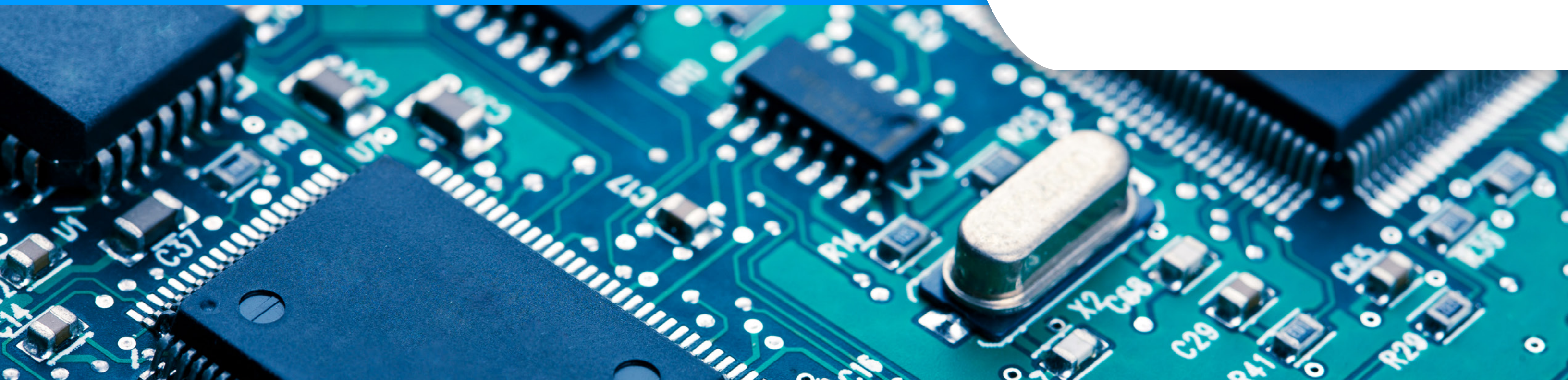
TECHNICAL UPDATE

CRAY VALLEY



BENEFITS

- Excellent reactivity
- Effective crosslinking
- Low D_k and D_f
- High T_g
- High thermal decomposition temperature
- Low water absorption
- Low coefficient of thermal expansion
- Excellent processability

TARGET MARKETS/ APPLICATIONS

- Copper clad laminate and printed circuit boards
- Structural composites
- Radomes
- Aerospace applications

ADDITIONAL INFO

- SDS/TDS: Ricon® 100, 130, 154, 157, and 181.
- Technical data sheet: Ricon® Resins – Peroxide Curing Data and Use as a Reactive Plasticizer in Polyphenylene Ether Based CCL and PWB

Ricon® Resins – Hardeners in Polyphenylene Ether (PPE) Based Formulations for CCL and PWB

Introduction

Ricon® resins are based on an electrically insulating and moisture-resistant polybutadiene backbone that is compatible with styrene-butadiene block copolymers and 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, the styrene and vinyl content of Ricon is shown to dramatically affect its viscosity and prepreg tackiness, as well as the cured T_g and dielectric properties of the co-reaction product with PPE.

Viscosity of Neat Ricon Resins

Several Ricon resins, blends of resins, and experimental resins are listed in Table 1. These vary in the styrene content in the copolymer, 1,2-vinyl content of the butadiene portion of the copolymer, and molecular weight. Their viscosities at both 25°C and 50°C are listed in Table 1.

TotalEnergies

Table 1: Composition, Molecular Weight and Viscosity of Ricon Polybutadiene-co-styrene Resins.

Product		Styrene (%)	1,2-Vinyl (%)	Mn[1], g/mol	Viscosity (at 25°C, cP[2])	Viscosity (at 50°C, cP[3])
Ricon 154	Low	0	90	5200	3,900,000	100,100
Ricons 154 and 130, 75/25 blend	Low	0	75	4090	190,000	12,000
Ricons 154 and 130, 25/75 blend	Low	0	44	2873	3,000	620
Ricon 130	Low	0	28	2500	750	270
Ricons 154 and 100, 75/25 blend	Low	6	86	4998	3,800,000	85,000
Ricons 154 and 181, 75/25 blend	Low	7	79	4497	700,000	32,000
Ricon 100	Medium	25	70	4500	850,000	22,000
Ricons 100 and 181, 75/25 blend	Medium	26	57	3963	200,000	10,000
Ricons 100 and 181, 25/75 blend	Medium	27	41	3449	40,000	3,900
Ricon 181	Medium	28	30	3200	17,500	2,800
Experimental Ricon 1	Medium	35	50	1800	200,000	8,000
Experimental Ricon 2	High	50	40	1190	700,000	17,700
Experimental Ricon 3	High	51	44	1130	5,000,000	52,000
Experimental Ricon 4	High	54	26	1478	100,000	5,700

[1] Typical measured Mn of neat resins; calculated Mn of blended resins.
[2] Extrapolated from viscosity vs temperature data.
[3] Measured viscosity.

