Mississippi Pultrusion

Pultrusion Research Report of The University of Mississippi
Composite Materials Research Group

Fall 2004/Winter 2005

201 Carrier Hall ♦ University, Mississippi 38677 ♦ E-Mail: jgv@pultrusion.me.olemiss.edu ♦ (662) 915-5378

Recent Publications

Ellen Lackey, J. G. Vaughan, and R. Patki, "Enhanced Pultrusion Using Photocure to Supplement Standard Thermal Cure," *Proceedings of Composites 2003 - CFA* (Composites Fabricators Association), published on CDROM, 2003.

Brief Abstract: A hybrid thermal/photo initiator process which uses photocure to supplement standard thermal cure was developed. Results demonstrate the potential offered by this hybrid thermal/photo initiator process; exposure to UV energy lead to an increase in degree of cure and mechanical properties in the thermal/photo initiated pultruded composites. This paper was named Best Pultrusion Paper Award Winner for Composites 2003. This is the fourth consecutive year that CMRG research papers have been selected for awards at the CFA annual convention.

Ellen Lackey and James Vaughan, "Resin Fillers and Additives: What Pultrusion Research has Learned about the 'Secret Herbs and Spices' of Composites," *Composites Fabrication*, 10 (3) 12-17, 36, March 2003.

Brief Abstract: Just as any chef knows that "secret herbs and spices" can turn an ordinary recipe into a culinary masterpiece, proper selection of resin fillers and additives used to formulate a resin system can result in polymeric composites with optimal properties.

CMRG Examines Pultruded Composites Reinforced with Natural Fibers

Researchers at the Composite Materials Research Group (CMRG) at the University of Mississippi (UM) have recently begun a research study supported by the U. S. Department of Agriculture (NRI-CSREES-USDA Award number 2003-35504-13627) examining natural fiber reinforcements (NFR). The objectives of this research are to demonstrate the feasibility of using the cost-effective pultrusion process to manufacture high quality polymeric composites using natural fiber reinforcements, to publish details concerning pultrusion using NFR in the open literature, and to quantify mechanical property variability for these composites. The initial pultrusion experiments conducted for this study utilized hybrid reinforcement composed of E-glass with unidirectional hemp yarn or woven hemp mat reinforcements.

> *"Agricultural crop fibers such as hemp and jute have the potential to act as replacements for glass fiber reinforcements in polymeric composites."*

As society begins to recognize the importance of utilizing renewable bioproducts that are beneficial to the environment, focus is beginning to return to agricultural materials. In this study, the use of agricultural products as constituent materials in composites is being reexamined, and new technology is being applied to efficiently utilize these materials. Agricultural crop fibers such as flax, kenaf, hemp, jute, and sisal have the potential to act as replacements for glass fiber reinforcements in polymeric composites.

Influenced by environmental concerns, the European automotive industry has been a leader in the commercialization of natural fiber composites in applications such as door panels, interior trim parts, structural headliners, and seat backs. This trend is now being adopted by the North American automotive industry. In addition to the automotive applications that have been commercialized, research work continues worldwide on the utilization of agricultural fibers as a substitute for glass fibers for applications with more demanding property requirements.

In general, natural fibers offer moderate mechanical properties, but, in some aspects, the properties of natural fibers can surpass those of E-glass. The acoustic insulating properties of the fibers are especially desirable for some applications. The low density (ρ) of natural fibers makes them competitive and even superior to E-glass in terms of specific strength (σ/ρ) and

Continued on page 3….

CMRG Research Profiles

The Composite Materials Research Group at the University of Mississippi emphasizes an interdisciplinary research approach. Presently, the research is focused on areas including structural modeling, mechanical and physical property characterization, thermal and kinetic modeling, surface science, and experimental process characterization/optimization. In this issue of *Mississippi Pultrusion*, a discussion of continuing research concerning the development of a new phenolic resin system is presented. Further details concerning this research are being presented in a paper coauthored by CMRG and ANGUS Chemical Co. researchers at the ACMA Composites 2004 annual conference and are available in the *Composites 2004 Proceedings*.

Development of New Novolac-Based Phenolic Resins for Pultrusion

Composite Materials Research Group engineers at the University of Mississippi have recently been involved in a project to develop improved phenolic resins for pultrusion processing. Instead of the traditional resole phenolic formulations that have been used with pultrusion in the past, this new resin system is a novolac-based resin. This research is being conducted with researchers from the ANGUS Chemical Company.

