N93-30853

DEVELOPMENT OF RESINS FOR COMPOSITES BY RESIN TRANSFER MOLDING

Edmund P. Woo, Paul M. Puckett, and Shawn J. Maynard
The Dow Chemical Company

The Dow Chemical Company was awarded a contract (NAS1-18841) by NASA Langley Research Center for the development of "Novel Matrix Resins with Improved Processability and Properties for Primary Aircraft Structures". The TRCO is Dr. Paul Hergenrother.

Designed to cover a wide range of resin technology and to meet the near-term and long-term needs of the aircraft industry, the Dow contract has three objectives as shown below.

Objectives

- RTM resins with improved processability and properties.
- Prepreg systems with high toughness and service temperature.
- New matrix resin concepts.

The contract awarded to Dow Chemical as a part of the ACT Program is divided into three distinct areas. At the facility in Freeport, TX work is being conducted on the development and evaluation of resin systems for use in resin transfer molding (RTM). The work in RTM involves formulating a number of commercial or near-commercial thermoset resins to reach the objectives of processability, service temperature, and toughness. At the facility in Midland, MI work is being conducted on the development of high temperature, highly damage tolerant prepreg composite systems. Also conducted in Midland is the development of new resin concepts which should lead to low viscosity resins that are thermally convertable to high T_g and tough polymers. Promising new resins will be studied for composite applications.

Overall Program

RTM Composite Technology

Task 1. RTM resins for 200°-300°F/wet service.

Prepreg Composite Technology

Task 2. Cyanate-based composite, 400°F/wet, CAI ≥40 ksi.

Task 3. Acetylene-based composite, 450°F/wet, CAI≥40 ksi.

New Resin Concepts

Task 4. BCB-based resins capable of linear polymerization.

Task 5. Arylene ether cyclic monomers.

The RTM task involves development of resin systems from commerical and near-commercial thermoset resins. There is no one perfect material that will be usefull in all processes and for all applications. The goal is to produce several materials which will meet the various needs in the aersopace industry including processing flexiblity, toughness and use in hot/wet service environments.

Objectives

Task 1. RTM Composite Systems

Develop a series of RTM resins for production of advanced composites that will

(a) be useful in "real-world" manufacturing and

(b) meet the needs for toughness and high temperature performance.

The RTM task will evaluate four classes of materials for their applicability to this process. The cyanate resins are a class of high T_g (≥250°C) thermosets that possess a true catalytic cure. These materials have demonstrated process flexibility, good toughenability, excellent composite properties, and retention of properties at elevated service temperatures. The vinyl esters are a well known class of materials that have demonstrated excellent potential for composite applications. New vinyl esters will be developed with higher T_g and toughness than currently available resins. Two classes of epoxy materials will be evaluated: epoxy resin formulations that are tough without the use of rubber for 200°F service environments; high T_g epoxy resin formulations that are rubber toughenable for 300°F service environments.

RTM Systems

Task 1.1. Cyanate-based composite systems

Improved toughness and processability,
Up to 300°F use temperature.

Task 1.2. Vinyl ester of hydrocarbon epoxy novolac

Excellent RT processability and fast cure,
Epoxy-like properties with improved toughness.

Task 1.3. Crosslinkable epoxy thermoplastics

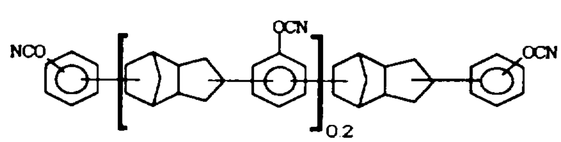
One-phase system with marked toughness improvement.

Task 1.4. High temperature epoxy resins

Up to 300°F use temperature,
Improved toughness and processability,
Based on readily available materials.