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Viscosities vs. 1,2-vinyl content and molecular weight are shown in Figures 1 and 2 respectively, at low, medium, and high levels of styrene. Viscosity increases as 1,2-vinyl content increases, but at different rates, depending on styrene content. Viscosity also increases with increasing molecular weight at no or low styrene content. But at higher styrene content, viscosity is actually higher at lower molecular weights. The complex interactions of 1,2-vinyl content, styrene content, and molecular weight with viscosity of Ricon resins are not taken into account here; Figures 1 and 2 are shown simply to demonstrate trends in viscosity.

Figure 1: Viscosity of neat Ricon resins vs. 1,2-vinyl content at 25°C (left) and 50°C (right).

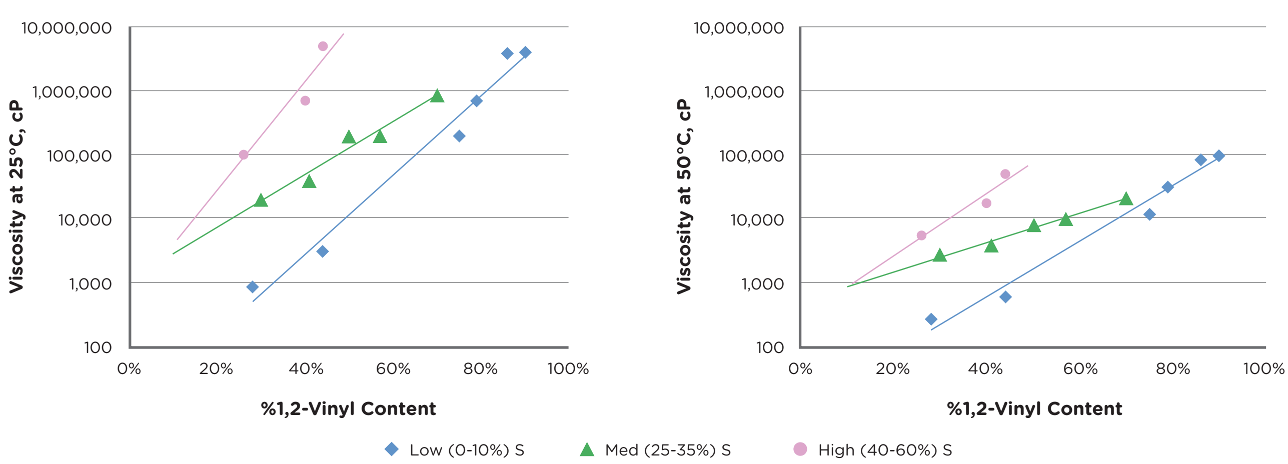
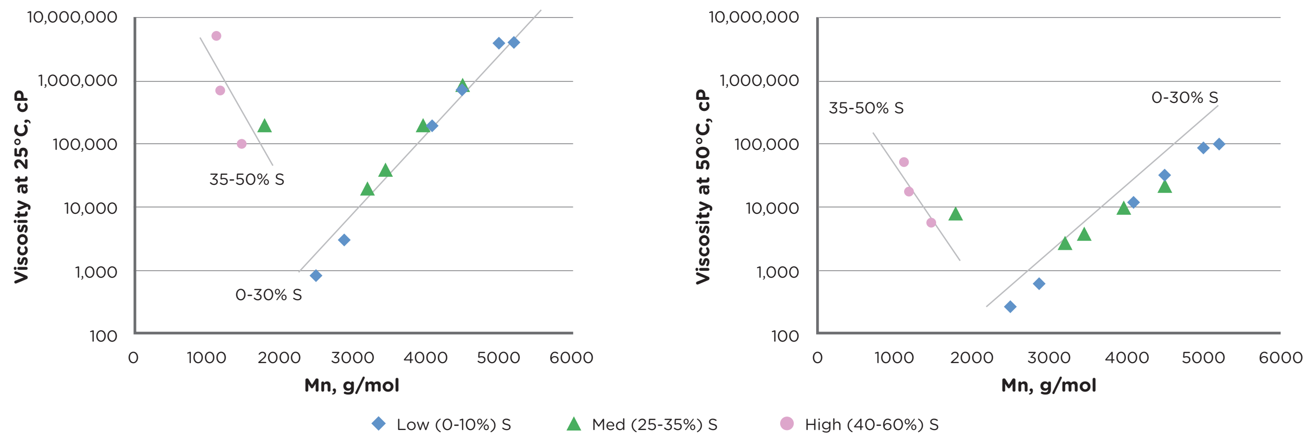


Figure 2: Viscosity of neat Ricon resins vs. molecular weight at 25°C (left) and 50°C (right).



