Improving Coating Performance with Biobased Epoxy Resins Derived from

Biobased materials are increasingly important in the coatings industry as more companies align their sustainability goals to reduce environmental footprints and develop more eco-friendly products to meet customer needs. However, widespread adoption of biobased materials in coating applications can be challenging due to the lack of available biobased materials that are both cost-effective and performance competitive.

To solve these challenges, we developed a series of cost-competitive biobased epoxy resins using distilled tall oil (DTO) as the feedstock. DTO, a bio-refinery product derived from crude tall oil, is a byproduct of the pinewood pulping process and is 100% biobased. DTO is a mixture of tall oil fatty acids (TOFA)—mainly oleic acid and linoleic acid—and tall oil rosin acids (rosin)—mainly abietic acid and its isomers. *Figure 1* shows the molecular structures of the main components in DTO.

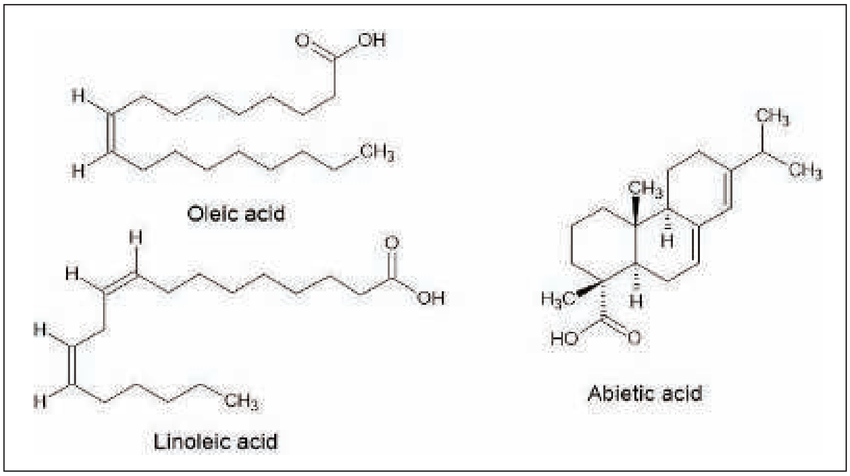
The properties of these novel DTO-based epoxy resins can be tuned by changing the ratio of TOFA to rosin in DTO. The three DTO-based epoxy resins listed in *Table 1* are amber color liquids at room temperature, have a biocontent range of 40% to 50% and an epoxy equivalent weight (EEW) ranging from 500 to 700 g/eq. They are designed for use in applications such as coatings, composites and adhesives, and performance enhancement(s) can be achieved with proper formulation. This article will demonstrate how these novel DTO-based epoxy resins can help improve miscibility and compatibility, water resistance, adhesion, flexibility, impact resistance, and chemical resistance in 2K epoxy coatings.

EXPERIMENTAL SECTION

Coating model formulations

The 2K epoxy coating formulations for this study are listed in *Table 2*. The name of each formulation represents the combination of the epoxy resins used. For example, the first formulation that only contains diglycidyl ether of bisphenol A (DGEBA) (EEW = 187 g/eq) in its epoxy part is named as DGEBA and used as the control. The other three formulations, EP100/DGEBA, EP125/DGEBA and EP150/DGEBA, all have a mixture of 50% by weight of DGEBA and 50% by weight of one of the DTO-based epoxy resins listed in *Table 1*. The amine hardener used in this study is Versamid 140, a polyamidoamine hardener from Gabriel. In each formulation, the ratio of epoxy to amine hardener was kept at 1:1 equivalent ratio.

FIGURE 1—Molecular Structures of Oleic Acid, Linoleic Acid, and Abietic Acid (The Dominant Species in DTO).



Distilled Tall Oil

By Wumin Yu, Ingevity Corporation USA

Characterization

The mixing study was conducted at room temperature (23 ± 2 °C) on a 150g formulation scale with a mechanical stirrer rotating at 300 rpm. For the curing behavior study, 150g of Part A (epoxy) and Part B (hardener) mixture in a plastic cup was placed in a 25 °C water bath and the viscosity and temperature of the mixture were closely monitored to obtain the gel time and exothermic peak temperature. The viscosity of the mixture was monitored by a Brookfield CAP 2000+ viscometer and the point at which the viscosity reached the maximum limit with a #03 cone spindle at 50 rpm and 50 °C was defined as the gel time.