Historically, attempts to pultrude phenolics have utilized resoles, which are “1-part” phenolic resin systems prepared with a phenol / formaldehyde ratio less than 1. This leads to a self reactive system which cures upon heating. This characteristic, while attractive to minimize formulation components, also leads to slow cure even at ambient temperature resulting in poor shelf-life. Thus resoles are often refrigerated during storage to minimize viscosity drift. In contrast, phenolic novolacs are typically prepared with a phenol / formaldehyde ratio greater than 1. As a consequence, few, if any, reactive sites remain in the resin. Without the potential for further reaction, storage of novolacs under ambient conditions without viscosity drift is typical. Curing of novolacs is typically effected by adding a source of formaldehyde. The physical handling of formaldehyde or its derivatives (e. g. hexamine, paraformaldehyde), however, poses significant worker exposure issues.

The pultrusion resin systems studied during this work are two-part formulations consisting of phenolic novolac resins and non-formaldehyde hardeners. Stored individually, the components have a shelf life greater than 6 months at room temperature. The two components are mixed just prior to use, and a mold release is added to facilitate processing. After mixing, the formulation has a pot life greater than 24 hours at room temperature. Because the resin component is a novolac rather than a resole, the pultrusion formulations do not need acid catalysis for rapid cure. These formulations, typically near pH 9, are also much less aggressive to the pultrusion die surface; hence, chrome plated dies are not required with this technology. Solvents such as ethanol are useful for adjusting formulation viscosity. A typical formulation contains 10 – 15 wt. % solvent.

The non-formaldehyde hardener component reacts thermally with the novolac resin to generate a cross-linked phenolic polymer. No significant amount of water or formaldehyde is generated in these reactions. Tests do not show any reportable quantities of free formaldehyde in this resin system. Additionally, there is essentially no formaldehyde release during cure as demonstrated by the total lack of formaldehyde odor during processing. The absence of formaldehyde generation was also quantified by badge testing. The ethanol, being an inert solvent, is discharged as a vapor at the exit of the die, and adequate ventilation to remove the vapors from the die exit is, of course, needed.

These resins are two-part formulations consisting of phenolic novolac resins and non-formaldehyde hardeners. Badge tests do not show any reportable quantities of free formaldehyde in this resin system.

The ratio of resin to hardener may be varied to achieve the desired cured resin mechanical properties. Good mechanical properties are routinely generated with formulations based on 2.75 parts of resin to 1 part of hardener. These formulations result in crosslink densities of approximately 75%, but useful properties have been demonstrated over the wider range of 60% to 90% crosslink density.

Pultrusion Processing Results: This novolac-based resin system offers numerous desirable processing characteristics. Phenolic resole systems for pultrusion are notoriously slow, with typical rates in the 15 – 36 in/min range, depending on the part geometry. This is due in part to the curing chemistry itself and also the need to flash off large quantities of solvent / water generated in the cured part. The addition of blocked-acid catalysts to accelerate cure rates is sometimes used, but this causes detrimental corrosion to expensive dies. In contrast, the present novolac-based pultrusion systems have a much lower solvent content and can be pultruded at much higher temperatures than a conventional resole. The combination of these two factors results in a fast curing system that can be pultruded at very high rates.

A study relating cure speed, cure temperature and part physical properties was performed. Using a uniform die temperature down the full length of the die, pultrusion was initiated at the lowest speed of interest. The pultrusion rate was then incrementally increased, with product being collected at each rate until further increases in line speed caused an under-cured part to result. The parts were then subjected to 3-point flexural testing to determine their integrity and the effect of pultrusion conditions on properties. The parameters measured were peak flexural stress, modulus, and peak strain at failure. Increased die temperature allowed processing at higher speeds, albeit with a sacrifice in the ultimate physical properties obtainable. Pultrusion above 60 in/min at 525F was not attempted, but the parts generated at 475F demonstrated excellent mechanical strength up to a pull rate of 52 in/min after which under-curing resulted in a rapid drop off in mechanical performance.

