethylamine can be used to formulate low-temperature cure wrinkle coatings.[29] It is noteworthy that epoxy cure catalysts that are not blocked with volatile compound do not cause wrinkle finishes, even when combined with MDSA. For example, the reaction of MDSA and epoxy resins can be catalyzed by imidazole–epoxy resin adducts.[30] There is no deblocking of catalyst; no volatile components are evolved; only one cure exotherm is present in the DSC thermogram of the formulation; and the coating is merely textured, not wrinkled.
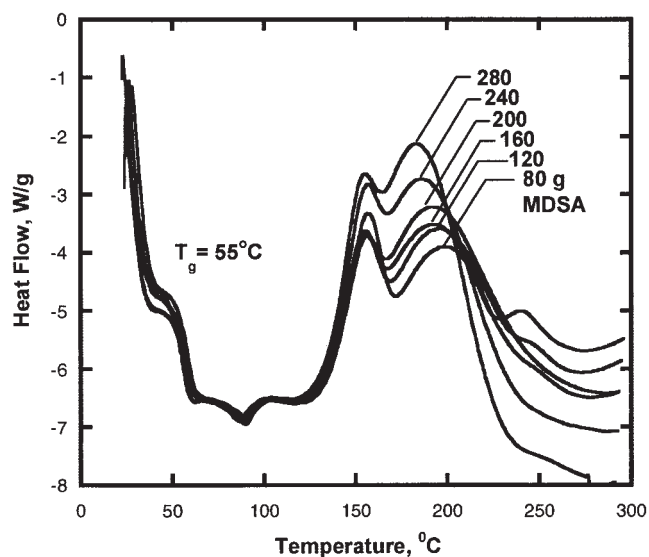
Homopolymerization
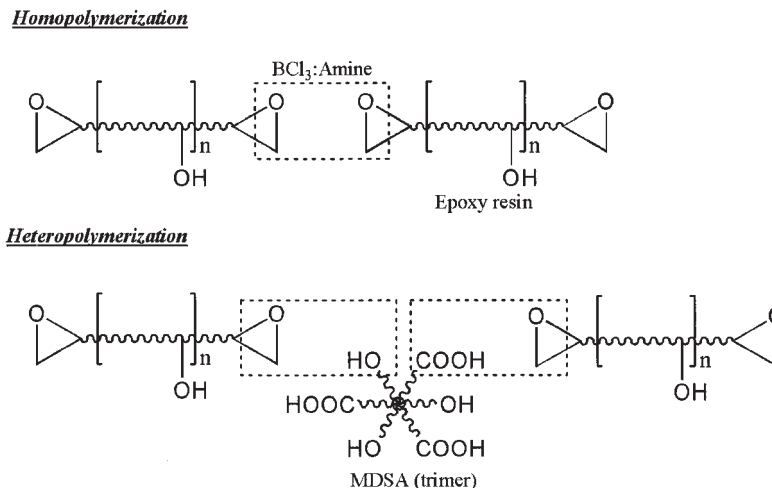

Heteropolymerization

Figure 14   Schematic representation of homopolymerization and heteropolymerization reactions. Simplified representations of epoxy resin and MDSA molecules are used. (Note: In homopolymerization, reaction between epoxy and secondary hydroxyl group is also possible but its occurrence is controversial.[22–26])

Effect of compositional parameters on critical reactions and wrinkling

Concentration of the catalyst and the crosslinker affect the critical reactions and the wavelength and amplitude of the wrinkles. The higher the catalyst concentration, the greater the proportion of homopolymerization reaction and the smaller is that of heteropolymerization reaction, as shown in Figure 9. The temperature of the homopolymerization peak did not shift appreciably with increase in catalyst concentration, whereas the temperature of the peak of the heteropolymerization reaction, which is catalyzed by the catalyst, diminished. Evidently the catalyst lowers the activation energy of the latter reaction. The area under the homopolymerization peak grows and that under the heteropolymerization peak shrinks as the catalyst concentration increases. That the sum of the two areas is about constant indicates that preferentially more bonds form via homopolymerization than heteropolymerization, the higher the catalyst concentration.

Raising the crosslinker concentration enhances the extent of both the homopolymerization and the heteropolymerization reactions, as shown in Figure 13. The temperature of the homopolymerization peak did not shift, whereas that of the heteropolymerization diminished. The sum of the areas under the peaks grew as crosslinker concentration was raised, indicating that more crosslinking takes place the higher the crosslinker concentration. (The third peak, which is at 235°C in Fig. 13, appears only at low crosslinker concentrations and is due to the reaction of the carboxylic acid groups present in the MDSA with the epoxy moieties.)

It is not yet clear why catalyst and crosslinker affect the wavelength and amplitude of the wrinkles in the way experimentally observed. However, it is known that the critical wavelength of buckling of an elastic layer is determined by the modulus and thickness of the layer and by the compressive stress in it at the onset of buckling instability.[10,31,32] The effects of catalyst and crosslinker on modulus, thickness, and compressive stress of the skin in a curing coating can be deduced by constructing and examining a theoretical model of the wrinkle mechanism hypothesized above. This is under way.[33]

CONCLUSIONS

Wrinkle formation in epoxy powder coating systems requires both crosslinking of the epoxy resins with crosslinkers such as MDSA (or its homologues) and the use of a blocked catalyst such as amine-blocked Lewis acid catalyst. In order for wrinkles to form, it appears that a depthwise gradient in solidification must be set up that results in a skin and that for a time the extent of polymerization in the skin must leave it swellable enough by unreacted oligomer from lower in the coating, yet with high enough elastic modulus, that swelling produces sufficient in-plane compressive elastic stress that it buckles into wrinkles. The gradient can be achieved by the use of amine-blocked catalyst: diffusion of the volatile (amine) blocker to the free surface, where its evaporation leads to a depthwise gradient in solidification so that the coating can form a mechanical skin. The crosslinking reactions are crucial to producing a stage of sufficient swellability and modulus and duration that swelling puts the skin into high enough in-plane elastic compressive stress that it buckles to form wrinkles before it becomes too rigidly solid. Experimentally observed compositional requirements for wrinkle formation are consistent with the proposed mechanism.

The size of the wrinkles can be controlled by varying the concentration of the catalyst and the

crosslinker. Increasing the amount of catalyst decreased both the wavelength and the amplitude of the wrinkle pattern. Increasing the amount of crosslinker initially increased the amplitude of the wrinkle; then, after reaching an optimum level, it decreased. DSC was a useful tool for understanding the importance of different reactions and studying the effect of composition changes on them.

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