

TARGET MARKETS/ APPLICATIONS

- Copper clad laminate (CCL) and printed wiring [Circuit] boards (PWB)
- Structural composites
- Radomes
- Aerospace applications

ADDITIONAL INFO

- **SDS /TDS:** Ricon 100, 154, 157, 184, 257

Ricon® Resins – Peroxide Curing Data and Use as a Reactive Plasticizer in Polyphenylene Ether Based CCL and PWB

Introduction

Ricon® resins are based on an electrically and moisture resistant polybutadiene backbone that is compatible with styrene-butadiene (SB) block copolymers and Polyphenylene Ether (PPE) resins, commonly used in copper clad laminate (CCL) and printed wiring board (PWB) formulations. Ricon resins also contain reactive vinyl groups which are easily cured by peroxides to provide high glass transition temperature (T_g) and thermal resistance. In this tech update, peroxide curing data will be shown to demonstrate that variation in vinyl content, molecular weight and styrene content of the resin structure dramatically affects the cured glass transition temperature (T_g).

Benefits

- Excellent reactivity to form highly crosslinked systems
- Compatibility with styrene-butadiene block copolymers, polyphenylene ether resins
- Variable 1,2-vinyl content, styrene content – effective crosslinker
- Low dielectric constant (D_k) and dissipation factor (D_f)
- High T_g (heat resistance, and high toughness for drilling processes)
- High thermal decomposition temperature (solder reflow resistance)
- Low water absorption (blister resistance in soldering process)
- Low coefficient of thermal expansion (CTE) for dimensional stability
- Excellent processability (appropriate viscosity, compatibility, solubility)

Peroxide Curing of Ricon Resins

Five Ricon resins shown in Table 1, varying in molecular weight, 1,2-vinyl content and styrene content, were used in the peroxide curing study. Each Ricon resin was blended with varying levels of dicumyl peroxide (2-6%). A differential scanning calorimeter (DSC) was used to monitor T_g before and after cure, enthalpy of reaction (J/g), and peak temperature of reaction.

Table 1: Ricon polybutadiene-co-styrene resins and properties

	Uncured T_g (DSC), °C	% Vinyl	% Sty	Mn	Viscosity, cP	Polymer type
Ricon 184	-58	30	28	8600	75,000 at 25 °C	Random
Ricon 157	-48	70	0	1800	6,000 at 25 °C	Random
Ricon 100	-24	70	25	4500	40,000 at 25 °C	Random
Ricon 154	-20	90	0	5200	250,000 at 45 °C	Random
Ricon 257	-38	70	35	5300	900 at 25 °C*	Block

*Note: 52% in toluene

Experimental – DSC sample preparation and scan method

- Dissolved peroxide in Ricon resin
- Placed sample in open pan in DSC
- Chose the atmosphere (N_2 or O_2)
- Cooled to below anticipated T_g for Ricon
- First ramp at 10 °C/min to 0 °C to measure initial T_g
- Rapidly heated to 100 °C
- Second ramp at 20 °C/min to 250 °C to monitor cure enthalpy
- Held at 250 °C for 15 minutes
- Second cooling to -75 °C
- Third ramp at 10 °C/min to 200 °C to measure T_g of cured material

Results

An example DSC scan is shown in Figure 1. Note that the onset temperature is where a line representing the fastest change in heat flow intersects with the base line. Curing actually starts 10-14 °C below this onset temperature.

Figure 1: Example DSC scan for Ricon resins.

