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Liquid 1,2-Vinyl Polybutadienes and Modified Polybutadienes as Resin Matrix in Laminates

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ABSTRACT

Liquid 1,2-vinyl polybutadiene homopolymers and copolymers with styrene have been used in thermoset applications for a number of years. The most common usages are coatings, electrical potting and laminates. The polybutadienes are used in those areas where high moisture resistance, chemical inertness and low dielectrics and loss factors are important.

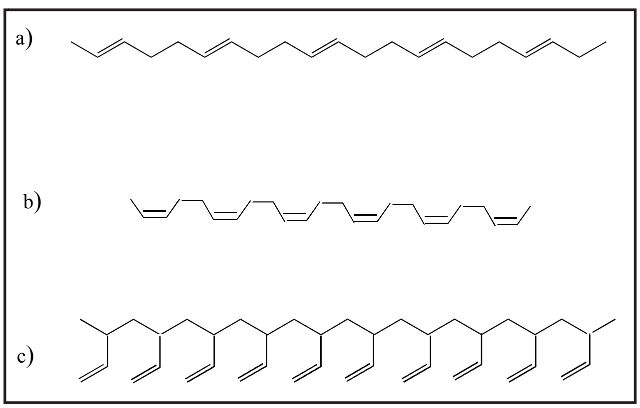
The first generation polybutadiene thermosets are peroxide cured and require somewhat special cure schedules in order to produce acceptable parts. The new polybutadiene based thermosets are expoxy/ anhydride chemistry in the cure mechanism. This chemistry allows handling and cure schedules similar to epoxies, while achieving properties similar to those of the peroxide cured systems.

These new resins are tougher and more versatile than the traditional polybutadienes. Prepregs for laminates and resin transfer injection molding (RTIM) are examples of areas where the properties of these new resins may be utilized.

INTRODUCTION

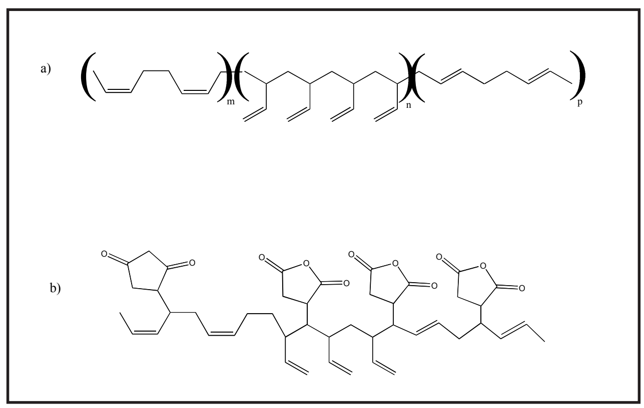
The polymerization of 1,3-butadiene has been known for many years. (1) 1,3-butadiene can be polymerized to produce three different types of unsaturated structures depending upon conditions and catalyst. One set of condition can give a 1,4 addition structure. The 1,4 structure can have either cis or trans configuration (Figures 1a and 1b). These materials when cured with peroxide or sulfur produce rubbery products. The third form is 1,2-vinyl unsaturation (Figure 1c). The peroxide cure of 1,2-vinyl polybutadienes produces very hard, brittle materials. The Ricon™ polybutadiene resins contain all three types of unsaturation with the 1,2-vinyl content being relatively high (Figure 2a). These materials cure to hard parts.

Figure 1



Configurations of polybutadiene: (a) 1,4-Trans, (b) 1,4-Cis and (c) 1,2-Vinyl.

Figure 2



Strucures for (a) Ricon 150 and (b) Maleic Anhydride adducted polybutadiene

Observing the structure of the polybutadiene molecule, one can visualize a number of chemical modifications that can be performed to toughen the cured resin. Modification with maleic anhydride has demonstrated good versatility[(2,3)]. The properties of the reaction products of "maleinized" polybutadiene with epoxies are very attractive for many applications.

The electrical properties of the polybutadiene resins have been documented in earlier papers[(3,4)]. These studies showed that polybutadienes being 100% hydrocarbon had excellent electrical properties[(2)]. In addition to the exceptional electrical properties, the polybutadienes have excellent high temperature stability and moisture resistance. The Ricotuff epoxy system is based on the maleinized polybutadienes and incorporates and takes advantage of these properties.