For tensile, dynamic mechanical analysis (DMA), Shore D hardness and water absorption test samples, the formulation mixtures were first cured in silicon molding at room temperature overnight and then removed from the silicon mold and post-cured at 100 °C for two hours. The tensile test was performed on an Instron 3365 universal testing machine at a crosshead speed of 10 mm/minute according to ASTM D638.

TABLE 1—Basic Properties of DTO-Based Epoxy Resins

DTO EPOXY RESIN	BIO-CONTENT (%)	EEW (G/EQ)	VISCOSITY (CP @ 50°C)
EP100	47	690	4740
EP125	44	666	1150
EP150	42	502	2910

TABLE 2—Model Formulations

FORMULATION ID	DGEBA	EP100/DGEBA	EP125/DGEBA	EP150/DGEBA
Part A (epoxy):				
DGEBA, parts by weight	100	50	50	50
EP100, parts by weight	0	50	0	0
EP125, parts by weight	0	0	50	0
EP150, parts by weight	0	0	0	50
Part B (hardener):				
Versamid 140, parts by weight	51	32	33	35

The DMA test was conducted using a 3-point bending geometry on a TA Instruments DHR-2 rheometer at a heating rate of 2 °C/minute and the tan delta curve maximum was used as the glass transition temperature (T_g) of each cured sample. The Shore D hardness was measured with a Shore D durometer.

The water absorption test was carried out by immersing a cured sample (44mm x 13mm x 3mm in dimension) in water at room temperature. Every three or seven days, the sample was taken out and water on the sample surface was wiped off before measuring the weight gain. The water absorption percentage after t days of water immersion was calculated as:

$$Water\ absorption\ (\%) = \frac{M_t - M_0}{M_0} \times 100\%$$

where M_0 and M_t are the initial sample weight and the sample weight after t days of water immersion, respectively.

The 2K epoxy formulations listed in *Table 2* were coated onto aluminum (type A, 3003 H14 alloy, smooth mill) and steel (type R, cold-rolled steel, dull matte) Q-panels using a 6-mil drawdown bar for coating-performance evaluation. The coating dry time was recorded with a GARDCO DT-5040 quadracycle electronic dry time recorder (ASTM D5895) on a 3-mil wet film drawn down on a Lenata 2A opacity chart. All Q-panels were cleaned with acetone and dried for 15 minutes before applying coatings.

The coated panels were kept at room temperature to cure for seven days with some coated panels going through an additional two hours of post-cure at 100 °C if needed before characterization. The dry film thickness was roughly 3 mils. The coating flexibility was measured with a TQC mandrel bend tester (ASTM D522). Impact-resistance measurements were performed with a BYK Gardner 1102 impact tester (ASTM D2794).

The tape test method (ASTM D3359) was used for coating adhesion evaluation. The chemical resistance of each coating sample was evaluated with a spot test method. Nearly one milliliter of each of the testing chemicals was placed on the surface of a coated panel and covered with a watch glass. Each chemical droplet was kept in contact with the panel for 24 hours and then the contact area was examined for damage after the residual chemical was wiped off.

RESULTS AND DISCUSSION

Ability of DTO epoxy to enhance miscibility and compatibility in 2K epoxy coatings

The epoxy and hardener in a 2K epoxy coating need to be mixed well to achieve a fully cured system for optimal performance. In a series of mixing studies, we found that the DTO-based epoxy resins can help enhance the miscibility between DGEBA and amidoamine or polyamidoamine hardeners, shortening mixing time and improving mixing efficiency significantly. *Figure 2* is a comparison of the mixing behavior between Formulation DGEBA (control) and Formulation EP125/DGEBA. Formulation DGEBA only contains DGEBA and Versamid 140 (polyamidoamine).