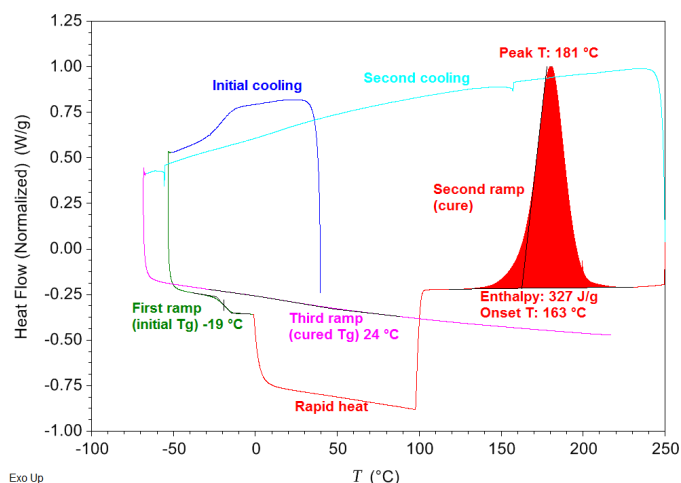


Figure 2 shows the cured T_g versus the peroxide level, for all five Ricon resins cured in both O_2 and N_2 atmospheres. In general, the resins achieve higher T_g when cured in O_2 vs. N_2 . Figure 3 summarizes the cured T_g of the resins with 6% dicumyl peroxide level and cured in oxygen.

Figure 2: T_g of Ricon Resins cured with increasing levels of dicumyl peroxide in both O_2 and N_2 .

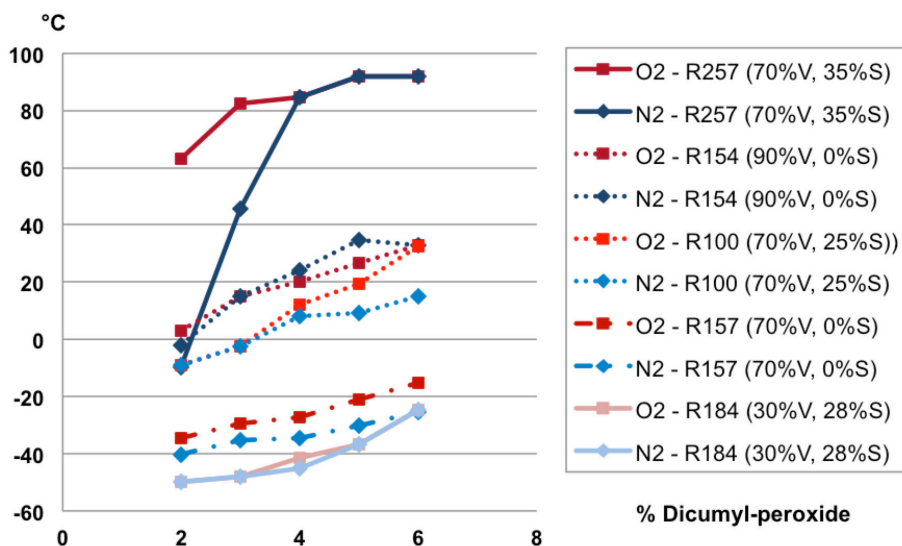
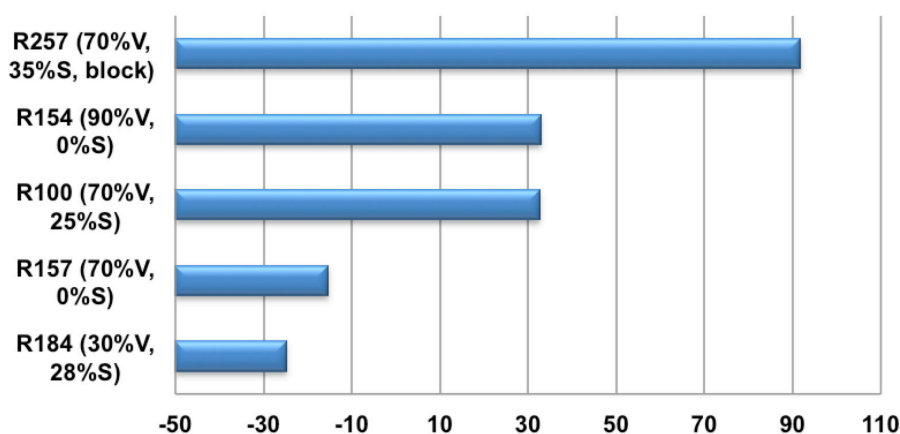


Figure 3: T_g of Ricon Resins with 6% dicumyl peroxide in O_2 .