Tackiness of Ricon Resin Fiberglass Prepregs

Ricon 100 and Experimental Ricon 4 were evaluated to see if prepreg tackiness could be decreased with changes in copolymer composition and viscosity. The resins were dissolved in methyl ethyl ketone, then applied to E-glass fiberglass woven cloth. The cloth was oven dried at 80°C to remove the solvent, then pressed at 100 psi / 110°C to produce fiberglass prepregs. The tackiness of the prepregs was evaluated using a Texture Analyzer (Stable Micro Systems) to measure the pull-away force of a ¼" diameter stainless steel probe pressed to the surface of the prepreg for 60 seconds at 3000g of force. The area under the pull-away force curve was also calculated as a measure of tack strength. The pull-away force of duct tape and masking tape was also measured for comparison. Duct tape had the highest pullaway force, followed by masking tape. Ricon 100, generally recognized as having high tackiness in pregregs, had a tack strength roughly 10 times lower than that of masking tape. Experimental Ricon 4 had even lower pull-away force and strength values, indicating prepreg tackiness can be reduced by formulating with resins having higher styrene content, or lower 1,2-vinyl content and viscosity.

Figure 1: Pull-Away Force of Ricon Prepregs.

Product	Styrene (%)	1,2-Vinyl (%)	Uncured (T_g,°C)	Viscosity of neat resin at (50°C, cP)	Peak pull-away force (g)	Tack strength (g x seconds)
Ricon 100 prepreg	25	70	-22	22,000	220-250	26-32
Exp. Ricon 4 prepreg	54	26	-27	5,700	30-130	2-7
Masking Tape	—	—	—	—	1230-1400	218-280
Duct Tape	—	—	—	—	2640-2740	820-840

Co-Reaction with Polyphenylene Ether (PPE) Resin

Polyphenylene ether (PPE) is a frequently used resin in CCL and PWB applications. Once crosslinked, it imparts strength and heat resistance to circuit board substrates. Triallyl isocyanurate (TAIC) is a tri-vinyl functional compound frequently used as a crosslinker for formulations with vinyl-functional PPE. However, at typical laminate cure temperatures of 150 – 200°C, TAIC can volatilize and degrade. Ricon resins can be substituted as non-volatile crosslinkers while also functioning as reactive plasticizers, imparting toughness to circuit board substrates.

Ricon resins were compared with TAIC as hardeners for vinyl-functional PPE (Noryl™ SA9000 PPO™, SABIC). Ricons were mixed with PPE at a 1:1 weight ratio into toluene at 55% solids with dicumyl peroxide at 3% solids basis. These solutions were applied to E-glass fiberglass woven cloth and dried at 80°C to remove solvent. Then three layers were stacked and cured at 100 psi and 160°C for three hours, then postcured at 200°C for one hour. Dielectric constant (Dk) and dissipation factor (Df) of the cured laminates were measured using a split post dielectric resonator (SPDR, QWED Ltd). Resin content of the cured laminate was measured via thermogravimetric analysis (TGA), then T_g was measured via dynamic mechanical analysis (DMA).

Figure 3: Structures of vinyl functional polyphenylene ether resin (left) and Ricon styrene-co-butadiene resin (right).

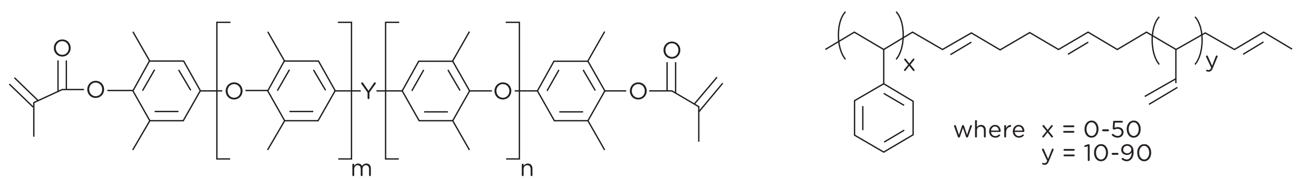


Table 3: Composition and Viscosity of Ricon Resins Co-Reacted with PPE at 1:1 Weight Ratio.

