

# Effects of *In Situ* Esterification on the Performance of Carboxyl Functionalized Rubber-Modified Epoxy Film Adhesives

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**ABSTRACT:** Epoxy-based film adhesive formulations were developed with 10 wt % solid carboxyl functional rubber. Due to the high rubber content and resulting viscosity restrictions, the rubber could not be prereacted with the epoxy before hot-melt filming. Therefore, an esterification catalyst was used to perform this reaction *in situ* before the epoxy curing reactions. The performance of this adhesive system is compared to that of one without the esterification catalyst. A significant difference in the flow characteristics was observed with incorporation of the esterification catalyst, but only small variations in mechanical performance were found. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 728–734, 2000

**Key words:** film adhesives; epoxy adhesives; carboxyl functionalized rubber-modified adhesives

## INTRODUCTION

Film adhesives are used in the transportation industry for many applications ranging from the bonding of metallic or composite structures to surfacing materials for aerodynamic surfaces. Typical adhesive compositions used for these applications are epoxy-based materials that require modifiers for the necessary performance and processing improvements.<sup>1</sup> In the past, a significant research effort has focused on improving cured resin fatigue resistance and fracture toughness.<sup>2–5</sup> However, significantly less attention has been given to understanding effects of the resin composition on the rheology and tack of the materials. These uncured characteristics not only effect the layup of a film adhesive material but also, to a great extent, the cured performance of the structure. This is especially true for situations

in which proper filleting is required for adequate bonding, such as in honeycomb structures.

Common materials used for the modification of epoxy resins are liquid or solid rubbers based on butadiene–acrylonitrile.<sup>6,7</sup> Depending on the state of the material, these elastomers may require dissolution in a suitable solvent, such as methyl ethyl ketone, for incorporation into the epoxy. The solvent can be subsequently removed for hot-melt processing. However, due to high molecular weight and inherent elasticity, the percentage of a dissolved solid rubber in a formulation is usually small unless the films are solvent-cast. Solvent casting requires an added step for the removal of the solvent and can also result in a significant volatile content in the final product. Furthermore, a much smaller quantity of the high-molecular-weight rubber can be added to a hot-melt formulation if the rubber is functionalized (e.g., with carboxyl groups) for coreacting with the epoxy. Since this step is typically performed during the resin formulation procedure with a common esterification catalyst, such as

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triphenylphosphine, the elasticity and viscosity increase dramatically due the large increase in molecular weight. As a result, only a small quantity of solid reactive rubber can be added, or hot-melt filming is not possible. This small quantity may not provide a distinguishable improvement in the performance of the adhesive system.

In this research, a method is described for developing hot-melt-processable film adhesives containing high quantities of solid reactive rubber. Instead of the typical method of prereacting the reactive rubber with the epoxy during formulating, a method of reacting the carboxyl functionalities with the epoxy after hot-melt filming and before epoxy cure was developed. This technique allowed a much higher quantity of solid functionalized elastomer to be incorporated into the film adhesive since the elasticity and viscosity were not increased through a prereaction step. Included in this article is a comparison of the physical and mechanical characteristics of model film adhesive systems with and without this technology.

## EXPERIMENTAL

### Adhesive Formulation

A combination of solid and liquid difunctional epoxy resins based on bisphenol A were used in the model adhesive formulation. The solid epoxy resin was D.E.R.<sup>®</sup> 661 from Dow Chemical Co. (Midland, Michigan), and the liquid epoxy resin was Epon<sup>®</sup> 828 from Shell Chemical Co. (Houston, Texas). Epoxy curing agents used in the formulation were dicyandiamide, Amicure<sup>®</sup> CG 1400 from Pacific Anchor Chemical Co. (Allentown, Pennsylvania), and diuron from Aldrich Chemical Co. (Milwaukee, Wisconsin). Chromium (2%) naphthenate, from OMG Americas Inc. (Cleveland, Ohio), was used as an epoxy/carboxyl esterification catalyst. The resin was modified with a solid butadiene-acrylonitrile rubber, which has randomly distributed carboxyl functionality, Nipol 1472 from Zeon Chemicals Inc. (Louisville, Kentucky). This material, available in crumb form, was washed before use with methanol to remove the surface talc. The base resin formulation consisted of 60 wt % solid epoxy, 30 wt % liquid epoxy, and 10 wt % rubber. The curing agents based on epoxy weight were 5-phr dicyandiamide and 1.5-phr diuron. Three different adhesive formulations were developed, differing only in the concentra-