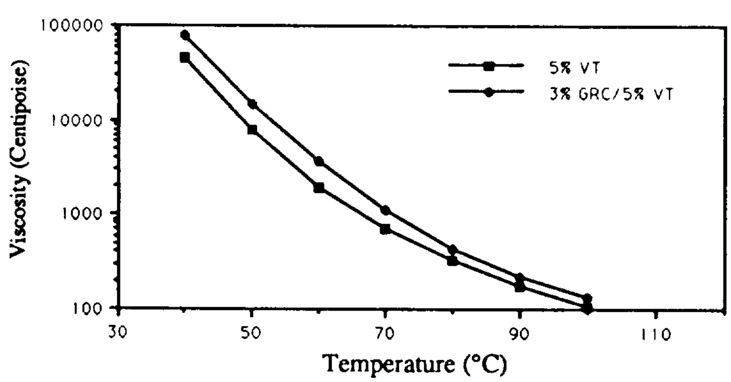
Two cyanate resin formulations have passed the screen established for RTM systems. Both formulations are one-pot systems which contain a latent catalyst. These resin systems are processable at 180-200°F (82-93°C) and provide pot-life of greater than 8 hours. Their room temperature storage stability is greater than 2 months. In addition, these formulations achieve RTM processability without losing the positive attributes of cyanate resin XU71787.02 -- high T_g, high modulus, low moisture absorption, and processing flexibility.

Cyanate RTM Resins



XU71787.02

Viscosity Profiles of Modified Cyanate Resin

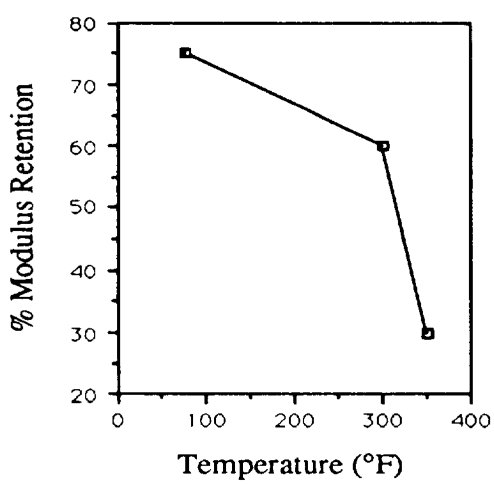


Two cyanate resin systems are being evaluated in composite form. The use of a latent catalyst in the RTM formulation provides a stable viscosity below 500 cps at 180°F (82°C) for molding. Increasing the temperature to 250°-350°F (121°-177°C) cures the resin within a few hours. A freestanding post cure of at least 475°F (246°C) is required for optimum properties. The cyanate with 5% vinyltoluene is the base resin. The same material with 3% GRC, a proprietary core-shell rubber, is being evaluated as a toughened RTM system for 300°F/wet applications. This toughened polymer system has demonstrated good fracture toughness, high modulus, high T_g and low moisture absorption.

Cyanate RTM Resins

5% VT/3% GRC

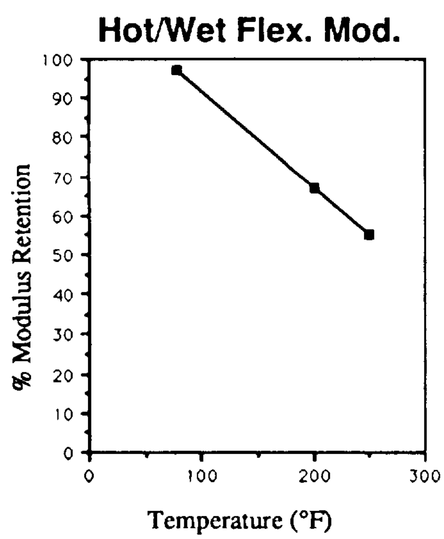
Hot/Wet Flex. Mod.



