Mississippi Pultrusion

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

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Jack McClurg, James Vaughan, and Ellen Lackey, "Combined Effects of Moisture, Temperature, and Load on Pultruded Composites," *Technical Papers Β CFA Composites 2002*, CDROM, 2002. (Selected as Best Pultrusion Paper and Co-winner for Best Overall Paper for Composites '02) Brief Abstract: The objective of this study was to thoroughly document the effects of heat, moisture, and loading conditions on the properties of a polyester pultruded unidirectional fiberglass reinforced composite material. The results show the major impact that relative humidity and immersion can have on polyester pultruded composites and also show a difference in the behavior of the moisture effect in the first few days versus the remaining exposure time. Data from this investigation provides information regarding the relationship between humidity exposure and water immersion property effects for these composites.

Rohit Joshi, James G. Vaughan, and Ellen Lackey, "Short-Term Aging Effects on Pultruded Composites," *48th International SAMPE Symposium*, Vol. 48, pp. 849-860, 2003.
Brief Abstract: Polyester/glass pultruded composites have been examined to determine room temperature post-cure aging effects on the mechanical properties of the composite. The intent of this study was to understand and quantify the effects that room temperature storage time can have on composite properties. The pultruded composites were purpose-

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CMRG Hosts Spring 2003 Pultrusion Industry Council

On May 22, 2003, researchers from the Composite Materials Research Group (CMRG) at the University of Mississippi (UM) had the pleasure of hosting the Spring 2003 meeting of the Pultrusion Industry Council (PIC) of the Composite Fabricators Association (CFA). Business meetings and research presentations highlighted the meeting, but CMRG personnel were also able to share some of the ambiance of Oxford and the Ole Miss campus as the members enjoyed an informal dinner on the historic Oxford square and campus tours.

The PIC is a subgroup of the CFA composed of members from firms manufacturing products using the pultrusion process, manufacturers and suppliers of products used in the pultrusion process, designers or suppliers of pultrusion products, end users of pultrusion products, and consultants to the pultrusion industry. The mission of the PIC is to promote the healthy growth of the pultrusion industry. This is accomplished through cooperatively representing the industry before government and code bodies; promoting the use of pultruded products over traditional materials; supporting the development of meaningful design standards; compiling and communicating relevant technical, statistical, and other data; and cooperatively addressing other issues that may impact the industry.

Following the call to order by Chairman Keith Liskey of Strongwell, the council spent the morning discussing business related to the PIC focus areas. After lunch featuring southern barbecue, CMRG researchers presented

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Pultrusion Industry Council members tour CMRG research labs.

CMRG Research Profiles

The Composite Materials Research Group at the University of Mississippi emphasizes an interdisciplinary research approach. Presently, the research is divided into four main areas — structural modeling, static and dynamic mechanical and physical property characterization, thermal and fluid modeling, and experimental characterization/optimization. In this issue of *Mississippi Pultrusion*, a discussion of current research related to the process development for polyurethane pultrusion is presented. This work has been done in cooperation with Bayer Polymers LLC and Nautilus Composites LLC. Further details concerning this research are being presented at the Composites 2003 Annual Conference and are available in the *Composites '03 Proceedings of the Composite Fabricators Association.*

Process Development for Pultrusion of Fast-Gel Thermoset Polyurethanes

Polyurethanes are unique among the various families of polymer chemistries because of their incredible versatility. Orders of magnitude ranges in modulus, density, strain to failure, and other critical properties can be achieved for these polymers with simple substitution of raw materials. Design variables in the raw materials include the length of the polymer chains, the types of linkages in those chains, as well as the number, location and shape of the branches. Over the last six decades, the chemical industry has developed a staggering array of these polymers for use in a wide range of applications. This array of polyols and isocyanates provides the ability to create designer macro-molecules with combinations of properties not possible with the resin chemistries currently used in composites. This wide array of commercially available raw materials also permits the design of the chemical reaction and processing conditions that result in these structures. In general, isocyanate groups are highly reactive, and the formation of a urethane linkage is an exothermic reaction. By selecting the type or types of polyols and isocyanates and an appropriate catalyst, the speed of the reaction and the energy released by it can be tailored to the manufacturing process employed.