tion of esterification catalyst incorporated. The esterification catalyst, chromium naphthenate, was included into the formulations in 0, 0.1, and 1.0 phr, based on epoxy weight.

The resin formulation procedure consisted of combining the solid epoxy and two-thirds of the total liquid epoxy with a rubber solution, made of one part crumb rubber and six parts methyl ethyl ketone. After adequate mixing, the resin solution was spread over a high surface area, and the methyl ethyl ketone was removed under vacuum at 110°C. This rubber-epoxy combination was then transferred to a mixing apparatus and cooled to 80°C. A paste consisting of the remaining liquid epoxy resin and the curing agents and catalyst was then incorporated into the resin. After thorough mixing, the adhesive formulation was quenched to room temperature and stored at 0°C until filming.

### Film Adhesive Development

The model film adhesives were developed by incorporating a spunbonded nonwoven polyester fiber scrim, Reemay<sup>®</sup> 2250, into the previously described adhesive formulations. The scrim was placed between two resin films and impregnated using a commercial-scale hot-melt prepreg machine. Resin filming was performed at 75°C, and scrim impregnation was performed at 80°C with minimal force from pressure rollers and a line speed of 0.91 m min. The film adhesives were quenched to 15°C immediately after impregnation and stored at 0°C until testing. All film adhesive thicknesses prior to cure were approximately 0.17–0.20 mm.

### Analysis

The uncured and cured model adhesive resins and films were analyzed using rheometry, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). Rheological data was generated with a Carri-Med TA Instruments CSL 100 controlled stress rheometer. The oscillation package was used with 40-mm parallel plates and a gap of 500  $\mu\text{m}$ . Temperature ramp experiments were performed using a heating rate of 5°C min through cure with an oscillation stress of 80  $\mu\text{N}$  m and an oscillation frequency of 1 Hz. A TA Instruments 912 DSC with a Thermal Analyst 2000 controller was used for the DSC experiments. Dynamic testing of the film adhesives was conducted using a heating rate of 5°C min to 300°C in a

nitrogen atmosphere. Model adhesives were also subjected to cure cycle experiments consisting of a 2.8°C min heating rate to 121°C, followed by a 90-min isothermal hold. The percentage of cure was determined by quenching the cured samples and ramping at 5°C min to 300°C. DMA experiments were performed on the cured film adhesives with a TA Instruments 983 DMA interfaced to a Thermal Analyst 2100 controller. A heating rate of 5°C min with a frequency of 1 Hz, and an oscillation amplitude of 0.3 mm was utilized in a nitrogen atmosphere. Subambient experiments, using a liquid nitrogen cooling system, were used to identify low-temperature transitions.

The composite material used for evaluating the adhesives was developed from Hexcel F 263 woven fabric prepreg. The cure cycle consisted of heating 2.8°C min to 177°C with a 2-h isothermal hold. Laminates were manufactured using a total consolidation pressure of 586 kPa, and the vacuum bag was vented to atmosphere when the autoclave pressure reached 103.5 kPa.

Mode I and mode II fracture energy specimens were fabricated with 18 plies of woven fabric prepreg with an adhesive layer in the midplane. Both precured and cocured specimens were fabricated. Precured composite laminates were solvent wiped with methyl ethyl ketone after a peel ply layer was removed before combination with the adhesive. A 5.08-cm fluorinated ethylene propylene (FEP) copolymer film layer was used as a crack starter and placed in the midplane of the sample. The final specimen dimensions were 33 by 1.27 by 4.10 cm. Mode I interlaminar fracture energy was measured using the double cantilever beam (DCB) method.<sup>8–10</sup> Each specimen was precracked in the mechanical testing apparatus to provide a sharp crack tip before testing. Fracture specimens were tested using a crosshead speed of 2.54 cm min until a displacement of 6.35 cm was reached at which point the crack extension was marked. Seven samples, each providing one  $G_{IC}$  value, were tested and averaged for each reported  $G_{IC}$  value. Standard deviations were calculated and are shown as error bars.