Tensile Strength	10.9 ksi
Tensile Modulus	434 ksi
Tensile Elongation	3.3%
Flexural Strength	18.2 ksi
Flexural Modulus	441 ksi
G(1c)	245 J/mm
Water Absorption	1.1%
Tg	255°C

Vinyl ester resins, because they are cured via a free radical mechanism, offer a flexibility in RTM processing not obtainble from most thermoset systems. This processing versatility, excellent thermal and mechanical properties, and corrosion resistance of these materials make them excellent candidates for composite fabrication. After screening a large number of vinyl esters, the system chosen for additional evaluation in composite applications is a 5% rubber modified material. This vinyl ester resin has demonstrated good modulus values, high T_g, and low water absorption. The material retains 55% of its room temperature modulus when tested at 250°F (121°C) following moisture saturation.

Vinyl Ester RTM Resin

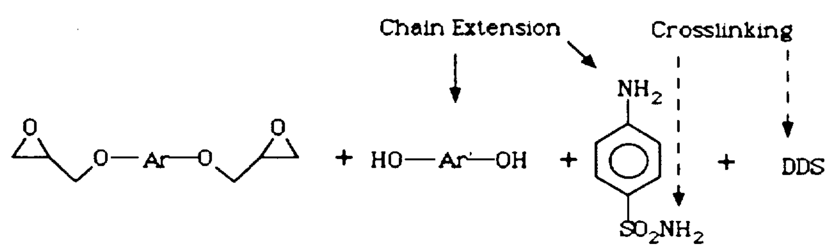


Tensile Strength	8.6 ksi
Tensile Modulus	405 ksi
Tensile Elongation	2.8%
Flexural Strength	18.3 ksi
Flexural Modulus	447 ksi
G(1c)	105 J/mm
Water Absorption	1.2%
Tg	171°C

Epoxy resins are the most widely used materials in advanced composites. A new class of epoxy materials has been developed that overcomes many of the deficiencies found in other "high performance" RTM systems. CET chemistry was originally formulated as a tough, homogeneous, prepreggable resin. The control of chain extension and crosslinking reaction rates provides the unique properties observed for this material. The combination of high polymer modulus, high ductility, and low moisture absorption produces a composite with excellent CAI and hot/wet compressive strength. The reactivity of this amine cured system makes it suitable for resin infusion molding but not, however, for liquid molding.

CET RTM Resins

Tactix® 695

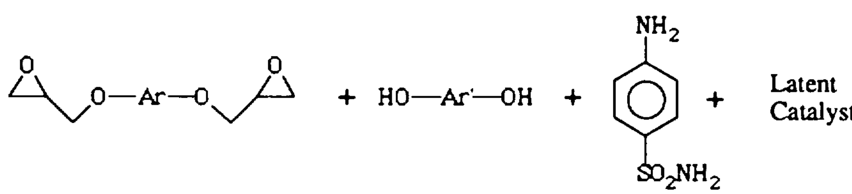


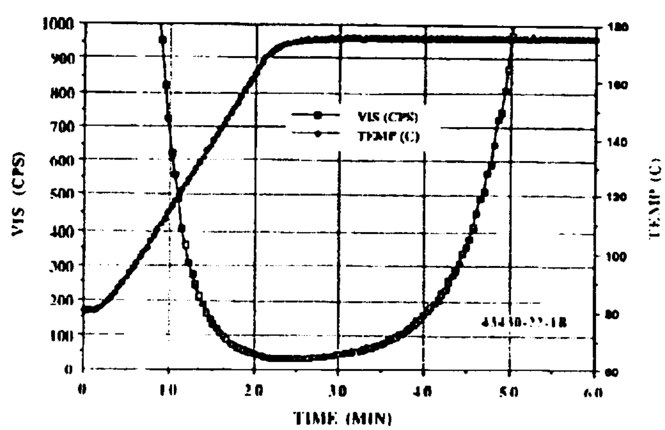
Resin Properties	
Flexural strength	22 ksi
Flexural modulus	520
Water absorption	1.3%
Tg	170°C

Composite Properties	
0° Comp. strength	
RTD	210 ksi
180°F/wet	170 ksi
CAI (1500 in-lb/in)	40 ksi

A new CET formulation has now been developed. This material is a one-pot system which contains resin, hardener, and latent catalyst. Control of chain extension and crosslinking reaction rates is also provided in this material. This formulation allows production of a ductile polymer with high modulus and improved resin viscosity stability at elevated temperatures (6% per hour increase at 80°C). Therefore, this material has potential for use in either resin infusion molding or in liquid molding. Molding viscosities of less than 500 cps are obtained at 250°F (121°C).