This paper will address all the Ricotuff properties with emphasis on the physical rather than the electrical, which have been addressed in an earlier paper[3]. Most of the test were performed on glass laminates of Ricotuff and 1581 glass (Hexcel's HX1564). The parts were tested both wet and dry at ambient and elevated temperatures.

EXPERIMENTAL

Polybutadiene resin casting were prepared by adding 1% - 2% dicumyl peroxide to the neat resin and cured at 320°F (160°C) for two hours then post cured at 428°F (220°C) for two hours. Modified polybutadiene/epoxy castings were prepared by mixing Part A, Part B and a catalyst in a 2:1:0.04 ratio and cured at 266°F (130°C) for two hours followed by a post cure at 500°F (260°C) for two hours. For the laminated parts, the resins were mixed as above then 1581 glass with F41 finish (A1100 amine) was impregnated to approximately 35% with resin. Eight (8) ply laminates were used in the tensile testing and ten (10) for all others. Parts were cured in an autoclave at 270°F (132°C) then post cured at 475°F (246°C) for 4 hours. Heat up was 2°F (1°C)/minute. Properties were determined at indicated temperatures. The following ASTM methods were used; Short Beam Shear (SBS):D2344; Flexural Strength and Modulus: D790; Tensile Strength and Modulus: D3039; Compression Strength and Modulus:D695.

DISCUSSION

The electrical properties of polybutadiene (Ricon) and the modified polybutadiene epoxy (Ricotuff) neat resins are listed in Table 1. The dielectric constants and loss tangent of Ricon and Ricotuff glass laminates are listed in Table 2. The Ricon and Ricotuff resins are viscous liquids with a very high degree of tack. Developing a prepreg for laminates was a high priority to better utilize moisture and chemical resistance and electrical properties of these resins. Laminates of the Ricons were developed using a mixture of high molecular weight resins and reactive monomers cured with peroxide catalyst. Hexcel's F-457-1 is an example of such a Ricon commercial prepreg.

Table 1

ELECTRICAL PROPERTIES OF NEAT POLYBUTADIENE RESINS		
Polymer	Dielectric Constant	Dissipation Factor
RICON	2.42	0.0005
RICOTUFF	2.58	0.0094

Table 2

ELECTRICAL PROPERTIES OF POLYBUTADIENE GLASS LAMINATES. X-BAND FREQUENCIES @ 24ºC (75ºF)		
Polymer	Dielectric Constant	Dissipation Factor
RICON	3.41	0.012
RICOTUFF	3.60	0.0095

Using the Ricotuff system, because it is a two part system plus a catalyst, meant developing a prepreg with proper tack and out time, which necessitated designing the proper resin combinations. The first approach was to adjust the catalyst and catalyst combinations and out time in order to reduce the very high tack. The next approach was to modify the part B epoxy to increase its viscosity and lower the room temperature tack. These experiments resulted in a Ricotuff system that made a very good prepreg. A Ricotuff/1581 glass has been prepared (Hexcel's HX1564) and most of the laminate data was developed from this prepreg. Some Physical properties of the Ricon and Ricotuff laminates are listed in Table 3.

Table 3

PHYSICAL PROPERTIES OF RICON AND RICOTUFF GLASS LAMINATES		
Test	Ricon	Ricotuff
Tensile Strength		
@77ºF (25ºC)	310 MPa	340 MPa
Flexural Strength		
@77ºF (25ºC)	366 MPa	545 MPa
@160ºF (71ºC)	186 MPa	----
@200ºF (93ºC)	----	366 MPa

The flexural strength of the Ricotuff glass laminate is 545 MPa (79,000 psi) which is 33% higher than the flexural strength of the Ricon glass laminate at 366 MPa (53,000 psi). The Ricotuff glass laminate loses 32% of its flexural strength at 200°F (93°C). The Ricon glass laminate loses 49% of its flexural strength at 160°F (71°C). The tensile strength of the glass laminate of Ricon and Ricotuff are 310 MPa (45,000 psi) and 340 MPa (49,300 psi), respectively. The data in Table 4 shows that the Ricotuff laminate retains 2/3 of its compressive strength with no loss in modulus at elevated temperatures. Another laminate test is the short beam shear (SBS). Ricotuff looses 34% at 180°F (82°C) and 43% at 200°F (93°C). (Table 4).