	HARDENER RESIN AS IS			CO-REACTED WITH PPE		
Product	**Styrene (%)**	**1,2-Vinyl (%)**	**Viscosity (50°C, cP)**	**T_g (°C[1])**	**D_k (at 5 GHz)**	**D_f (at 5 GHz)**
PPE as is[2]				160	2.540	0.00070
E-glass Fiberglass[3]					6.800	0.00700
TAIC	0	100	—	186	4.139	0.00565
Ricon 154	0	90	100,100	207	4.166	0.00557
Ricons 154 and 130, 75/25 blend	0	75	12,000	203	3.865	0.00512
Ricons 154 and 130, 25/75 blend	0	44	620	193	3.397	0.00481
Ricon 130	0	28	270	187	3.593	0.00501
Ricons 154 and 100, 75/25 blend	6	86	85,000	209	4.083	0.00580
Ricons 154 and 181, 75/25 blend	7	79	32,000	207	3.654	0.00544
Ricon 100	25	70	22,000	178	4.059	0.00492
Ricons 100 and 181, 75/25 blend	26	57	10,000	186	3.968	0.00517
Ricons 100 and 181, 25/75 blend	27	41	3,900	185	3.570	0.00438
Ricon 181	28	30	2,800	123	3.889	0.00478
Developmental Ricon 1	35	50	8,000	138	4.123	0.00466
Developmental Ricon 2	50	40	17,700	122	4.094	0.00464
Developmental Ricon 3	51	44	52,000	128	3.747	0.00481
Developmental Ricon 4	54	26	5,700	104	4.061	0.00502

[1] Determined by tan δ peak, DMA.
[2] Noryl™ Resin SA9000 Technical Data Sheet, SABIC. Dk and Df reported at 1 MHz.
[3] D_k and D_f reported at 10 GHz. Frederick Wallenberger, editor. Fiberglass and Glass Technology, Springer, 3rd Ed., 2009, page 186.
[4] At 25°C, 52% solution in toluene.

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As seen in Figure 4, T_g of the cured PPE/Ricon co-reaction increases with increasing vinyl content of the Ricon, due to the higher availability of crosslinks. At high styrene content with low vinyl content, T_g is low but dramatically increases as vinyl content increases. At low styrene content, the T_g increases only slightly with increasing vinyl content. The relationship of T_g with vinyl content is more variable at medium (5-27%) levels of styrene in the Ricon copolymer. In general, T_g increases with increasing molecular weight of Ricon as well. Higher T_g values can be achieved with Ricon resins compared to TAIC.

Dk of the cured PPE/Ricon co-reaction shows little correlation with 1,2-vinyl content of the Ricon, as shown in Figure 5. Dk varies between 3.4 and 4.2 regardless of vinyl content, styrene content, molecular weight of the Ricon, or resin content of the cured laminate. However, Df does correlate with vinyl content, increasing as vinyl content increases. Lower Dk and Df values are generally desirable for PWB applications, while higher T_g and lower viscosity are desirable. Higher T_g values, as well as significantly lower Df values, can be achieved with Ricon resins compared to TAIC. These co-reaction properties and their relationship to vinyl content, styrene content, and molecular weight of the Ricon are summarized in Table 4. A balance of properties can be achieved by appropriate selection of the Ricon resin.

Figure 4: T_g of cured PPE/Ricon fiberglass laminates vs. vinyl content (left) and molecular weight (right).