Mode II interlaminar fracture energy was measured using the end-notch flexure (ENF) test.<sup>8,9</sup> A three-point bending apparatus with stationary posts set 10.16 cm apart was used to create shear fracture of the specimen along the midplane. The crack front was set 2.54 cm from the stationary post, and the loading point was set 5.08 cm from this post. All specimens were precracked in the mechanical apparatus to provide a sharp crack tip

before testing. A displacement rate of 0.254 cm min was used to load the specimen in flexure until the crack propagated. The crack front was then located with an optical microscope fixture and moved back to 2.54 cm from the stationary post. This was repeated until the sample was cracked down its entire length. Eight  $G_{IIC}$  values were obtained for each specimen and averaged for the reported  $G_{IIC}$  value and standard deviation.

2024-T3 aluminum was phosphoric acid anodized and primed before use for adhesive bonding. The cure cycle for the bonded aluminum specimens was 2.8°C min to 121°C with a 2-h isothermal hold. A compaction pressure of 310 kPa was applied throughout the cure.

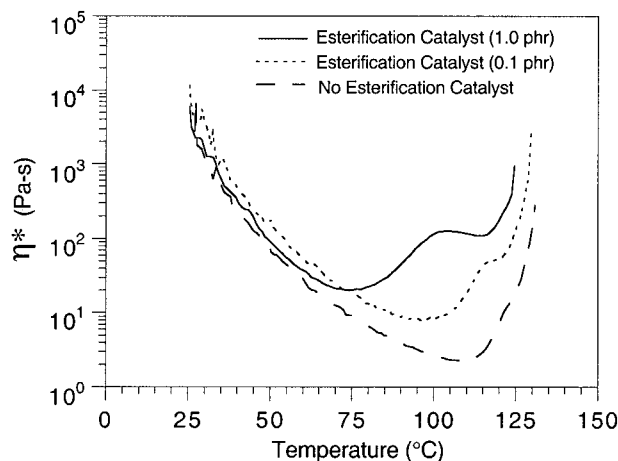
Aluminum single lap shear specimens, 2.54 cm wide with a 1.27 cm overlap, were developed for evaluating the model adhesives. Lap shear specimens were tested at four different temperatures, as follows: -55, 22.2, 82.2, and 121.1°C. Three specimens were tested for each adhesive at each temperature, and the averages and standard deviations are reported. A loading rate of 0.127 cm min was used for all testing.

Bell peel specimens, 2.54 cm wide by 19 cm long, were made with aluminum adherends to test the model adhesives. A loading rate of 10.2 cm min was used for the specimens. Three specimens were tested for each model adhesive, and the averages and standard deviations are reported.

Scanning electron microscopy was used to examine the morphology of polished adhesive samples and fracture surfaces after being sputter-coated with Au/Pd. An accelerating voltage of 20 kV and a working distance of 48 mm was used for all experiments.

## RESULTS AND DISCUSSION

The incorporation of high quantities of solid carboxyl functional rubber into hot-melt epoxy-based film adhesives is made possible by delaying the carboxyl/epoxy esterification until after film adhesive manufacture. Once the film adhesive is developed, it can be heated so that the esterification reaction is promoted before utilization. After the carboxyl/epoxy reaction is completed, the film can be quenched so as not to react the curing agents with the epoxy. The result is a highly elastic, high-viscosity adhesive system. Previously, Martin and coworkers used this method for the development of highly elastic rubber modified