Table 4

RICOTUFF GLASS LAMINATE PROPERTIES AT AMBIENT AND ELEVATED TEMPERATURES			
Test	77ºF (25ºC)	180ºF (82ºC)	200ºF (93ºC)
Tensile			
Strength	340 MPA		
Modulus	21 GPa		
Compression			
Strength	419 MPa	283.5 MPa	
Modulus	20.7 GPa	20.7 GPa	
Flexural			
Strength	545 MPa		366 MPa
Modulus	17.8 GPa		19.3 GPa
SBS	49.1 MPa	31.4 MPa	26 MPa

The SBS and the compression properties of Ricotuff under dry, wet and hot test conditions are listed in Table 5.

Table 5

WET AND DRY COMPARISON OF SBS AND COMPRESSION OF RICOTUFF GLASS LAMINATE TESTED DRY AFTER 14 DAYS @ 160ºF (71ºC)		
Test	77ºF (25ºC)	180ºF (82ºC)
SBS		
Dry	49.1 MPa	29.7 MPa
Wet	39.7 MPa	25.3 MPa
Compression Strength		
Dry	419 MPa	283.5 MPa
Wet	386.9 MPa	253.1 MPa
Compression Modulus		
Dry	22.8 GPa	20.5 GPa
Wet	22.8 GPa	19.9 GPa

Ricotuff retains over 51% under hot wet conditions in SBS, and over 60% of its properties in compression. Modifying the structure of the part A resin was done to maximize the Ricotuff system and make it a good impregnating resin. Because the part A is a modified polybutadiene, many of the steps taken to make Ricon laminates will also apply. Modification of molecular weight and micro-structure (ratio of cis, trans, and vinyl unsaturation) can be varied to prepare a suitable resin. A resin, Ricotuff LAM, has been developed using this approach and is currently undergoing tests. Table 6 shows some of the electrical properties for the Ricotuff LAM neat resin. The dielectric constant of 2.60 for the Ricotuff LAM is very close to 2.58 for Ricoftuff. The Ricotuff loss tangent is .0094 and the Ricotuff LAM loss tangent is .0085. All electrical data measured at 12-18 GHz. With electricals that correspond as well as they do to the Ricotuff and with the change in the base resin, the Ricotuff LAM should be superior the Ricotuff.

Table 6

ELECTRICAL PROPERTIES OF RICOTUFF LAM	
Property	
Dielectric Constant	2.60
Dissipation Factor	0.0085

Other areas being explored but not covered in this paper include peroxide cures of Ricotuff for improved heat and chemical resistance and copolymerization of polybutadienes and modified polybutadienes with polyesters and polyimides.

CONCLUSIONS

Laminates have been prepared from the Ricotuff epoxy system. The testing of these laminate have demonstrated that the Ricotuff laminates retain much of the excellent properties of Ricon polybutadiene resins and imparts a greater toughness to the cured polybutadienes/epoxy resin. The possibility exists that these properties can be transferred to other resin systems, such as, polyesters and phenolics.

REFERENCES

1. M. Morton, “Rubber Technology”, Secon Ed., Van Nostrand Reinhold Co., N.Y. 1973 p. 201

2. R. E. Drake and J. M. Labriola, “Ricon Mad: A New Polymeric Curative for Polychloroprene”, ACS Rubber Division, Atlanta, GA. 1986 paper no. 5

3. H. R. Sessions, J. M. Labriola, R. E. Drake, “Polybutadiene and Modified Polybutadiene Thermosets as Low Dielectric Polymer Matrix and Coatings for Radoms and Antennas”, International SAMPE Conference Series, 4, 1990, p. 158-166

4. R. E. Drake, “1,2-Polybutadienes-High Performance Resins for the Electrical Industry”, SPE, ANTEC 1984. Paper no. 362

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