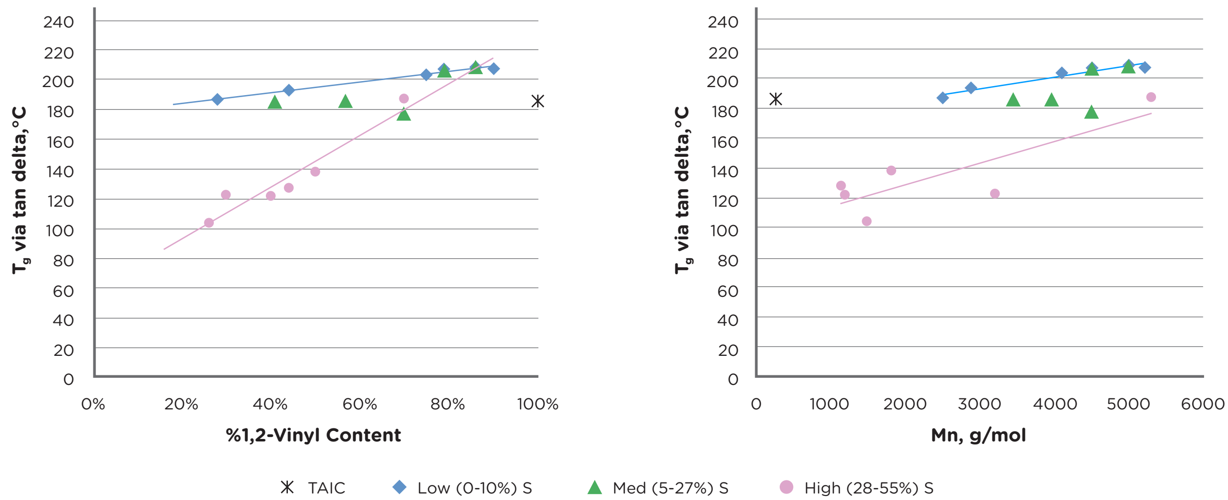

Figure 5: Dk (left) and Df (right) of cured PPE/Ricon fiberglass laminates vs. vinyl content.

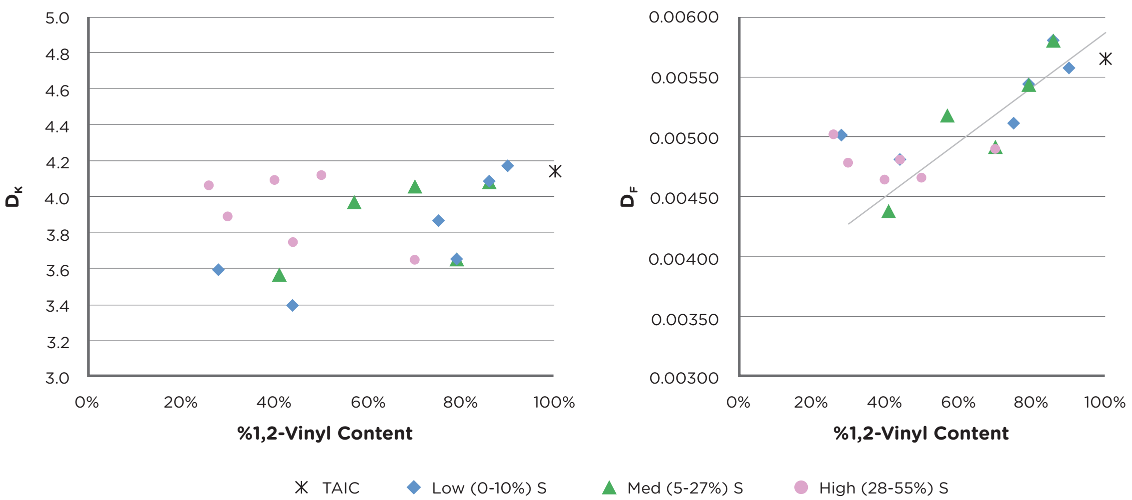

Table 4: Summary of the Effects of Ricon Composition on Ricon Viscosity and Cured PPE/Ricon.

RICON COMPOSITION	At Low Styrene Content		At High Styrene Content	
	As 1,2-Vinyl ↑	As Mol Wt ↑	As 1,2-Vinyl ↑	As Mol Wt ↑
Viscosity of Ricon (lower is generally better)	↑	↑	↑	↓
T_g of cured PPE/Ricon (higher is generally better)	↑	↑	↑	↑
D_k of cured PPE/Ricon (lower is generally better)	–	–	–	–
D_f of cured PPE/Ricon (lower is generally better)	↑	–	↑	–

Note: Green and red indicate desirable and undesirable effects respectively. **Bold** indicates effect is more significant.

Summary

Ricon resins are available at a variety of copolymer compositions, molecular weights, and viscosities. In general, the higher the 1,2-vinyl content, the higher the viscosity, although this varies with styrene content and molecular weight. Tackiness of prepregs prepared with Ricon can be improved with higher styrene content and lower vinyl content. T_g of the cured reaction product with PPE increases with increasing 1,2-vinyl content of the Ricon, however Df increases as well. Higher T_g values, as well as significantly lower Df values, can be achieved by replacing TAIC with Ricon resins. T_g, dielectric properties, and resin viscosity can be balanced with appropriate selection of Ricon.

About Cray Valley

Cray Valley is a global supplier of specialty chemical additives, hydrocarbon specialty chemicals, and liquid and powder tackifying resins used as ingredients in adhesives, rubbers, polymers, coatings, and other materials. 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 manufacturing, electronics, and other demanding applications.

For more information, please visit **www.crayvalley.com**.

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