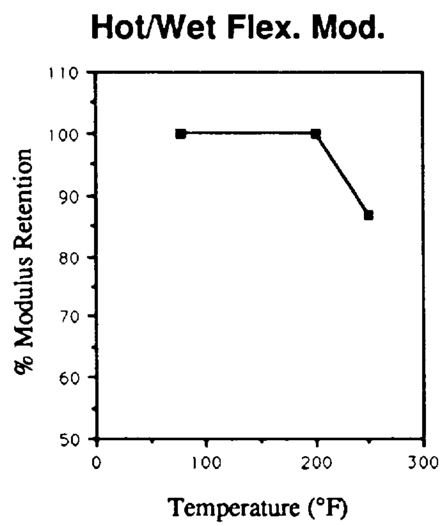
New CET Formulation





A one-pot curable resin composition has been developed that can be molded via resin infusion or liquid injection molding at temperatures greater than 250°F (121°C). It is cured at 350°F (177°C). Freestanding post cure at 400°F (204°C) is recommended for optimum properties. The polymer formed is ductile with a high tensile elongation and toughness which should provide excellent microcracking resistance and damage tolerance in the composite. The high modulus of the polymer should also produce good compressive strength. The very low moisture absorption of the polymer allows a high retention of properties (e.g. modulus) even at 250°F/wet.

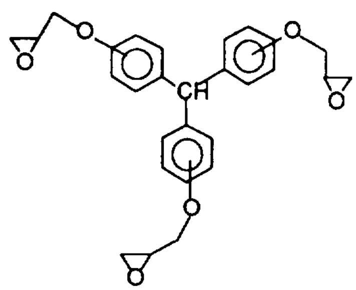
New CET Formulation



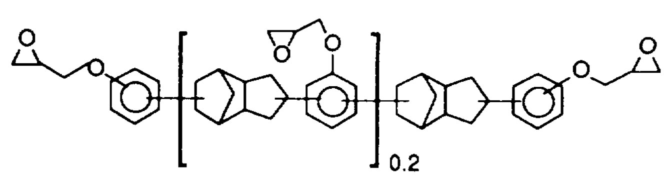
Tensile Strength	13.1 ksi
Tensile Modulus	472 ksi
Tensile Elongation	7.1%
Flexural Strength	20.7 ksi
Flexural Modulus	512 ksi
G(1c)	200 J/mm
Water Absorption	0.7%
Tg	154°C

Liquid epoxy resin systems are now commonly used for RTM applications. The processing advantages provided by low viscosity difunctional epoxies (e.g. bisphenol A and bisphenol F) are sometimes compromised by lower polymer modulus and T_g values. By use of selected higher functional materials that resist water uptake we believe we can produce improved RTMable formulations. These systems when toughened with rubber should generate high modulus, high T_g polymers which in turn should provide durable composites with good retention of properties at elevated service temperatures.

High Temperature RTM Epoxy Resins



Tactix® 742



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Summary of Accomplishments

- Program balanced between near and longer term.
- Resin development phase for RTM near completion. Preferred resin identified in 3 of the 4 sub-tasks. Composite studies in progress.
- Results of RTM work shared with other ACT contractors and samples sent for evaluation.
- Close to meeting target performance of Task 2.
- Task 3 has led to a ≥450°F/wet, low viscosity resin.
- Discovered low viscosity, high Tg, high toughness BCB-based resins in Task 4.