As shown in *Figure 2(a)* and *Figure 2(b),* after 30 minutes of mixing, the mixture still appeared cloudy. Only after 40 minutes of mixing, the mixture started to become homogeneous. In Formulation EP125/DGEBA, the epoxy part contains 50% of DGEBA and 50% of DTO-base epoxy EP125. The mixing was 20 times faster, as shown in *Figure 2(c)*. The formulation mixture became homogeneous

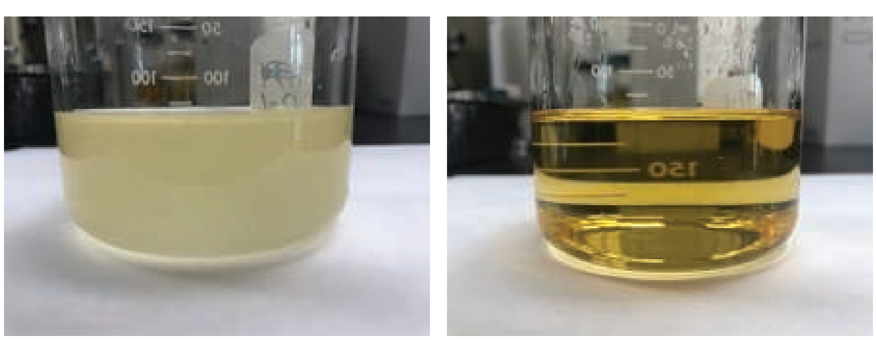
FIGURE 2—Mixing Comparison Between DGEBA and Versamid 140 With and Without DTO-based Epoxy

(a) Formulation DGEBA: after 30 minutes of mixing

(b) Formulation DGEBA: after 40 minutes of mixing

(c) Formulation EP125/DGEBA: after two minutes of mixing

FIGURE 3—Mixing Comparison Between DGEBA and EPON 58034 With and Without DTO-based Epoxy



(a) Mixing of 80% DGEBA and 20% EPON 58034 for more than one hour

(b) Mixing of 64% DGEBA, 16% EP125 and 20% EPON 58034 after one minute

with only two minutes of mixing. We determined this benefit could be achieved at levels as low as 20% with EP125 in the epoxy part to effectively mix the formulation in about three minutes under the same mixing conditions.

In some applications, rubber or rubber-modified epoxy resins such as carboxyl-terminated copolymer of acrylonitrile and butadiene (CTBN) modified epoxy resins are incorporated in 2K epoxy formulations to improve toughness. To achieve a satisfactory toughening effect, a good miscibility between the rubber or rubber-modified epoxy components and other epoxy components in the formulation is very important. In this study, we first mixed DGEBA with EPON 58034 (a CTBN rubber-modified epoxy resin from Hexion) in an 80:20 weight ratio at room temperature with a mechanical stirrer at 300 rpm and found that the mixture was still hazy after more than one hour of mixing, as shown in *Figure 3(a)*. *Figure 3(b)* shows that a transparent mixture was obtained after one minute of mixing under the same mixing conditions with incorporating less than 20% of the DTO-based epoxy EP125. DTO epoxy helped greatly improve the miscibility between DGEBA and the rubber-modified epoxy resin EPON 58034.

Figure 4 is the comparison of the appearance of the coating films drawn down on Lenata 2A opacity charts between formulation DGEBA and formulation EP125/DGEBA after a seven-day room-temperature cure. The coating film from formulation DGEBA shows an "orange peel" appearance, while a very smooth surface was observed in the coating film based on formulation EP125/DGEBA. This is also a sign of better compatibility in the formulation with adding DTO-based epoxy resins.