**Figure 1** Viscosity profiles of the model adhesive resins (heated at 5°C min).

prepreg systems, where a coordinated transition metal catalyst (chromium-III 2-ethylhexanoate) was used for reacting the epoxy with the carboxyl functionality of the rubber after prepregging.<sup>11</sup> In contrast, a much lower initial viscosity and viscosity during cure result if the esterification reaction is not performed before utilization but allowed to occur *in situ* during cure (but before epoxy cure). The film adhesives developed in this study were used according to this methodology. This method allowed a high quantity of rubber to be used while still maintaining the necessary flow characteristics. A significantly lower rubber content must be used for similar flow characteristics and elasticity if the rubber is prereacted with the epoxy before utilization. It should be noted that the reactivity of coordinated transition metal catalysts is concentration and temperature-dependent and, therefore, requires formulation considerations if the out-time and, hence, shelf life of a product is a concern.<sup>12</sup>

### Adhesive Development and Characterization

Three model adhesive resins were developed, differing only in the quantity of the catalyst used for the epoxy/carboxyl esterification. Differences in the rheological behavior of these resins are shown in Figure 1. As seen in the figure, increasing the quantity of esterification catalyst in the resin formulation increased the minimum viscosity and reduced the temperature at which it occurred. Without an esterification catalyst, the minimum viscosity of the resin was 1.5 Pa s and occurred at 110°C. When 1.0 phr of the esterification catalyst

was used, the minimum viscosity was increased by an order of magnitude over that of the uncatalyzed resin, and the temperature shifted to about 75°C. After this reaction, the material behaved in a more elastic manner. With the use of a lower quantity of the catalyst (0.1 phr), the epoxy/carboxyl reaction occurred at a higher temperature during the heating ramp. Both of these quantities of catalyst were sufficient to complete the epoxy/carboxyl reaction, as evident by the leveling of the viscosity before the main epoxy/curing agent cure. It is shown in Figure 1 that when the high quantity of esterification catalyst was used, the viscosity decreased slightly after the carboxyl/epoxy reaction until the curing agents reacted with the epoxies. The reason for this was that all available carboxyl groups had reacted with the epoxy. Therefore, when more thermal energy was supplied to the resin, the viscosity decreased until more bonds were formed in the cure reaction. It is worth noting that in all resins, an accelerator (diuron) was used for the main curing agent (diacydiamide), which may have promoted the epoxy/carboxyl reaction in the absence of the chromium naphthenate. Diuron, which dissociates upon heating into an isocyanate and dimethylamine, could have induced the carboxyl/epoxy reaction slightly before epoxy cure or cocontinuously.<sup>13</sup> This may have been responsible for the repeatable asymmetric viscosity curve observed after minimum viscosity of the resin when no chromium naphthenate was used. Previously, the epoxy/carboxyl esterification reaction, without the use of a catalyst (and no curing agent present), has been shown not to occur until approximately 150°C when using a 5°C min heating rate.<sup>11</sup>

Since a catalyst concentration of 0.1 phr was sufficient to complete the epoxy/carboxyl reaction prior to the curing reactions, it was selected as the concentration for use in comparison with the noncatalyzed system. Also, by using this lower concentration of catalyst, the resin could be filmed at 75°C without causing the esterification to occur during filming. Lastly, this concentration resulted in a controlled flow viscosity during cure, which was not obtained for the noncatalyzed adhesive resin formulation.

The model adhesives were subjected to dynamic DSC experiments. No significant differences were observed in the heat of reactions or the reaction onset, peak, or end temperatures because the amount of carboxyl groups per molecule of the reactive rubber was relatively small.<sup>2</sup> This