To demonstrate which property has the largest effect on T_g , Figures 4, 5 and 6 below group resins according to vinyl content, styrene content and molecular weight at varying levels of dicumyl peroxide.

Figure 4: Impact of styrene content on ΔT_g of resins with same 1,2-vinyl content (70%) at 2, 4 and 6% peroxide.

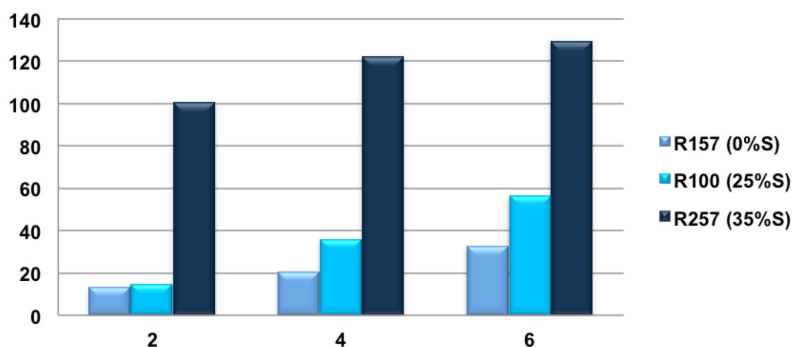


Figure 5: Impact of 1,2-vinyl content on ΔT_g of resins with similar styrene content (25-35%) at 2, 4 and 6% peroxide.

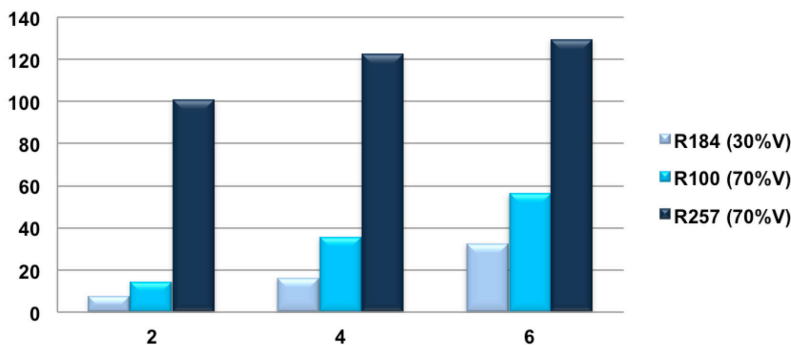
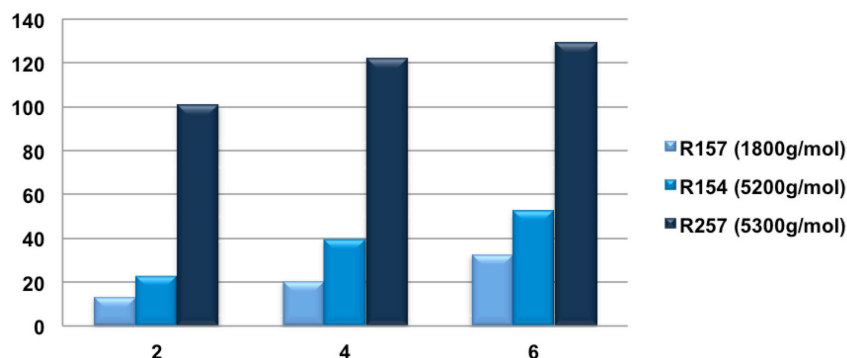
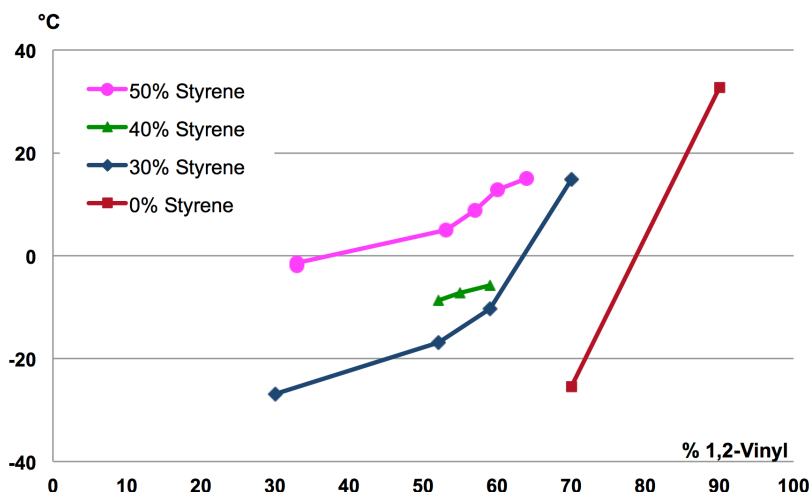