Orders of magnitude ranges in modulus, density, strain to failure, and other critical properties can be achieved for these polymers with simple

For the purposes of this research, several molecular structures were selected for testing. Some of the selected structures exhibit mechanical and thermal properties consistent with those of existing composite matrix resins; however, others were selected because they have unconventional properties that could potentially expand the applications for pultruded composites. Also, the mixes of polyols and isocyanates were selected to optimize the processing characteristics for pultrusion. These characteristics included:

- low viscosity, to ensure good fiber wetting,
- long relative gel time to make set-up and shut down easy and forgiving,
- rapid polymerization to allow for high process speeds and a good surface finish, and
- competitive cost.

The final resin chemistry selection included several different proprietary blends of polyols and a highly reactive isocyanate. In all cases, there was a significant exotherm; however, the exotherm was complete before the resin reached its gel state. This was considered an important goal in keeping the pultrusion pull forces from becoming excessive and stopping the process.

This process development research involved both pultrusion processing experiments and mechanical property testing. Pull force data was monitored during the runs and was used in the evaluation of the system processability. Examination of surface quality as the part exited the pultrusion die was also used in the evaluation of system processability. Process thermocouple data was collected during selected experiments to determine the heating profiles experienced by the composite within the die. The initial experiments used 113-yield Owens Corning Type 30 (366-AD-113) glass fiber, yielding a fiber volume of 68 percent. Due to the reactivity of the polyurethane resin system, a resin injection system was used for resin introduction. Resin was pumped into the injection chamber at a single point on the top surface, midway down the length of the chamber. The two components of the resin were pumped at a rate that matched the rate of resin consumption and maintained sufficient pressure in the injector box to insure adequate wetout. A standard 30-element disposable static mixing tube was used to mix the two resin components just before they entered the resin injector box. This approach is commonly used when working with polyurethanes because it minimizes the amount of mixed resin that has to be discarded if an emergency shut-down is necessary. During the experimentation, it was determined that a gear pump that could accurately maintain the component ratios provided the best delivery of resin to the injector system.

Processing Results

Processing trials examining numerous process parameters and resin formulations were conducted in order to establish a processing window. After initial examinations were performed, all resin chemistries selected for further research could be processed at speeds at or above 48 inches per minute with a highly glossy surface finish. The following conditions were selected for examination in the second phase of the experiments.

Typical starting conditions were as follows:

Start speed: 24 inches per minute

Mechanical Property Results			
Resin	**ASTM D790 Flexural**		**ASTM D2344**
	Stress (ksi)	Elongation (%)	Short-Beam Strength (ksi)
Hi-Mod Range	210 - 245	3.3 - 3.5	10 - 12.5
Hi-Mod Typical	232	3.4	11.5
Lo-Mod Range	200 - 220	3.0-3.3	9 - 10.7
Lo-Mod Typical	219	3.2	9.9

Entry cooling: On
Die entry set temperature: Preset at 80°F (although measured temperatures were near 150°F)
Mid die set temperature: 395°F
Die exit set temperature: 260°F

Typical settings at speed were as follows:
Process speed: 48 - 60 inches per minute
Entry cooling: On
Die entry set temperature: Preset at 80°F (although measured temperatures were higher than 150°F)
Mid die set temperature: 475°F
Die exit set temperature: 260°F

While these conditions proved to be usable for shorter runs, extended experimental runs demonstrated that modifications were necessary to achieve consistent processing results. As time passed, the temperature in the entry section of the die began rising well above the previous trial temperatures. After two hours of running, with the mid-die temperature typically at 475°F to 495°F, the thermocouples in the entry section of the die measured 170°F to 190°F. As a result, the reacting polyurethane resin was reaching gel very early in the die before it had fully wet out the fiber. As the part exited the die, it was possible to observe some of the glass ends in the part. This had not been observed in the previous processing trials; excellent wetout of the fiber had made it possible to read a newspaper through the part. As expected, the poor wetout resulted in a serious deterioration of mechanical properties in the pultrusions produced under these high temperature conditions. As further evidence that the high temperature die entry caused the deterioration in fiber wet out, pultrusions from early in the same runs, before the entry temperatures had begun to climb, had mechanical properties comparable to those observed in the earlier trials.