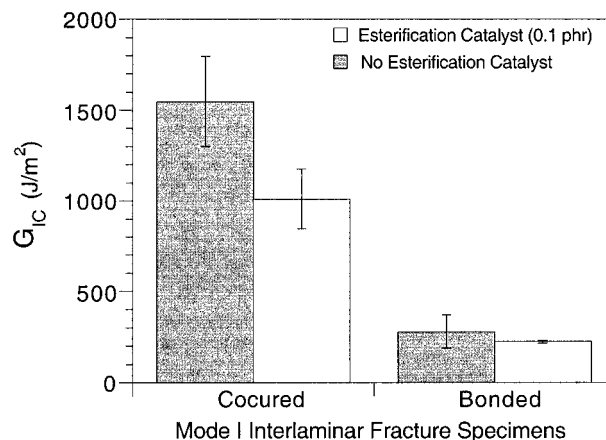
also showed that the chromium naphthenate did not accelerate the cure or inhibit the reaction of the curing agents. Past work by Browning showed that chromium octoate promoted the epoxy/carboxyl reaction and did not induce epoxy homopolymerization.<sup>12</sup> The adhesive resins were found to have nearly 100% conversion after being exposed to the 121°C cure cycle, as determined by DSC.

Dynamic mechanical analysis was used to identify the cured transitions of the film adhesives. The glass transition temperature of the film adhesives were found to be 115°C. These results identified that the carboxyl/epoxy reaction initiated by chromium naphthenate prior to epoxy cure did not affect the cured structure so as to alter the glass transition temperature. Differences in the glass transition temperature would not have been expected, even if the rubber material did not react since the amount of carboxyl functionality was so small in comparison to the overall bonding sites.<sup>2</sup>

Subambient DMA experiments were performed from -100°C, and no low-temperature transitions were identified in either the catalyzed or uncatalyzed cured adhesives. Therefore, it was concluded that the rubber did not completely phase-separate and remained mostly in the continuous epoxy phase. Interestingly, the viscosity difference and catalyst had no significant effect on the phase separation process.<sup>14</sup> Scanning electron microscopy was performed on both polished samples and fracture surfaces and verified that the rubber did not form a discrete second phase. This is in contrast to the resins developed by Diamant and Moulton, which showed that the solid reactive rubber phase-separated during cure to form approximately 1.0- $\mu\text{m}$  irregularly shaped domains.<sup>2</sup>

### Mechanical Analysis

The mode I fracture energies were determined for the model adhesive systems when used with composite adherends. Figure 2 shows the  $G_{IC}$  values for the model adhesives when used with cocured and bonded composite applications. As seen in the figure, the bonded specimens had a much lower fracture energy than the cocured specimens. This was a result of the significantly different failure mechanisms. Cocured specimens failed cohesively, while bonded specimens failed adhesively. The model adhesive containing the esterification catalyst had a lower  $G_{IC}$  value than the uncatalyzed adhesive when used in cocured specimens, but no significant difference was seen for the

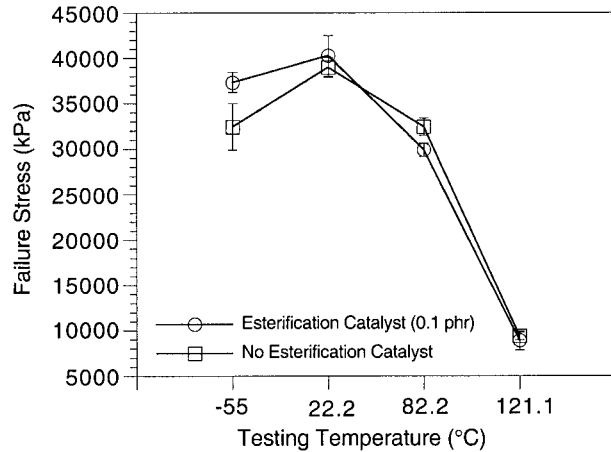


**Figure 2** Mode I interlaminar fracture energy of cocured and bonded composite specimens.

bonded samples. Differences observed for the cocured values could have been a result of resin flow and resin mixing of the adhesive with the prepreg resin.