FIGURE 4—Coating Film Appearance

a) Formulation DGEBA (b) Formulation DGEBA/EP125

TABLE 3—Gel-time, Exothermic Peak, and Tack-free Time

SAMPLE ID	DGEBA	EP100/DGEBA	EP125/DGEBA	EP150/DGEBA
Gel time @25 °C, hour	2.2	1.8	2.0	1.9
Exothermic peak, °C	39.7	44.6	48.0	46.0
Tack-free time @ 25 °C, hour	10.0	10.5	11.0	9.2

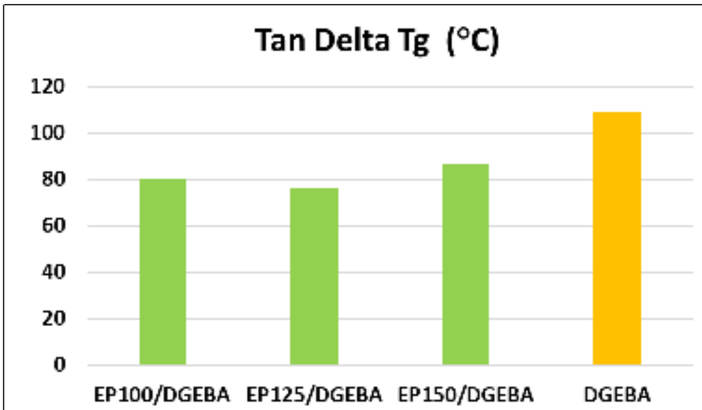
Curing behavior comparison of model coating formulations

Table 3 lists the gel time, exothermic peak temperature, and tack-free time of each model formulation. Compared with the control formulation, all the DTO epoxy containing formulations show similar tack-free time, slightly lower gel time and higher exothermic peak temperature.

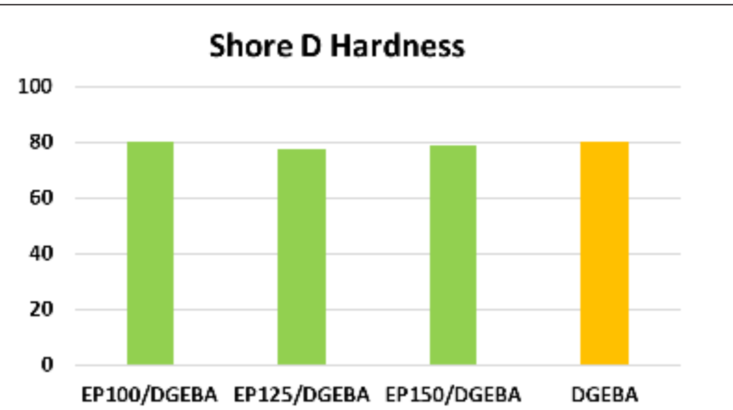
Effect of DTO epoxy on glass transition temperature and hardness of cured samples

As shown in *Figure 5(a)*, with adding up to 50% of DTO epoxy in the formulation, there was a 20-to-30 degree drop in the glass transition temperature (Tan Delta T_g) in the fully cured samples, which could be a result of the higher content of flexible fatty chains in the cured samples brought in by DTO epoxy. If T_g is a major concern in applications, a low amount of DTO epoxy should be used. In terms of hardness, *Figure 5(b)* demonstrates that all the DTO epoxy containing samples are comparable to the control in terms of Shore D hardness.

FIGURE 5—Comparison of Tan Delta T_g and Shore D Hardness of Cured Samples



(a) Tan Delta T_g



(b) Shore D hardness

Ability of DTO epoxy to improve tensile properties in 2K epoxy coatings

All samples for tensile tests went through 100 °C post-cure for two hours. *Table 4* lists the tensile properties of the cured samples based on the formulations in *Table 2*. Compared with the control formulation DGEBA, all DTO epoxy containing formulations show higher tensile strength and elongation while maintaining similar Yong's modulus. Especially for formulation EP125/DGEBA, the tensile strength is roughly 25% higher and elongation at break is 60% higher when compared with the control.

Ability of DTO epoxy to enhance water resistance in 2K epoxy coatings

The results of water absorption tests on the cured samples at ambient temperature versus immersion time are shown in *Figure 6*. All DTO epoxy containing formulas show lower water absorption over time than the control formula. The EP100/DGEBA formulation exhibits the best performance on resisting water uptake, which could be due to its higher rosin content.