Figure 6: Impact of molecular weight on ΔT_g at 2, 4 and 6% peroxide.



Ricon 257 has the highest cured T_g , combining high 1,2-vinyl content with high styrene content and relatively high molecular weight. However, these properties lead to higher viscosity, thus the resin is diluted in solvent for ease of use. There may be an optimum composition and molecular weight combination to allow high cured T_g along with ease of processing and solvent-free handling. Figure 7 shows the T_g of several developmental Ricon resins of varying 1,2-vinyl and styrene content. Although the T_g is lower than that of Ricon 257 in general, these resins may provide opportunity to formulate without solvent but still gain the benefits of Ricon resins.

Figure 7: T_g of developmental Ricon resins with 6% dicumyl peroxide in N_2 .



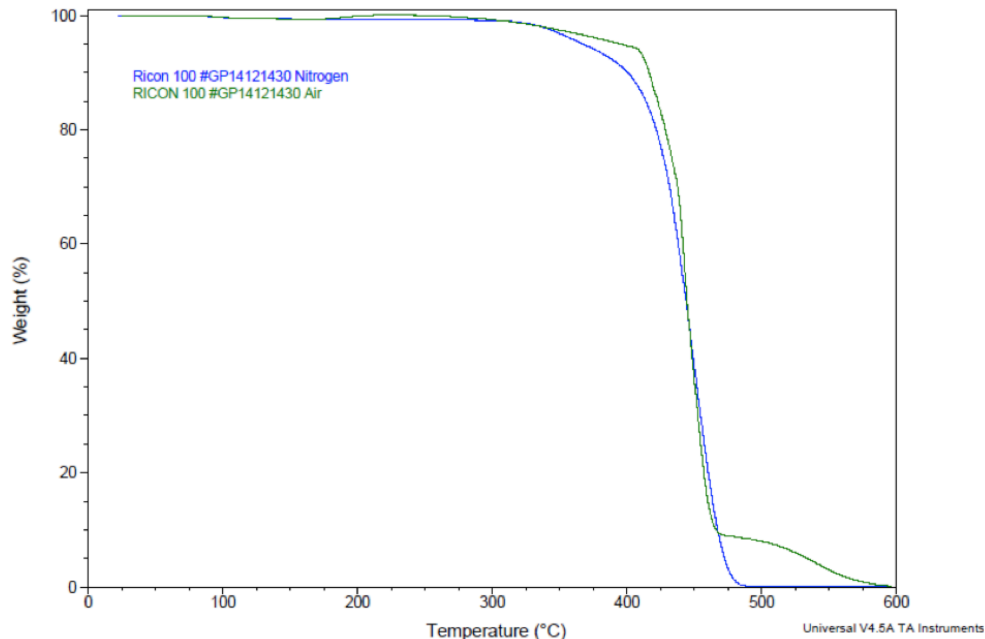
The combination of higher styrene and higher vinyl content in general increases the T_g of cured Ricon resins. But clearly other factors, such as polymer structure and molecular weight, have an effect on cured T_g as well.