Based on the temperature profiles that had been employed earlier in the project, it was postulated that the parts could be pultruded with an effective 24 inch heated die and a 24 inch cooled resin injector region. The final round of process trials reinforced this belief; results indicated that such a configuration with good insulation of the long injector from the hot die would provide the best combination of fiber wetout, mechanical properties, and speed.

Mechanical Property Results

A summary of the typical mechanical properties measured for the final series of pultrusion experiments run at a pull speed of 48 to 60 inches per minute is shown in the table above. These properties compare very favorably with product manufactured using conventional pultrusion resin chemistries. The results of the mechanical testing showed that there was considerable latitude in the resin chemistry with respect to mechanical properties. Deliberate changes of ±10% of the nominal resin mix ratio of the two component polyurethane systems showed only minor variation in the resulting three-point flexural strength. The lack of significant variation in mechanical properties is welcome information for pultruders since resin chemistry control appears to have a reasonably wide processing window. Small variations in the ratio of the polyol and the iscocyanate only led to minimal variations in the flexural and short-beam mechanical properties.

Conclusions

It is clear from the results of these pultrusion trials that polyurethane resin systems can make a significant contribution to the advancement of pultruded composites. Basic pultrusion processing parameters have been established and fundamental insight has been gained for advancing the processability of these resins even further. Mechanical and physical properties compare very favorably with conventional pultruded composite properties and offer some benefits not present with conventional systems

Recent Publications (cont.)

fully manufactured with a wide range of initial degrees of cure as they exited from the die to determine the effect of aging for varying initial degree of cure conditions. The properties studied were Barcol hardness and short-beam strength. These properties were correlated with measurements of the degree of cure of the composites over the aging period as determined from differential scanning calorimetry. Results show that composites that are not fully cured as they exit the die exhibit significant aging effects over the first week of room temperature storage after production. Results from this study can be used to validate mechanical property testing of recently pultruded composites against properties of composites stored for lengthy times before use.

Ellen Lackey, James G. Vaughan, and Rahul Patki," "Utilization of Photocure Techniques in Conjunction with Thermal Cure for Increasing Productivity of the Pultrusion Process," *RadTech Report*, May/June, pp. 42-49, 2003. Brief Abstract: One area for potential development is the utilization of photocure techniques in conjunction with the pultrusion process. One drawback associated with previous approaches to the use of photoinitiated resins with the pultrusion process is the need for special tooling and special pultrusion equipment. The objective of this research was to demonstrate the feasibility of a photocure pultrusion process that utilizes standard pultrusion tooling and equipment. Results from this study demonstrated the feasibility of the use of a hybrid thermal/photocure strategy as exposure to UV energy was seen to successfully increase the degree of cure of the hybrid thermal/phtocure composite compared to that for thermal cure only composites.

Spring 2003 PIC Meeting (cont.)

overviews of research areas currently underway at UM. Dr. Jim Vaughan gave an overview of the CMRG facilities and capabilities. Dr. Ellen Lackey discussed ongoing research related to durability of pultruded composites, gave a brief update about ongoing research related to polyurethane pultrusion, and discussed an upcoming project examining the use of natural fiber reinforcements with the pultrusion process. Dr. Jeff Roux presented research concerning fluid modeling of the pultrusion process. Dr. Raju Mantena discussed dynamic analysis of structural foam, and Dr. Ahmed Al-Ostaz presented an overview of a statistical approach for predicting composite failures. Following the presentations, council members joined Jim Vaughan as he led a tour of the CMRG research facilities. Following the tours, council members had the opportunity to view CMRG student poster presentations and meet with CMRG students.

CMRG Research Paper Selected as Best Pultrusion Paper and As Co-Winner of Best Overall Technical Paper for Composites 2002

The technical paper entitled "Combined Effects of Moisture, Temperature, and Load on Pultruded Composites" authored by Jack McClurg, James Vaughan, and Ellen Lackey was selected for this award at the CFA Composites 2002 annual convention. This paper focused on composite durability studies at various exposure temperatures and humidity levels and related these conditions to immersion test results more commonly available to the composites community. This is the third consecutive year that CMRG research papers have been selected for awards at the CFA convention.