Ability of DTO epoxy to improve coating adhesion to different substrates in 2K epoxy coatings

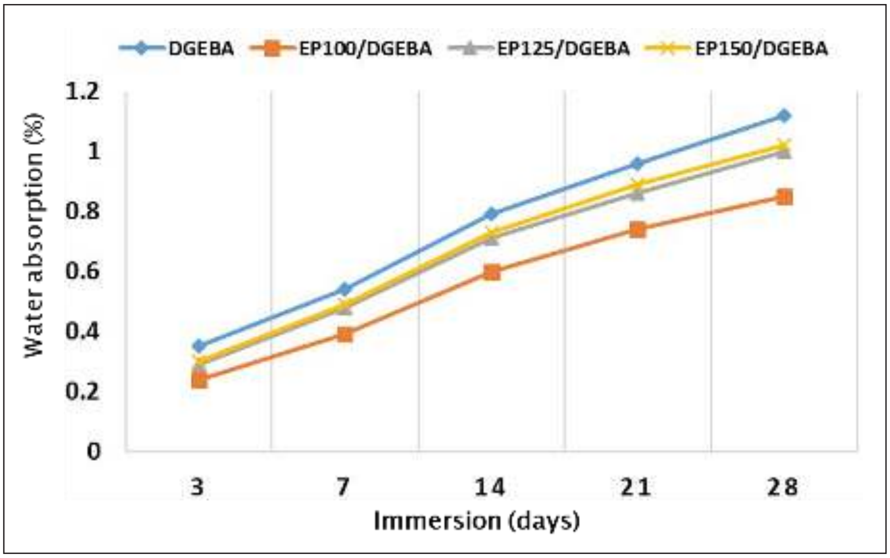
The tape test method (ASTM 5339) was used to evaluate the coating adhesion on both aluminum (type A) and steel (type R cold-rolled steel) substrates. The adhesion rating scale is from 0B to 5B with 5B the best adhesion rating. The adhesion assessment was first conducted on seven-day room-temperature (23 ± 2 °C) cured samples. The dry film thickness of the coatings was roughly three mils. On aluminum substrates, all the DTO epoxy containing samples showed 2B rating and the control only showed 1B rating, while on steel substrates, all samples including the control exhibited 5B rating.

For the samples that went through post-cure at 100 °C for two hours, *Figure 7* shows the images of the cross-cut areas on the coated panels after the tape tests with the corresponding adhesion rating marked in the bottom of each image. On aluminum substrates, the control still exhibited 1B rating while all the DTO epoxy containing samples showed 3B to 5B ratings. The DTO epoxy containing samples also showed better adhesion rating than the control on steel substrates (5B vs 3B). In a similar study, better coating adhesion to glass substrates was also observed with adding DTO epoxy to the formulation. All these results demonstrate that DTO epoxy helps improve the adhesion of 2K epoxy coatings to different substrates.

TABLE 4—Tensile Properties of Cured Samples

FORMULATION ID	YONG'S MODULUS (GPA)	TENSILE STRENGTH (MPA)	ELONGATION AT BREAK (%)
DGEBA	1.69 ± 0.07	38.86 ± 4.00	2.64 ± 0.39
EP100/DGEBA	1.74 ± 0.05	46.45 ± 5.58	3.31 ± 0.63
EP125/DGEBA	1.64 ± 0.05	48.01 ± 1.96	4.08 ± 0.47
EP150/DGEBA	1.60 ± 0.05	40.22 ± 2.78	2.99 ± 0.28

FIGURE 6—Plot of Water Absorption of Cured Samples at Ambient Temperature vs Immersion Time



Ability of DTO epoxy to improve coating flexibility and impact resistance in 2K epoxy coatings

The Mandrel Bend Test (ASTM D522) is a convenient method used to evaluate the flexibility of coatings. *Figure 8* shows the images of the coating films on aluminum substrates after the mandrel bend test. The coating film based on the control formula showed significant cracking, while the coating films from the formulas that contain DTO epoxy EP100 or EP125 did not show any cracking, suggesting an improvement in flexibility.

The impact test method according to ASTM D2794 measures the resistance of a coating film subject to rapid deformation. In this test, a standard weight is dropped from different distances to strike an indenter to deform the coating and the substrate to determine the point at which cracking failure occurs. The higher the value, the better the ability of a coating to resist cracking caused by impacts. *Table 5* lists the impact-resistance results of the four coatings on steel substrates with both intrusion and extrusion indentions. Formulation EP125/DGEBA shows improvement in impact resistance for both intrusion and extrusion indentions over the control formulation DGEBA with the incorporation of DTO epoxy EP125.