Table 1. Optimized Flexural Properties of 2-Part Phenolic Novolac Resin System

Pultrusion Speed (in/min)	3-point Flex Str. (ksi)	Flexural Modulus (Mpsi)	Peak Flexural Strain (%)
40	208	7.3	3.1
44	199	7.2	3.1
48	205	7.2	3.1
52	191	7.1	2.9

Optimized Processing Condition: Based on knowledge developed concerning the effects of formulation viscosity and stability, cure temperature, crosslink density and pull speeds, an optimization of the formulation for a given set of process conditions was performed. It was determined that pultrusion temperatures exceeding 500F were undesirable from a personal safety and operational viewpoint. Based on this, and the desire to maintain high processing rates, conditions were focused on creating a system that would give optimal pultrusion performance and excellent physical properties when processed in the 475 – 500F range. The resulting optimized resin / hardener system is as follows:

Resin / Hardener ratio – 2.75:1
Formulation Viscosity – 1200 cps @ 77F (25C)
Working Pot Life – 24 hours
Suggested Cure Temperature – 475F

The properties attainable with the above formulation / processing conditions are shown in Table 1. However, what Table 1 does not show is the dynamic operating range of the resin system. Start up conditions for initial trials can be extremely conservative, e. g. 12 in/min, without fear of seizing the die. Additionally, process upsets causing prolonged pull stoppages (1 – 3 min) have not caused operational problems. The surface finish attainable on all roving parts was exceptional, with high gloss, and no surface dusting, blemishes or pitting.

Conclusions: Formaldehyde-free, 2-part phenolic novolac pultrusion resin systems have been shown to have excellent shelf and pot life. The processing conditions and mechanical properties of the new system have also been demonstrated to be far superior to typical pultrusion phenolics, in many cases rivaling polyester resins. These improvements in properties are achieved without sacrificing the outstanding fire-smoke-toxicity (FST) characteristics inherent with phenolic resins.

Natural Fiber Reinforcements (cont.)

specific modulus (E/ρ).

Natural fiber reinforcements also offer value-added properties such as the beneficial environmental impact of these renewable resources, less abrasive nature of the fibers for reduced tool wear, and less skin irritation for workers. Challenges associated with the use of these fibers include the affinity of the fibers for moisture absorption and variable quality of the fibers due to growing conditions. These limitations can be addressed through the application of technologies such as fiber surface treatments, proper selection of resins and additives, and the proper design of fiber layup architecture for the fiber reinforcement in composites.

This research has demonstrated the potential for the use of natural fiber reinforcements with the pultrusion process. Pultrusion experiments conducted for this study have shown that hemp yarn and woven hemp mat can be successfully used in pultrusion. Based on the success achieved in the pultrusion of hybrid natural fiber/E-glass reinforcement composites, the focus of this research has been expanded to more thoroughly examine details of the use of natural reinforcement materials. The potential for the use of other types natural reinforcement materials is being examined. Also, additional factors such as moisture absorption of the natural fiber and surface modifications of the fiber to promote better wetout and resin adhesion to the natural fiber are being studied.

ACMA Certified Composites Technician (CCT) Program Participation at the UM School of Engineering

As part of its overall educational program, the University of Mississippi has begun participating in the Certified Composites Technician (CCT) program administered by the American Composites Manufacturers Association (ACMA). The first CCT's from UM were certified in Spring 2004. The CCT program was conceived by ACMA to provide a framework for a common body of knowledge of the composites workforce and to enhance individual performance through an understanding of the basic technology and principles used throughout the industry. Through participation in this program, the University of Mississippi strives to enhance students' understanding of composites manufacturing and materials. Knowledge of composite materials is critical for today's engineers, and participation in the CCT program provides a broad introduction to the field of composite materials to a wide range of students. The CCT program, which focuses on the broad scope of open molding technology, provides an ideal complement to the pultrusion research at UM.

Through successful completion of the CCT program, students with less than one year of experience earn the CCT-Associate designation, and students who have been directly involved in hands-on composites manufacturing for over one year earn the CCT designation.

In addition to providing the opportunity for UM students to complete the CCT program, UM also looks forward to providing service to the composites industry through participation in the CCT program. The CCT-Instructor designation, held by Dr. Ellen Lackey, qualifies her to teach CCT study courses to employees industry-wide as well as to administer the CCT examination. Dr. Lackey may be contacted at elackey@pultrusion.me.olemiss.edu for more information.

Recent CCT's from the University of Mississippi. Pictured from left to right – Brittany Hancock, Ellen Lackey (CCT-I), and Jarrad Zaiser. Not pictured – Bridget Knight, Vinod Namilakonda, and Vaishali Paliwal.

Mississippi Pultrusion WWW Homepage

http://www.olemiss.edu/depts/compmatl

- **Pultrusion-related literature search**
  - **SAMPE Conference Proceedings**
  - **SPI Conference Proceedings**
  - **CFA/ACMA Proceedings**
  - **General pultrusion publications**
  - **Abstracts of all CMRG publications**
- **Virtual tour of CMRG facilities**
- **Research overview**
- **Newsletter back issues**
- **Research contact information**