Mode II fracture toughness was also tested for the model adhesives. The cocured specimens showed significantly different results than the adhesively bonded composite specimens. All cocured specimens either failed in compression (through-thickness normal to the adhesive layer) or were found to delaminate in the prepreg plies. As a result of failure in the prepreg, mode II adhesive fracture energy for the cocured specimens could not be quantitatively determined only that it was greater than the interlaminar prepreg value. Hence, the model adhesives' performance was more than adequate for this type of loading for cocured applications. The bonded specimen  $G_{IIC}$  values were found to be similar for the uncatalyzed 1500  $\text{J m}^2$  (std. 267) (no esterification catalyst) and catalyzed 1623  $\text{J m}^2$  (std. 154) model adhesives. A combination of adhesive and cohesive failure was identified in the specimens. The higher mode I and mode II values for cocured applications indicated that primary bond formation across the interface and resin mixing (prepreg/adhesive) may have been responsible for the increased fracture energy when compared to the role that mechanical interlocking provided in the bonded specimens. An opposite effect was observed in previous work using preformed particles to modify a similar adhesive formulation, where the  $G_{IC}$  values of the bonded specimens exceeded or equaled the cocured values.<sup>14</sup>

The failure stress of adhesively bonded aluminum lap shear joints at different temperatures is



**Figure 3** Failure stress as a function of testing temperature of bonded aluminum lap shear specimens.

shown in Figure 3. After testing at the different temperatures, all specimens showed cohesive failure. From the figure, it appears as though the adhesive containing the esterification catalyst increased the failure stress over that of the uncatalyzed adhesive at lower temperatures. This is especially evident at  $-55^{\circ}\text{C}$ . However, this trend reversed when the temperature was increased. This was assumed to be a result of the differences in the rubber structure caused by reacting the rubber with the epoxy at a lower temperature through the use of the esterification catalyst, and in completion before epoxy cure. In contrast, it is not known when or how many of the carboxyl groups reacted in the uncatalyzed adhesive, except that the reaction would have occurred at a much higher temperature. At lower temperatures, the rubber molecules would be more elongated (less entanglement), possibly causing more reactive sites to be available. Once the epoxy molecules are reacted with the rubber, a more elongated, stiffer rubber molecule should result after cure. These materials may therefore have had different internal stresses affecting their low- and high-temperature utilization.

The Bell peel strength of the two model adhesive systems was tested in aluminum bonding applications. The peel strength of the adhesive containing the esterification catalyst was 420.9 kPa (std. 20.7), and the peel strength of the uncatalyzed adhesive was 379.5 kPa (std. 34.5). A combination of both adhesive and cohesive failure was observed in the specimens. The slight increase in average peel strength of the catalyzed adhesive was also shown in the lap shear testing.

## CONCLUSIONS

It was shown in this article that high quantities of solid carboxyl functional rubber can be incorporated in a hot-melt epoxy-based film adhesive if the carboxyl/epoxy esterification is delayed until after the film adhesive is developed. The use of a coordinated transition metal catalyst was shown to promote carboxyl/epoxy esterification prior to the reaction of the epoxy/curing agent. The result was a controlled flow resin with the same initial viscosity, elasticity, and tack and drape characteristics as a resin manufactured with a nonfunctionalized solid elastomer. Mechanical properties of film adhesives with and without the esterification catalyst were investigated using both composite and aluminum bonding applications. Differences were observed in the mode I fracture performance of the cocured composite specimens. Use of the esterification catalyst resulted in a higher viscosity during cure and, in turn, a lower  $G_{IC}$  value. This was likely the result of less resin mixing (adhesive/prepreg) during cure. When comparing the mode I and mode II fracture energies of the cocured versus bonded specimens, significantly higher values were obtained for the adhesives utilized in cocured composite applications. Therefore, resin mixing and primary bond formation across the interface versus mechanical interlocking were assumed to be responsible for the increased fracture energy. The mechanical response of the film adhesives used for aluminum bonding was also evaluated. When the failure stress of lap shear specimens was tested at four different temperatures, it was found that the esterification reaction prior to cure increased the lower temperature ( $-55^{\circ}\text{C}$ ) failure stress over that of the uncatalyzed adhesive. This was assumed to be due to the difference in the rubber structure caused by the esterification catalyst. These adhesive materials may therefore have had different internal stresses affecting their low-temperature utilization. Collectively, this research described the method of developing film adhesive systems containing large quantities of solid carboxyl functional rubber and evaluated the mechanical performance of the systems when used for both composite and aluminum bonding applications.

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