FIGURE 7—Evaluation of Coating Adhesion by Tape Test on (a) Aluminum and (b) Steel Substrates

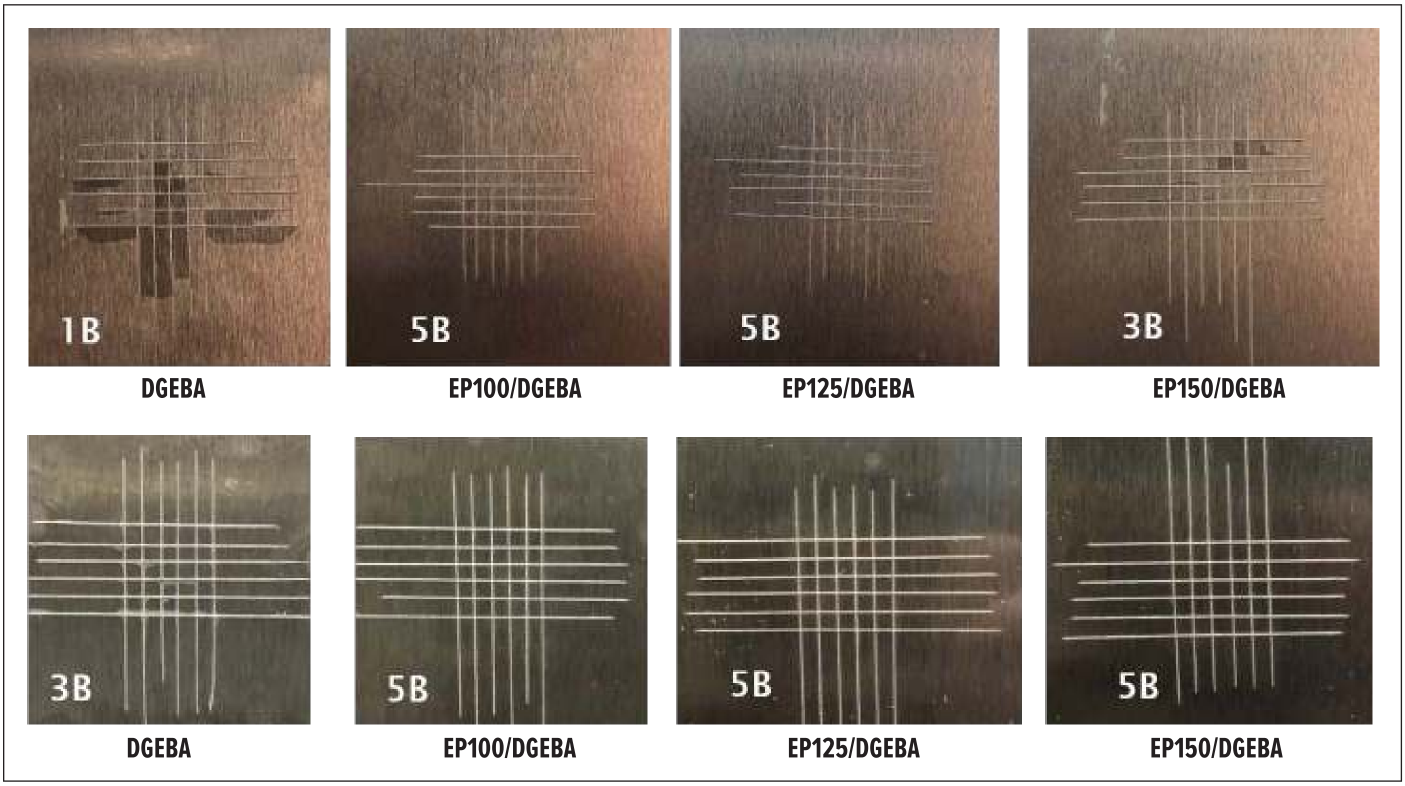


FIGURE 8—Mandrel Bend Test Results

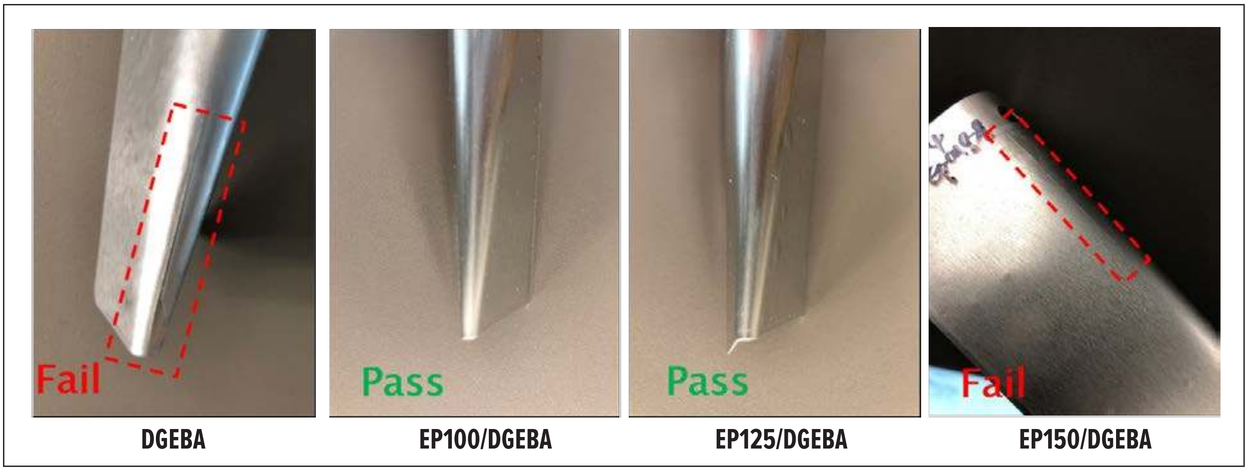


TABLE 5—Impact-resistance Test Results

FORMULATION ID	IMPACT RESISTANCE (IN. LB)	
	Intrusion	Extrusion
DGEBA	70	10
EP100/DGEBA	70	10
EP125/DGEBA	90	50
EP150/DGEBA	70	30

TABLE 6—Chemical-resistance Results by 24-hour Spot Tests

FORMULATION ID	DGEBA	EP100/DGEBA	EP125/DGEBA	EP150/DGEBA
Acetic acid (10%)	3	5	5	4
Sulfuric acid (50%)	3	5	5	4
Sodium hydroxide (50%)	3	5	5	5
Ammonium hydroxide (10%)	3	4	4	4
Xylene	5	5	5	5
Total	17	24	24	22

Ability of DTO epoxy in enhancing chemical resistance in 2K epoxy coatings

Table 6 lists the chemical-resistance results by 24-hour spot tests. Five chemicals were used for the spot tests, including 10% acetic acid, 50% sulfuric acid solution, 50% sodium hydroxide solution, 10% ammonium hydroxide solution, and xylene. The damage was rated on a scale from 1 to 5 (5: no damage; 4: slight damage; 3: moderate damage; 2: considerable damage; 1: very strong damage).

Overall better chemical performance was observed with the coatings based on the formulations that contained one of the three DTO epoxy resins.

CONCLUSION

Experimental results indicated that DTO epoxy resins helped enhance the miscibility and compatibility between DGEBA and Versamid 140 (a polyamidoamine), significantly improving mixing efficiency and reducing coating defects. The mixing study between DGEBA and EPON 58034 also demonstrated that the miscibility between the CTBN modified epoxy and DGEBA was greatly improved with incorporating DTO epoxy resins.

When curing DGEBA with Versamid 140, the incorporation of DTO epoxy resins helped increase tensile strength and elongation of the cured samples. The cured samples also exhibited better water resistance in the water-immersion test. In terms of coating performance, incorporation of DTO epoxy resins resulted in higher flexibility and impact resistance, enhanced adhesion to different substrates and better chemical resistance. ❇

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