Method for Determining Number of Hydroxyl Content per Mole of Oligomeric Coproduct (OCP). A recorded weight of OCP was spiked with a recorded amount of cyclohexane (C$_6$H$_{12}$). The sample was then dissolved in CDCl$_3$ and NMR experiments were run. From the NMR spectra, the peaks corresponding to the protons on C$_6$H$_{12}$ (1.43 ppm) and the protons on the phenolic hydroxyl groups (~5.5 ppm) were integrated, using the cyclohexane peak as a reference. This is based on the knowledge that the given peak corresponds to 12 protons per mole of C$_6$H$_{12}$. From this integration and the recorded weights of OCP and C$_6$H$_{12}$ in the NMR sample, a back calculation (Equation 1) was performed to determine the amount of phenolic hydroxyls are present in OCP, where $i$ is the area under the hydroxyl peak. The moles of OCP were determined by using the weight average molecular weight ($M_w$) that was obtained through APC analysis.

\[
\text{moles of } C_6H_{12} \times \frac{12 \text{ moles of } C_6H_{12} \text{ protons}}{1 \text{ mole of } C_6H_{12}} \times \frac{i \text{ moles of hydroxyl protons}}{12 \text{ moles of } C_6H_{12} \text{ protons}} \quad (1)
\]

Extent of Cure Determination Details. The extent of cure for the cured epoxy-amine resins was measured using a Nicolet iS50 FT-IR operating in the near-IR range. Near IR spectra were obtained operating in the range of 7000-4000 cm$^{-1}$ for 32 scans at a resolution of 2 cm$^{-1}$. In this range, there are absorbance bands characteristic of amine and oxirane groups, allowing for a quantitative analysis of the groups present before and after curing. The peak corresponding to the oxirane used in this quantification is found around 4530 cm$^{-1}$. Primary amines have a characteristic absorbance at 4925 cm$^{-1}$; however, an absorbance at 6535 cm$^{-1}$ represents both primary and secondary amines. The epoxy-amine resins were analyzed before the curing process by placing them in a 3 mm thick glass vessel. The cured resins were cleaned with acetone and allowed to fully dry before FTIR experiments were run. Throughout the curing process, both oxirane peaks at 4350 cm$^{-1}$ and 6060 cm$^{-1}$ and both amine peaks at 4925 cm$^{-1}$ and 6535 cm$^{-1}$ will decrease in size and thus, absorbance. For this work, the area of the oxirane peak at 4350 cm$^{-1}$ was utilized to calculate extent of cure. The peaks appearing around 5790-6000 cm$^{-1}$ were used as internal references for quantitative purposes. Equation 2 was used to estimate the extents of cure.

\[
\text{Extent of Cure} = \frac{\left(\frac{\text{Abs}_{4530}}{\text{Abs}_\text{ref}}\right)_{\text{pre-cure}} - \left(\frac{\text{Abs}_{4530}}{\text{Abs}_\text{ref}}\right)_{\text{post-cure}}}{\left(\frac{\text{Abs}_{4530}}{\text{Abs}_\text{ref}}\right)_{\text{pre-cure}}} \quad (2)
\]

TGA, DSC, DMA, and Fracture Testing Details. Thermogravimetric analysis (TGA) of the cured resins was performed on a TA Instruments Discovery TGA 550. Approximately 10 mg of sample was loaded into
a platinum pan and heated at 10 °C min\(^{-1}\) until the pan reached 700 °C in an N\(_2\) atmosphere (balance gas flow rate of 40 mL min\(^{-1}\) and sample gas flow rate of 25 mL min\(^{-1}\)). This procedure was repeated in air. The thermogravimetric properties reported from this experimentation include the initial decomposition temperature (\(IDT\)), temperature at 50% weight loss (\(T_{50\%}\)), temperature at maximum decomposition rate (\(T_{\text{max}}\)), and char content. Experiments were performed in triplicates.

Thermal analysis was performed using a TA Instruments Discovery 2500 DSC. Approximately 10 mg of sample was loaded into a Tzero aluminum pan with a hermetic lid and crimped to seal. The pan was then heated to 200 °C at a rate of 10 °C min\(^{-1}\) under N\(_2\). From this analysis, a glass transition temperature (\(T_g\)) was reported for the epoxy-amine thermoset samples. Experiments were performed in triplicates.

The viscoelastic properties of the polymers in this work were characterized using a TA Instruments Q800 DMA. The analysis was executed on cured resin samples of uniform dimensions of 35 x 11 x 2.5 mm\(^3\) using the single cantilever geometry. The experiments were run with a frequency of 1.0 Hz, Poisson’s ratio of 0.35, and deflection amplitude of oscillation of 7.5 µm. Samples were heated from 0 °C to 200 °C at a rate of 2 °C min\(^{-1}\). The peaks of the loss modulus (\(E''\)) and tan δ thermograms were used to determine the \(T_g\) of the cured resins. Experiments were performed in triplicates.

Fracture testing was performed to gather an introductory understanding of the fractural properties of the cured resins. This testing was performed in accordance with ASTM D5045 using an Instron 5966 with a 1 N load cell and a 3-point bend flexure fixture at a cross-head speed of 10 mm min\(^{-1}\). Samples of uniform dimension (44 x 10 x 4 mm\(^3\)) were prepared by combining the coproduct and Epikure W as previously described. Using a diamond saw, the samples were notched, and a razor blade was used to propagate a crack before testing. The critical strain energy release rate, \(G_{IC}\), and the plane strain fracture toughness, \(K_{IC}\) upon fracture were obtained. \(K_{IC}\) and \(G_{IC}\) are related via the Poisson’s ratio (\(\nu\)) and the modulus (\(E\)) of the material. Experiments were performed in triplicates.
Figure S1. Representative chemical structure of Epon 164, the chemical structure of Epon 828 and the chemical structure of Epikure W.
Figure S2. Representative $^1$H-NMR spectrum of the E-OCP.

Table S1. Comparison of E-OCP synthesized with 15.0 eq. and 30.0 eq. of epichlorohydrin.

| Epichlorohydrin Content | $M_n$ (Da)   | $M_w$ (Da) | $D$     | EEW (g/eq.) |
|-------------------------|--------------|------------|---------|-------------|
| 15.0 eq.                | 861 ± 105    | 940 ± 48   | 1.1 ± 0.09 | 207 ± 4.7   |
| 30.0 eq.                | 710 ± 52     | 792 ± 38   | 1.1 ± 0.06 | 203 ± 12    |
Figure S3. Representative overlay of near-IR spectra of the E-OCP and Epikure W before and after cure.

Table S2. TGA data for the cured resins in N₂ (10 °C/min heating rate). IDT = the initial decomposition temperature (taken at 5% weight loss); T₅₀ = temperature at 50% weight loss; Tmax = temperature at maximum decomposition rate.

| Cured Resin       | IDT (°C) | T₅₀ (°C) | Tmax (°C) | Char content (wt%) |
|-------------------|----------|----------|-----------|--------------------|
| E-OCP : Epikure W | 345 ± 9  | 392 ± 3  | 354 ± 5   | 0.5 ± 0.3           |
| Epon 164 : Epikure W | 361 ± 3  | 442 ± 2  | 352 ± 3   | 0.25 ± 0.1          |

*Char content at 700 °C.

Figure S4. Representative TGA thermograms of the cured resins in air.
Figure S5. Representative tan δ thermograms for the cured resins.

Figure S6. Load displacement curves for cured E-OCP : Epikure W resin test coupons.