Ricon resin properties in CCL applications

Ricon resins have traditionally been used as an additive in thermoset rubber compounds. The 1,2-vinyl content increases the crosslink density in the cured rubber compound, which improves the physical properties of manufactured rubber goods such as tires, automotive belts and hoses. The hydrophobic nature of the polybutadiene backbone also imparts excellent water resistance. These properties extend to PWB and CCL applications, where Ricon resins can also increase crosslink density and water resistance as well as provide toughness and lower dielectric constant (Dk) and dissipation factor (Df). Ricon resins containing styrene, such as Ricon 100, 181 and 184, can improve gas barrier properties and further improve electric properties compared to polybutadiene homopolymers.

In addition, Ricon resins attain high thermal decomposition temperatures as seen in thermogravimetric analysis (TGA) results of Ricon 100 in Figure 8, which can improve hot solder flow resistance.

Figure 8: TGA of cured Ricon 100.



Ricon Resins in Polyphenylene Ether (PPE) based formulations

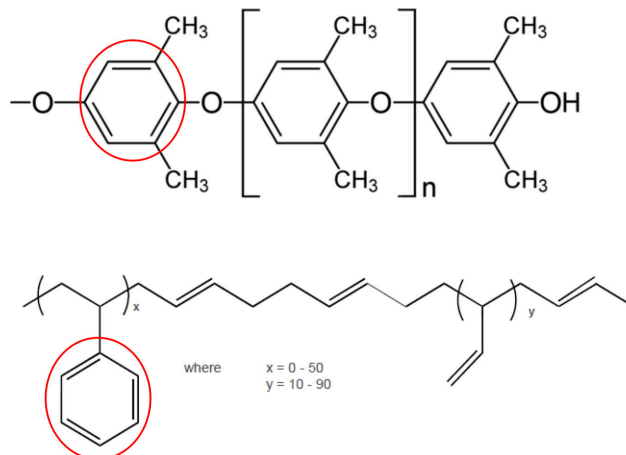
-as a Reactive Plasticizer

Ricon 257 contains 35% styrene which makes it very compatible with the aromatic rings of the Polyphenylene ether (PPE) resins (Figure 9) that are used in PWB and CCL applications.

-as substitute Triallylisocyanurate (TAIC) crosslinker

Triallyl Isocyanurate (TAIC) is a tri-vinyl functional compound that is commonly used as a crosslinker for PPE based PWB. However, TAIC is volatile (bp = 150 °C) and degrades at laminate cure conditions (>200 °C). Ricon styrene-co-butadiene resins are used as a substitute for TAIC because the Ricon resins are multi-vinyl functional, and are non-volatile at curing conditions.

Figure 9: Structures of Polyphenylene ether resin and Ricon styrene-co-butadiene resin.



Summary

Ricon resins can be peroxide cured, and the cured T_g depends on the styrene and 1,2-vinyl content as well as the molecular weight and polymer structure of the resin. Ricon 257 with the highest styrene content and 70% 1,2-vinyl content achieves the highest T_g of the Ricon resins tested. Other Ricon resins are being developed to achieve a balance of cured T_g with improved physical properties, while being easy to process and free of solvent.

Ricon styrene-co-butadiene resins like Ricon 100 and 257 are compatible with PPE resins, affording their use as reactive plasticizers in PPE based PWB and CCL applications. The Ricon imparts excellent thermal resistance. Lastly, Ricon resins are currently being used as a substitute for TAIC curing agent in PPE-based formulations.

About Total Cray Valley

Total Cray Valley is the premier global supplier of specialty chemical additives, hydrocarbon specialty chemical, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings, and other materials. Total Cray Valley has pioneered the development of these advanced technologies, introducing hundreds of products that enhance the performance of products in energy, printing, packaging, construction, tire manufacture, electronics, and other demanding applications.

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